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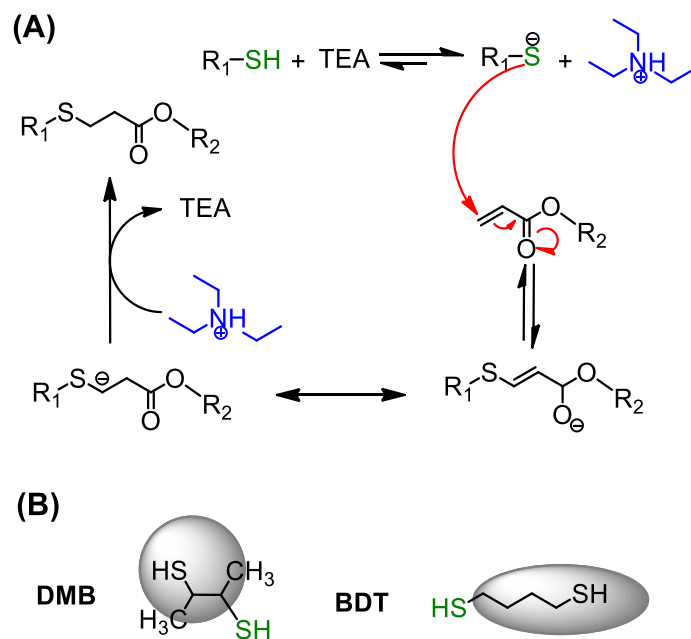
Polymerization kinetics, oxidation-responsiveness, and the in vitro anticancer efficacy of poly(ester-thioether)s

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Scheme S1 (A) The proposed mechanism of the thiol-Michael addition reaction catalyzed by TEA. Only one thiol group in the dithiol monomer was involved in the reaction for clarity. (B) The chemical structures of DMB and BDT and their steric hindrances for nucleophilic addition.

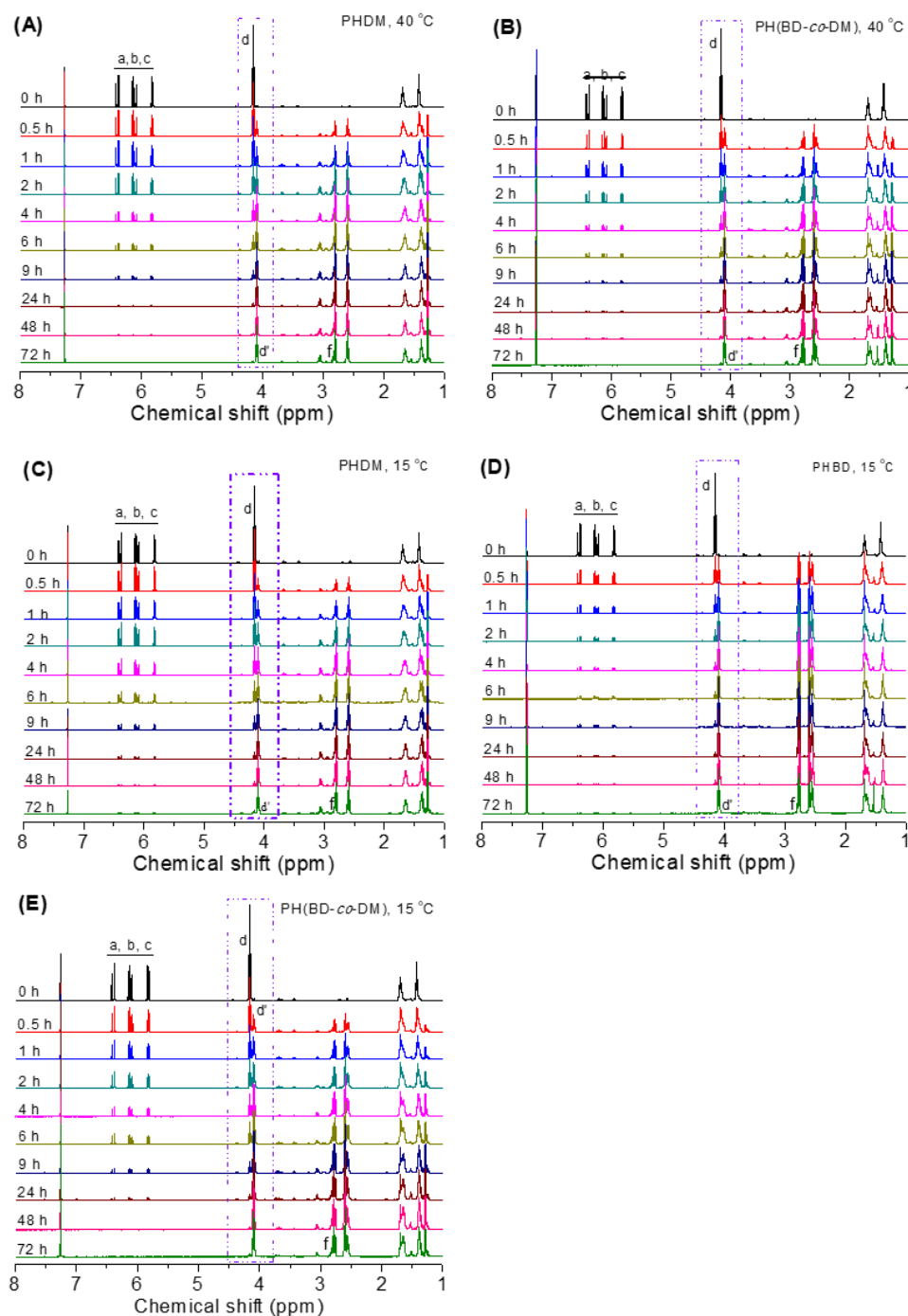
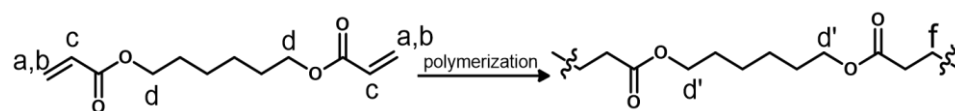


Fig. S1 The polymerization kinetics of poly(ester-thioether)s at 40 °C (A and B) and 15 °C (C, D, and E). The scheme shows the characteristic protons used for calculation of HDA conversion.

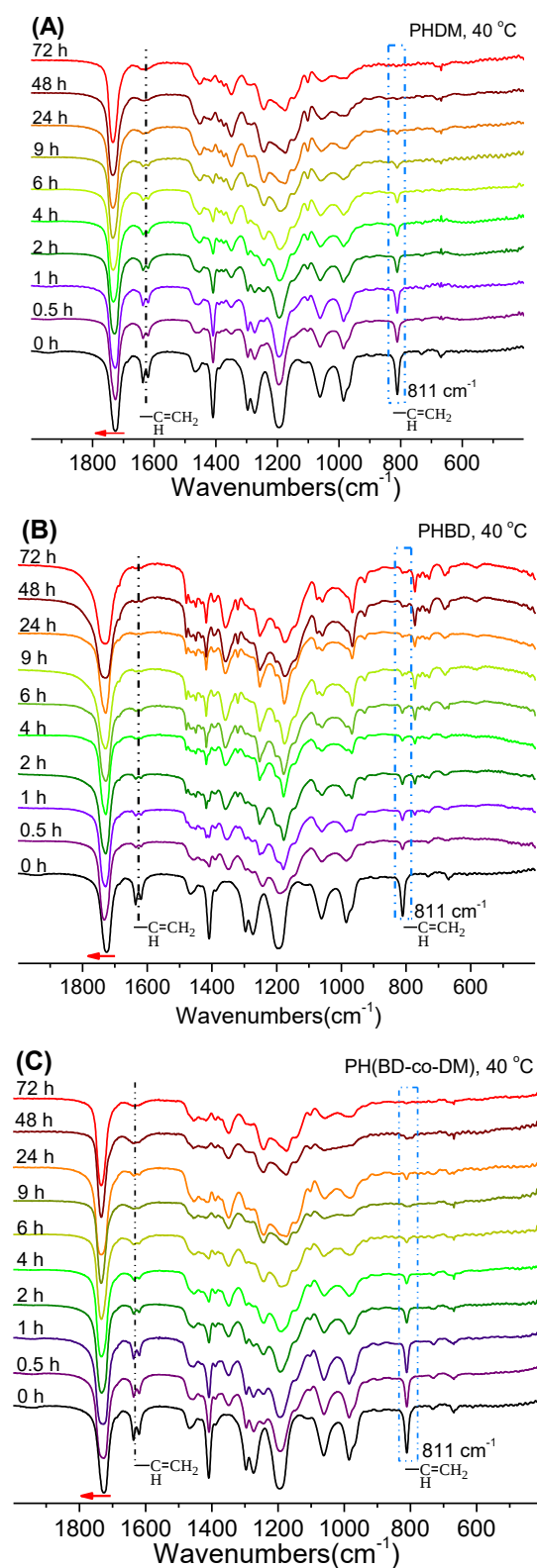


Fig. S2 The polymerization kinetics study of poly(ester-thioether)s at 40 °C by FTIR.

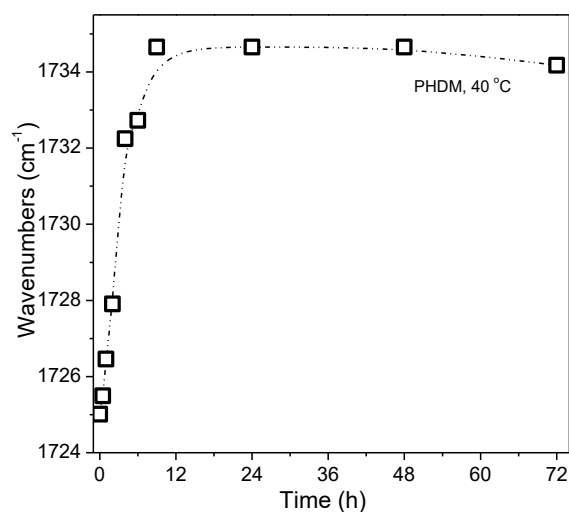


Fig. S3 Change of characteristic absorption band of carbonyl groups in HDA in the polymerization of PHDM at 40 °C.

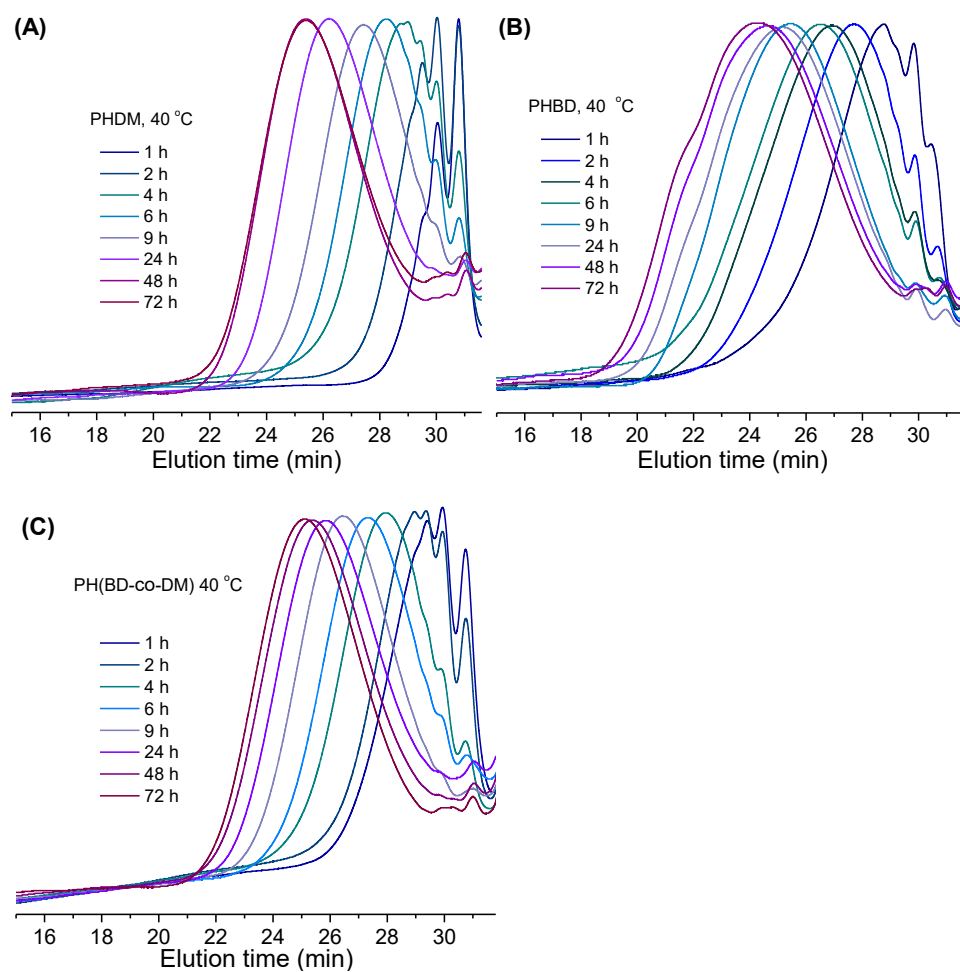


Fig. S4 The polymerization kinetics study of poly(ester-thioether)s at 40 °C by GPC.

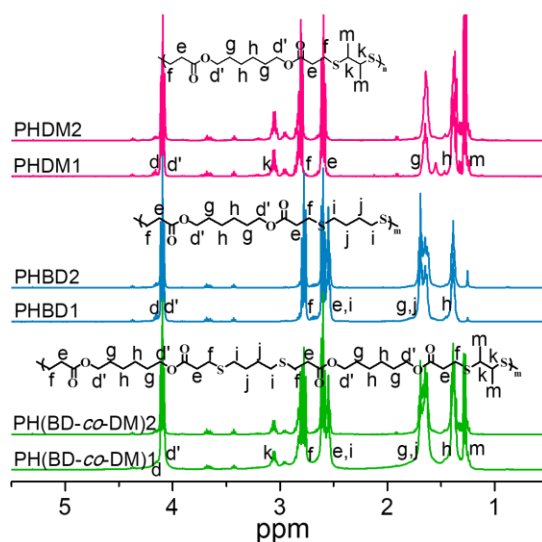


Fig. S5 ^1H NMR spectra of PHDMs, PHBDs, and PH(BD-co-DM)s in CDCl_3 .

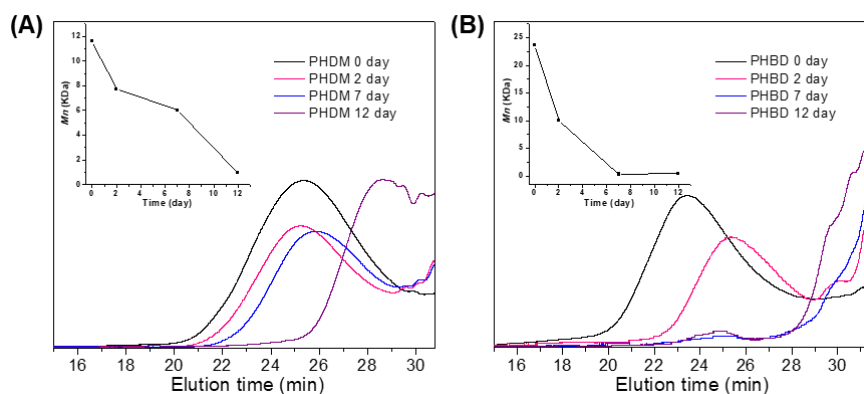


Fig. S6 Degradation of PHDM and PHBD studied by GPC.

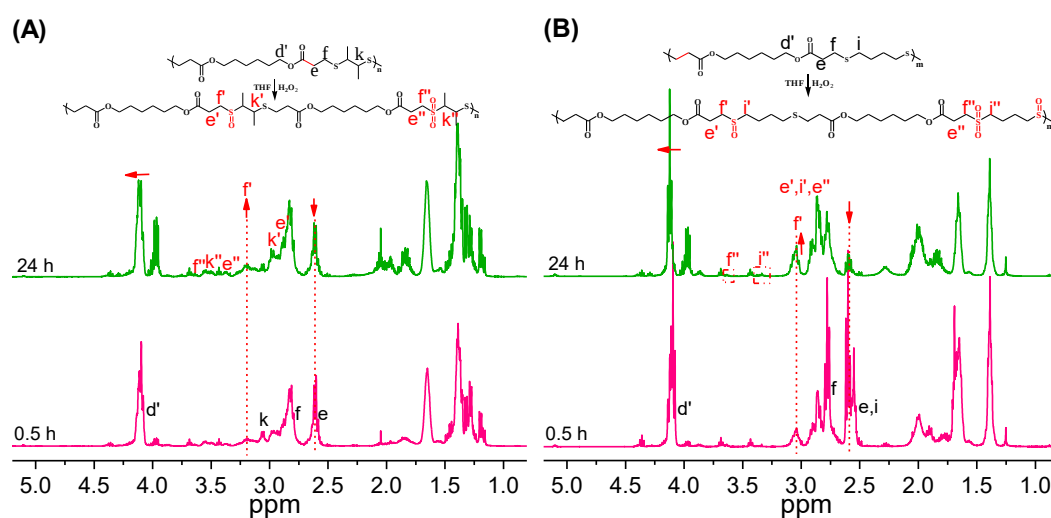


Fig. S7 ^1H NMR spectra of PHDM (A) and PHBD (B) treated with 0.05 M H_2O_2 for 0.5 and 24 h in THF.

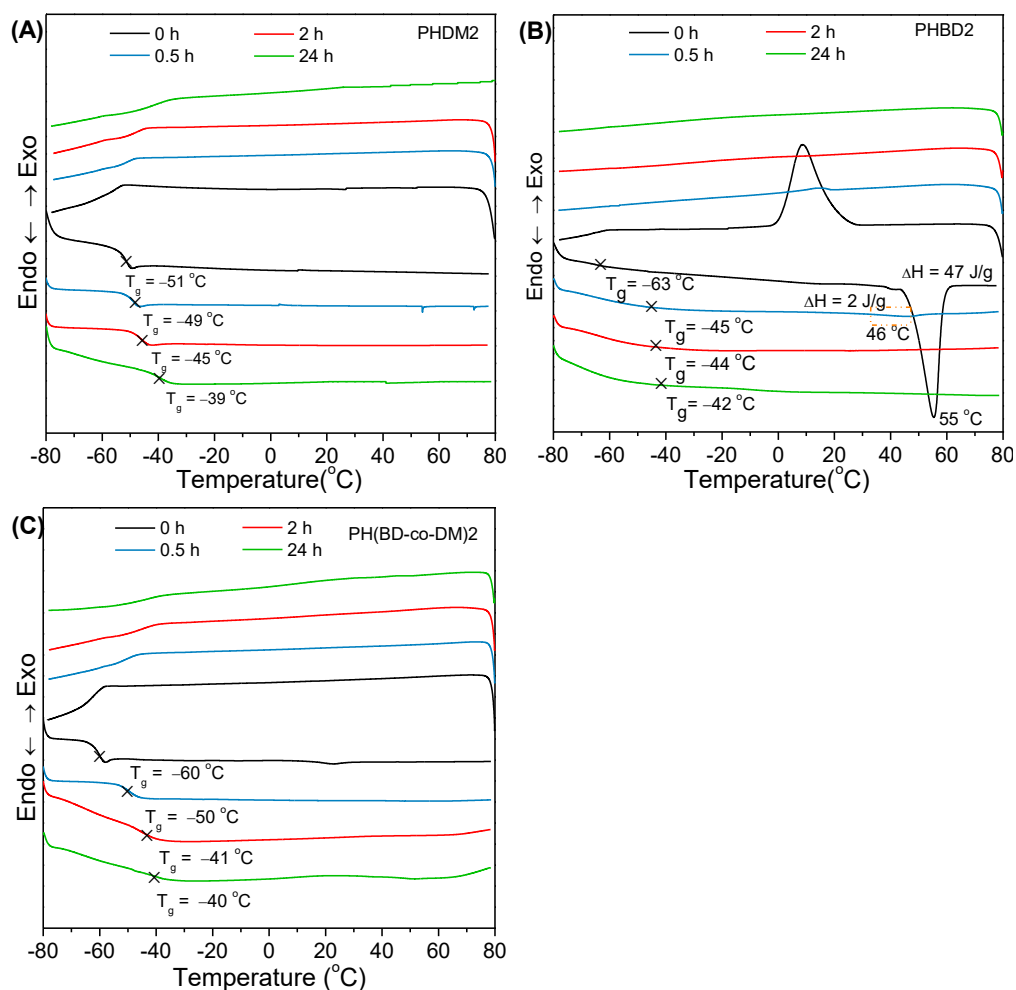


Fig. S8 DSC thermograms of PHDM2 (A), PHBD2 (B) and PH(BD-co-DM)2 (C) before and after oxidation by 0.1 M H_2O_2 in THF for different incubation times at 37 °C.

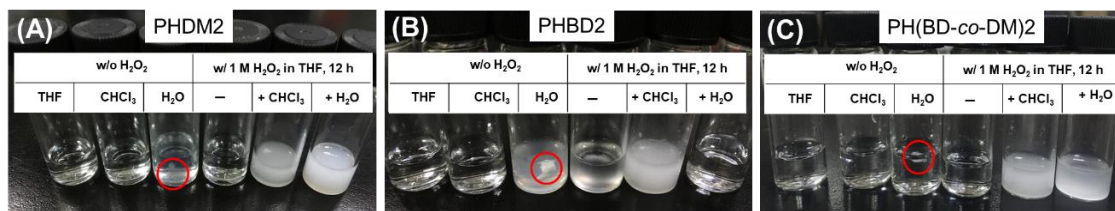


Fig. S9 Images of poly(ester-thioether)s in organic solvents or their mixed solvents before and after oxidation by 1 M H_2O_2 in THF.

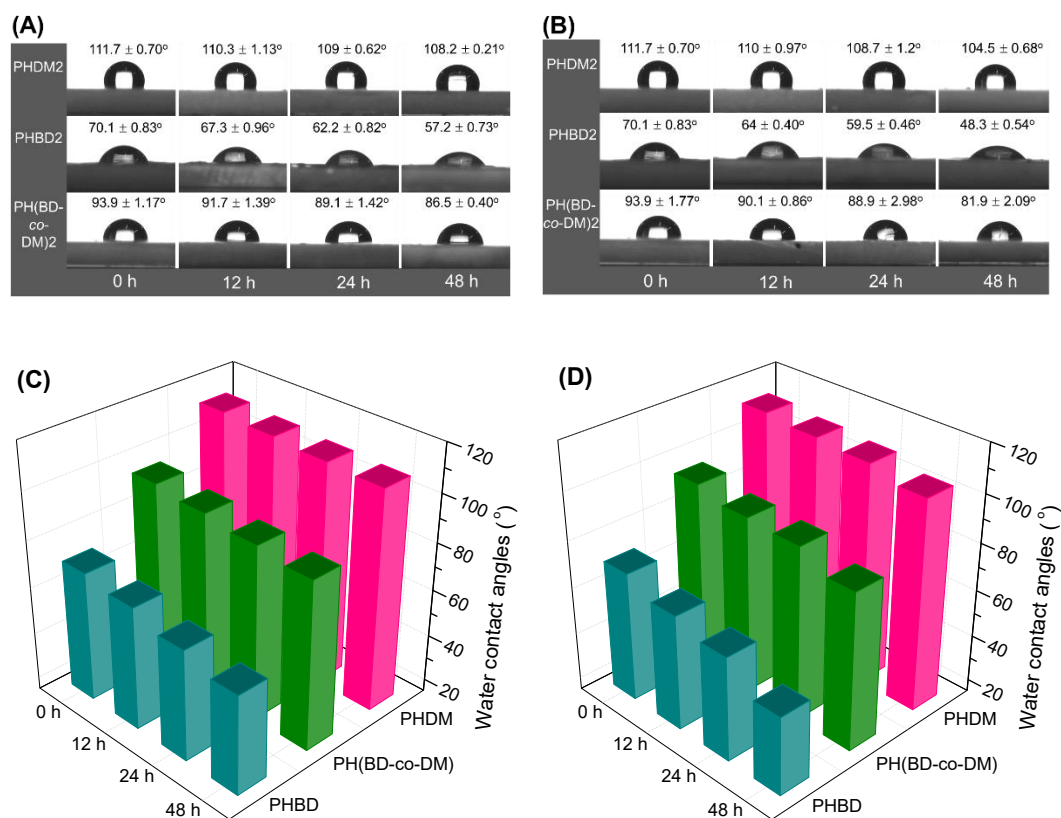


Fig. S10 The contact angles of poly(ester-thioether)s' films before and after H₂O₂ treatment (A, C: 0.1 M H₂O₂; B, D: 0.5 M H₂O₂) for different times.

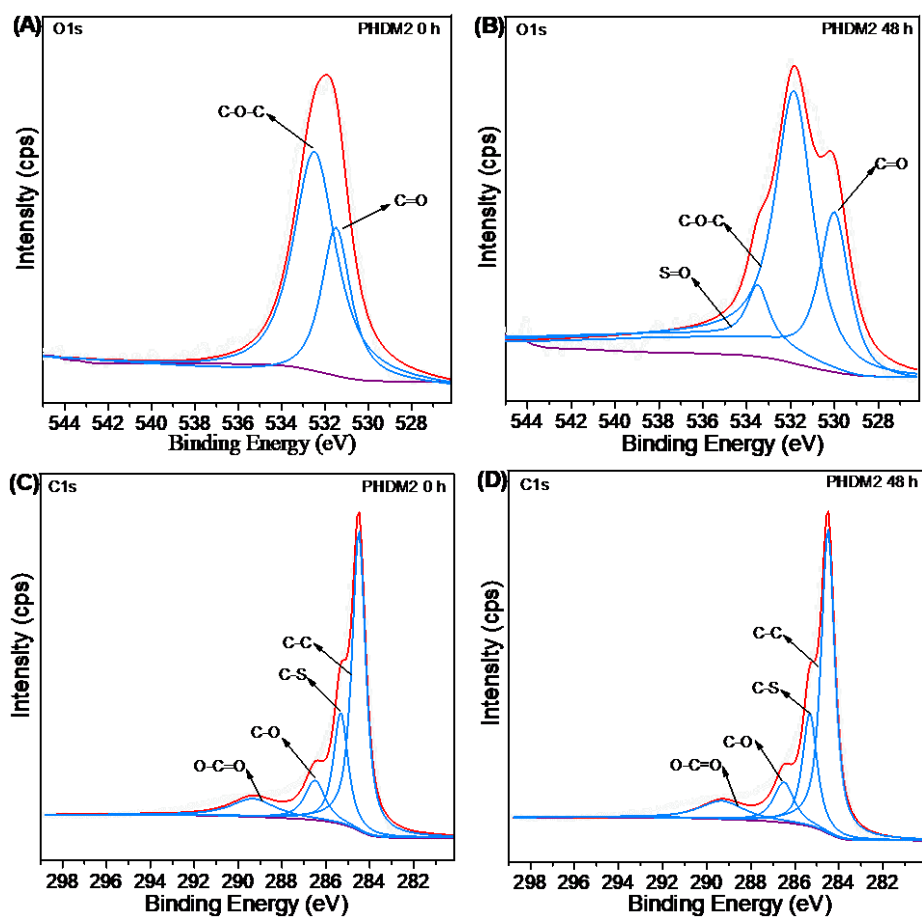


Fig. S11 O1s (A, B) and C1s (C, D) XPS spectra of PHDM2 films after oxidation by 1 M H₂O₂ for 0 and 48 h.

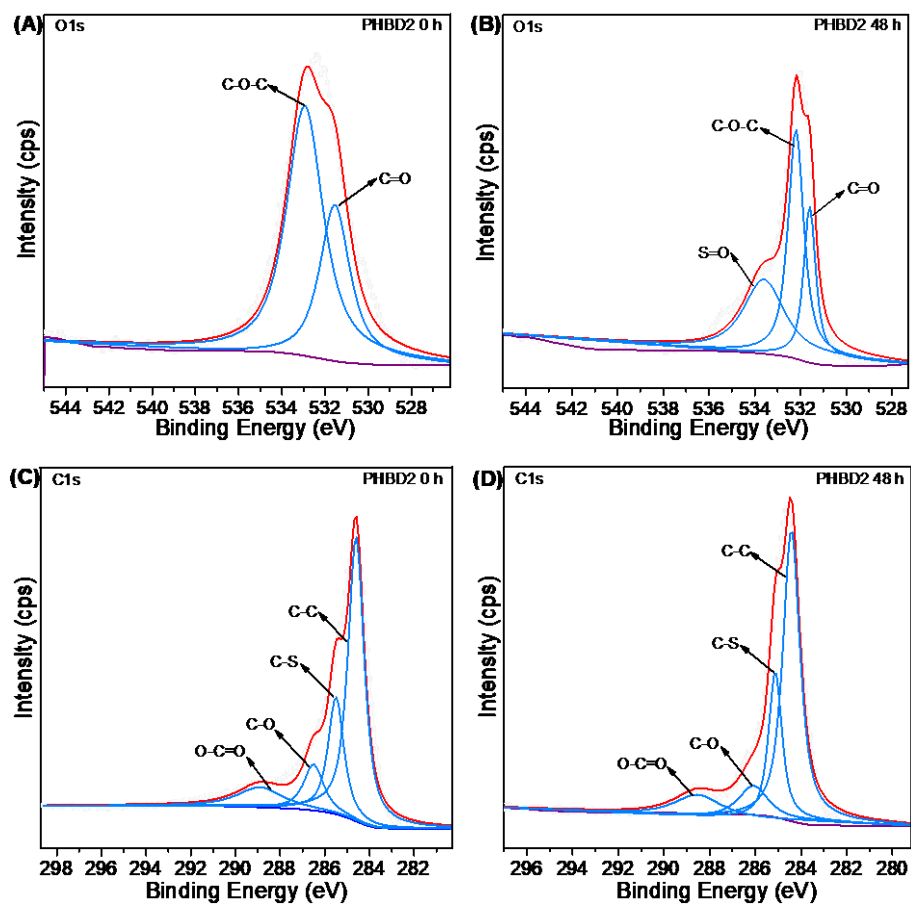


Fig. S12 O1s (A, B) and C1s (C, D) XPS spectra of PHBD2 films after oxidization by 1 M H₂O₂ for 0 and 48 h.

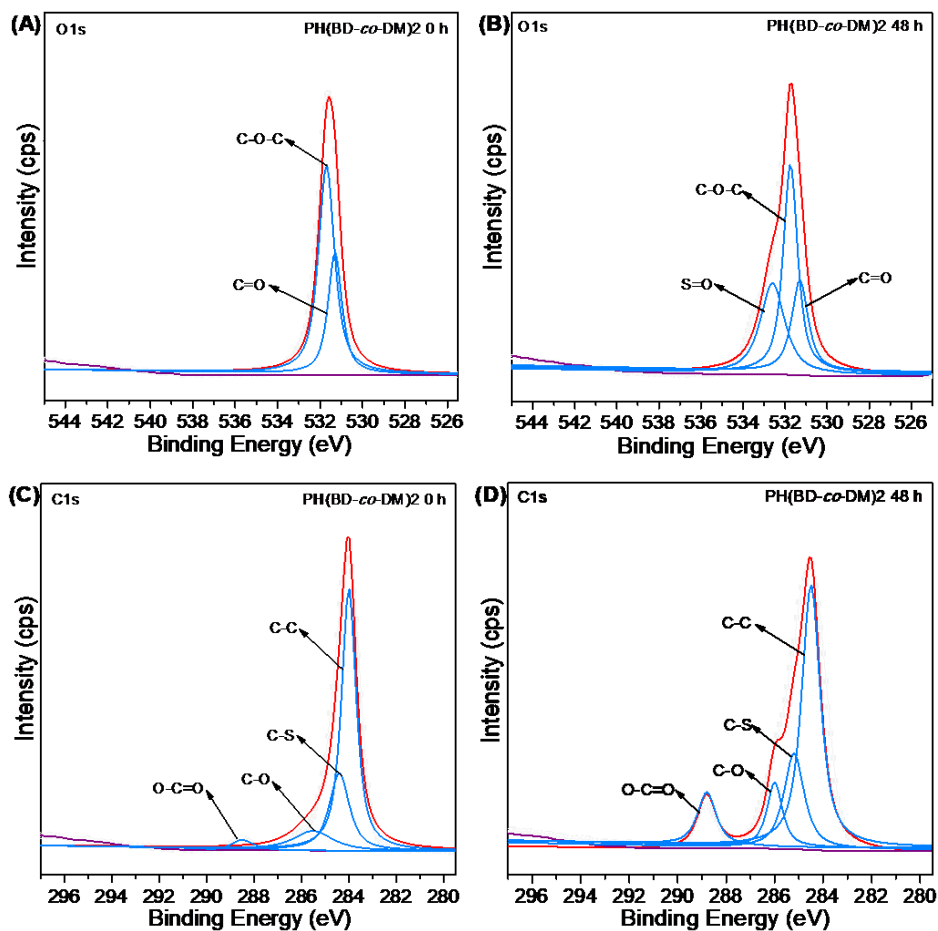


Fig. S13 O1s (A, B) and C1s (C, D) XPS spectra of PH(BD-co-DM)2 films after oxidization by 1 M H₂O₂ for 0 and 48 h.

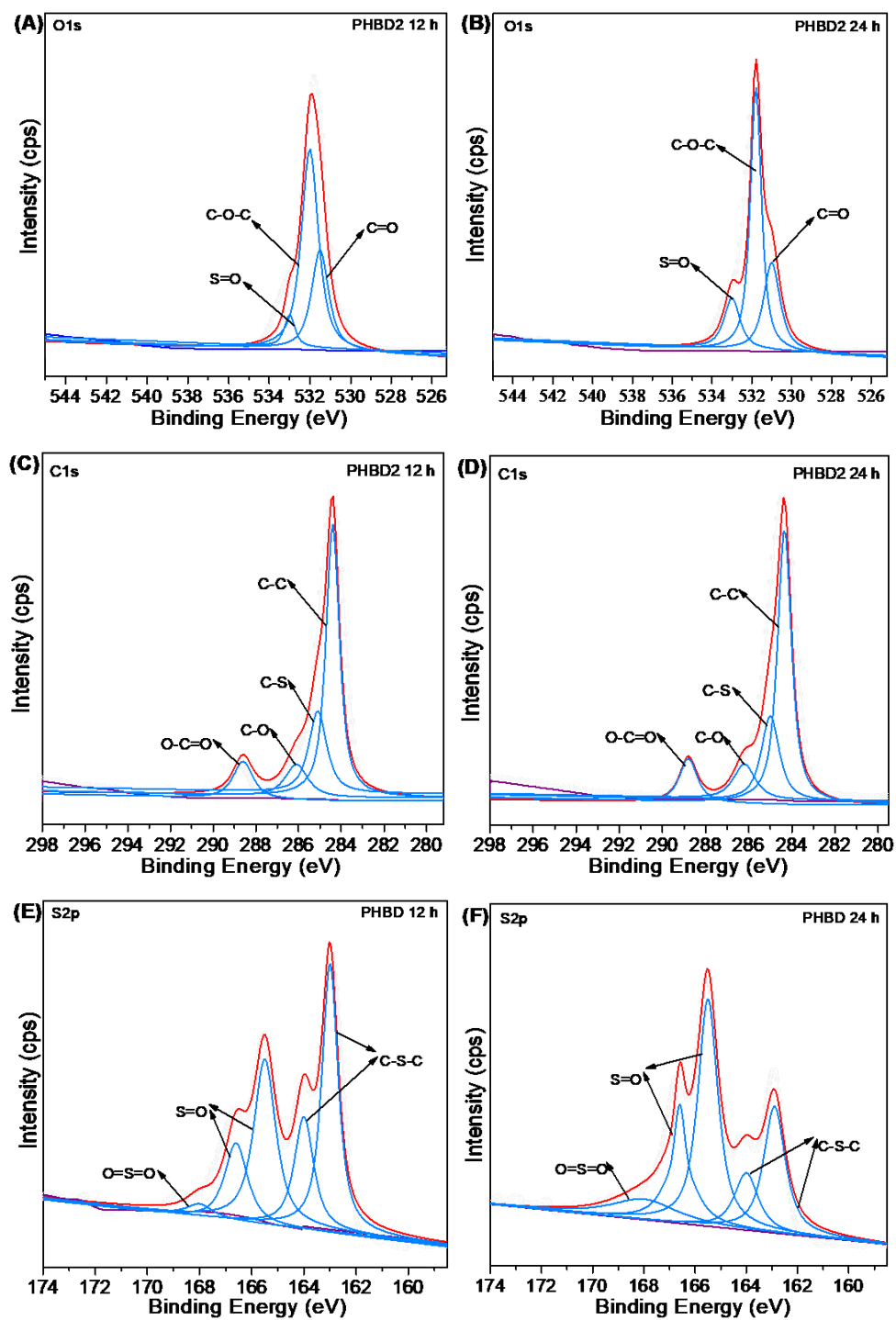


Fig. S14 O1s (A, B), C1s (C, D) and S2p (E, F) XPS spectra of PHBD2 films after oxidization by 1 M H_2O_2 for 12 and 24 h.

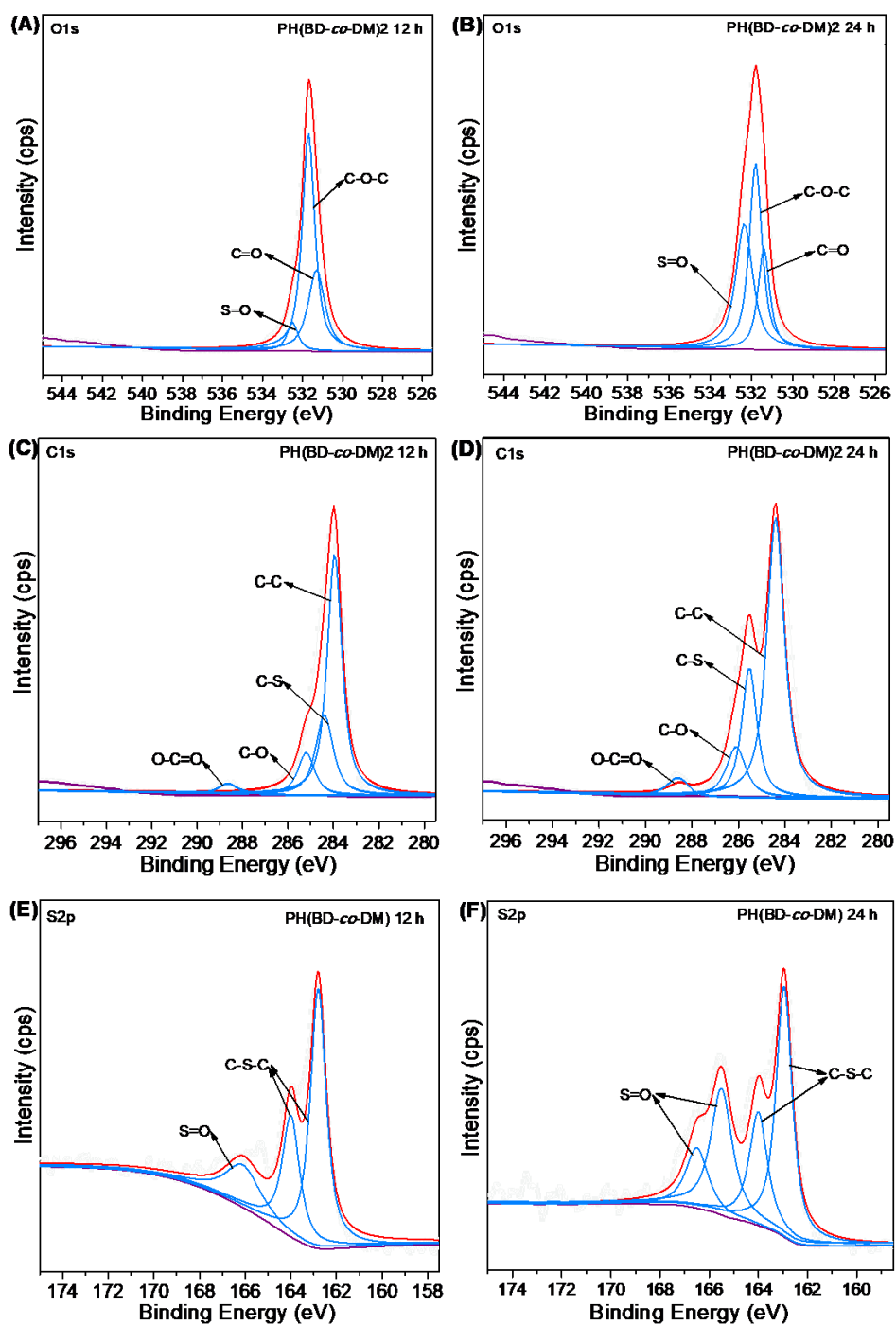
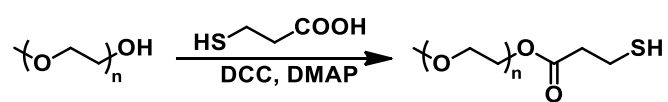


Fig. S15 O1s (A, B), C1s (C, D) and S2p (E, F) XPS spectra of PH(BD-co-DM)2 films after oxidization by 1 M H₂O₂ for 12 and 24 h.



Scheme S2 Synthetic scheme of mPEG-SH.

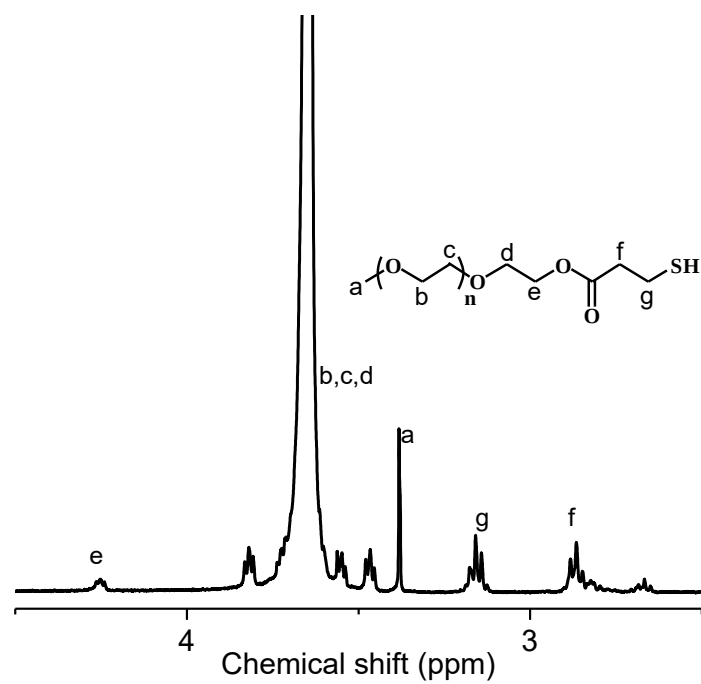


Fig. S16 ^1H NMR spectrum of mPEG-SH.

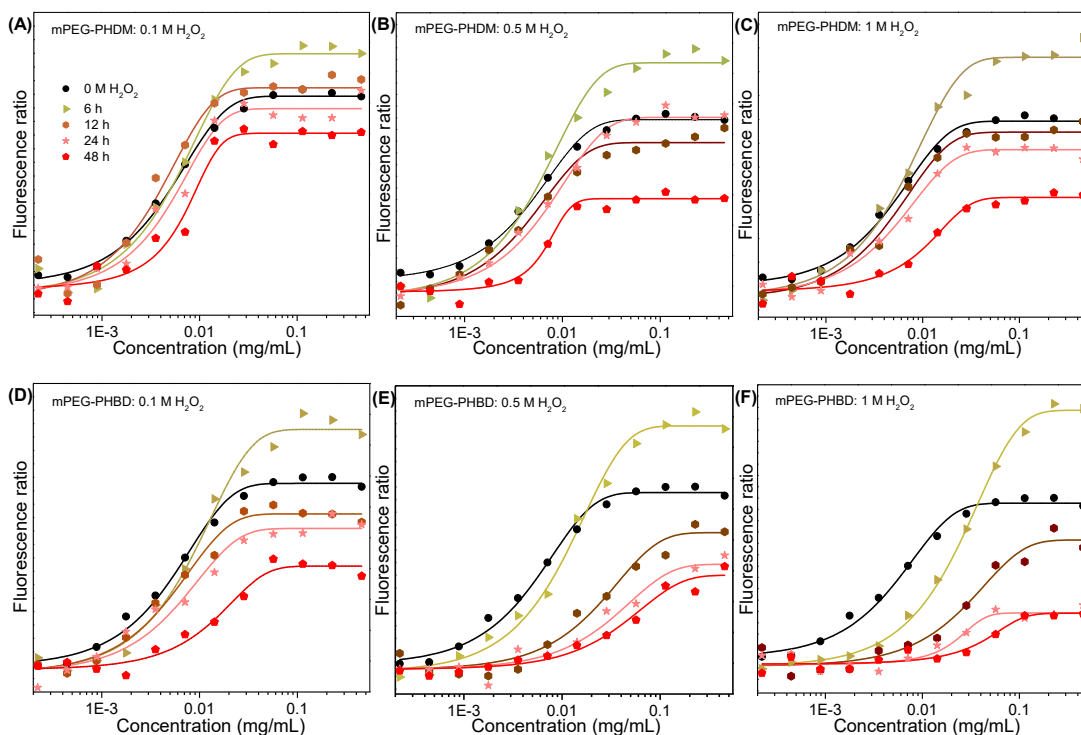


Fig. S17 Oxidation-triggered critical micelle concentration (CMC) changes of mPEG-PHDM (A–C) and mPEG-PHBD (D–F) after oxidation by H_2O_2 (0.1, 0.5 and 1 M) for different times.

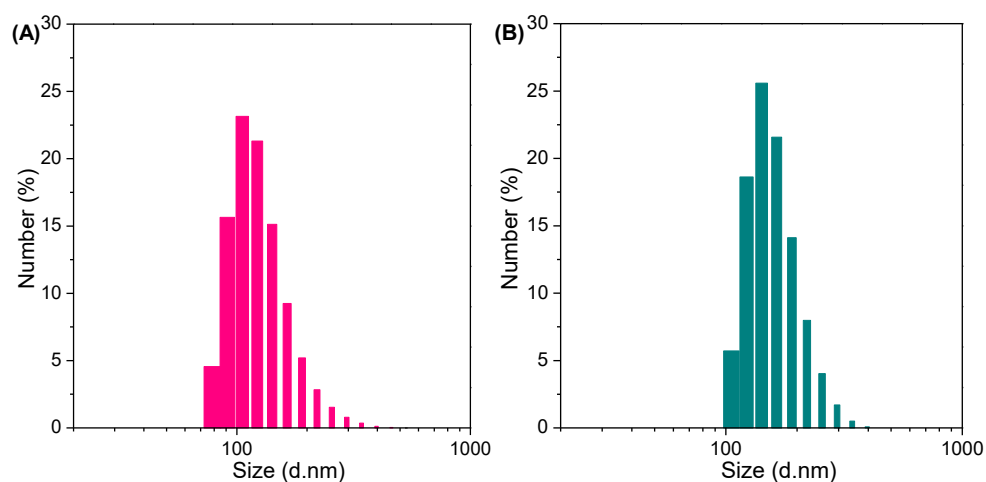


Fig. S18 DLS results of mPEG-PHDM (A) and mPEG-PHBD (B) blank micelles ($n = 3$).

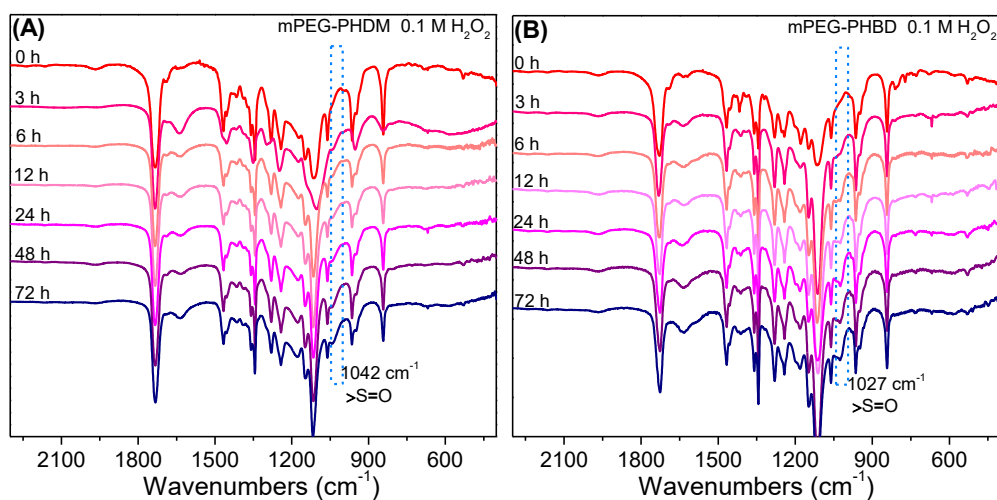


Fig. S19 FTIR spectra of mPEG-PHDM (A) and mPEG-PHBD (B) micelles treated with 0.1 M H₂O₂ for different incubation times.

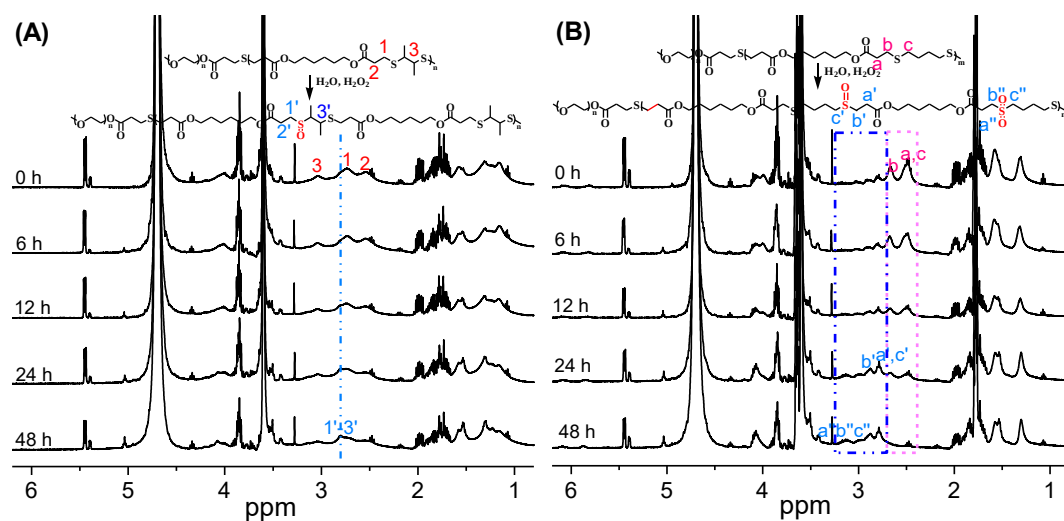


Fig. S20 ¹H NMR spectra of mPEG-PHDM (A) and mPEG-PHBD (B) micelles treated with 0.1 M H₂O₂ for different incubation times.

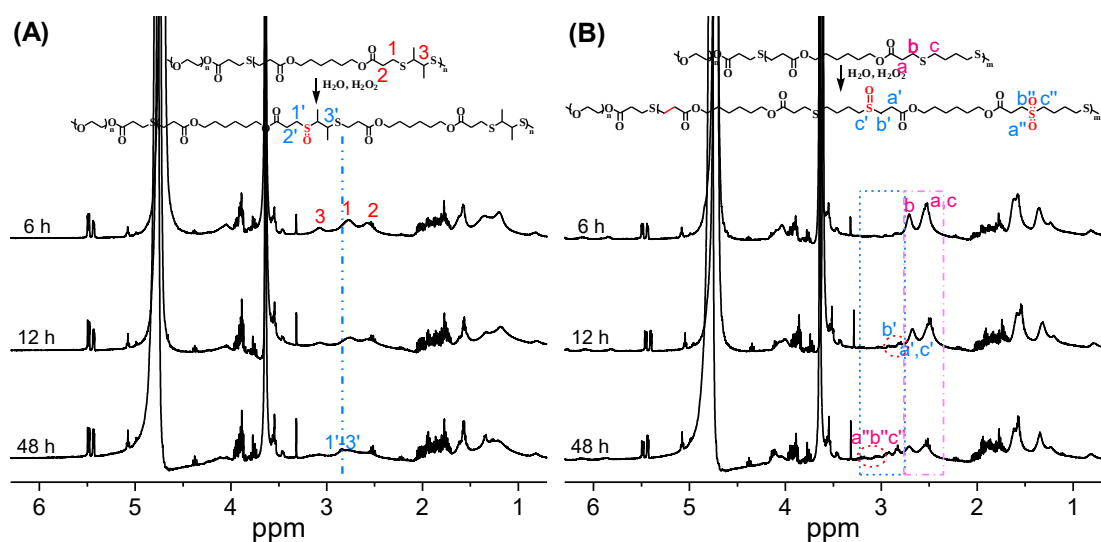


Fig. S21 ^1H NMR spectra of mPEG-PHDM (A) and mPEG-PHBD (B) micelles

treated with 0.05 M H_2O_2 for different incubation times.

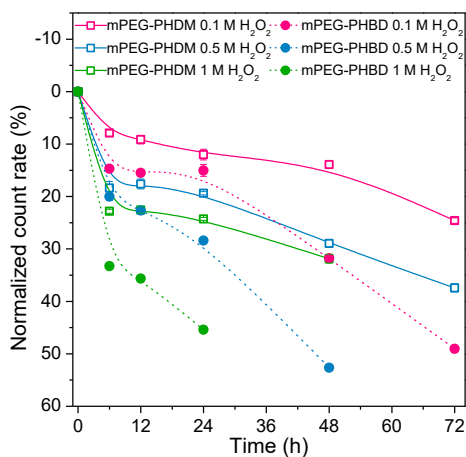


Fig. S22 Normalized count rates of blank micelles treated with H_2O_2 (0.1, 0.5 and 1

M) for different incubation times.

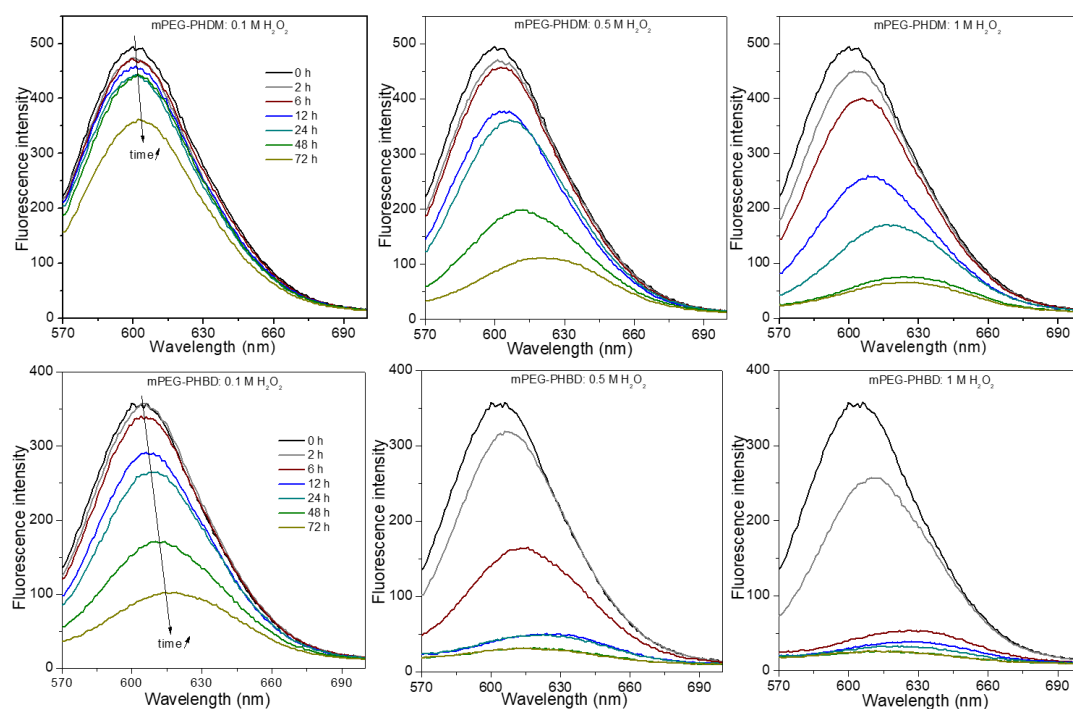


Fig. S23 Fluorescence intensity of Nile Red encapsulated mPEG-PHDM and mPEG-PHBD micelles treated with H₂O₂ (0.1, 0.5 and 1 M) for different incubation times.

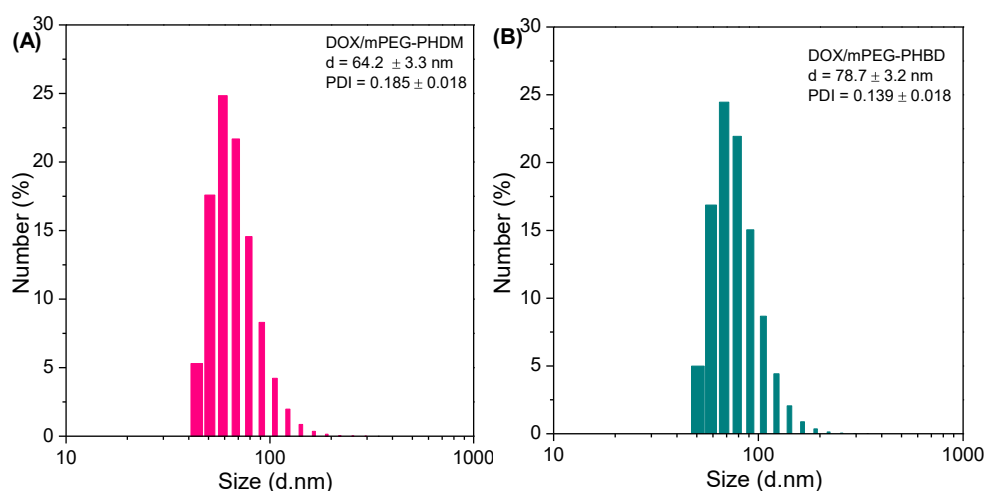


Fig. S24 The DLS results of DOX-loaded mPEG-PHDM and mPEG-PHBD micelles (n = 3).

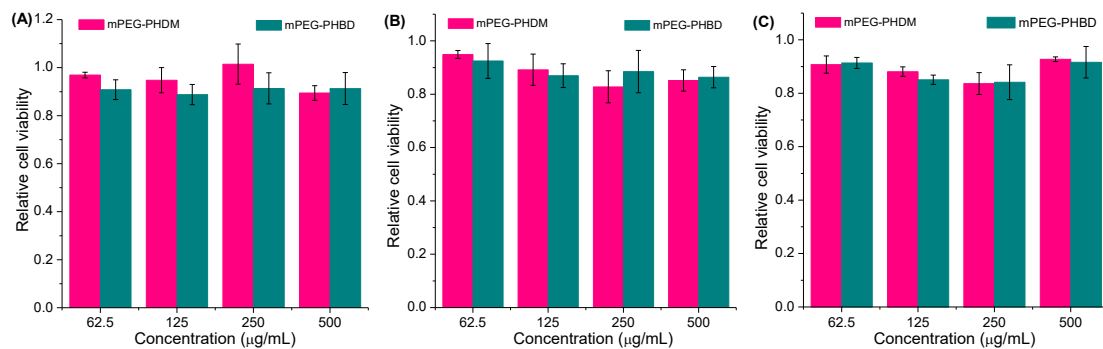


Fig. S25 Cell viability of NIH/3T3 (A), MCF-7 (B) and 4T1 (C) cells after incubation with blank mPEG-PHDM and mPEG-PHBD micelles for 48 h (n = 5).

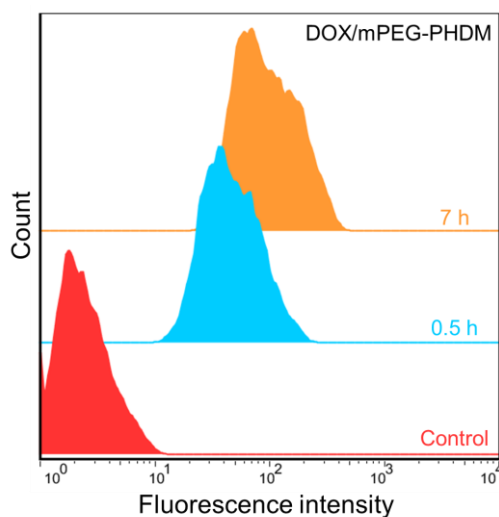


Fig. S26 Flow cytometry results of 4T1 cells treated with DOX/mPEG-PHDM micelles for 0.5 h and 7 h.