**Supporting Information** 

## Synthesis of gradient copolymers by concurrent enzymatic monomer transformation and RAFT polymerization

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**SFig. 1.** Cumulative RMA mole fraction ( $F_{RMA}$ ) as a function of normalized chain length during random copolymerization of HMA and TFEMA.

## **Supporting Data**



**SFig. 2.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of gradient copolymers pHMA-*g*-pTFEMA catalyzed by different concentrations of enzyme after purification.



**SFig. 3.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of gradient copolymers based on different alcohols after purification. [CETPA] = 12.5 mM; [ABVN] = 4.2 mM; [TFEMA]<sub>0</sub> = 1.0 M; [ROH]<sub>0</sub> = 1.0 M

(BzOH and mPEG) or 2.0 M (2-octanol); [TEA] = 1.0 M; [Novozym435] = 8.3 mg/mL in 6.0

mL of toluene at 55 °C.

polymer	$F_{RMA}(\%)$	$\mathbf{M}_{\mathbf{n}}$	PDI	Tg <sup>onset</sup> (°C)
pTFEMA-g-pHMA	56	12800	1.25	21.6
pTFEMA-r-pHMA	60	11500	1.39	39.1
pTFEMA-g-pBzMA	42	8300	1.44	21.5
pTFEMA-r-pBzMA	50	10600	1.22	80.0
pTFEMA-g-pOMA	34	12600	1.22	28.3
pTFEMA-r-pOMA	50	7800	1.32	34.3

STab. 1. Information of gradient and random copolymers