Polymer Chemistry

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ARTICLE

Scalable Synthesis and Derivation of Functional Polyesters Bearing Ene and Epoxide Side Chains

Cite this: DOI: 10.1039/xoxxoooooox

Yunfeng Yan and Daniel J. Siegwart*

The University of Texas Southwestern Medical Center
Simmons Comprehensive Cancer Center
Department of Biochemistry
Dallas, Texas 75390, U.S.A.
E-mail: daniel.siegwart@utsouthwestern.edu

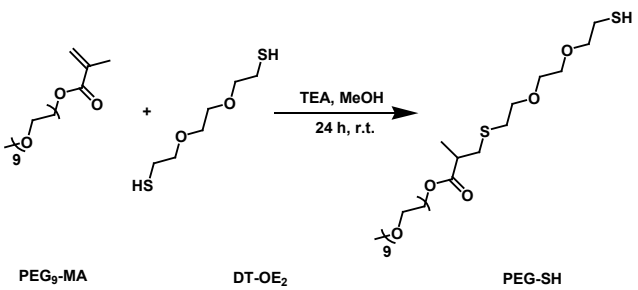
Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Supplementary Information

Preparation of thiol-terminated poly(ethylene glycol) (PEG-SH). PEG-SH was synthesized via Michael addition of PEG methylacrylate (PEG_9-MA) and 2,2'-(ethylenedioxy)diethanethiol ($DT\text{-}OE_2$) in methanol with triethylamine (TEA) as catalyst at room temperature (**Scheme S1**). 40 mmol of $DT\text{-}OE_2$ (6.855 mL) and 40 mmol of TEA (5.6 mL) were added into 50 mL of methanol. After the mixture was purged with N_2 for 5 min, 10 mmol of PEG_9-MA (4.63 mL) was added and the mixture was stirred for 24 h at r.t. under N_2. After evaporation of methanol, the product was purified using flash chromatography (75% toluene/20% acetonitrile/5% methanol, v/v/v) and the structure was verified by ^{1}H NMR (**Figure S1**). 4.5 g of pure PEG-SH was isolated in 65% yield based on one equivalent $DT\text{-}OE_2$.



Scheme S1. Synthesis of PEG-SH via PEG methylacrylate-dithiol addition.

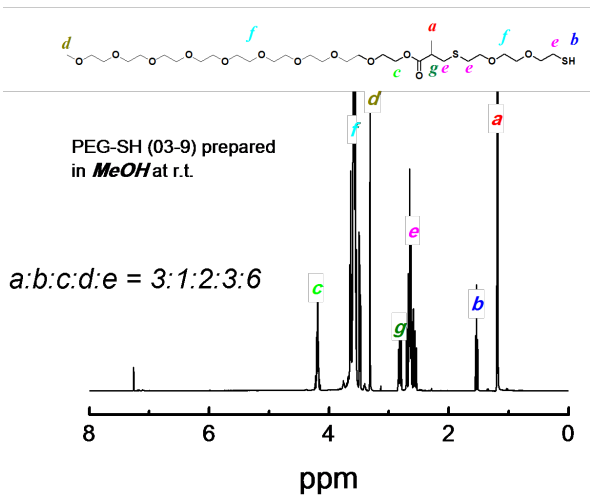


Figure S1. ^{1}H NMR spectrum of PEG-SH in $CDCl_3$.

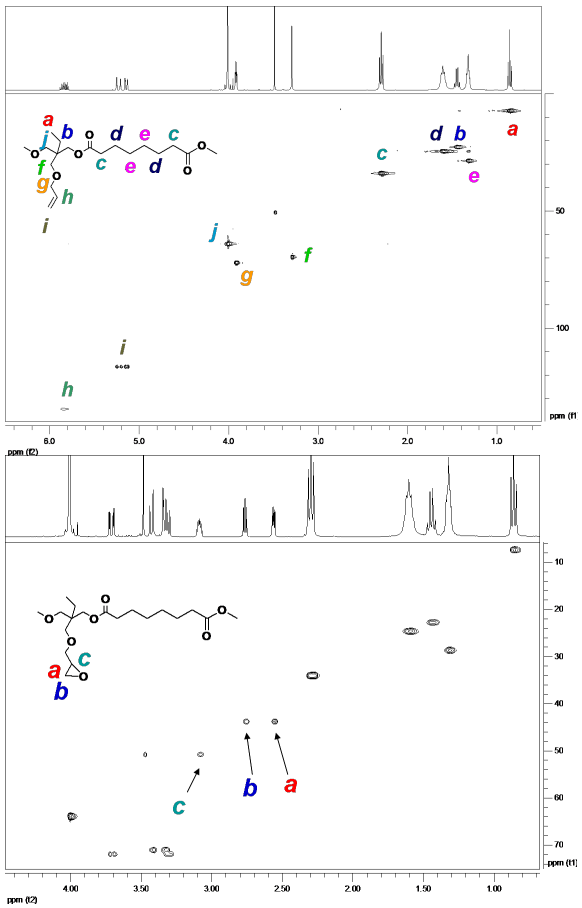


Figure S2. C-H COSY NMR spectra (gHSQCAD) of polyesters before (PE8-2) and after epoxidation (PE8EP) in $CDCl_3$.

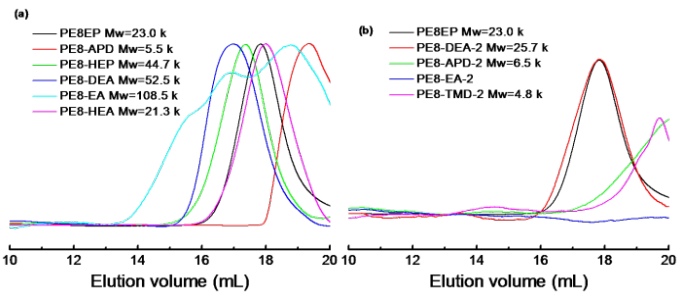


Figure S3. GPC (DMF) curves of modified polyesters via epoxy-amine strategy. (a) Modification at 40 °C for 24 h with 10 equiv. amines; (b) Modification at 55 °C for 2 h with 2 equiv. amines.