Supporting Information for

# Oxygen-enriched thermosensitive hydrogel for the relief of hypoxic tumor microenvironment and enhancement of radiotherapy

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## Supplementary Methods

**Micellization of synthesized copolymers in water.** The micellar hydrodynamic diameters ($D_h$) of copolymer solutions at different concnetrations were measured via a laser light scattering instrument (Zetasizer Nano, ZS90, Malvern) with light scattering angle at 90º. The aqueous polymer solutions were filtered with 0.45 μm filters and equilibrated at test temperature for 15 min before testing. Stokes-Einstein equation was employed to calculate the $D_h$s of various polymeric micelles. Microscopic images of micelles in 0.5 wt% copolymer solution were acquired via a transmission electron microscope (TEM, Tecnai G2 20 TWIN, FEI). A drop of solution was added to a copper grid placed on a filter paper and dried at room temperature for 12 h. The images were acquired using TEM with an accelerating voltage of 200 kV.

## Supplementary Results

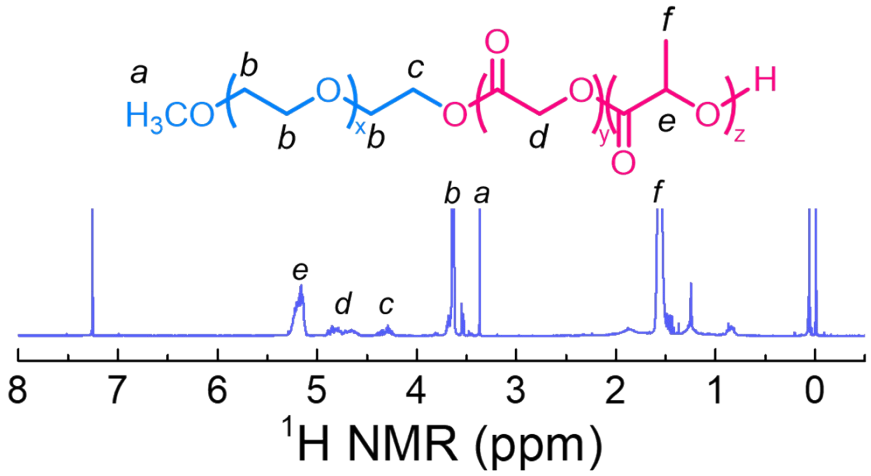


Figure S1. $^{1}$H NMR spectrum of synthesized mPEG-PLGA copolymer.

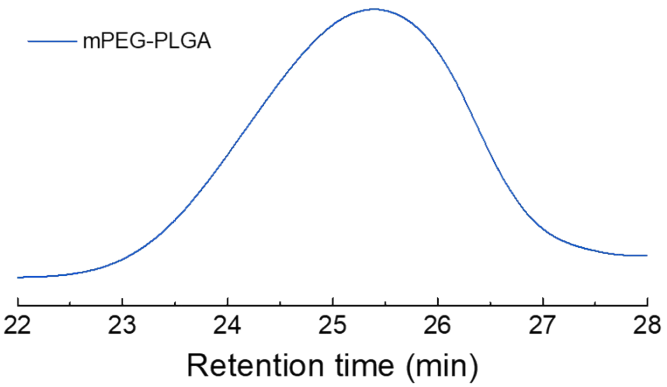


Figure S2. GPC trace of synthesized mPEG-PLGA diblock copolymer.

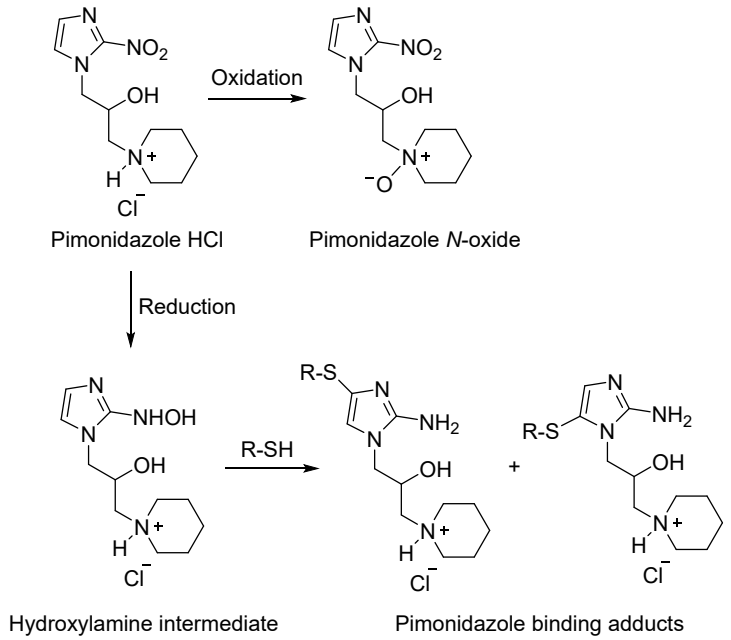


Figure S3. Schematic of action mechanism of hypoxia probe (pimonidazole HCl) *in vivo*. In the presence of adequate oxygen, pimonidazole is oxidized to pimonidazole *N*-oxide, which cannot bind to -SH-containing molecules. In hypoxic cells, pimonidazole is activated via reduction and the reduced pimonidazole forms adducts with thiol groups in proteins, peptides, and amino acids and accumulate in tissue.

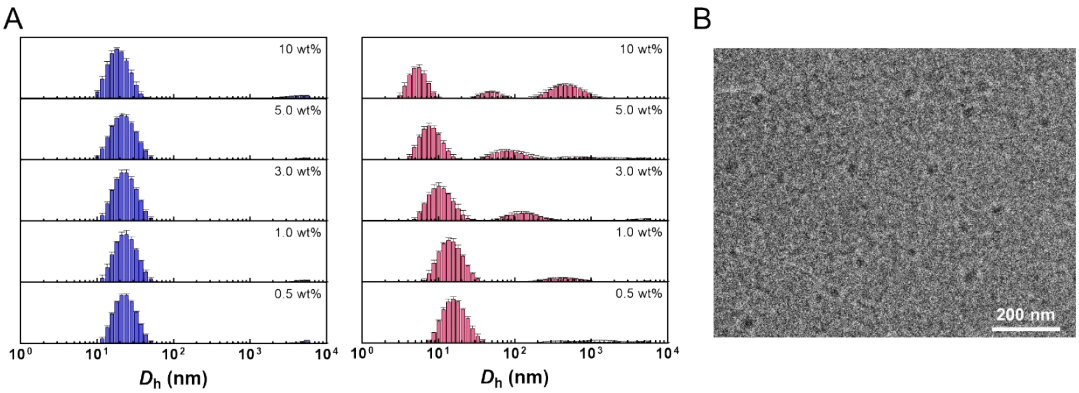


Figure S4. The sizes and distributions of polymeric micelles. (A) The micelle sizes and distributions of mPEG-PLGA copolymer solution (blue) and mPEG-PLGA-PFOA copolymer solution (red) in a series of concentrations detected by DLS at 25 ℃. (B) Typical TEM image of micelles in 0.5 wt% mPEG-PLGA-PFOA aqueous solution at room temperature.

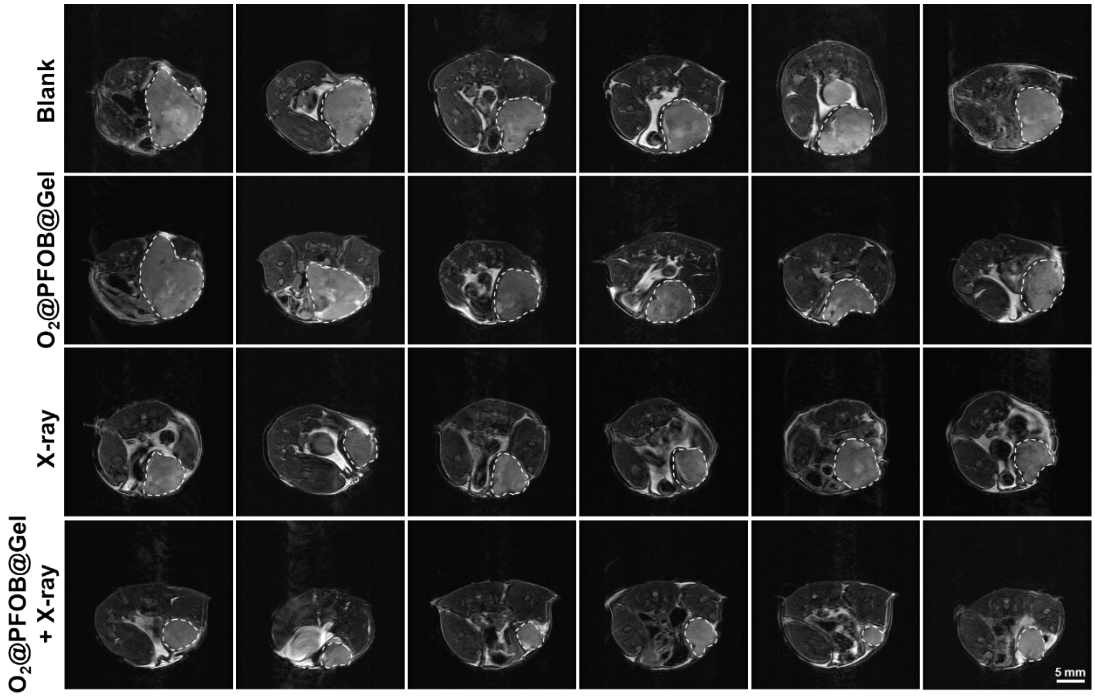


Figure S5. The maximum MRI cross-sectional images of all tumors in each group on day 16. The tumors were marked with white dashed circles.