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Supporting Information

Filling Polymersomes with Polymers by Peroxidase-Catalyzed Atom Transfer Radical Polymerization

Maria Valentina Dinu[1], Mariana Spulber[1], Kasper Renggli, Dalin Wu, Christophe A. Monnier, Alke Petri-Fink, Nico Bruns*

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Dr. M. V. Dinu, Dr. M. Spulber, Dr. K. Renggli, D. Wu, Prof. N. Bruns
Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

Dr. K. Renggli
Department of Biological Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139, USA

C. A. Monnier, Prof. A. Petri-Fink, Prof. N. Bruns
Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland
E-mail: nico.bruns@unifr.ch

[1]These authors contributed equally to this work.

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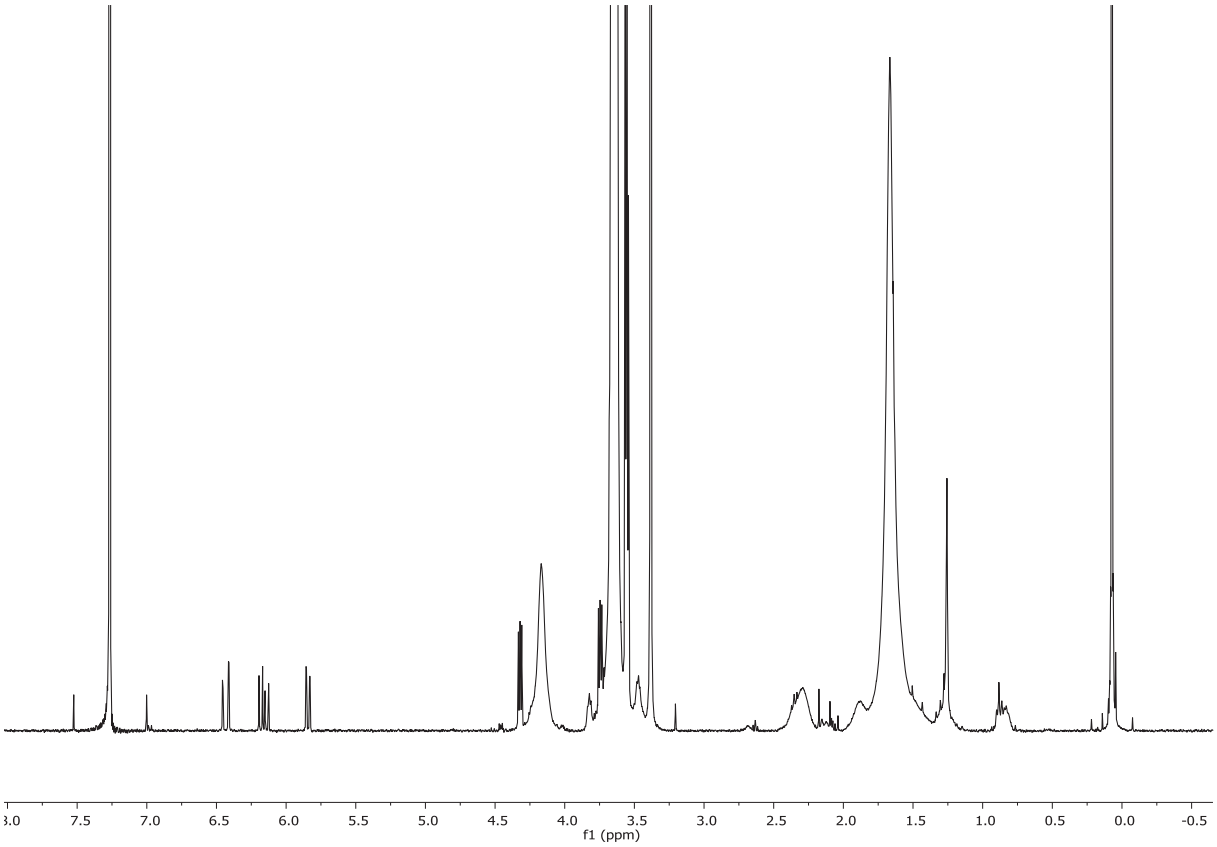

Figure S1. ^{1}H-NMR spectrum of poly(PEGA) synthesized by HRP in PP-OH-photopermeabilized PDMS-*b*-PMOXA polymersomes before purification by SEC. The spectrum of the reaction mixture was used to determine the conversion of the polymerization.

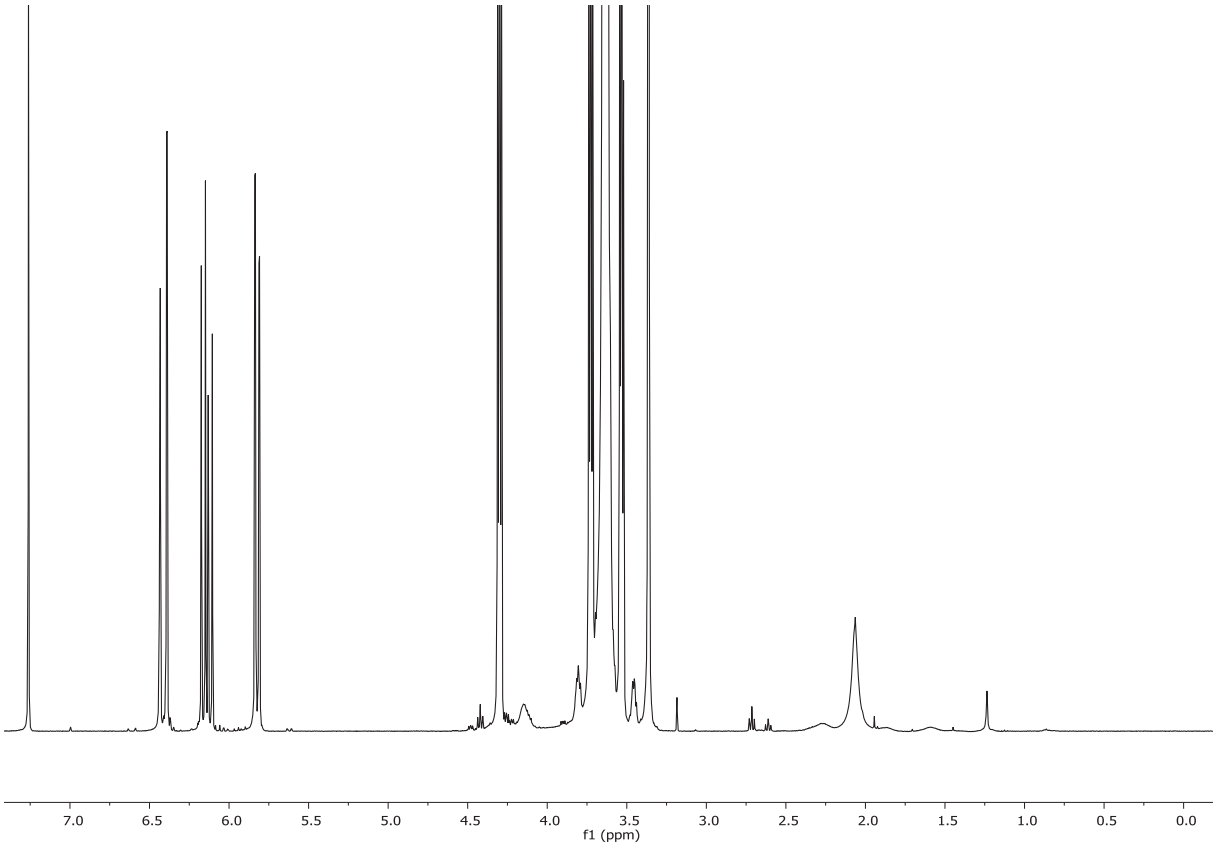

Figure S2. ^{1}H-NMR spectrum of poly(PEGA) synthesized by free HRP before purification by SEC. The spectrum of the reaction mixture was used to determine the conversion of the polymerization.

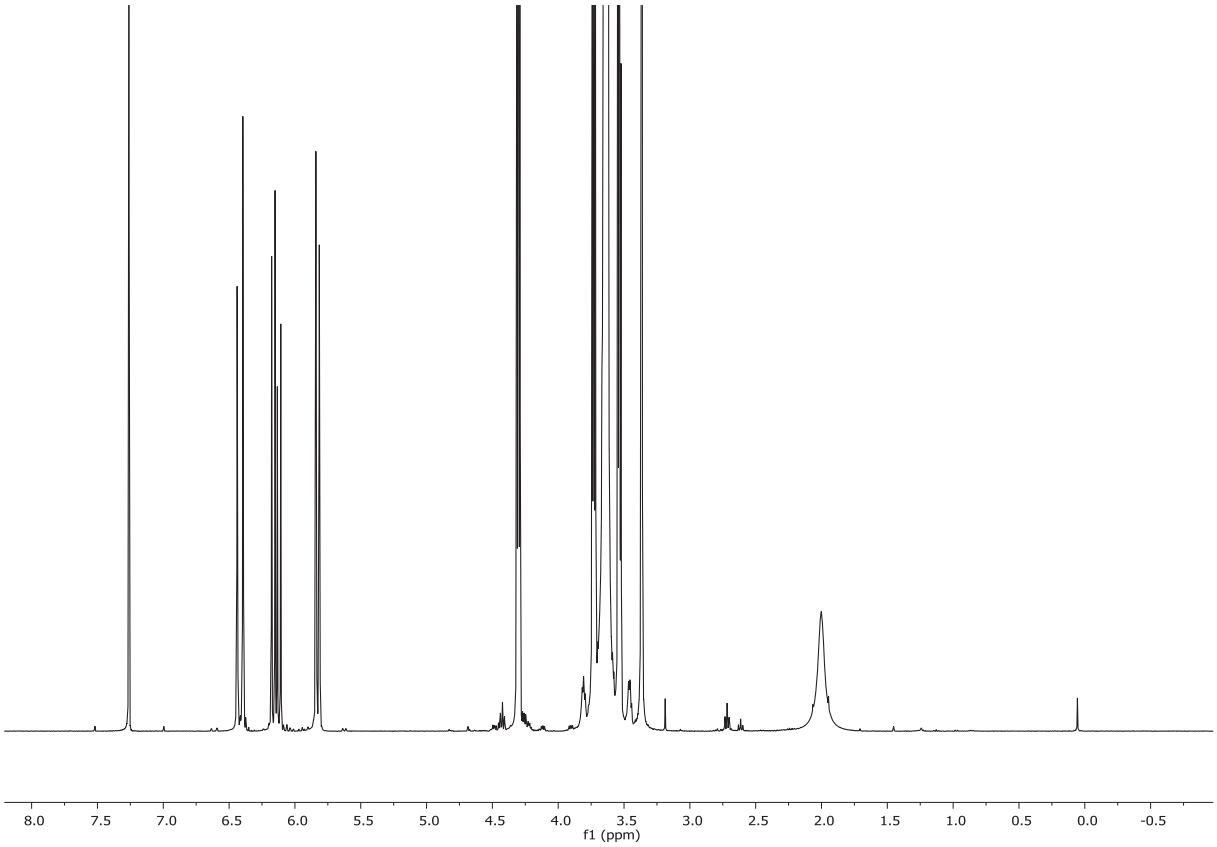

Figure S3. ^{1}H-NMR spectrum of PEGA polymerization with HRP-loaded PDMS-*b*-PMOXA polymersomes that had not been photoreacted with PP-OH. The spectrum of the reaction mixture shows that no conversion occurred when polymersomes were not permeabilized with PP-OH.

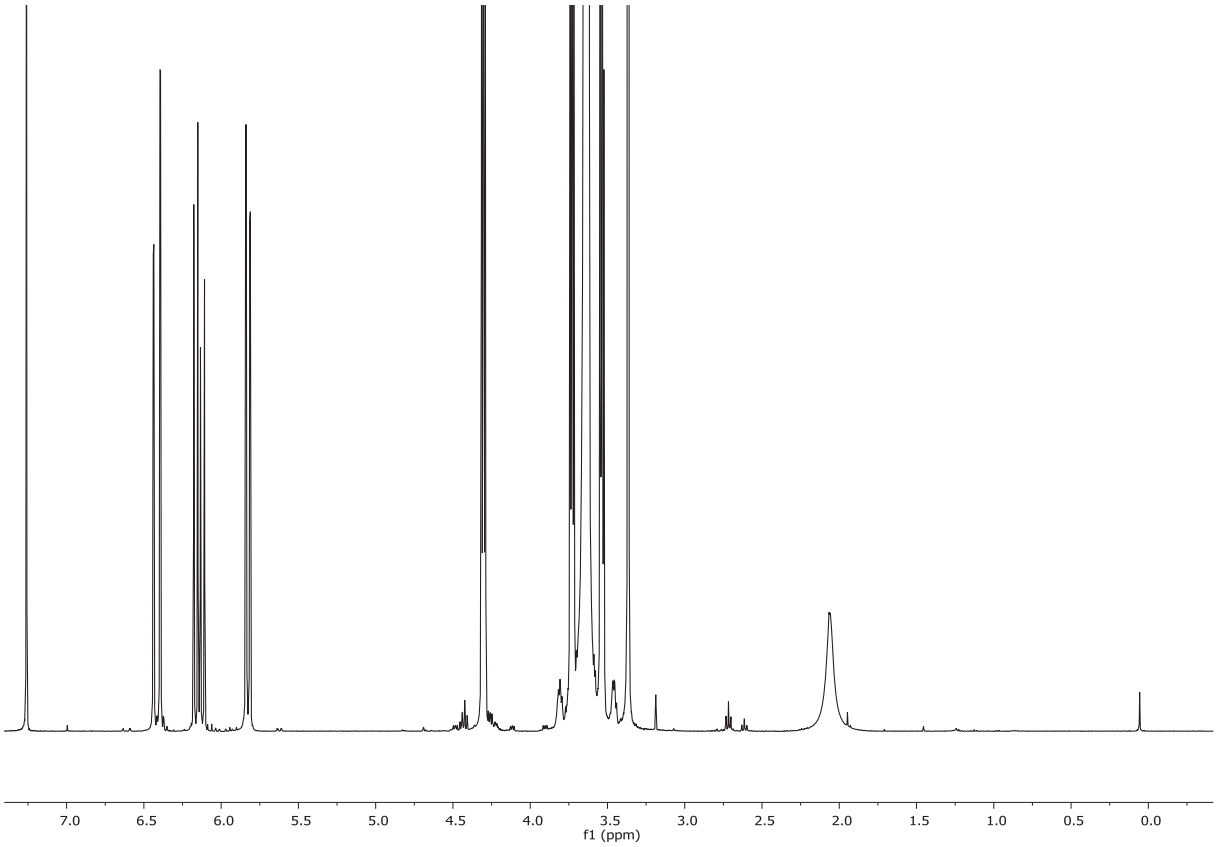

Figure S4. ^{1}H-NMR spectrum of a control reaction in which PEGA was exposed to PP-OH-photopermeablized PDMS-*b*-PMOXA polymersomes that did not contain enzyme. The spectrum of the reaction mixture shows that no conversion occurred when polymersomes lacked HRP.

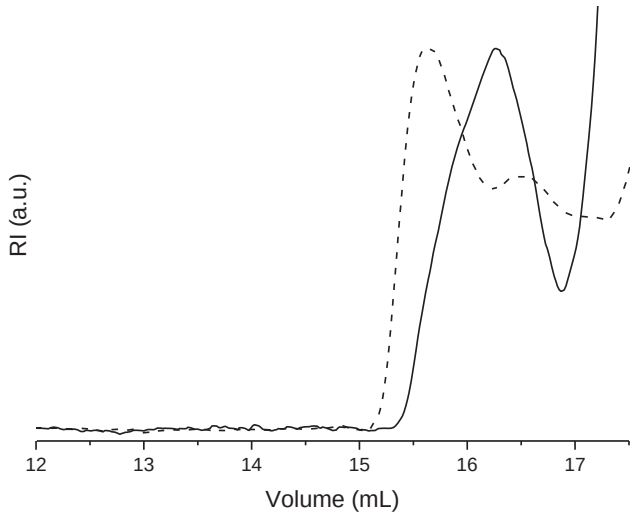

Figure S5. GPC elugrams. (- - -) poly(PEGA) obtained by HRP-catalyzed PEGA polymerization in PP-OH-photopermeabilized PDMS-*b*-PMOXA polymersomes; (——) poly(PEGA) synthesized by free HRP. At an elution volume of > 17 mL the monomer and small molecular weight compounds elute.

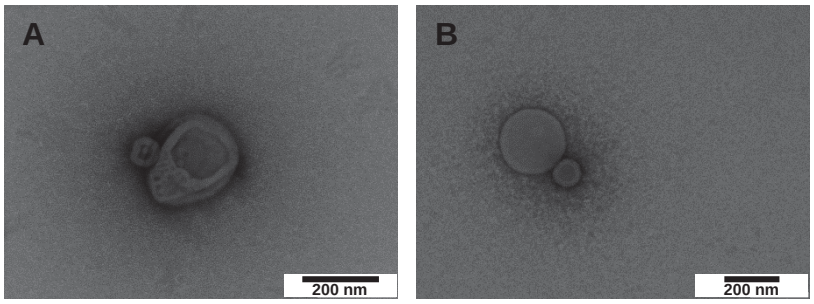

Figure S6. A and B) Additional TEM micrographs of poly(PEGA)-filled polymersomes obtained by HRP-catalyzed ATRP within photo-permeabilized PMOXA-*b*-PDMS polymersomes.

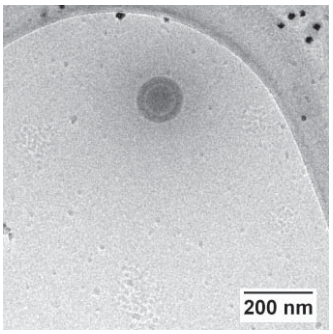

Figure S7. Additional cryo-TEM micrograph of a poly(PEGA)-filled polymersome obtained by HRP-catalyzed ATRP within photo-permeabilized PMOXA-*b*-PDMS polymersomes.