Supporting information

for

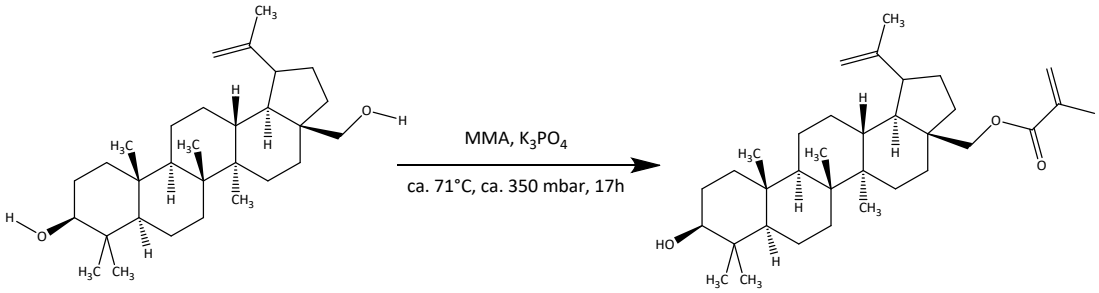
Biobased triblock thermoplastic elastomer with Betulin- or Carvacryl-methacrylate end-blocks by RAFT polymerization

Aniello Vittore,[a] Pauline Shamraienko,*[b] Ilka Hermes,[b] Qiong Li,[b] Brigitte Voit,[b, c] and Lorella Izzo*[a]

a) Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, via J.H. Dunant 3, 21100 Varese, Italy
b) Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany
c) Organic Chemistry of Polymers, TUD Dresden University of Technology, 01062 Dresden, Germany

Contents

1 Synthesis of betulin methacrylate (BetuMA)



Scheme S1 Reaction scheme of synthesis of betulin methacrylate by transesterification

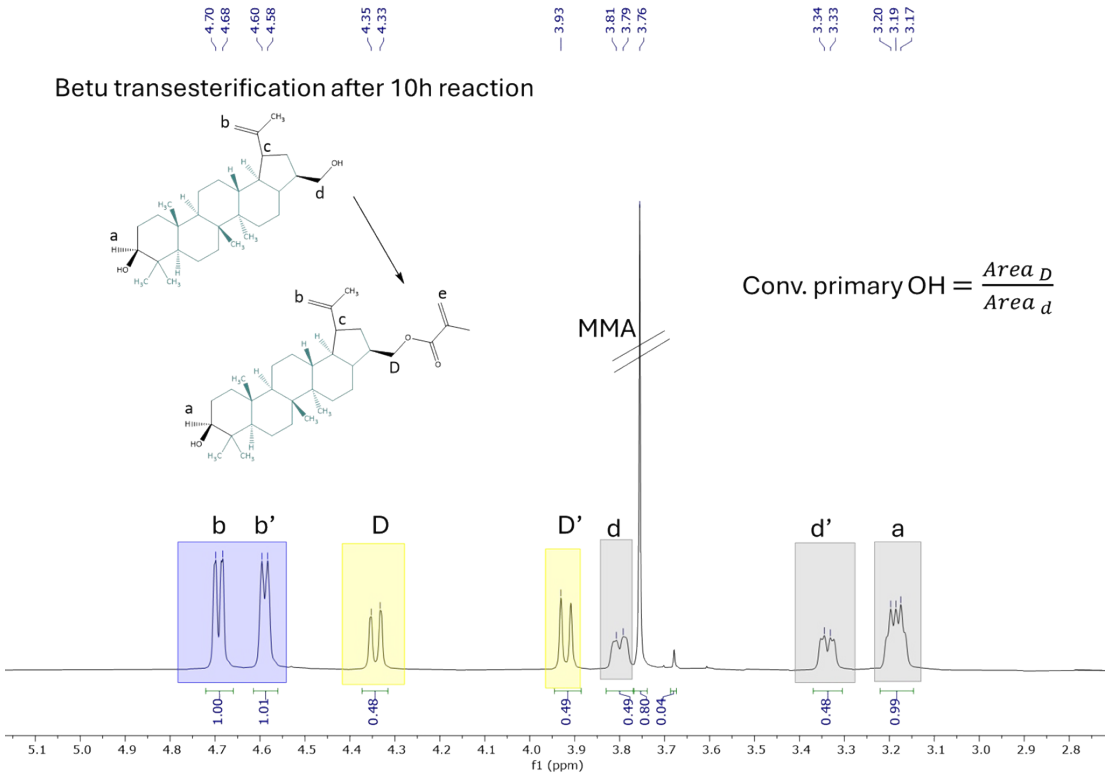


Figure S1 ^{1}H-NMR representative spectrum of the crude mixture of betulin transesterification and equation used to calculate the conversion of primary hydroxyl group.

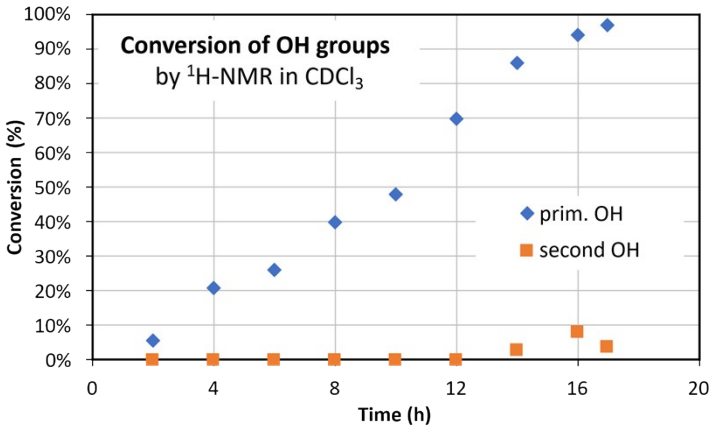


Figure S2 Conversion of betulin hydroxyl groups as evaluated by ¹H-NMR spectroscopy

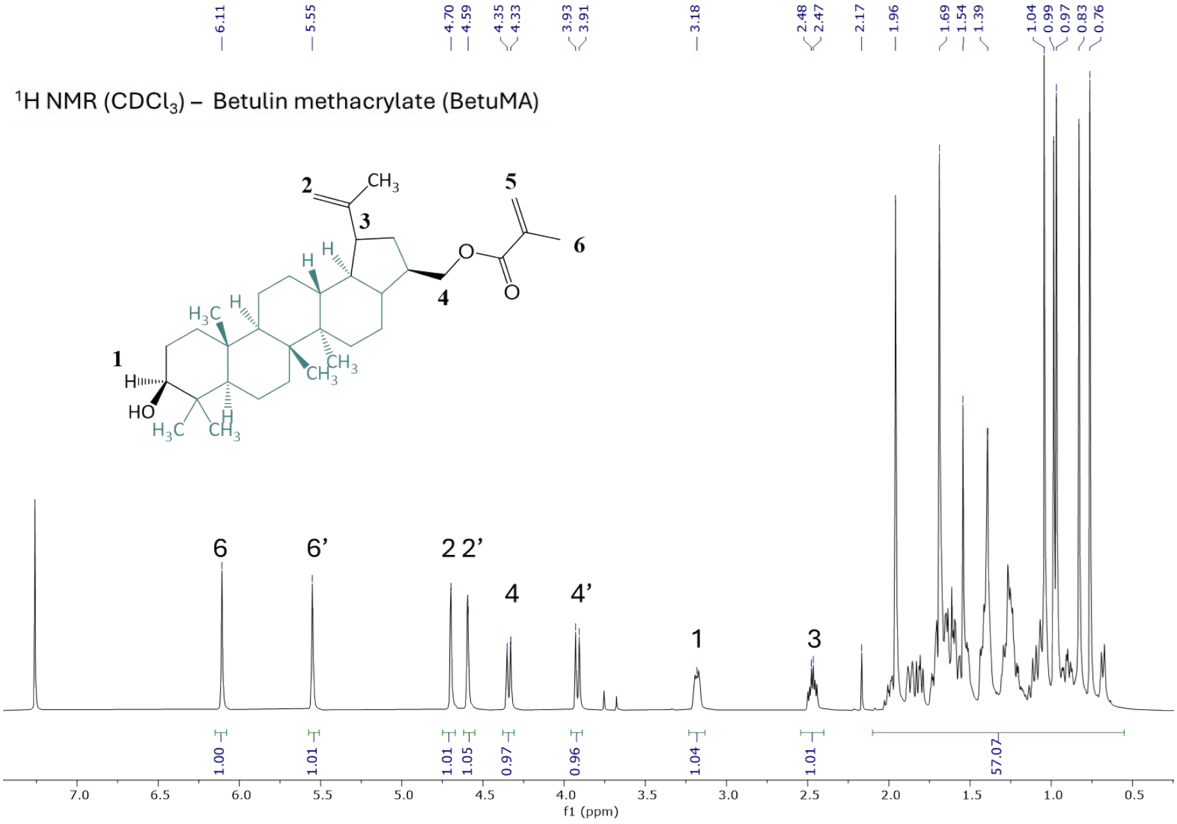


Figure S3 ¹H-NMR spectrum ($CDCl_3$, room temperature) of purified Betulin methacrylate (BetuMA)

2 CaMA and BetuMA RAFT homo-polymerization

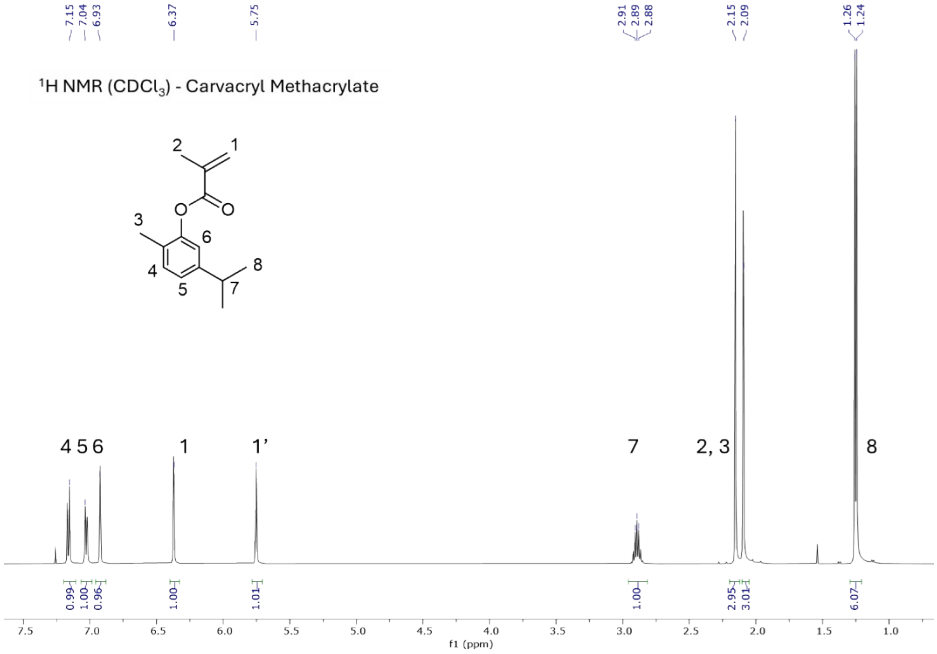


Figure S4 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of Carvacryl methacrylate (CaMA)

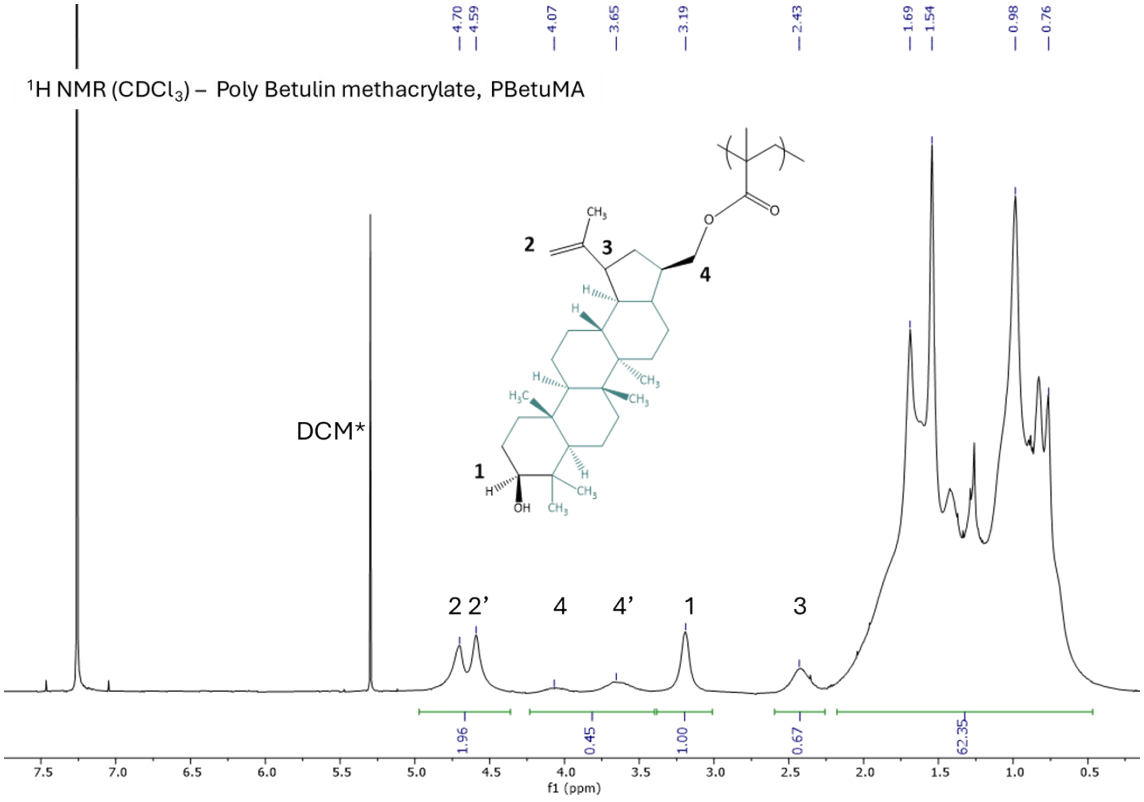
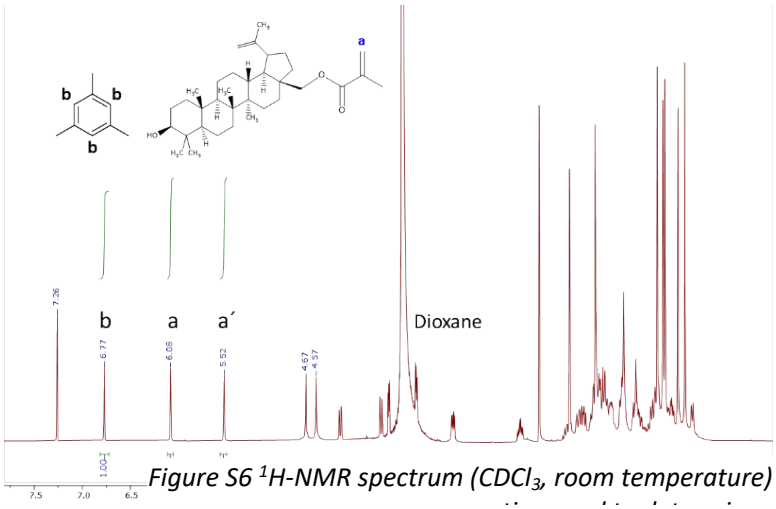


Figure S5 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of Poly(Betulin methacrylate) (PBetuMA)

2.1 BetuMA polymerization conversion

Conversion of methacrylate group during BetuMA polymerization were calculated by ^{1}H-NMR ($CDCl_3$) of crude reaction mixture. The monomer/internal standard (IS=Mesitylene) ratio at time **t** ratio at time **0** were used to calculate conversion as reported:



$$Conversion = 1 - \frac{\left(Area_{monomer}/Area_{IS}\right)_{time=t}}{\left(Area_{monomer}/Area_{IS}\right)_{time=0}} = 1 - \frac{\left(Area_a/Area_b\right)_{time=t}}{\left(Area_a/Area_b\right)_{time=0}}$$

Figure S6 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of the crude mixture of BetuMA RAFT polymerization and ...dard.

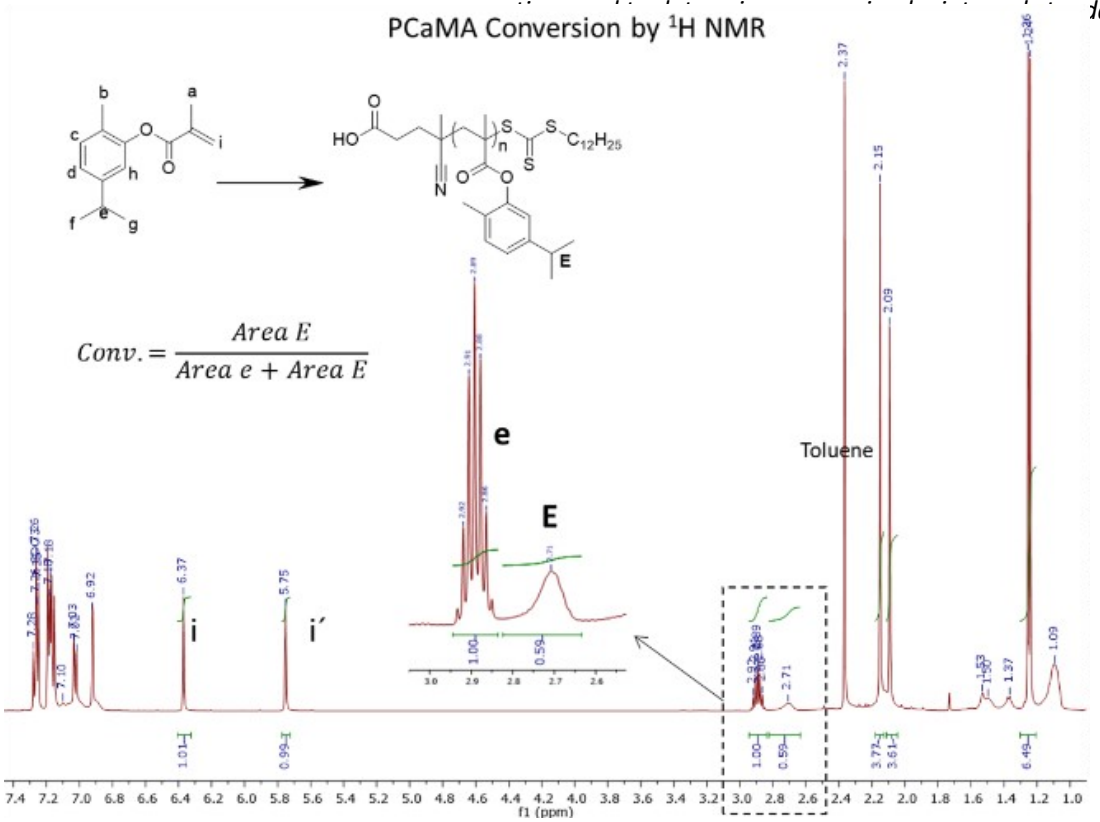


Figure S7 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of the crude mixture of CaMA RAFT polymerization and equation used to determine conversion.

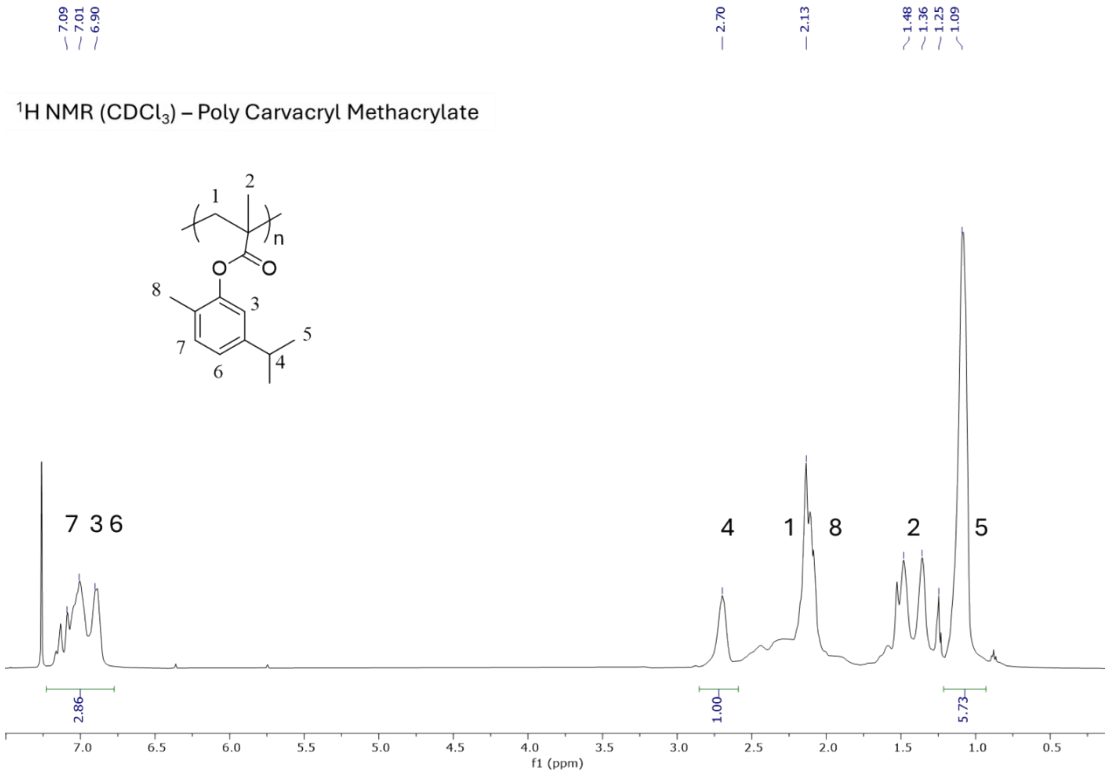


Figure S8 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of poly(carvacryl methacrylate) (PCaMA)

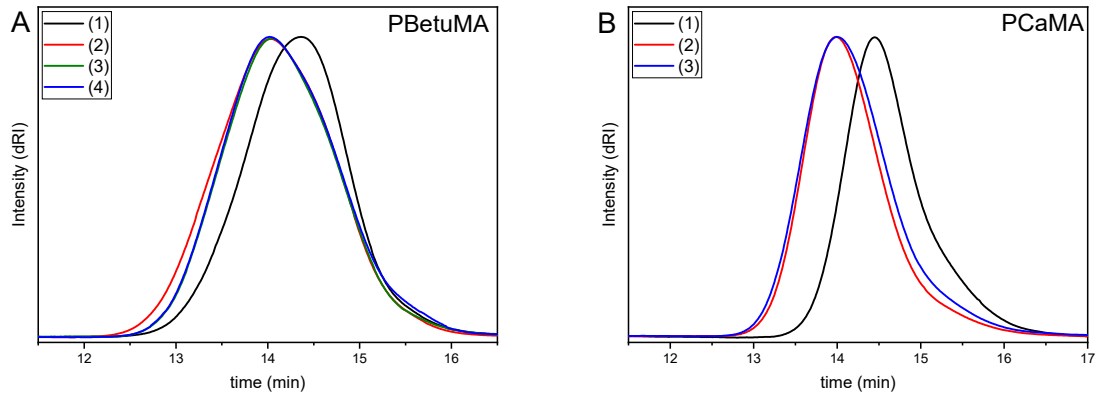


Figure S9 GPC traces (dRI) of A) PBetuMA and B) PCaMA as obtained from condition reported in the main text (see Table 1 for BetuMA and Table 2 for CaMA).

3 Synthesis of ET13 macroCTA

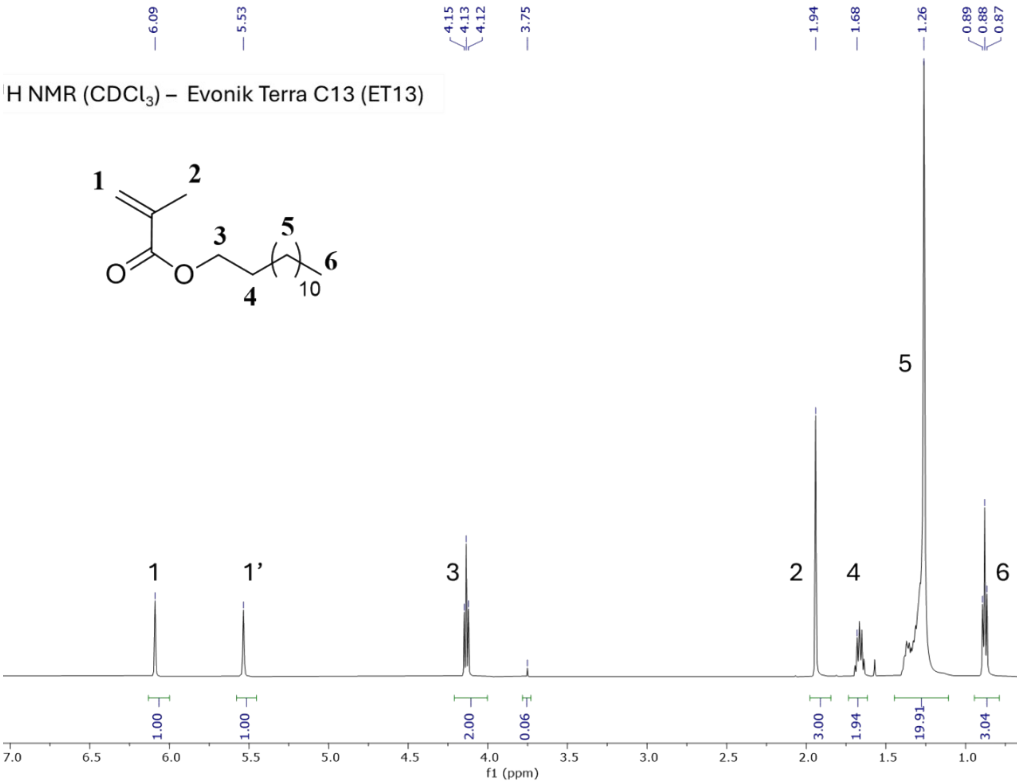
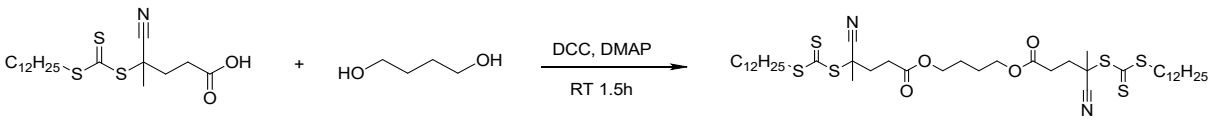


Figure S10 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of Evonik Terra C13 (ET13)

3.1 Synthesis of the RAFT agent Bis-CDP



Scheme S2 Reaction scheme of the synthesis of bis-CDP

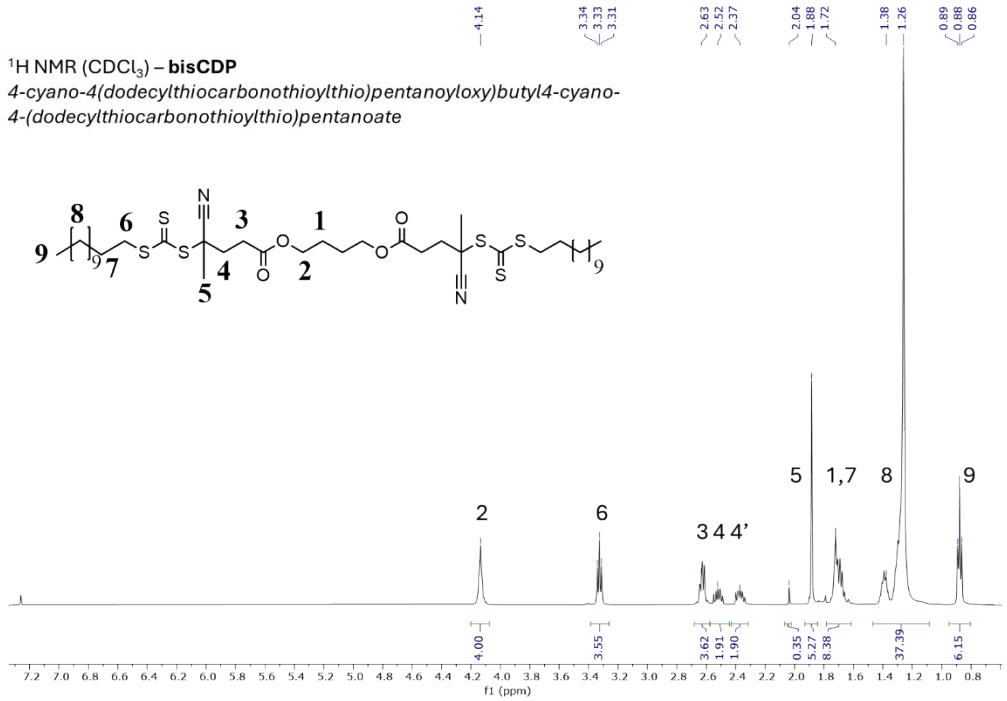


Figure S11 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of bifunctional RAFT agent bis-CDP

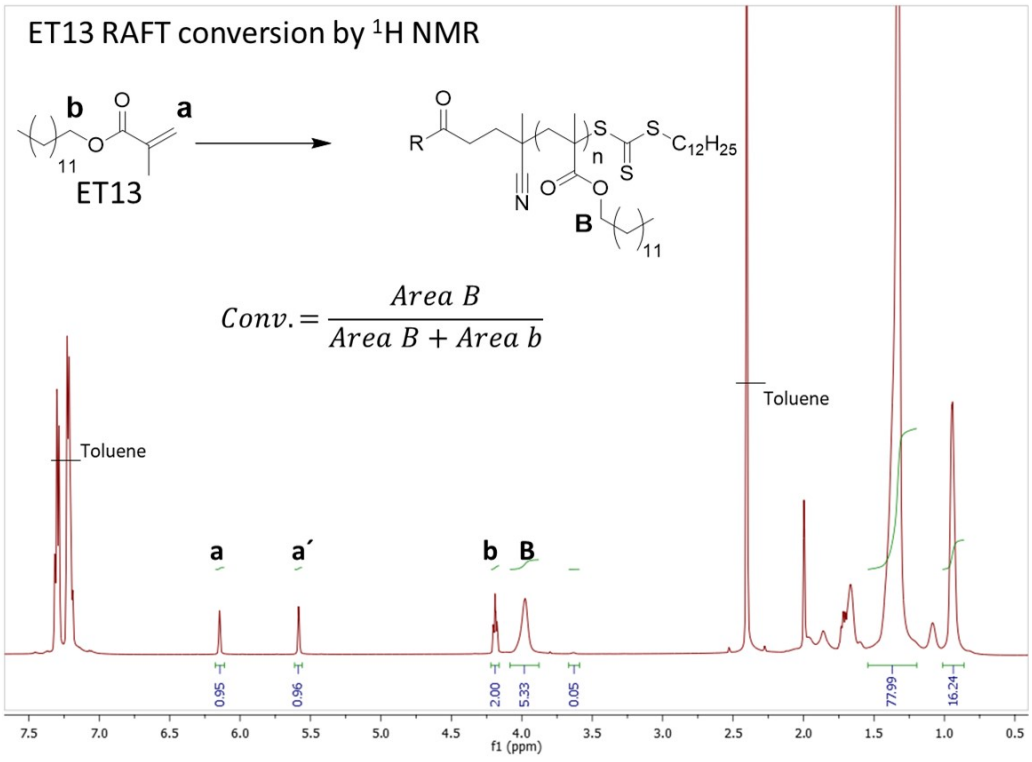


Figure S12 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of crude mixture of ET13 RAFT polymerization and equation used to determine monomer's conversion.

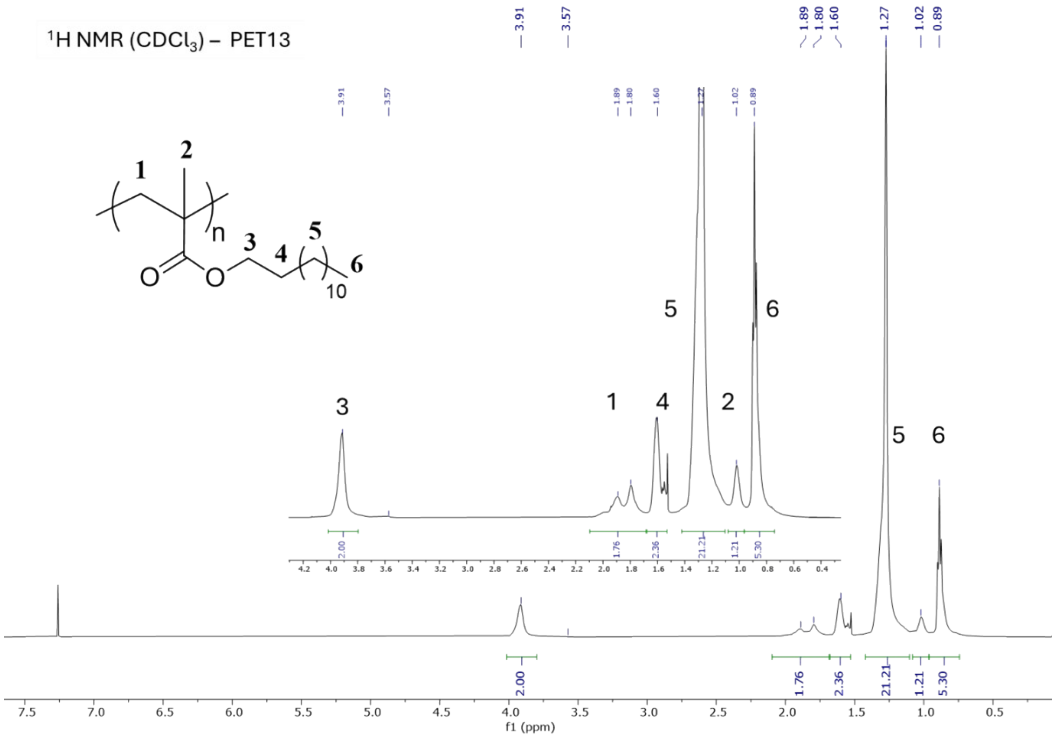
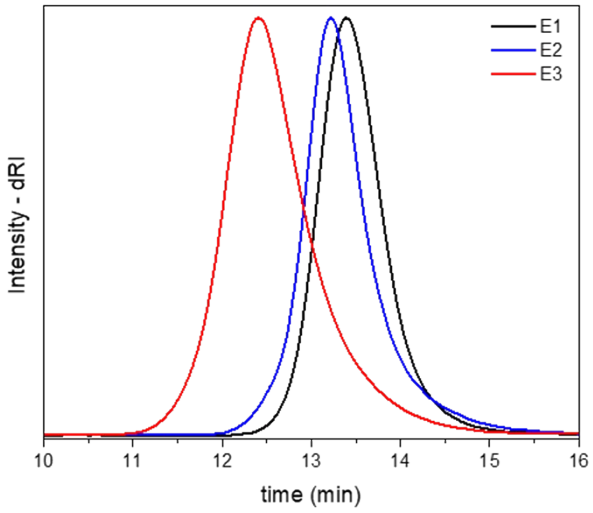


Figure S13 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of PET13



Sample	M_n (Kg/mol)	Đ
E1	84.1	1.10
E2	108	1.11
E3	229	1.25

Figure S14 GPC traces (dRI) of the three macro-CTA (E1, E2, E3) and the relative M_n and Đ.

4 ABA triblock copolymers

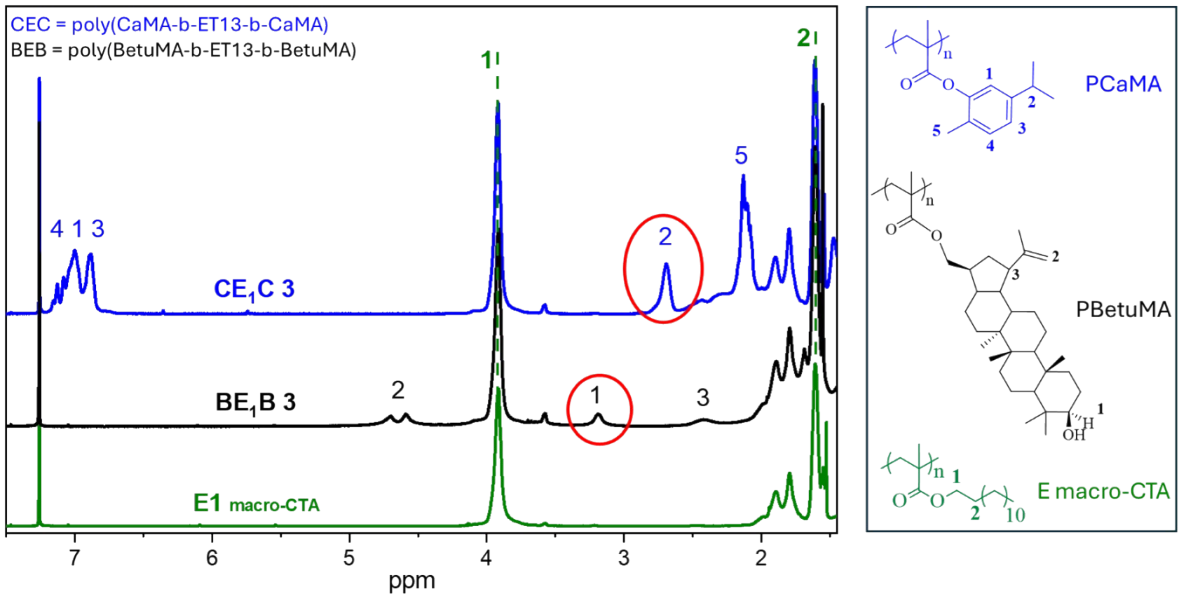


Figure S15 Representative ^{1}H-NMR spectra of, from bottom: PET13 macroCTA, BEB and CLC triblock copolymers (encircled signals were used to calculate the composition of glassy blocks).

Table S1 Copolymers composition calculation by ^{1}H-NMR analysis as molar and weight fraction of the glassy blocks

$Molar\ fraction_{BetuMA} = \frac{I_{CH_2O\ PBetuMA}}{I_{CH_2O\ PBetuMA} + I_{CH_2O\ PET13}} * \frac{2}{3}$	$Molar\ fraction_{CaMA} = \frac{I_{CH(CH_3)\ PCaMA}}{I_{CH_2O\ PET13} + I_{CH(CH_3)\ PCaMA}} * \frac{2}{3}$
$Weight\ fraction_{BetuMA} = \frac{Molar\ fraction_{BetuMA} * Molar\ mass_{BetuMA}}{Molar\ fraction_{BetuMA} * Molar\ mass_{BetuMA} + (1 - Molar\ fraction_{BetuMA}) * Molar\ mass_{ET13}}$	$Weight\ fraction_{CaMA} = \frac{Molar\ fraction_{CaMA} * Molar\ mass_{CaMA}}{Molar\ fraction_{CaMA} * Molar\ mass_{CaMA} + (1 - Molar\ fraction_{CaMA}) * Molar\ mass_{ET13}}$
Where, Molar Mass$_{CaMA}$= 218.29 g/mol, Molar Mass$_{BetuMA}$= 510.80 g/mol, Molar Mass$_{ET13}$= 268 g/mol.	

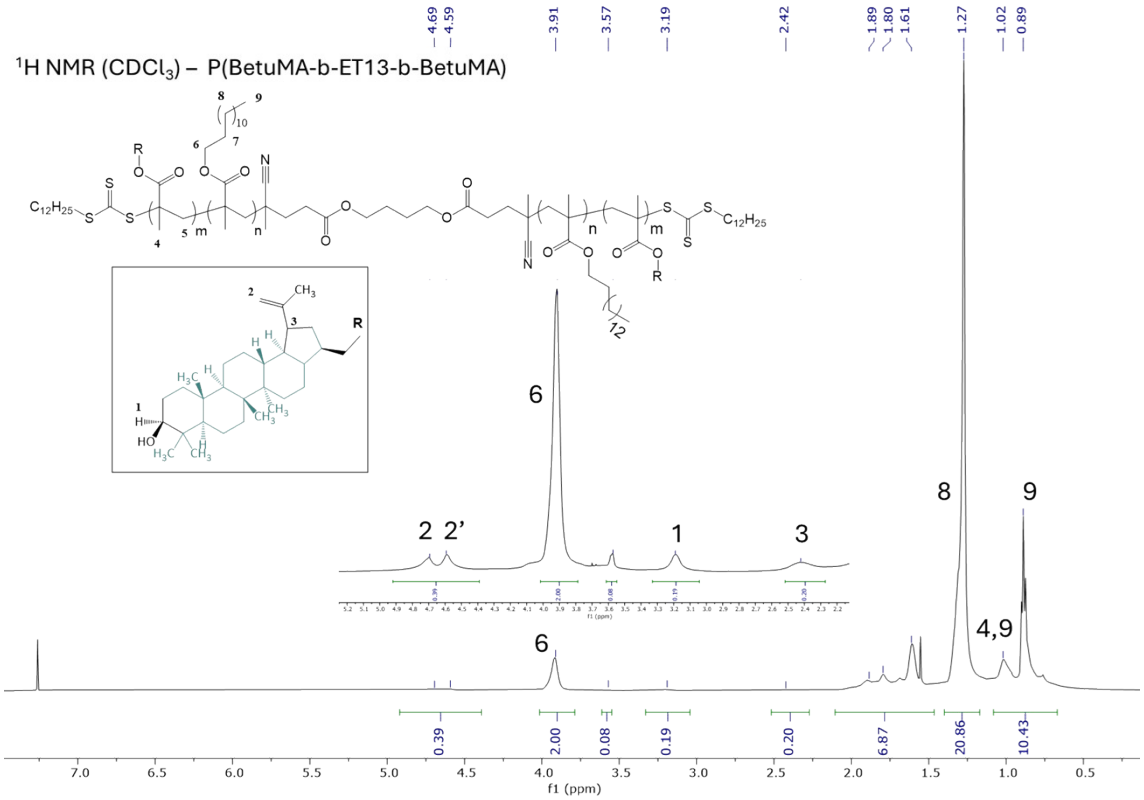


Figure S16 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of P(BetuMA-b-ET13-b- BetuMA), ***BEB***

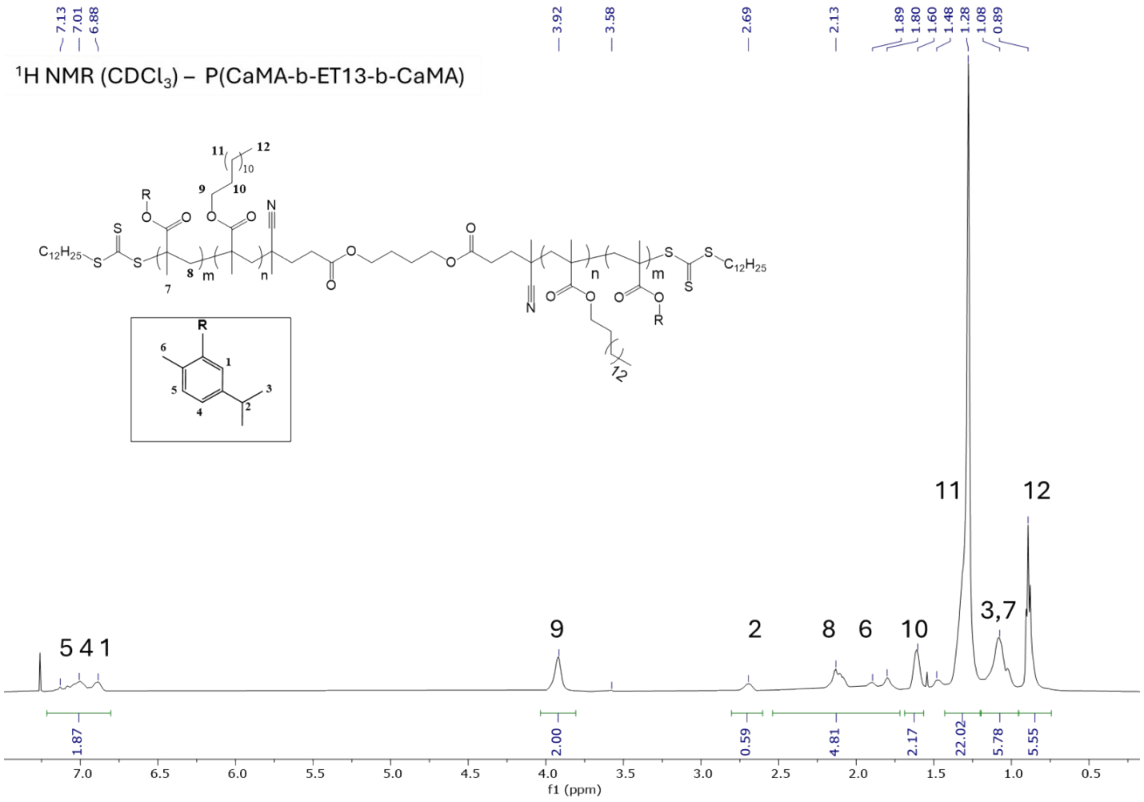


Figure S17 ^{1}H-NMR spectrum ($CDCl_3$, room temperature) of P(CaMA-b-ET13-b-CaMA), ***CEC***

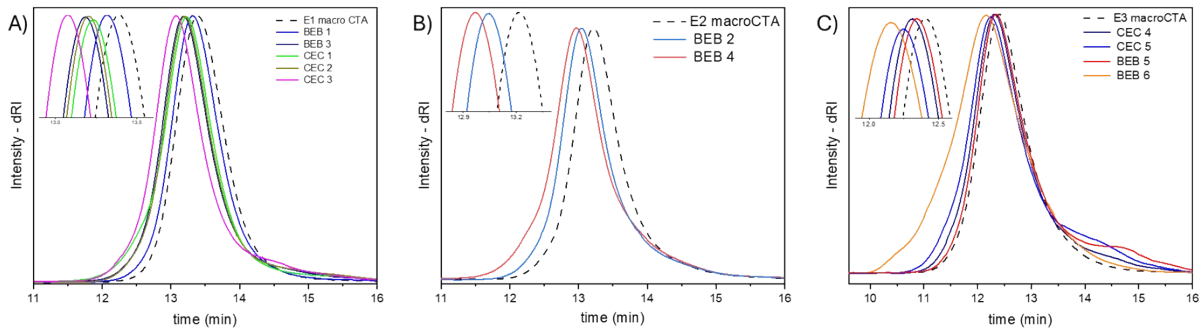


Figure S18 GPC chromatogram traces of PET13 macroinitiators A) E1, B) E2, C) E3 and the relative triblock copolymers BEBs and CECs.

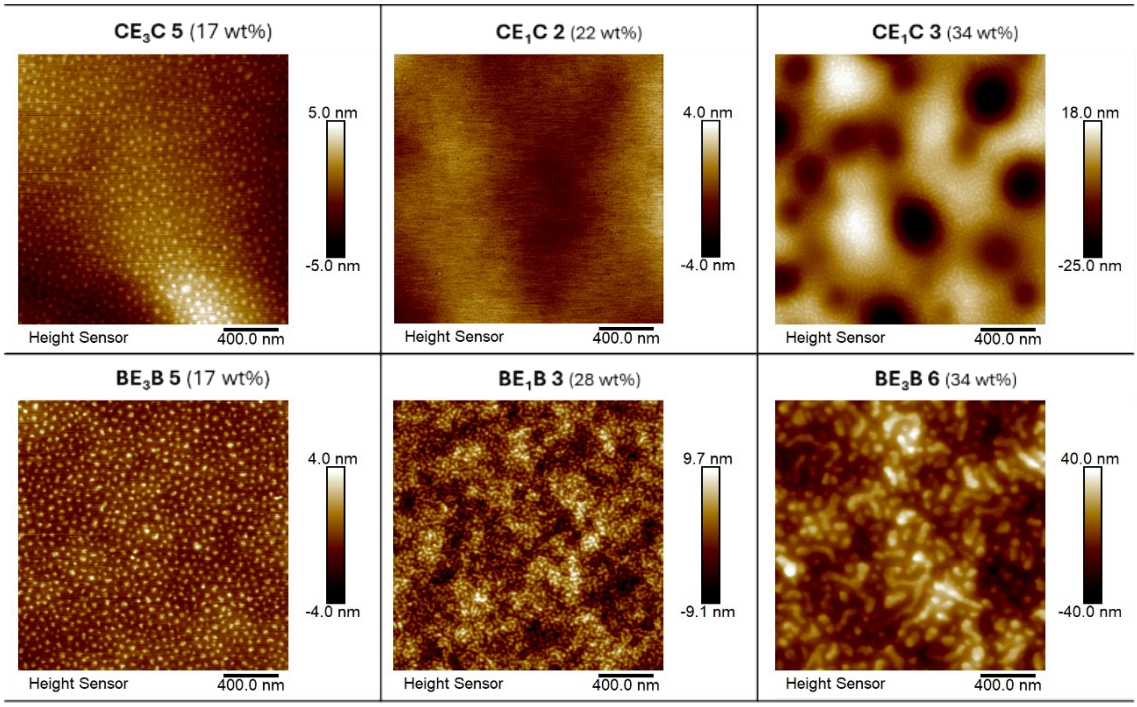


Figure S19 AFM topography images of triblock copolymer with PCaMA (CEC 5, 2 and 3) or PBetuMA (BEB 5, 3 and 6) as external blocks corresponding to AFM phase images in Figure 8 in the main manuscript.

For the determination of the domain sizes, we applied a polynomial line alignment and a 3-pixel Gauss filter to the phase images. The domains of higher phase were then masked with a threshold of the values listed below and used for size determination.

Table S2 List of thresholds of the values for the domain size determination.

CE_3C 5	Masked above 3 deg
CE_1C 2	Masked above 5 deg

CE_1C 3	Masked above 10 deg
BE_3B 5	Masked above 3.5 deg
BE_1B 3	Masked above 9 deg
BE_3B 6	Masked above 8 deg