Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Synthesis and Adhesion Control of Glucose-based Bioadhesive via Strain-Promoted Azide-Alkyne Cycloaddition

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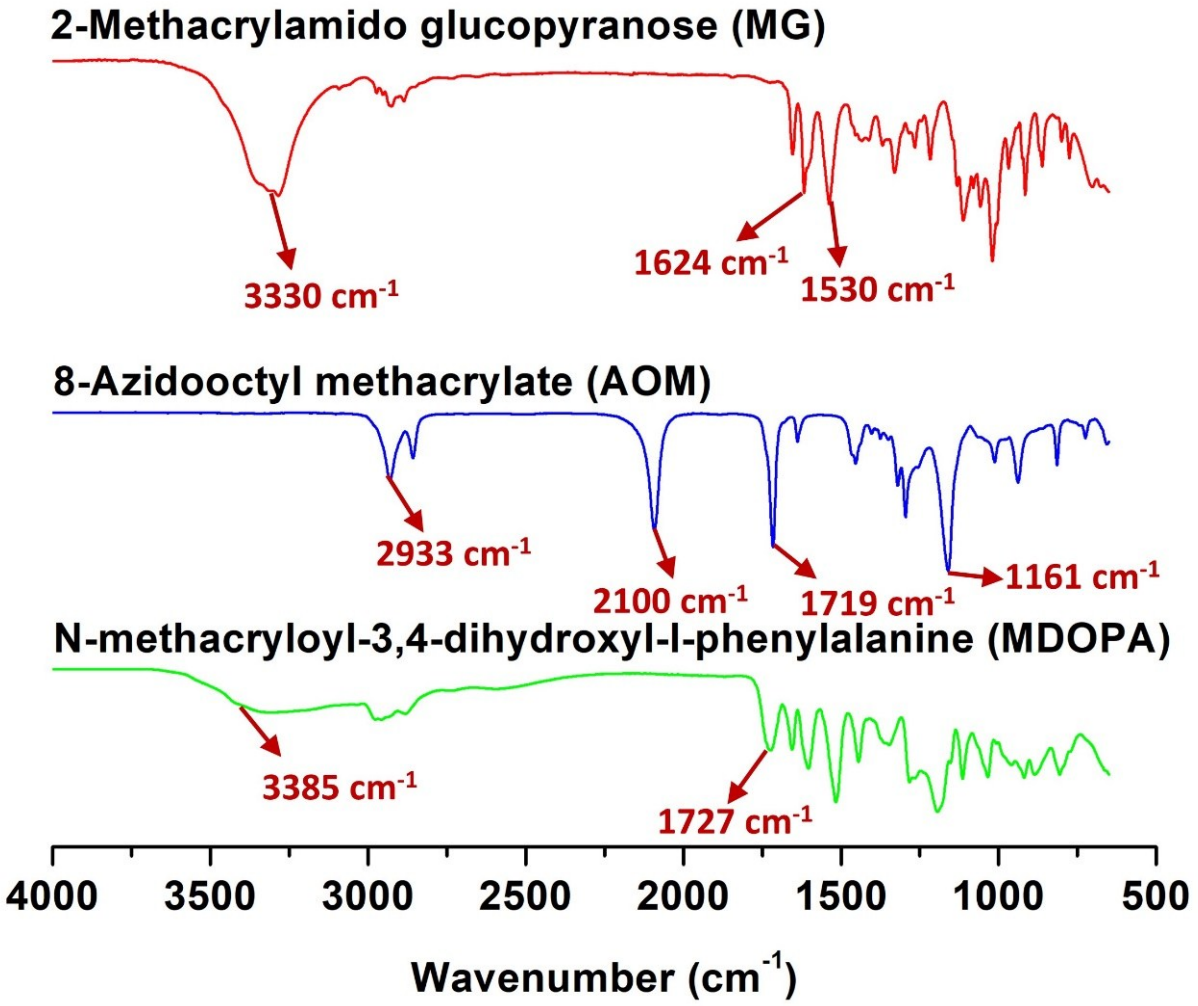


Fig. S1. FT-IR spectra of synthesized monomers. Broad peak at 3330-3385 cm^{-1} region represents OH stretching. The peaks at 2933 cm^{-1} is due to sp^3 C-H stretching whereas the strong peak at and 2100 cm^{-1} identifies the azide group in the AOM **3**. The peak at 1727 cm^{-1} is due to the carboxylic acid C=O stretch from the MDOPA **2**. The strong peak at 1719 cm^{-1} is due to the C=O stretching in acrylate whereas the peak at 1161 cm^{-1} portrays the stretching of C-O-C in acrylate. Finally, the amide vibration peaks in MG **1** monomer are represented by peaks at 1624 and 1530 cm^{-1}.

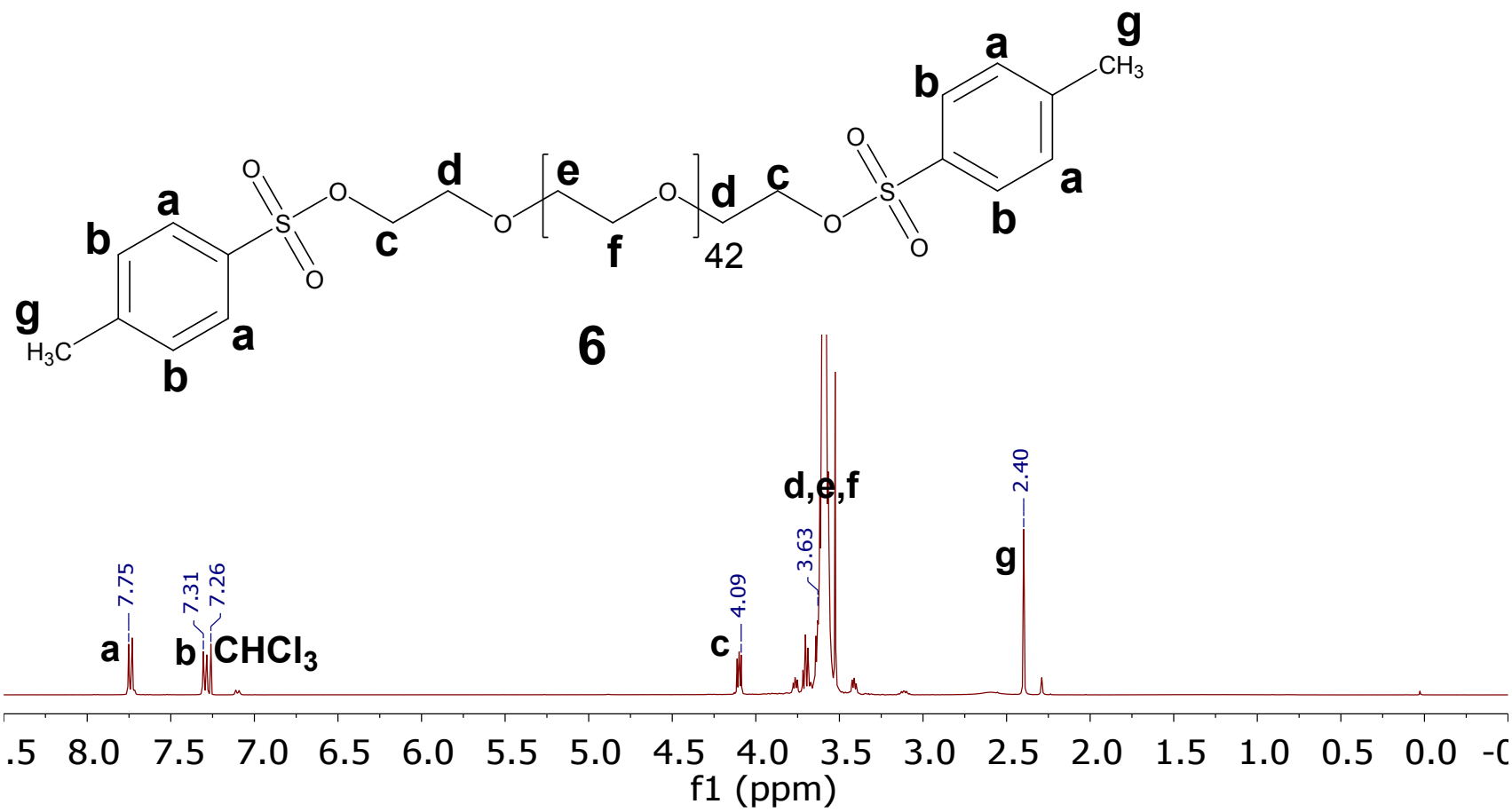


Fig. S2. ^{1}H-NMR ($CDCl_3$) – Ditosylated poly(ethylene glycol) **6**.

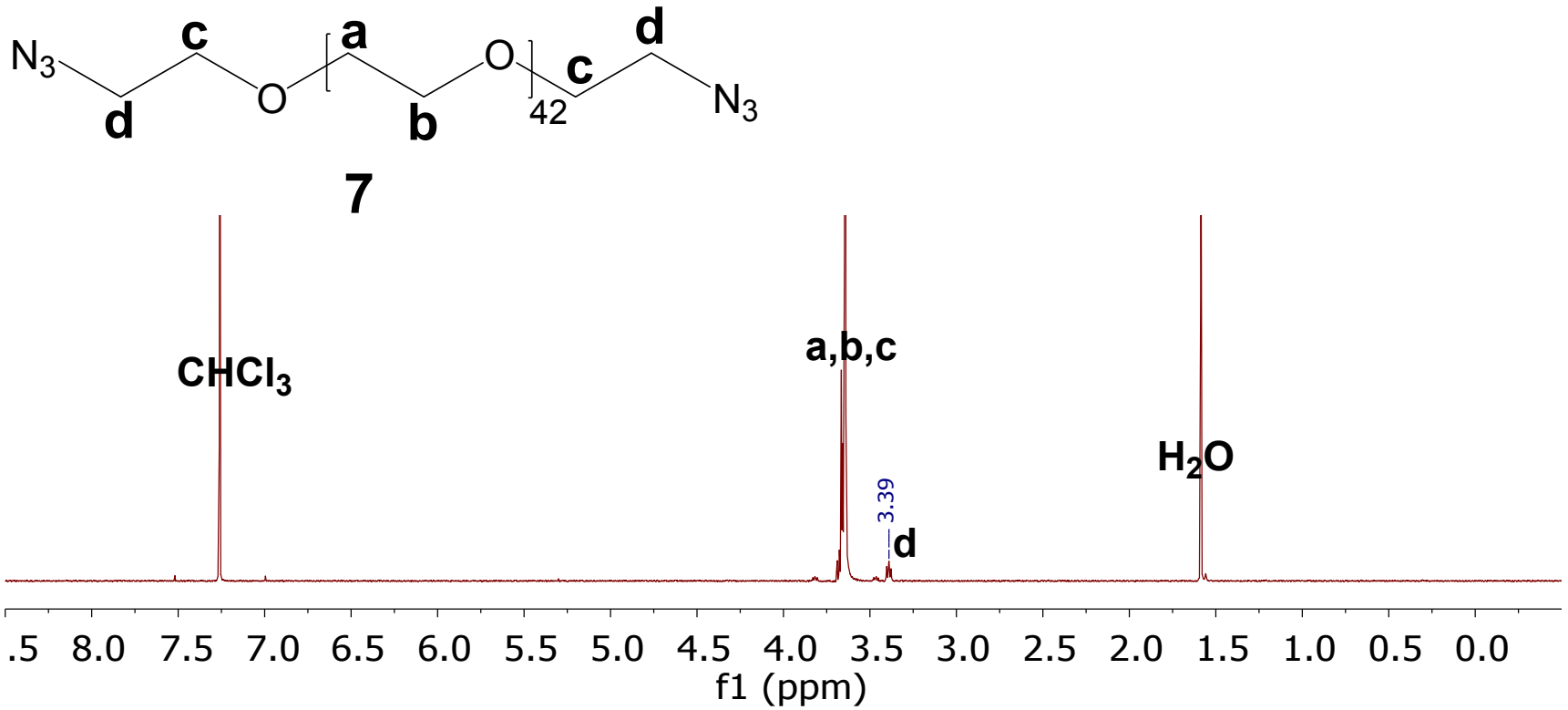


Fig. S3. ^{1}H-NMR ($CDCl_3$) – poly(ethylene glycol)-diazides **7**.

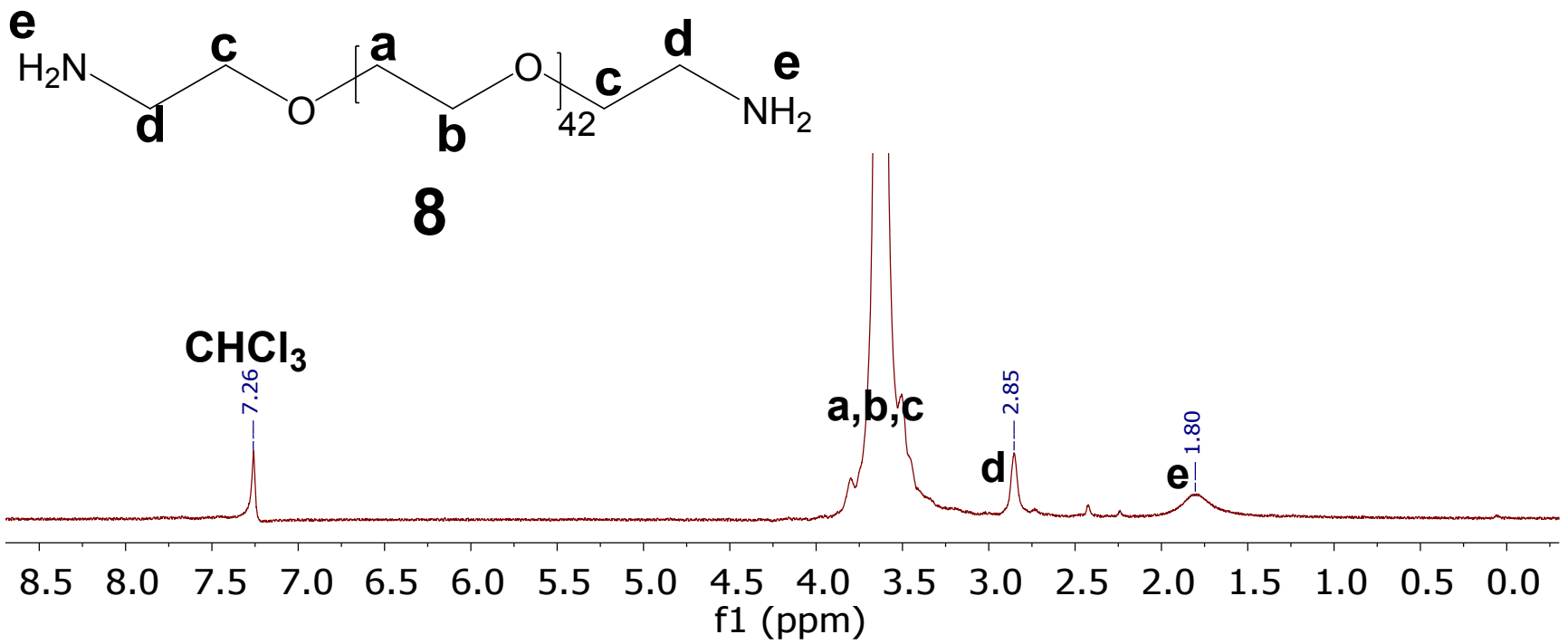
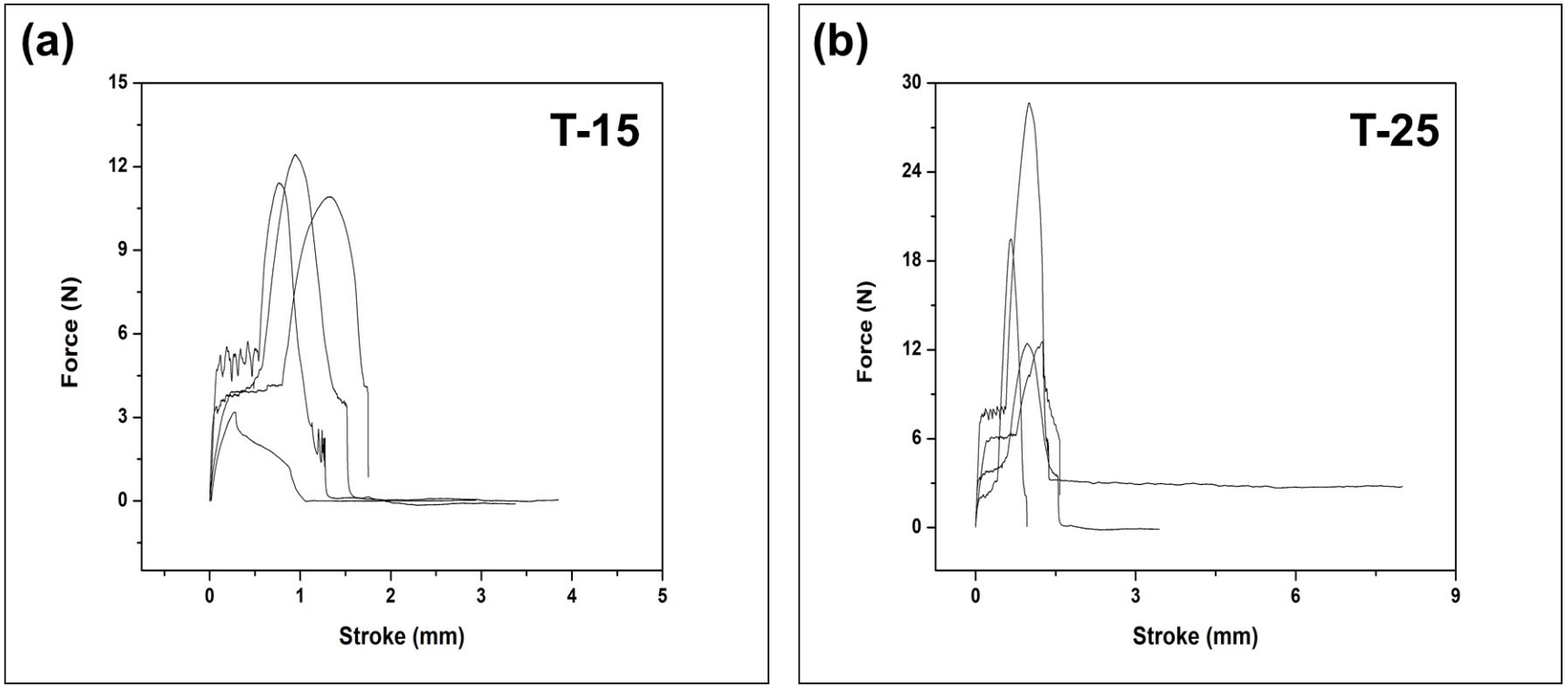
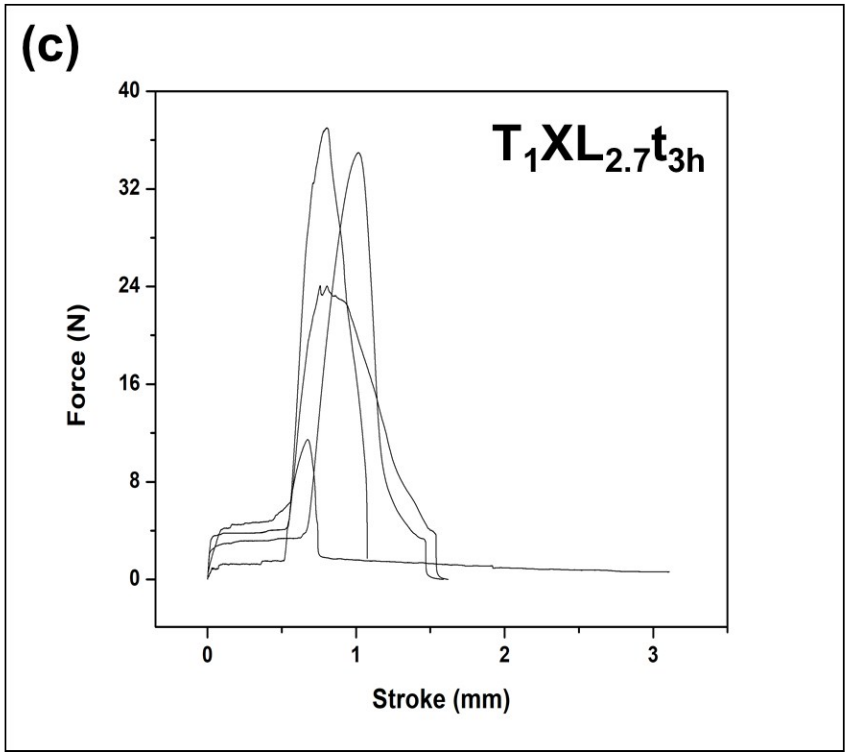


Fig. S4. ^{1}H-NMR ($CDCl_3$) – poly(ethylene glycol)-diamines **8**.


(a)
T-15
Force (N)
Stroke (mm)
0
3
6
9
12
15
0
1
2
3
4
5
(b)
T-25
Force (N)
Stroke (mm)
0
6
12
18
24
30
0
3
6
9


(c)
$T_1XL_{2.7}t_{3h}$
Force (N)
Stroke (mm)
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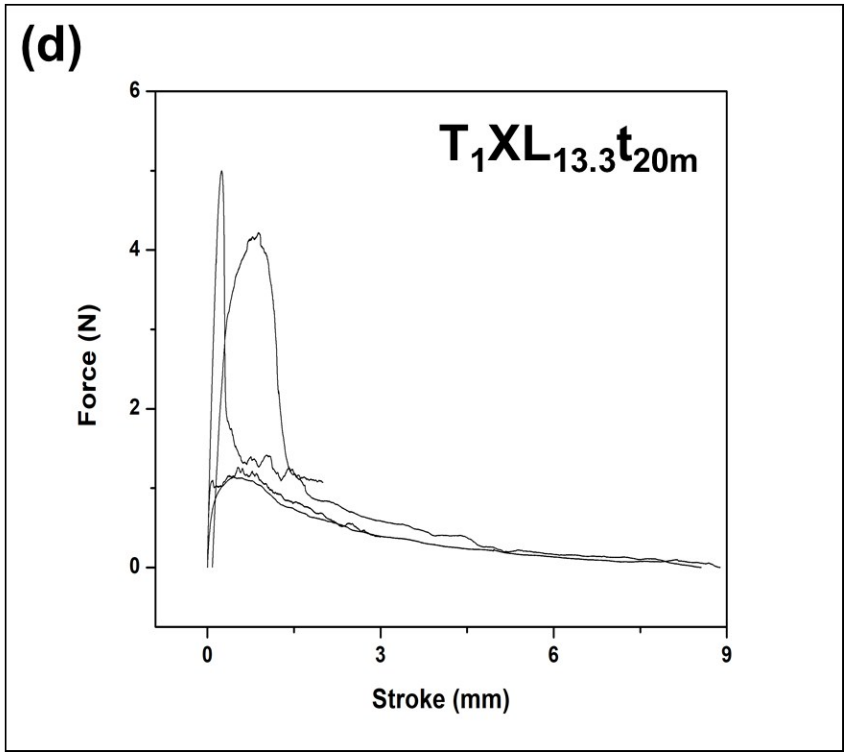
8
16
24
32
0
1
2
3


(d)
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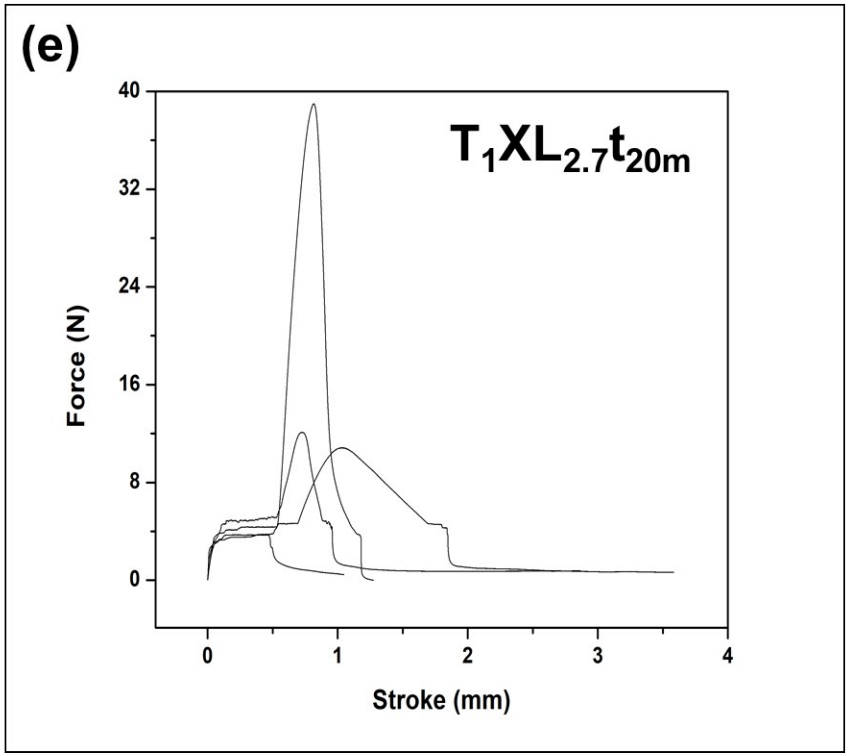
6
0
3
6
9


(e)
$T_1XL_{2.7}t_{20m}$
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Stroke (mm)
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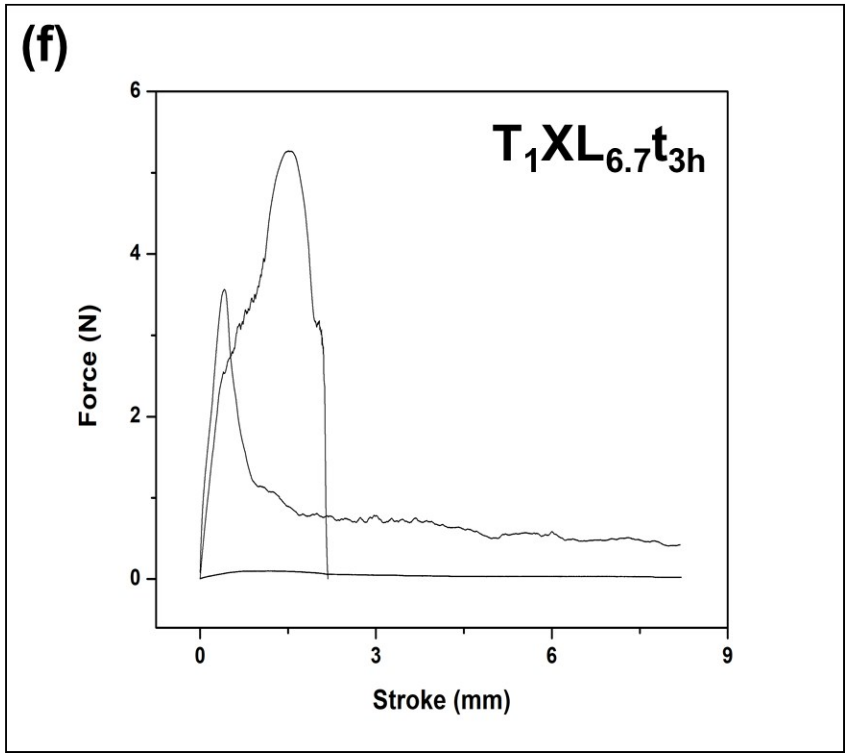
16
24
32
40
0
1
2
3
4


(f)
$T_1XL_{6.7}t_{3h}$
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Stroke (mm)
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6
0
3
6
9

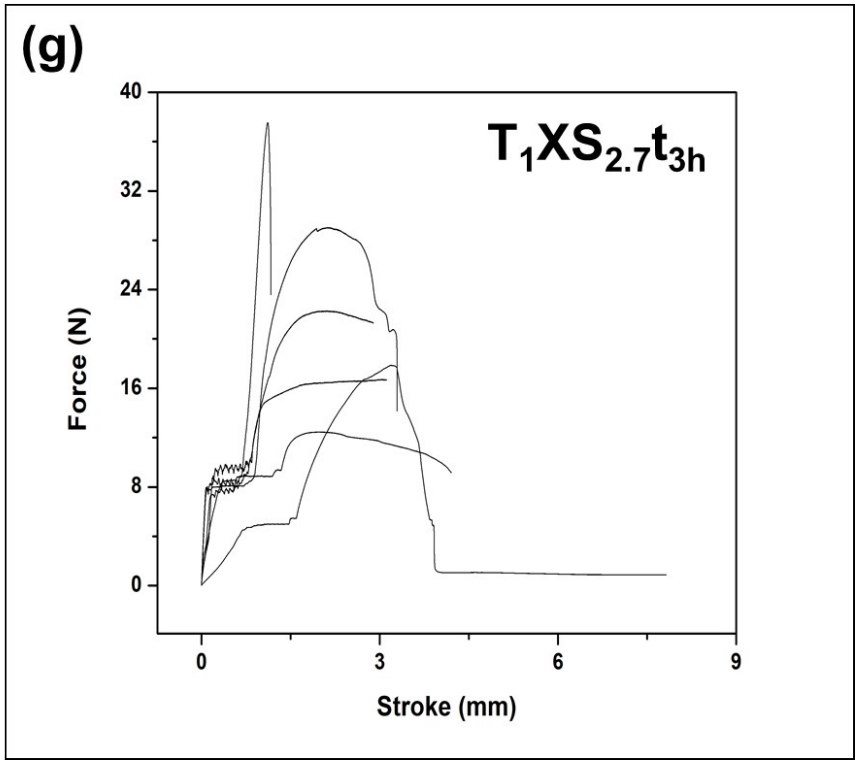

Fig. S5. Lap shear test data, force *vs.* displacement on porcine skin substrates. (a) Pure 15 mg terpolymer (T15), (b) Pure 25 mg terpolymer (T25) the, (c) terpolymer + 2.7 wt % long crosslinker at 3 h crosslinking time, (d) terpolymer + 13.3 wt % long crosslinker at 20 min crosslinking time, (e) terpolymer + 2.7 wt % long crosslinker at 20 min crosslinking time, (f) terpolymer + 6.7 wt % long crosslinker at 3 h crosslinking time, and (g) terpolymer + 2.7 wt % short crosslinker at 3 h crosslinking time. The maximum adhesion strength was obtained from the highest peak of force divided by the area of porcine skins covered by adhesive. Work of adhesion is energy of adhesion per unit area, which can be calculated by integration of plot (force vs. displacement) divided by the area of porcine skins covered by adhesive. The test was repeated at least 4 times (unless specified) to get average values and error bars. The error bar is the standard error of the mean.

Fig. S6. Crosslinked 8-azidooctyl methacrylate (AOM **3**) monomer. First, BCN-PEG$_{6000}$ **11** crosslinker and AOM **3** monomer were completely dissolved in chloroform in separate vials. As soon as two solutions were mixed, white precipitate was formed immediately because of rapid metal-free click reaction.

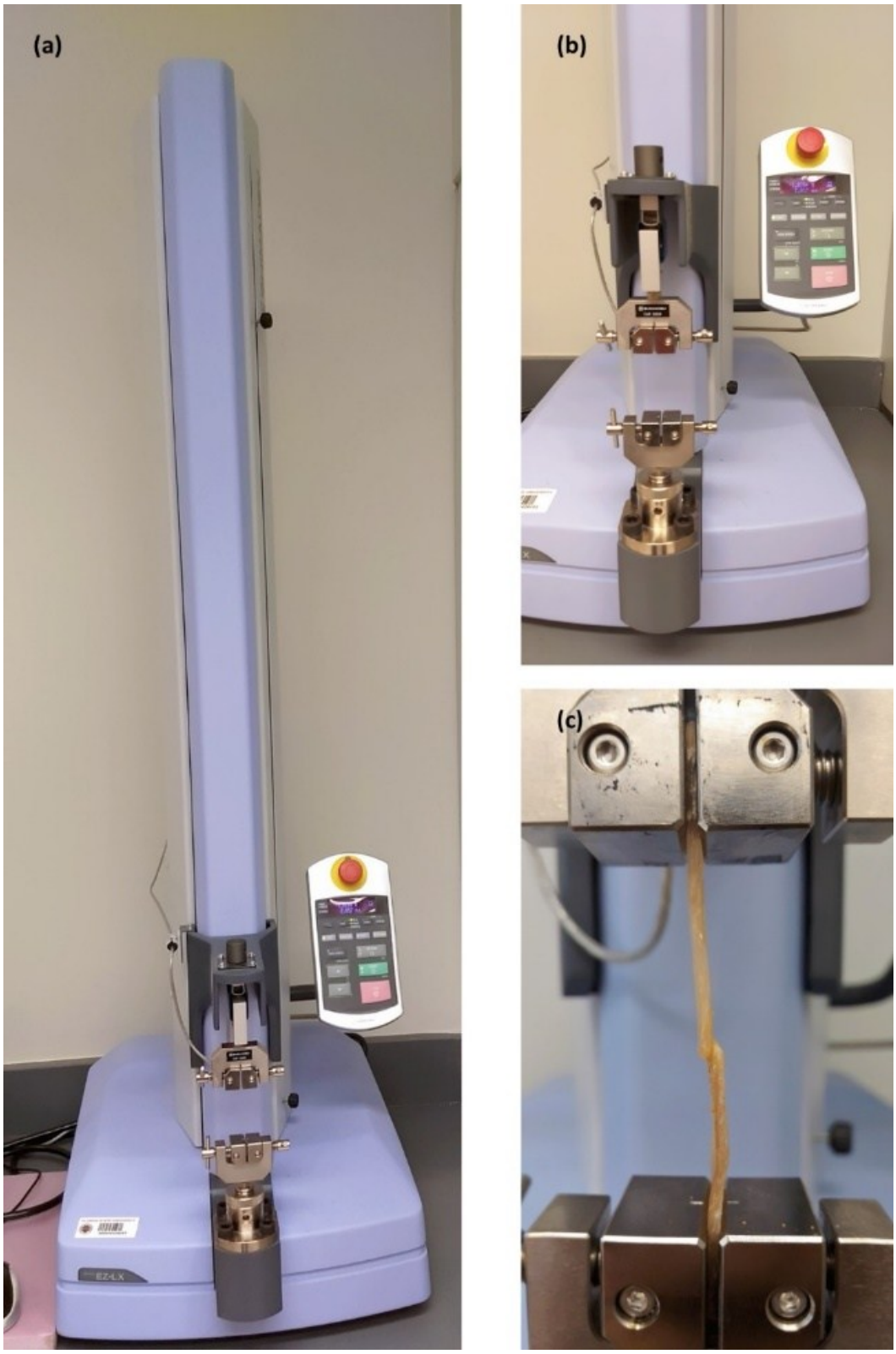

Fig. S7. **(a)** Lap shear test instrument (Shimadzu EX Test EZ-LX), **(b)** sample holders/grips, and **(c)** glued porcine skins for testing.

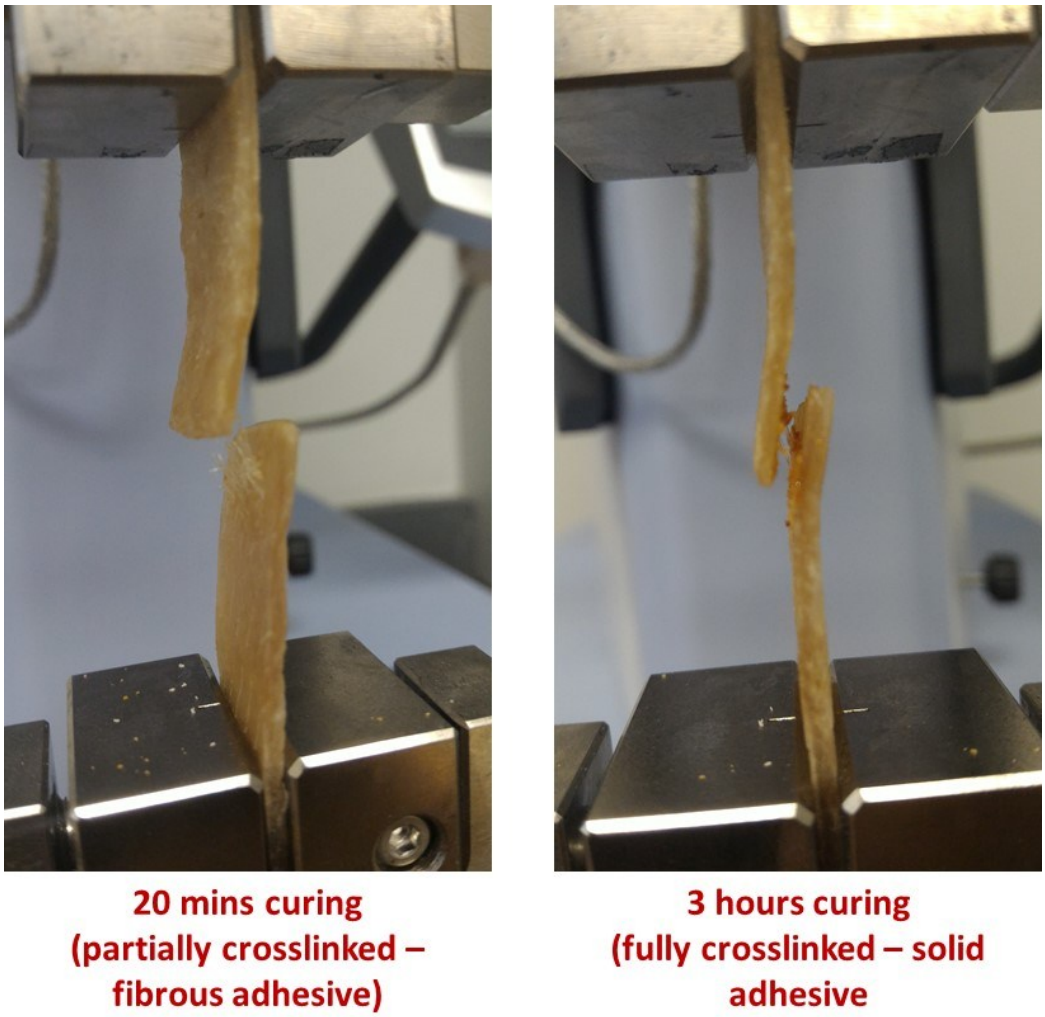

Fig. S8. Comparison of curing time of crosslinked (BCN-PEG$_{6000}$)-poly(MG-*co*-MDOPA-*co*-AOM) **14**. At crosslinking time t = 20 minutes, fibers were observed between two detached porcine skins; whereas at t = 3 hours, polymer became solid due to full crosslinking.