Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Homogeneous polymerization of hydrophobic monomers in bio-based DL-menthol/1-tetradecanol eutectic mixture by ATRP and RAFT polymerization

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Table S1. Composition and pH of different DL-menthol-based EM and solubility of hydrophobic monomers in the EM. S: soluble and INS: insoluble

EM	Molar ratio	pH	Tested monomers		
			MA	MMA	Sty
DL-menthol: acetic acid	1:1	4.0	S	S	S
DL-menthol: pyruvic acid	1:2	*	S	S	S
DL-menthol: lactic acid	1:2	2.3	S	S	INS
DL-menthol: 1-tetradecanol	2:1	6.0	S	S	S

* Not determined

Table S2. Reaction conditions and molecular weight parameters of PMA-Br prepared by SARA ATRP in 100 % EM (DL-menthol/1-tetradecanol).

Entry[a]	DP	k_p^{app} (h^{-1})	t (h)	Conv (%)	$M_n^{th} \times 10^{-3}$	$M_n^{SEC} \times 10^{-3}$	$Đ$
1	222	0.17	10.9	73	14.2	13.6	1.13
2	100	0.42	6.1	80	7.2	7.4	1.16
3	50	0.69	6.0	86	4.1	4.2	1.19
4[b]	100	0.75	1.7	72	7.2	7.3	1.06
5	500	-	10.0	52	22.1	19.7	1.12
6[c]	500	-	20.0	30	13.1	12.7	1.27

[a]Polymerization conditions:$[MA]_0/[EBiB]_0$ = DP/1 (molar); Cu(0): l = 5 cm and d = 1mm; $[Me_6TREN]_0/[CuBr_2]_0$ = 5 (molar); $[CuBr_2]_0$ = 225 ppm (in comparison to the amount of monomer); $[MA]_0$/[DL-menthol/1-tetradecanol] = 0.75/1 (v/v); T = 30 ℃; [b]4EBiB was used as the initiator; [c] $[MA]_0$/[DL-menthol/1-tetradecanol] = 0.5/1 (v/v).

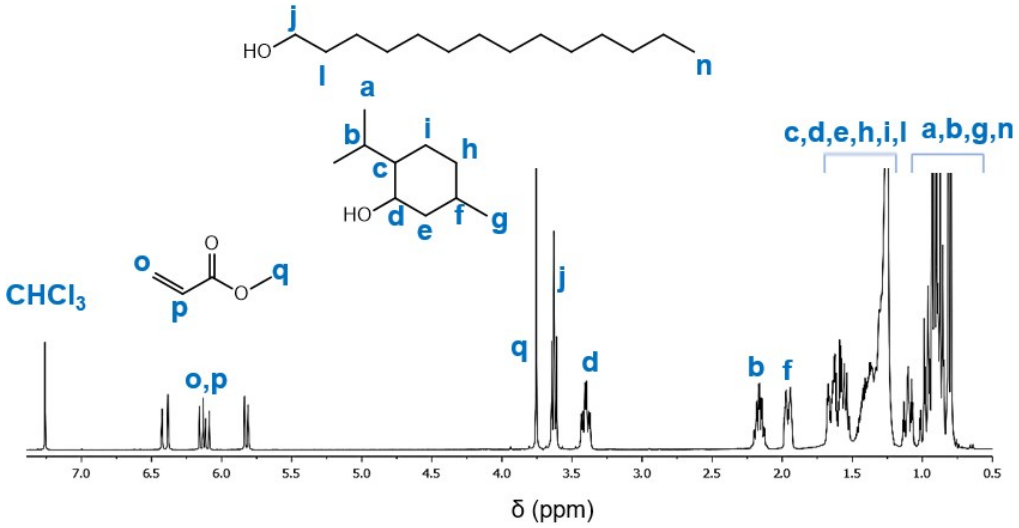

Figure S1. ^{1}H NMR spectrum of the final liquid phase from SARA ATRP reaction in EM, corresponding to the EM and monomer.

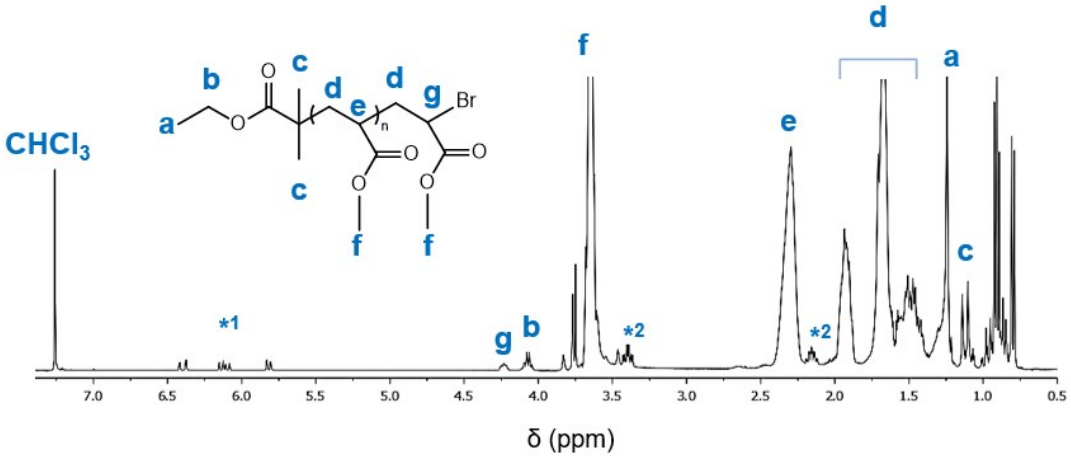

Figure S2. ^{1}H NMR spectrum of the final solid phase from SARA ATRP reaction in EM, corresponding to PMA-Br, traces of monomer (*^{1}) and EM (*^{2}).

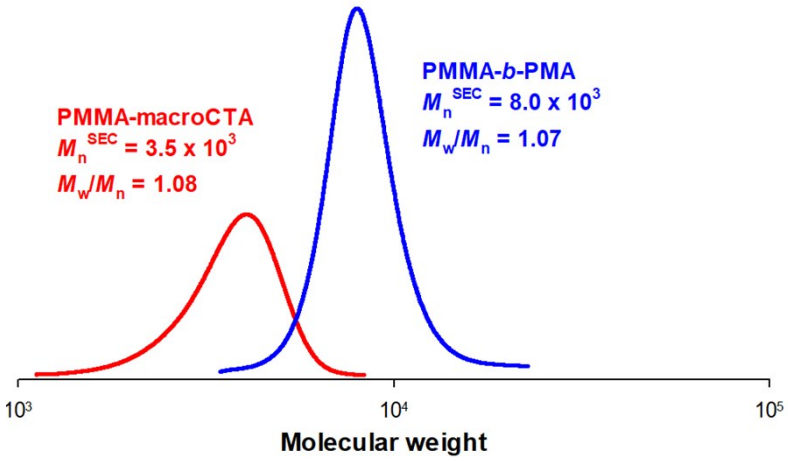

Figure S3. Normalized SEC traces of PMMA-macroCTA and PMMA-*b*-PMA block copolymer obtained after chain extension by RAFT in DMSO.