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Supporting Information

On-Demand and Negative-thermo-swelling Tissue Adhesive Based on Highly Branched Ambivalent PEG-catechol Copolymers

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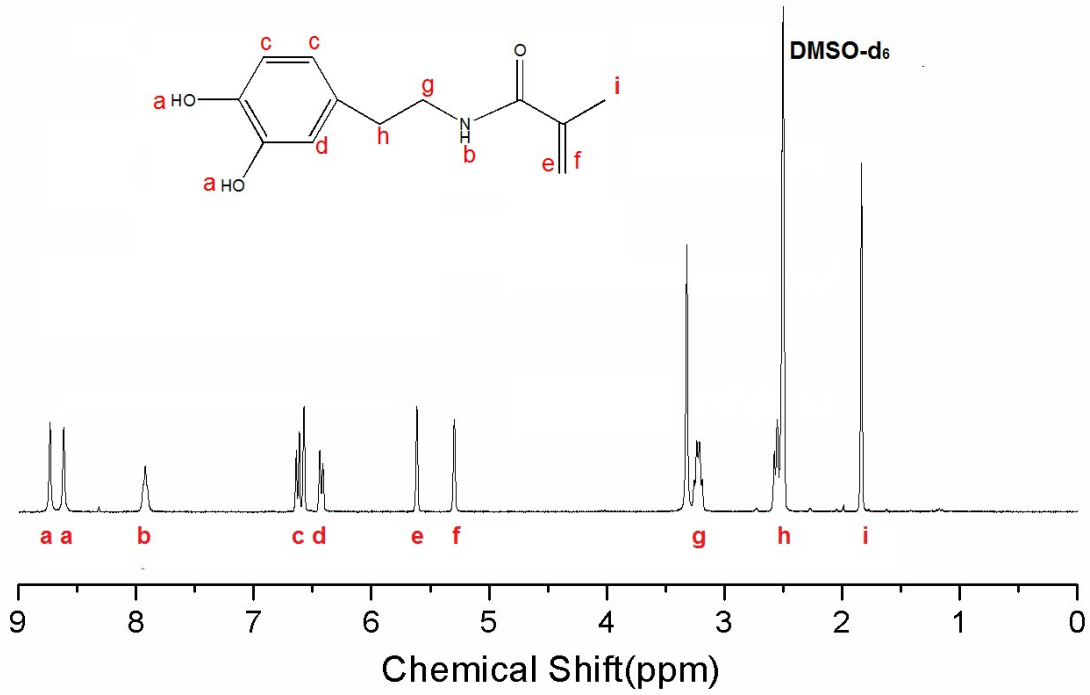
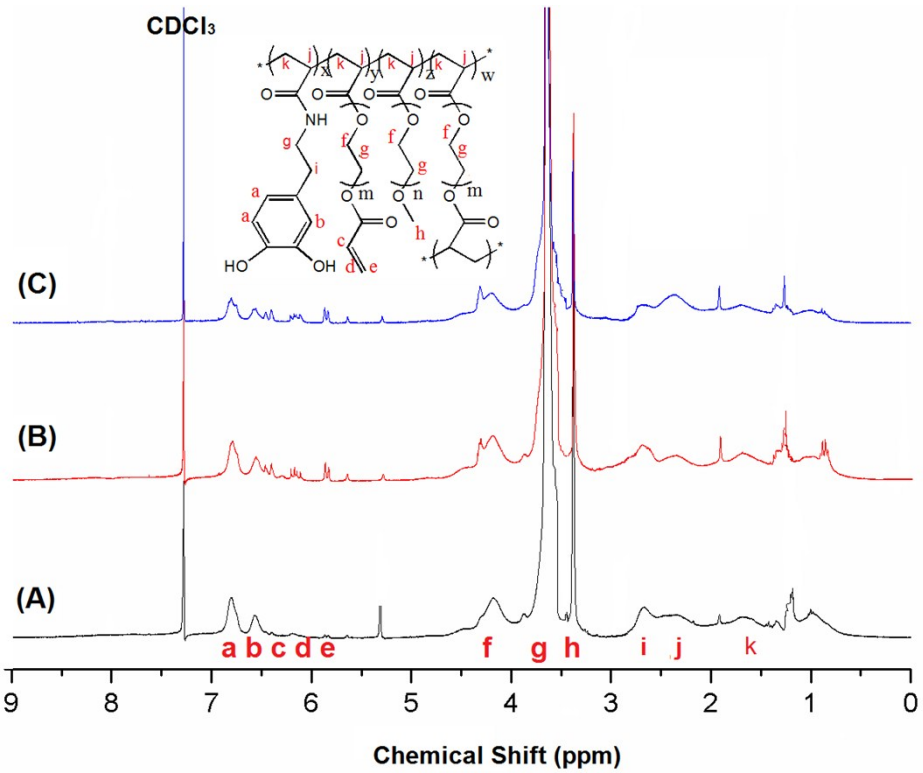
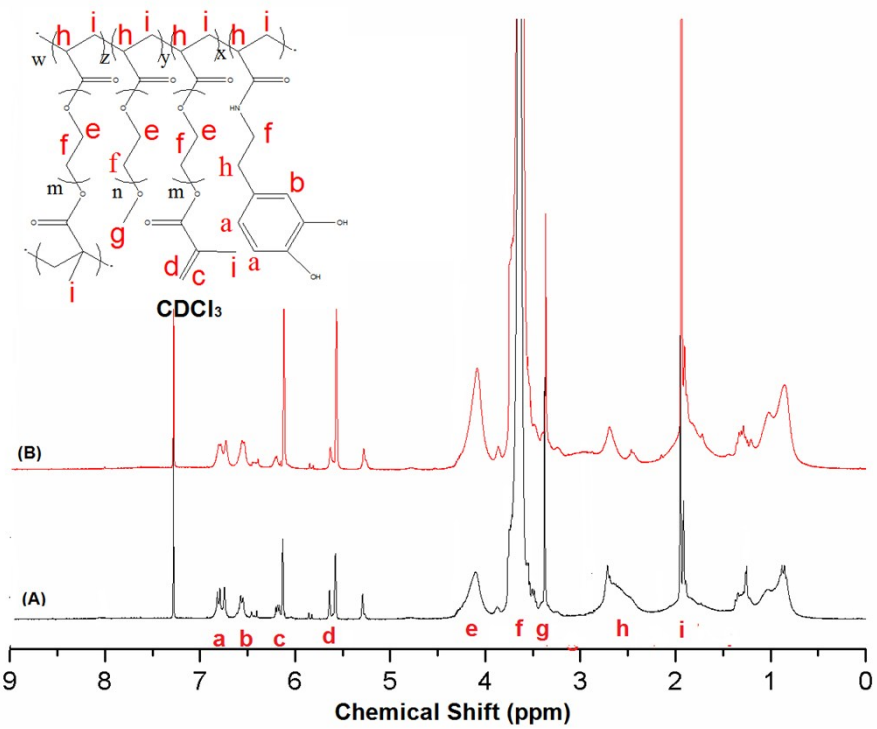


FigureS1. ^{1}H NMR spectrum (400 MHz, DMSO-D_6) of purified dopamine methacrylamide (DMA).



FigureS2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified (A) Poly(DMA_{40}-$PEGMEA_{40}$-$PEGDA_{20}$) (B) Poly(DMA_{40}-$PEGMEA_{30}$-$PEGDA_{30}$) (C)Poly(DMA_{40}-$PEGMEA_{20}$-$PEGDA_{40}$). Signals from spectrum have been assigned hydrogen atom groups (a to j) in the structure on the left.



FigureS3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified (A) Poly(DMA_{40}-$PEGMEA_{30}$-$PEGDMA_{30}$) (B) Poly(DMA_{40}-$PEGMEA_{20}$-$PEGDMA_{40}$). Signals from spectrum have been assigned hydrogen atom groups (a to i) in the structure on the left.

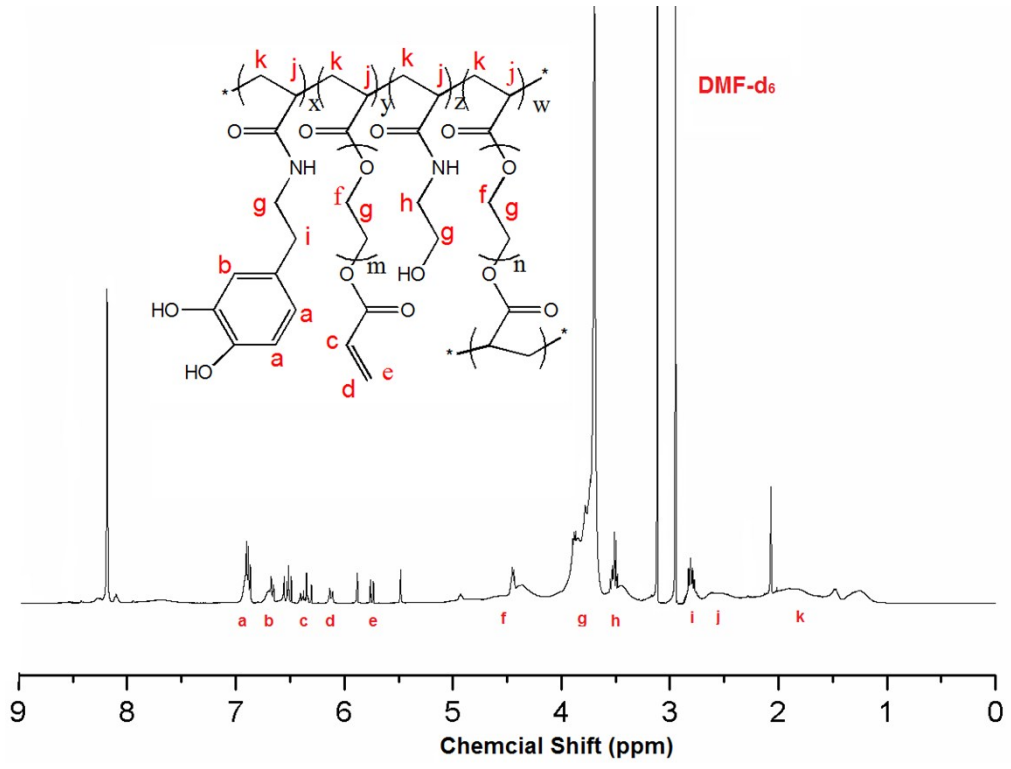
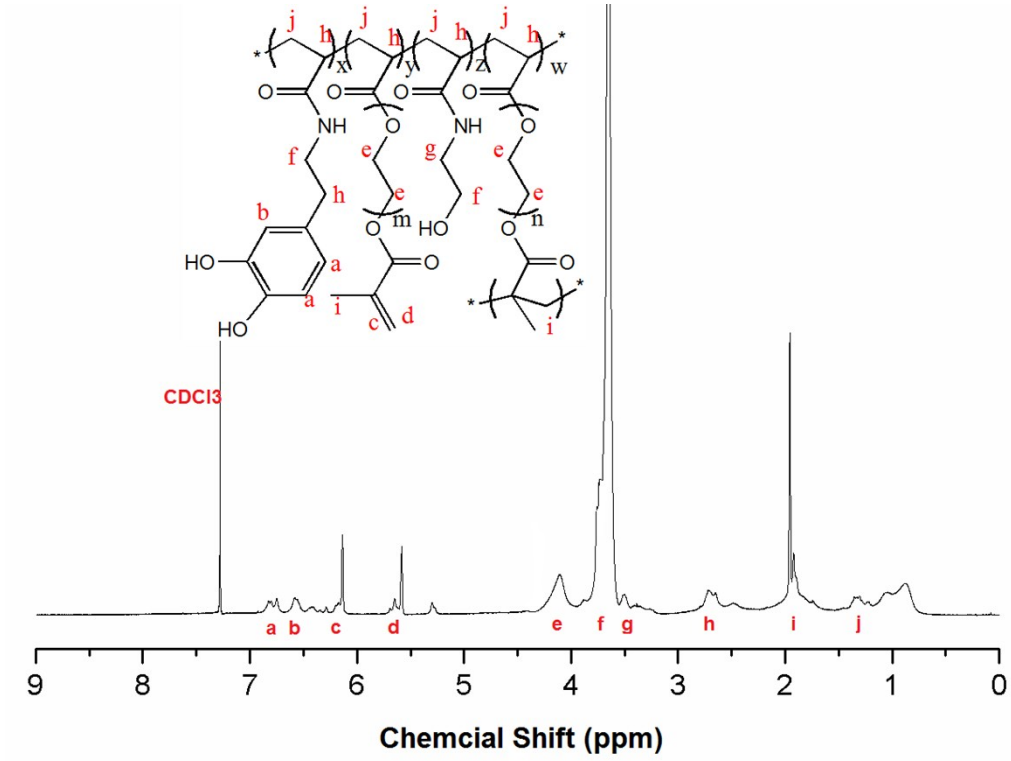
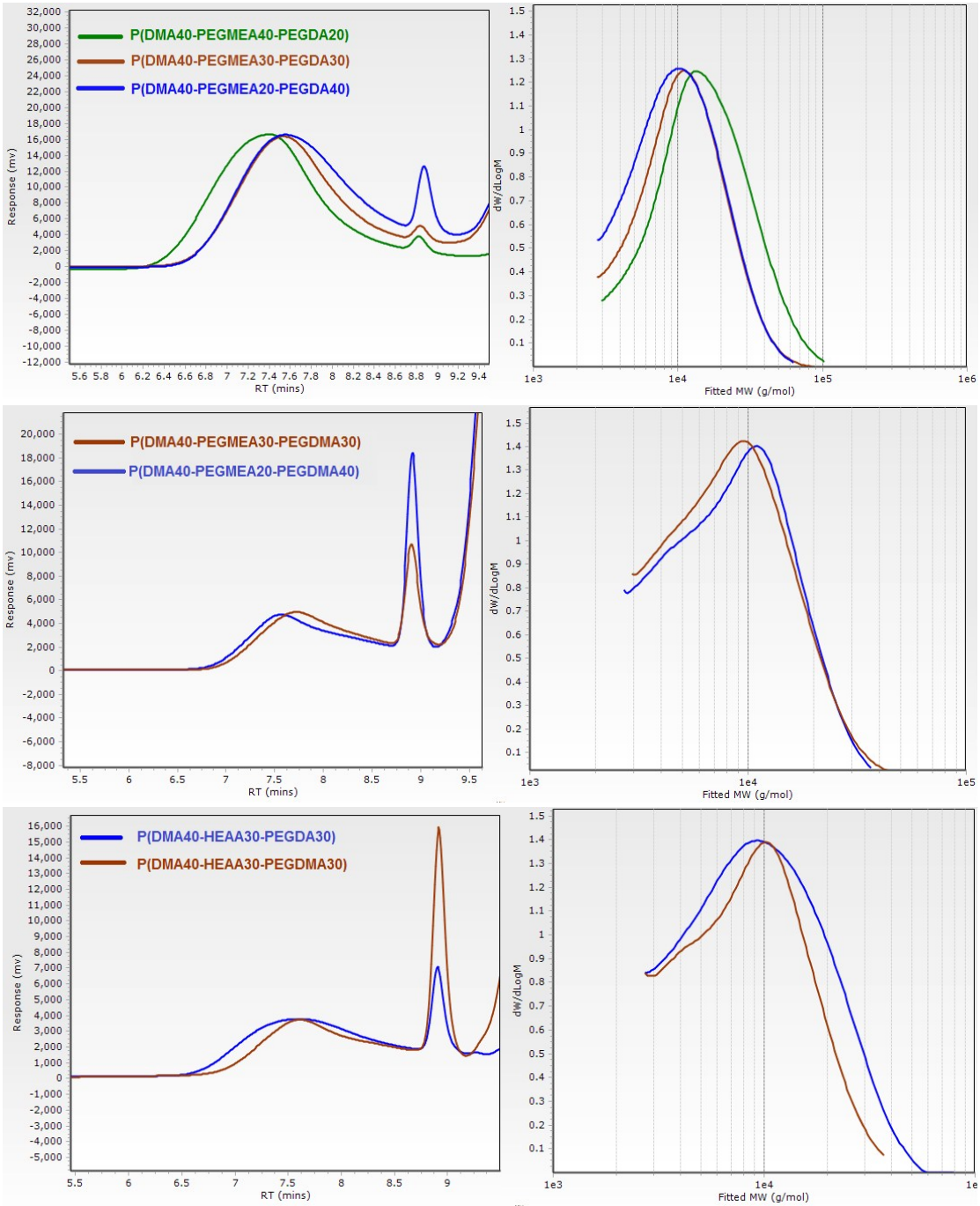


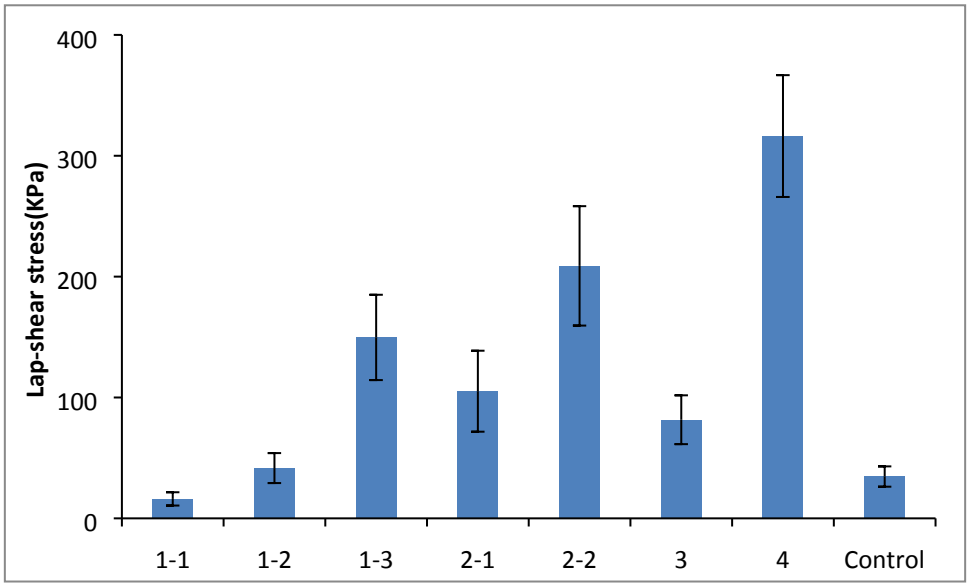
Figure S4. ^{1}H NMR spectrum (400 MHz, DMF-d_6) of purified Poly(DMA_{40}-$HEAA_{30}$-$PEGDA_{30}$). Signals from spectrum have been assigned hydrogen atom groups (a to K) in the structure on the left.



FigureS5.^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified Poly(DMA_{40}-$HEAA_{30}$-$PEGDMA_{30}$). Signals from spectrum have been assigned hydrogen atom groups (a to j) in the structure on the left.



FigureS6. Gel Permeation Chromatography (left) and molecular weight distribution (right) traces for all DOPA-PEG polymers.



FigureS7. Adhesion properties of copolymers evaluated through lap shear adhesion with borosilicate glass as surfaces. *n=5, 1-1: Poly(DMA_{40}-$PEGMEA_{40}$-$PEGDA_{20}$); 1-2: Poly(DMA_{40}-$PEGMEA_{30}$-$PEGDA_{30}$); 1-3: Poly(DMA_{40}-$PEGMEA_{20}$-$PEGDA_{40}$); 2-1: Poly(DMA_{40}-$PEGMEA_{30}$-$PEGDMA_{30}$); 2-2: Poly(DMA_{40}-$PEGMEA_{20}$-$PEGDMA_{40}$); 3: Poly(DMA_{40}-$HEAA_{30}$-$PEGDA_{30}$); 4: Poly(DMA_{40}-$HEAA_{30}$-$PEGDMA_{30}$); Control: P($PEGDA_{25}$–$PEGMEMA_{50}$).

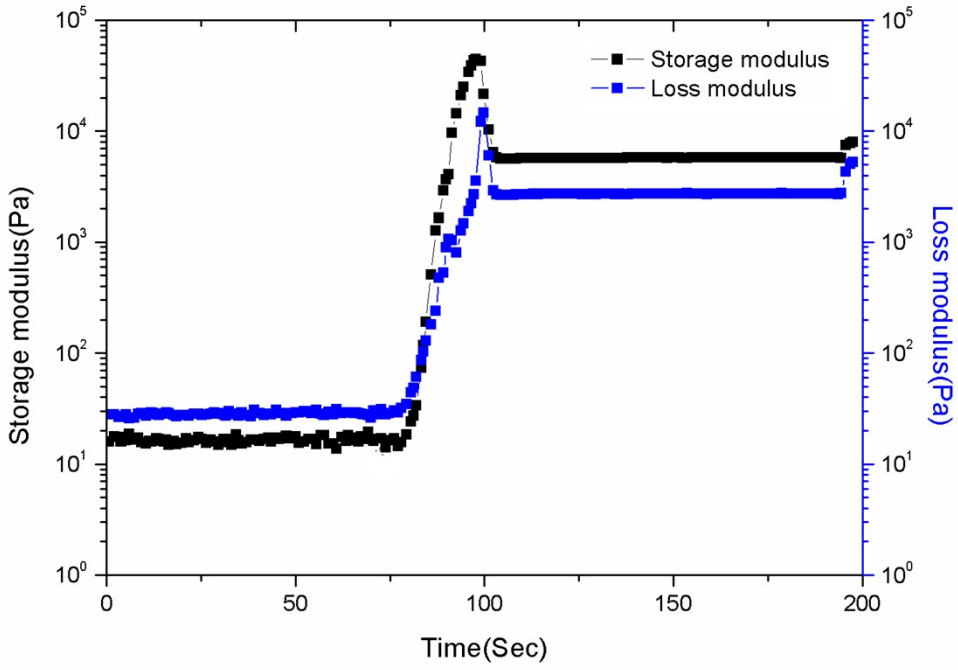


Figure S8. Real-time photocrosslinking rheological measurements of the P(DMA_{40}-$PEGMEA_{20}$-$PEGDMA_{40}$) hydrogel. The samples were exposed to UV light for 2 mins after the first minute of data collection. The black symbols represent the storage modulus G' and the blue symbols represent the loss modulus G''.