## Lipoates as Building Blocks of Sulfur-Containing Branched Macromolecules

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# **Supporting information**

### 1. Copolymerization of LpA and EA

AIBN (0.005 g, 3.29×10<sup>-5</sup> mol), LpA (0.678 g, 3.29×10<sup>-3</sup> mol), and EA (0.35 mL, 3.29×10<sup>-3</sup> mol) were dissolved in DMAc (2 mL) in a reaction tube, to which a magnetic stir bar had been inserted. Benzonitrile (0.05 mL) was added as internal standard for calculation of conversion by <sup>1</sup>H NMR spectroscopy, the tube was capped with a rubber septum, immersed in an ice bath, and the mixture was purged with nitrogen for 30 min. The reaction tube was then transferred into an oil bath preheated to 65 °C to start the polymerization. Samples (ca. 0.02 mL) were periodically withdrawn with a nitrogen-purged syringe to monitor the monomer conversion and the apparent molecular weights and molecular weight distributions of the polymers. The rates of consumption of the two comonomers (Figure S1) were very close. After 20 h, the reaction mixture was dialyzed using a membrane with cutoff molar mass of 2,000 Da against methanol for 2 days, during which period the solvent was regularly decanted and replaced by a fresh solvent. The solvent from the polymer solution was removed on a rotary evaporator to yield the final copolymer poly(LpA-*co*-EA) (0.436 g). As expected from the polymerization kinetics and based on NMR analysis (Figure S2), the copolymer contained 50 mol % of each repeat unit.



Figure S1. Kinetics of radical copolymerization of LpA and EA initiated by AIBN at 65 °C in DMAc.

#### 2. Methylation of poly(LpA-co-EA)

Poly(LpA-*co*-EA) (0.436 g, ca. 1.43 mmol of carboxylic acid groups from LpA) was dissolved in a mixture of THF (2 mL) and methanol (2 mL) in a reaction tube equipped with a magnetic stir bar. Solution of TMSDAM (2 M in ether, 2.1 mL, 4.20 mmol) was added to the solution dropwise. Bubbles (N<sub>2</sub>) appeared during the addition of TMSDAM and the color of the final solution was yellow. The reaction mixture was stirred overnight (ca. 12 h). The solvents were then removed on a rotary evaporator to yield the product poly(MLp-*co*-EA) (0.452 g). The polymer was analyzed by <sup>1</sup>H NMR spectroscopy (in acetone-d<sub>6</sub>), which revealed that the ratio of the integrals of protons a\*, b\*, and c\* was 1.0 : 1.0 : 1.5, indicating that the methylation of the carboxylate groups was complete (the ratio of the integrals of protons a and b in the starting material was 1.0 : 1.0).



Figure S2. Methylation of poly(LpA-co-EA) to poly(MLp-co-EA)

#### 3. Reductive degradation of poly(MLp-co-EA)

The copolymer poly(MLp-*co*-EA) (ca. 5 mg) was dissolved in THF (1 mL) and analyzed by SEC. Following that,  $Bu_3P$  (20  $\Box$ L) was added to the SEC vial, the mixture was shaken at r.t., and analyzed again by SEC after 2 h and after 10 h (Figure S3).



**Figure S3.** SEC traces of poly(MLp-*co*-EA) (solid line) and the products of its reductive degradation in the presence of Bu<sub>3</sub>P in THF at r.t. after 2 h (dashed line) and after 10 h (dotted line).

### 4. Reaction between EA and Bu<sub>3</sub>P

The reaction between EA (6.6 mg,  $6.6 \times 10^{-5}$  mol) and Bu<sub>3</sub>P (0.03 mL,  $1.3 \times 10^{-4}$  mol) was carried out in CDCl<sub>3</sub> (0.5 mL) in an NMR tube at r.t. First, the spectrum of EA was collected, then Bu<sub>3</sub>P was added, the mixture was vigorously shaken, and the timer was started. The first NMR spectrum of the reaction mixture was collected in 5 min, and a second one was collected after 1 h. Within 5 min, the acrylate was completely consumed (Figure S4).



Figure S4. Reaction between EA and Bu<sub>3</sub>P in CDCl<sub>3</sub> at r.t.