Supporting Information

Hemoglobin and Red Blood Cells Catalyze Atom Transfer Radical Polymerization

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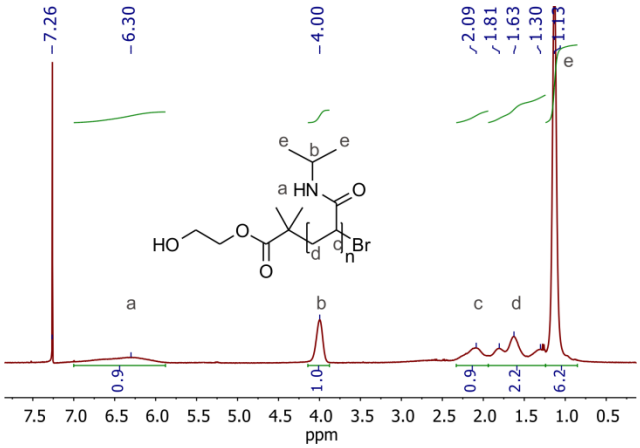

Figure S1. ^{1}H NMR spectrum of a purified PNIPAAm sample obtained from a polymerization catalyzed by native Hb. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ/ppm = 7.00 – 5.88 (bm, n·1H), 4.14 – 3.88 (bm, n·1H), 2.33 – 1.94 (bm, n·1H), 1.94 – 1.24 (bm, n·2H), 1.24 – 0.88 (bm, n·6H).

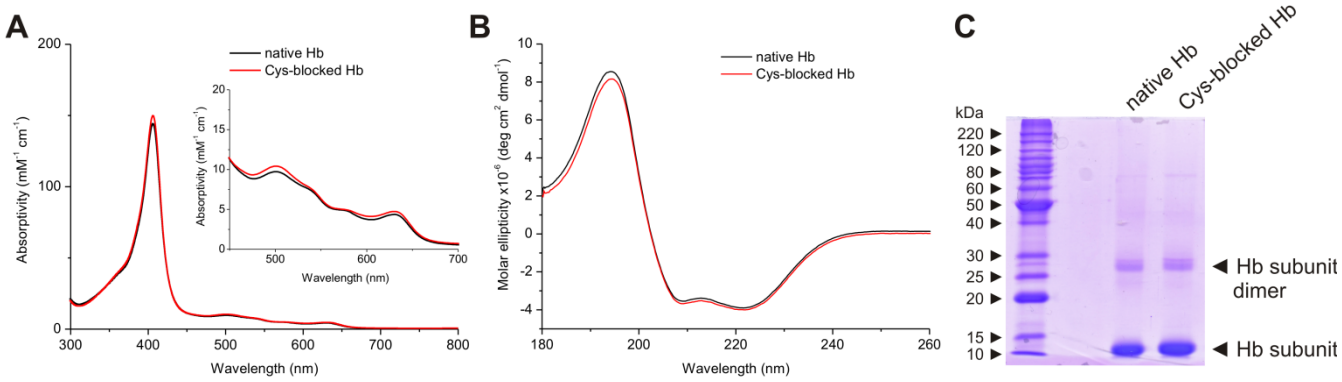

Figure S2. Characterization of native Hb and Cys-blocked Hb. A) UV-Vis spectra, B) circular dichroism spectra, C) SDS gel electrophoresis.

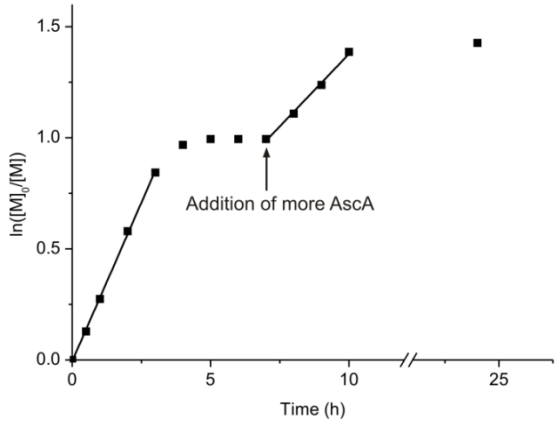

Figure S3. Kinetic plot of a polymerization of NIPAAm catalyzed by Cys-blocked Hb under ARGET ATRP conditions. An additional deoxygenated aliquot of AscA (20 mg dissolved in 2 ml of water) was added to the reaction mixture after 7 h. Initial experimental conditions: Ratio of HEBIB/NIPAAm/AscA/Hb 1:78:1:0.008.

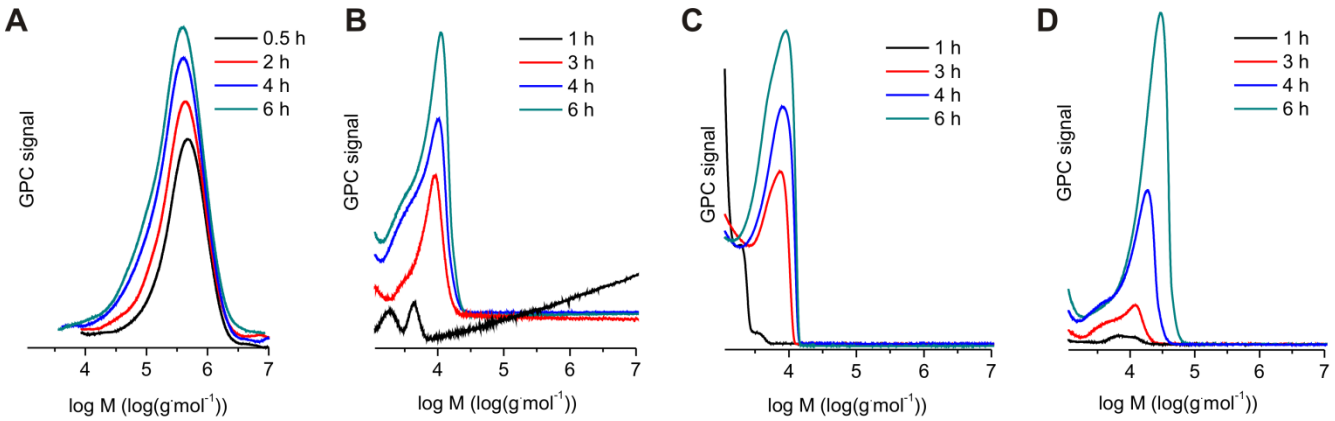

Figure S4. A-C) Selected GPC traces of kinetic experiments reported in the manuscript in Figure 3: (A) NIPAAm, (B) PEGA, (C) PEGMA. D) Selected GPC traces of the kinetic experiment reported in Figure 4. (As monomer and polymer were not separated prior to GPC measurements during kinetic experiments, the non-reacted monomers PEGA and PEGMA give rise to a GPC signal below log M ≈ 3.2).

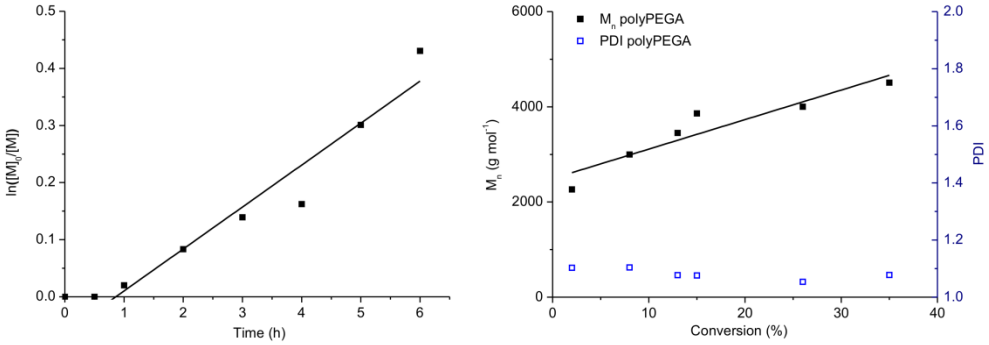

Figure S5. Kinetic investigations of a BPN-initiated polymerization of PEGA catalyzed by Cys-blocked Hb under ARGET ATRP conditions. The kinetic plot, and the evolution of molecular weight and PDI as a function of conversion are shown. Experimental conditions: Ratio of BPN/PEGA/AscA/Hb 1:74:1:0.007.

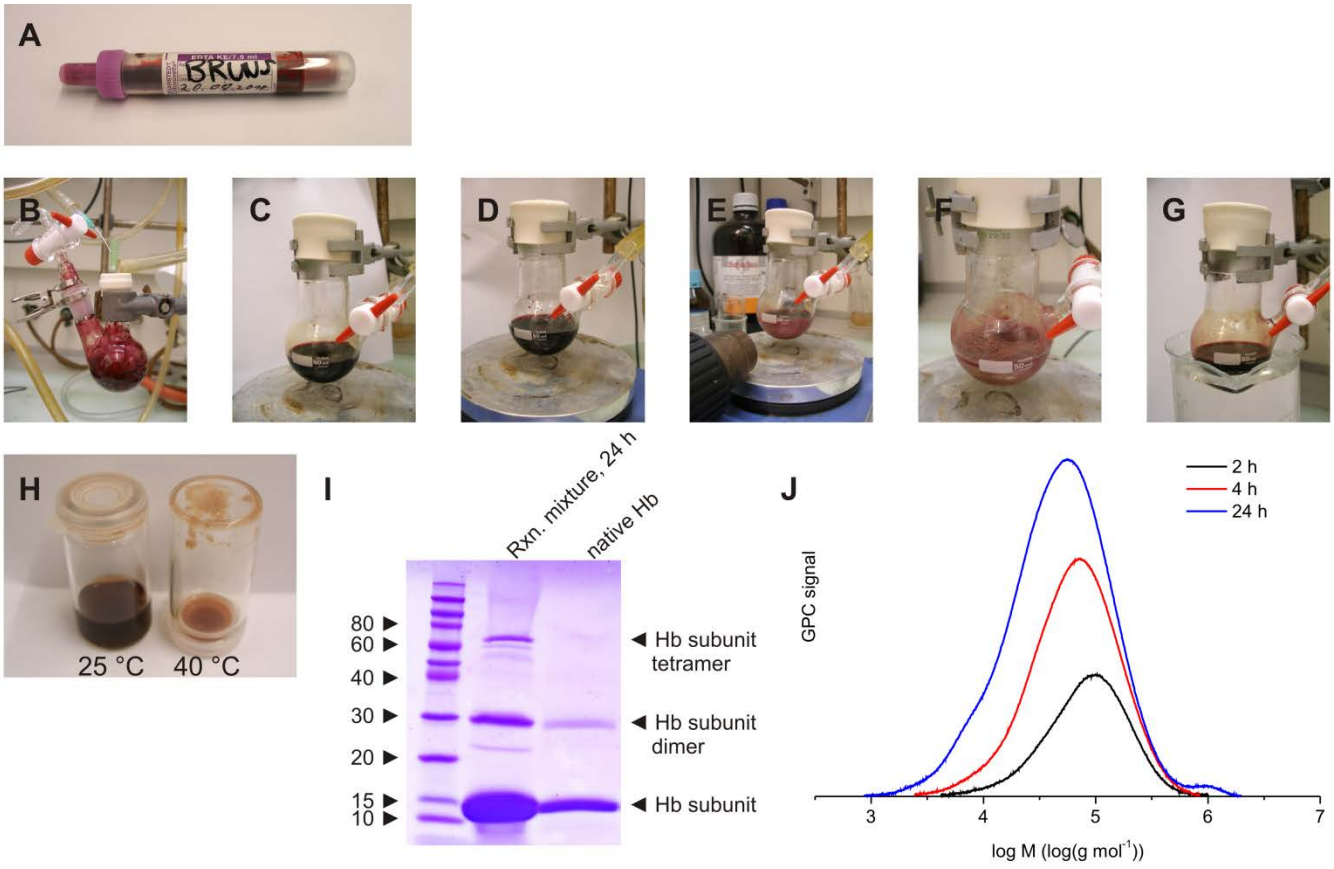

Figure S6. Polymerization of NIPAAm under ARGET ATRP conditions using human erythrocytes as catalyst. A-H) Photographic documentation: A) Fresh sample of erythrocytes from the corresponding author, B) deoxygenation of erythrocytes by purging with argon, C) reaction mixture at the beginning of the polymerization, D) reaction mixture after overnight stirring, E) a precipitate formed upon gentle heating of the reaction mixture, indicating the presence of PNIPAAm, F) precipitate at approx. 40 °C, G) upon cooling to room temperature, the precipitate dissolved, H) reaction mixture after filtration through a plug of neutral aluminium oxide, I) SDS gel electrophoresis of reaction mixture and native Hb, J) evolution of GPC traces during polymerization (t_{rxn} = 2 h: M_n= 55100 g mol^{-1}, PDI = 2.09, conversion= 40%; t_{rxn}=4 h: M_n=39900 g mol^{-1}, PDI = 2.37, conversion= 78%; t_{rxn}=24 h: M_n= 23900 g mol^{1}, PDI = 3.48, conversion= 100%).

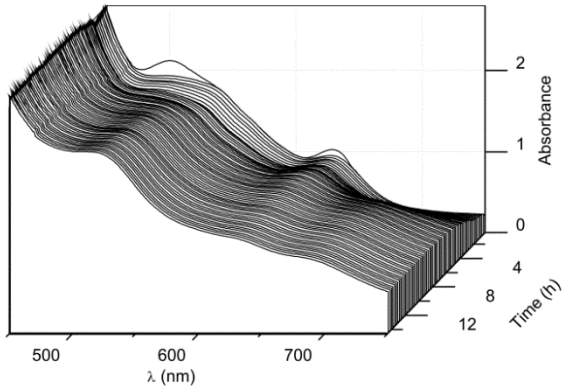

Figure S7. Time dependent Vis spectra of a NIPAAm polymerization catalyzed by Cys-blocked Hb under ARGET ATRP conditions. Experimental conditions: Ratio of HEBIB/NIPAAm/AscA/Hb 1:79:1:0.008. The first spectrum was recorded after the addition of AscA. Spectra were recorded every 4 min.