

## Supplementary Information

### Mechanistic insights on the incorporation of higher alpha-olefins into acrylate copolymers via photoATRP

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#### 1. Computational details of density functional theory (DFT)

The quantum chemistry programme suite Gaussian 16<sup>1</sup> is used for all computations. For the geometry optimization of all the species, including reactants, reactant complexes, transition states, product complexes, and products, the hybrid density functional B3LYP<sup>2-3</sup> is employed. Copper (Cu) is modelled using the LanL2DZ (Los Alamos pseudopotential) basis set,<sup>4</sup> and the other elements are computed using Pople's 6-311+G (d, p) basis set. All stationary locations underwent frequency calculations to determine whether they were minima or transition states. A first visual examination of the atomic displacement vectors, which appear as one and only

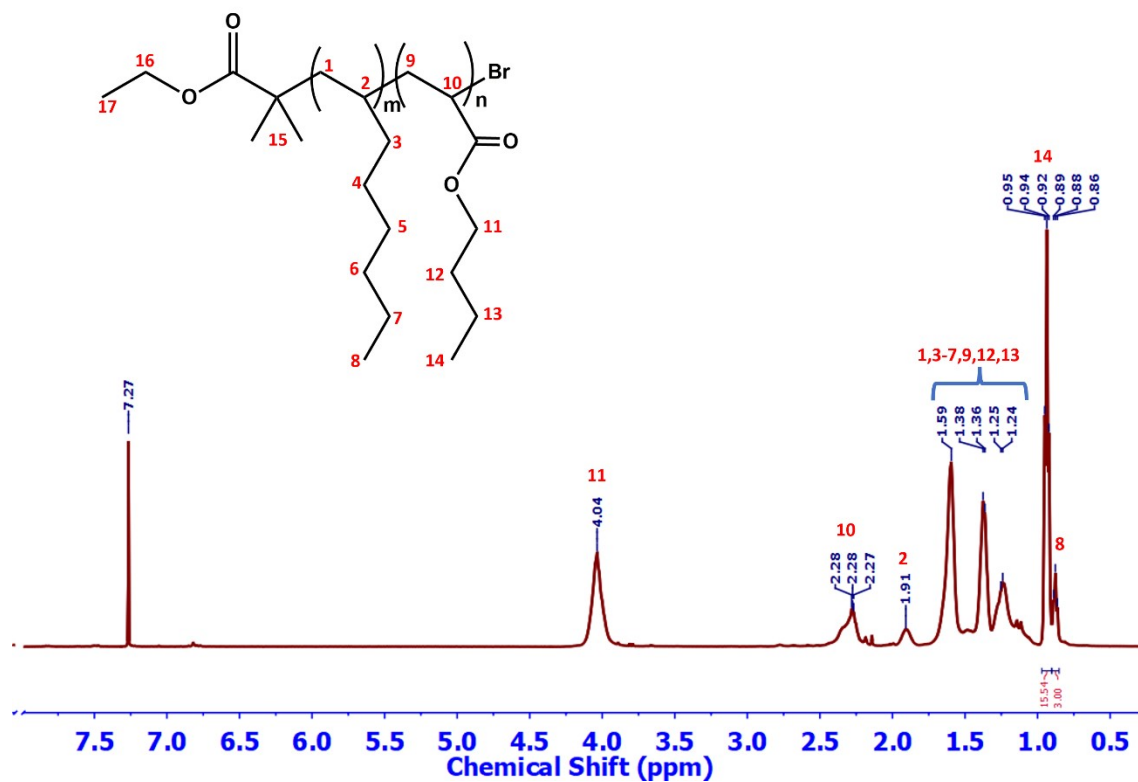
one imaginary frequency of the desired reaction coordinate, is used to characterize the transition states (TS).

A Hessian index of zero is used to describe all other minima. Intrinsic reaction coordinate (IRC) computations are done on the transition states to ensure they connect to the reactants and products on either side of the first-order saddle point.<sup>5</sup> The continuum solvation model SMD devised by Truhlar and Cramer <sup>6</sup> addressed the solvent's influence. Since the reaction occurred in methanol (CH<sub>3</sub>OH), we utilized its continuum dielectric constant ( $\epsilon = 32.7$ ) in the following computations.

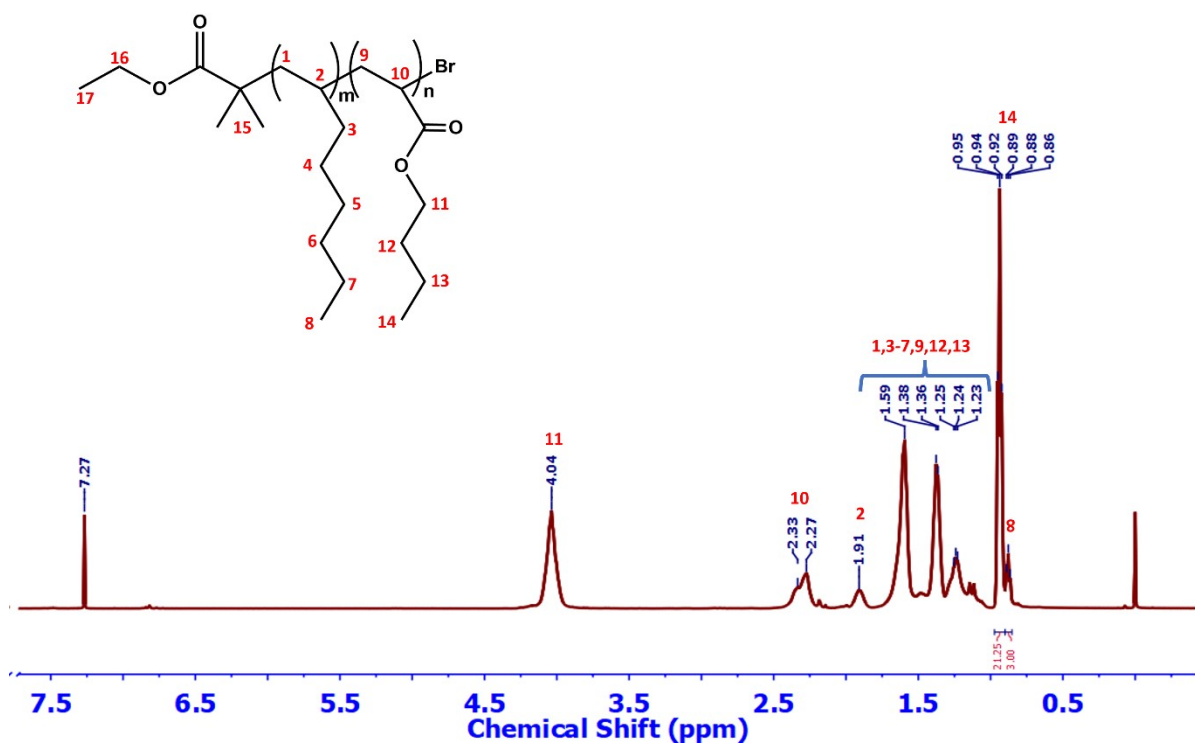
At the SMD (Methanol) / LanL2DZ(Cu),6-311+G (d, p) (C, H, N, O, Br)// B3LYP/LanL2DZ(Cu),6-311+G (d, p) (C, H, N, O, Br) level of theory, the single-point energies of all the stationary points are determined. The zero-point vibrational energy (ZPVE), thermal, and entropic corrections from the gas-phase calculations are added to give the Gibbs free energies and enthalpies for all stationary places in the condensed phase.

The single-point energies of all the stationary points are obtained at the SMD (Methanol)/ LanL2DZ(Cu),6-311+G (d, p) (C, H, N, O, Br)// B3LYP/LanL2DZ(Cu),6-311+G (d, p) (C, H, N, O, Br) level of theory. The Gibbs free energies and enthalpies for all stationary points in the condensed phase are obtained by adding the zero-point vibrational energy (ZPVE), thermal and entropic corrections obtained from the gas-phase computations. Therefore, the presented results and discussion are on the basis of the Gibbs free energies in both the gas phase and solvent phase.

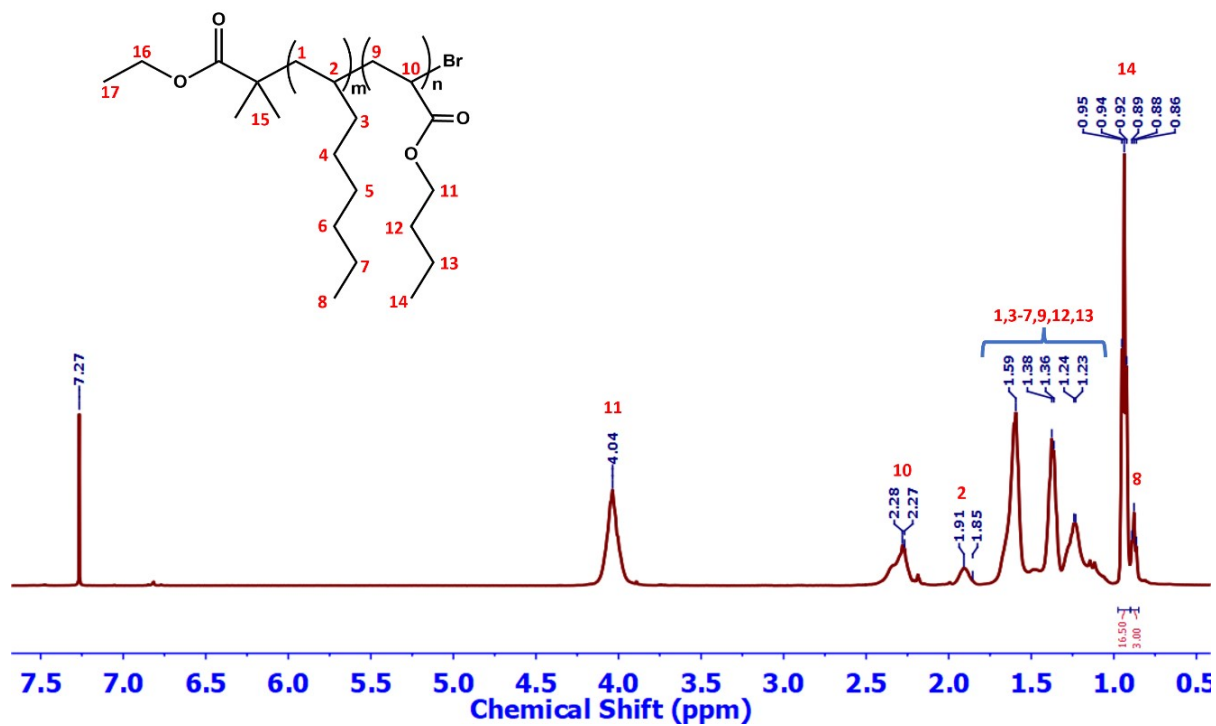
## 2. $^1\text{H}$ NMR analysis



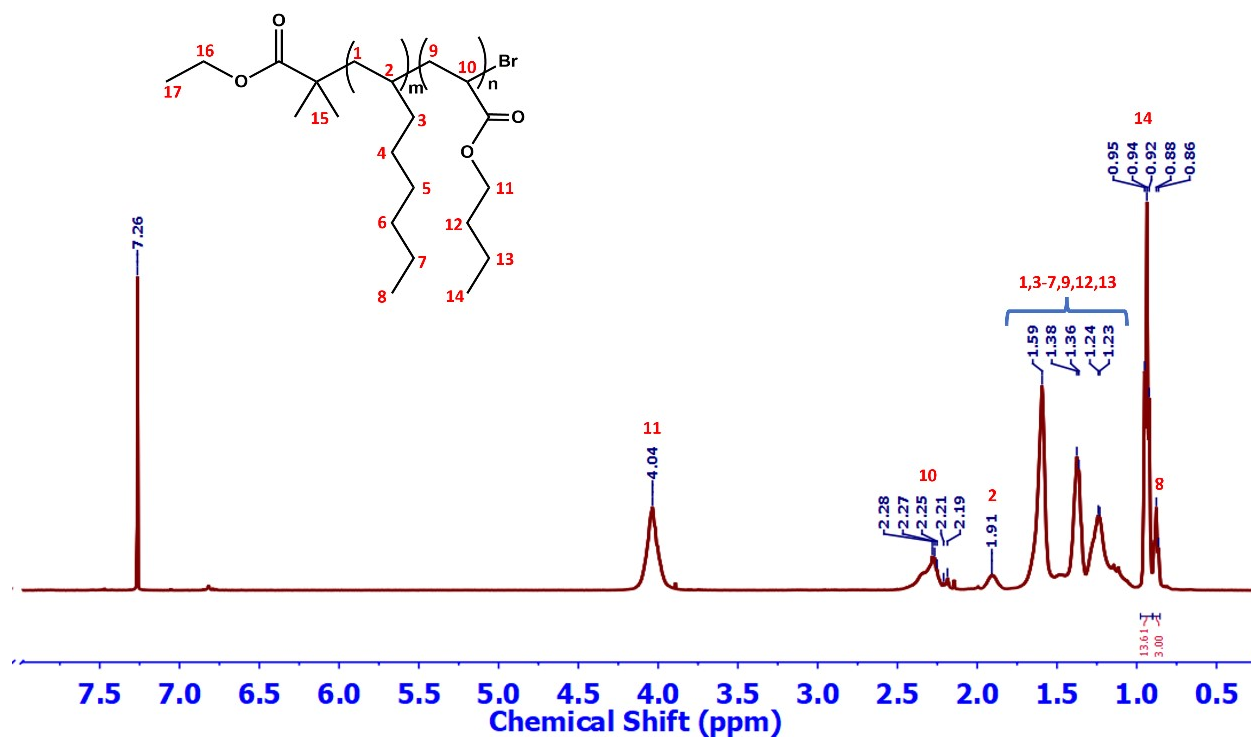
**Figure S1.**  $^1\text{H}$  NMR of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions (a) *n*-BA/1-octene/ $\text{Cu}^{\text{II}}$ /PMDETA/EBiB/BAPO = 100/100/0.1/1.8/1/1.



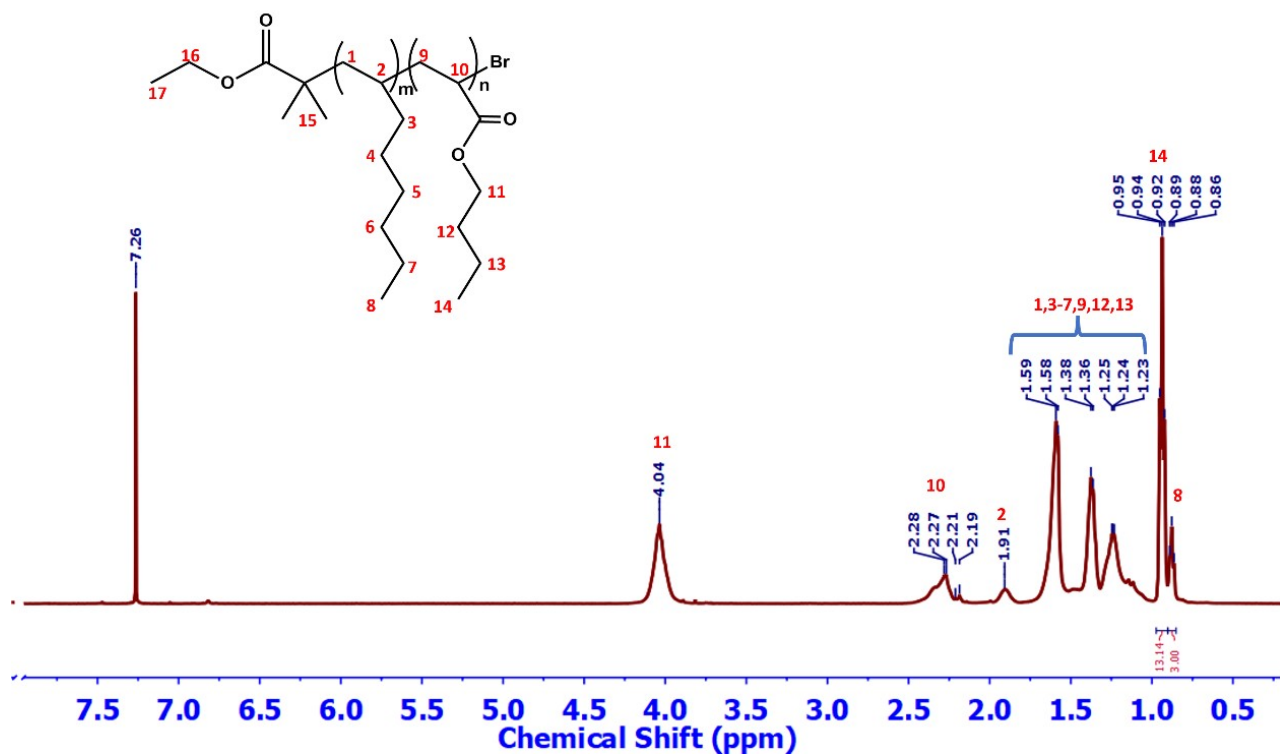
**Figure S2.** <sup>1</sup>H NMR of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions (a) *n*-BA/1-octene/Cu<sup>II</sup>/PMDETA/EBiB/BAPO = 100/100/0.1/0.6/1/0.5.



**Figure S3.** <sup>1</sup>H NMR of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions (a) *n*-BA/1-octene/Cu<sup>II</sup>/Tren/EBiB/BAPO = 100/100/0.1/0.6/1/1.

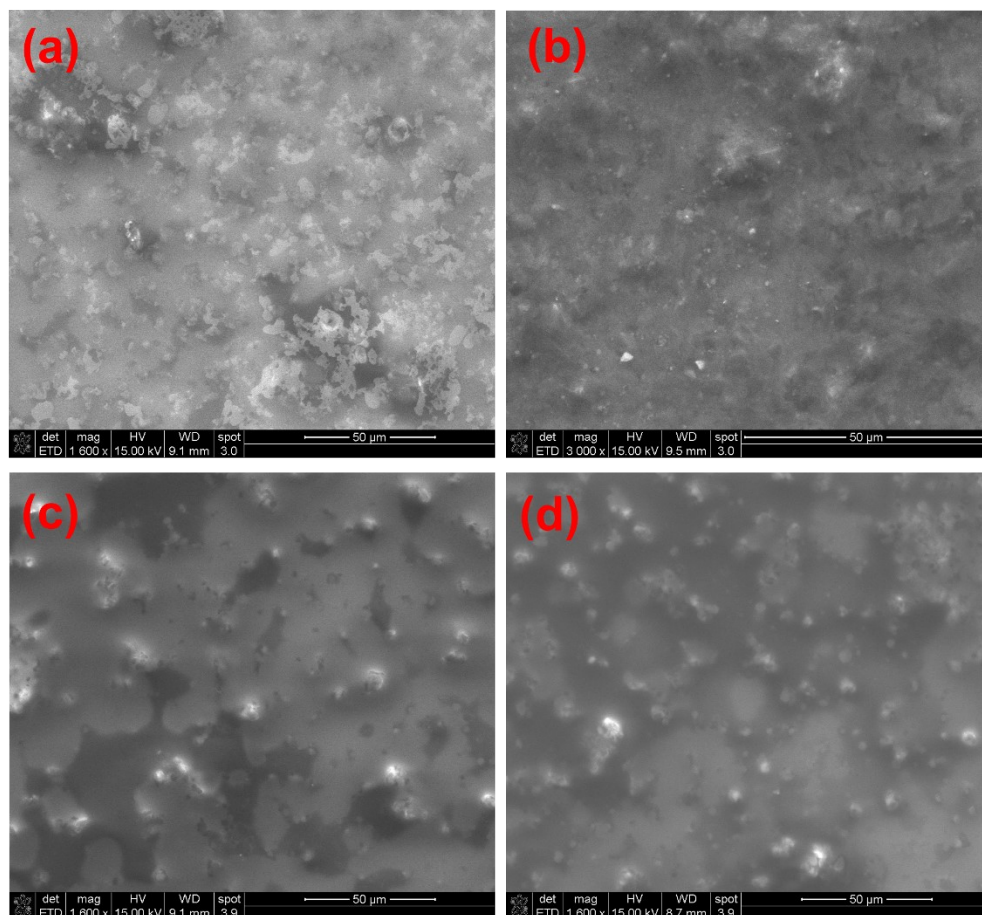


**Figure S4.** <sup>1</sup>H NMR of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions (a) *n*-BA/1-octene/Cu<sup>II</sup>/TPT/EBiB/BAPO = 100/100/0.1/0.6/1/1.



**Figure S5.** <sup>1</sup>H NMR of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions (a) *n*-BA/1-octene/Cu<sup>II</sup>/PMDETA/EBiB/BAPO = 100/100/0.1/0.1/1/1.

### 3. Scanning electron micrograph (SEM) analysis



**Figure S6.** SEM images of poly(*n*-BA-co-1-octene) synthesized at the reaction conditions **(a)** *n*-BA/1-octene/Cu<sup>II</sup>/PMDETA/EBiB/BAPO = 100/100/0.1/0.6/1/1, **(b)** *n*-BA/1-octene/Cu<sup>II</sup>/PMDETA/EBiB/BAPO = 100/100/0.01/0.06/1/1, **(c)** *n*-BA/1-octene/Cu<sup>II</sup>/Tren/EBiB/BAPO = 100/100/0.1/0.6/1/1, and **(d)** *n*-BA/1-octene/Cu<sup>II</sup>/TPT/EBiB/BAPO = 100/100/0.1/0.6/1/1.

### References

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