Electronic Supplementary Material (ESI) for RSC Applied Polymers.

Supporting information

Salicylhydroxamic Acid Containing Structural Adhesive

Md Saleh Akram Bhuiyan, Kan Wang, Fatemeh Razaviamri, and Bruce P. Lee*

Department of Biomedical Engineering, Michigan Technological University, Houghton, MI 49931, United States of America

* Corresponding author: Bruce P. Lee

E-mail: bplee@mtu.edu

1. Experimental Design

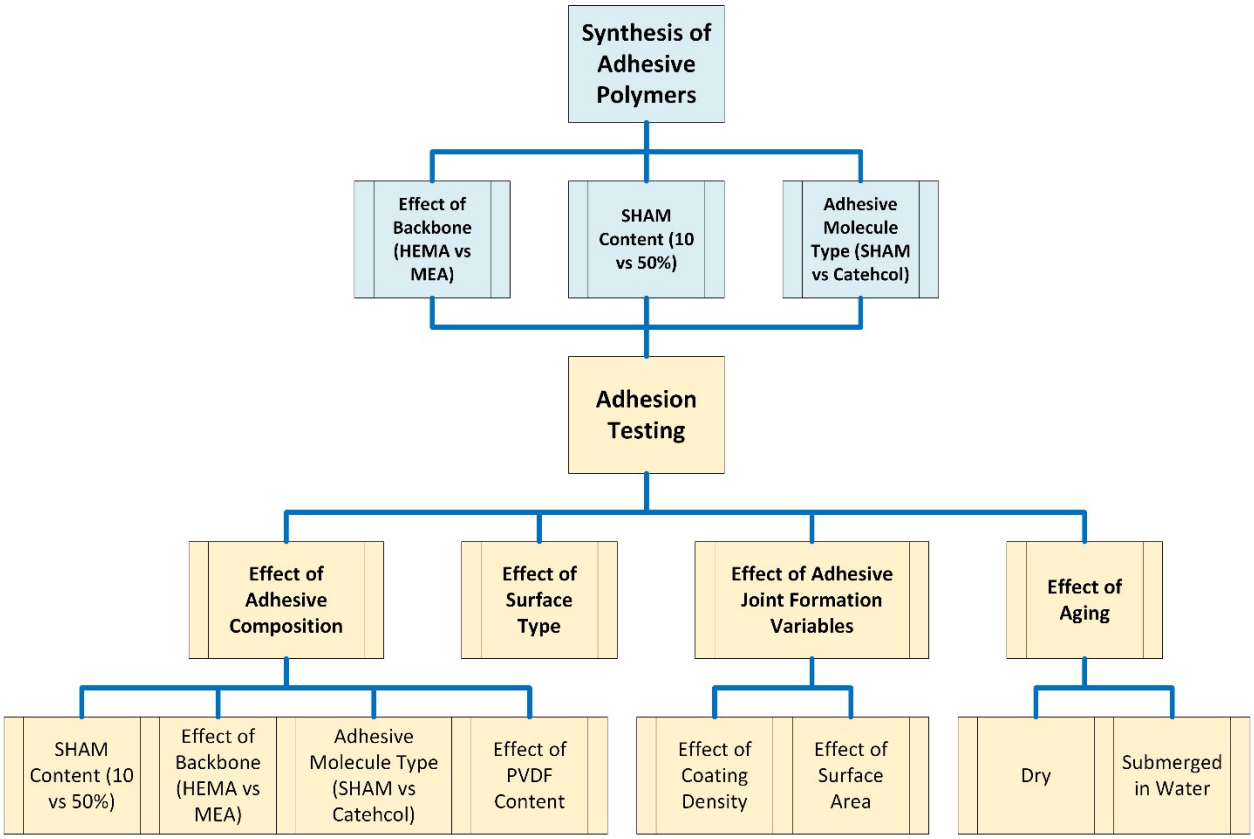

Figure S1: Diagram outlining the experimental design of this study.

2. Preparation of adhesively bonded sample for lap shear adhesion test

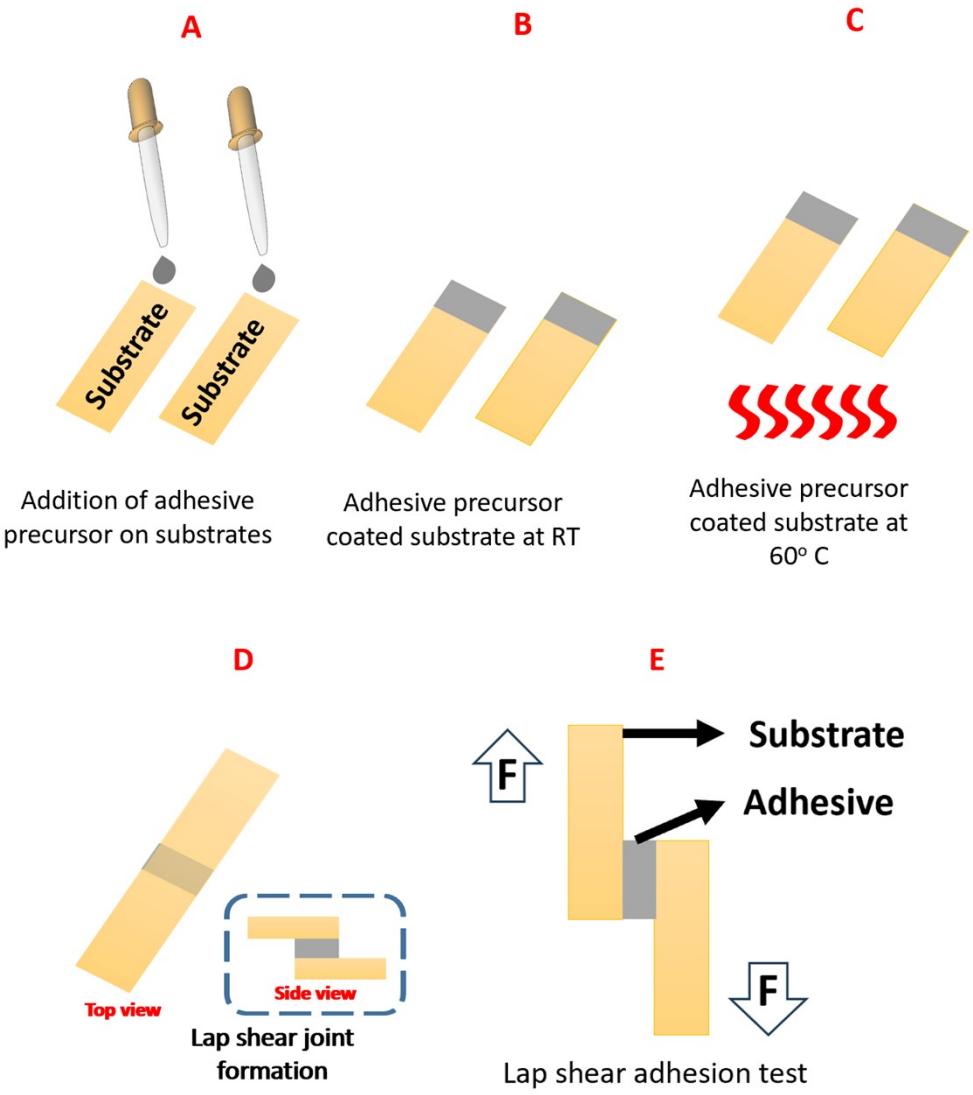

Figure S2: Stepwise process of preparing sample for lap shear adhesion testing. A) drop coating of adhesive precursor on the substrates, B) coated substrate at RT for 15 min, C) coated substrate at 60° C to remove solvents. D) formation of lap shear joint between two substrates, and E) lap shear adhesion test of prepared sample.

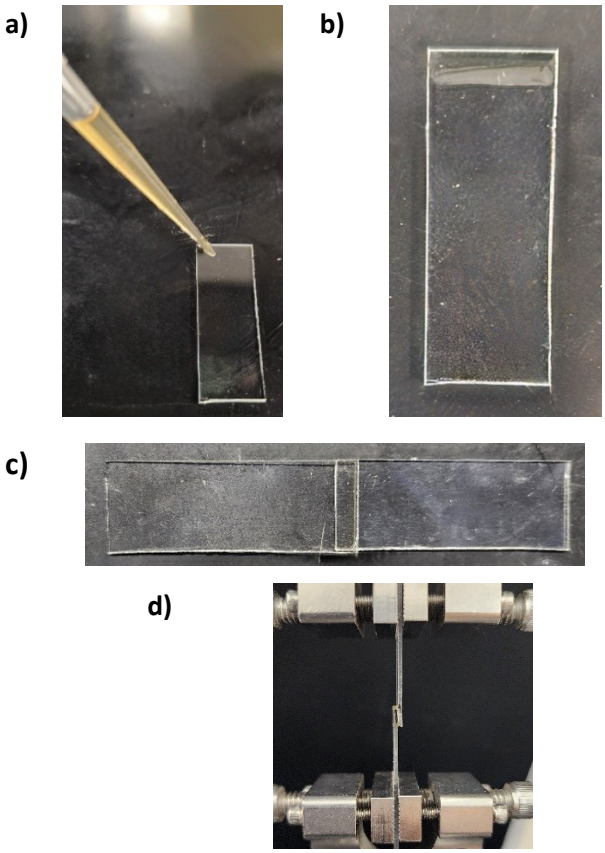

Figure S3: Image of the stepwise process of preparing samples for lap shear adhesion test. (a) Drop coating of adhesive precursor on a glass substrate. (b) Glass substrate with the adhesive precursor after baking at 60 ^{o}C. c) Lap joint sample prepared by attaching two substrates, and (d) image of sample during the lap shear adhesion test.

3. NMR characterization of prepared copolymer

3.1. NMR Spectra of p(HEMA)

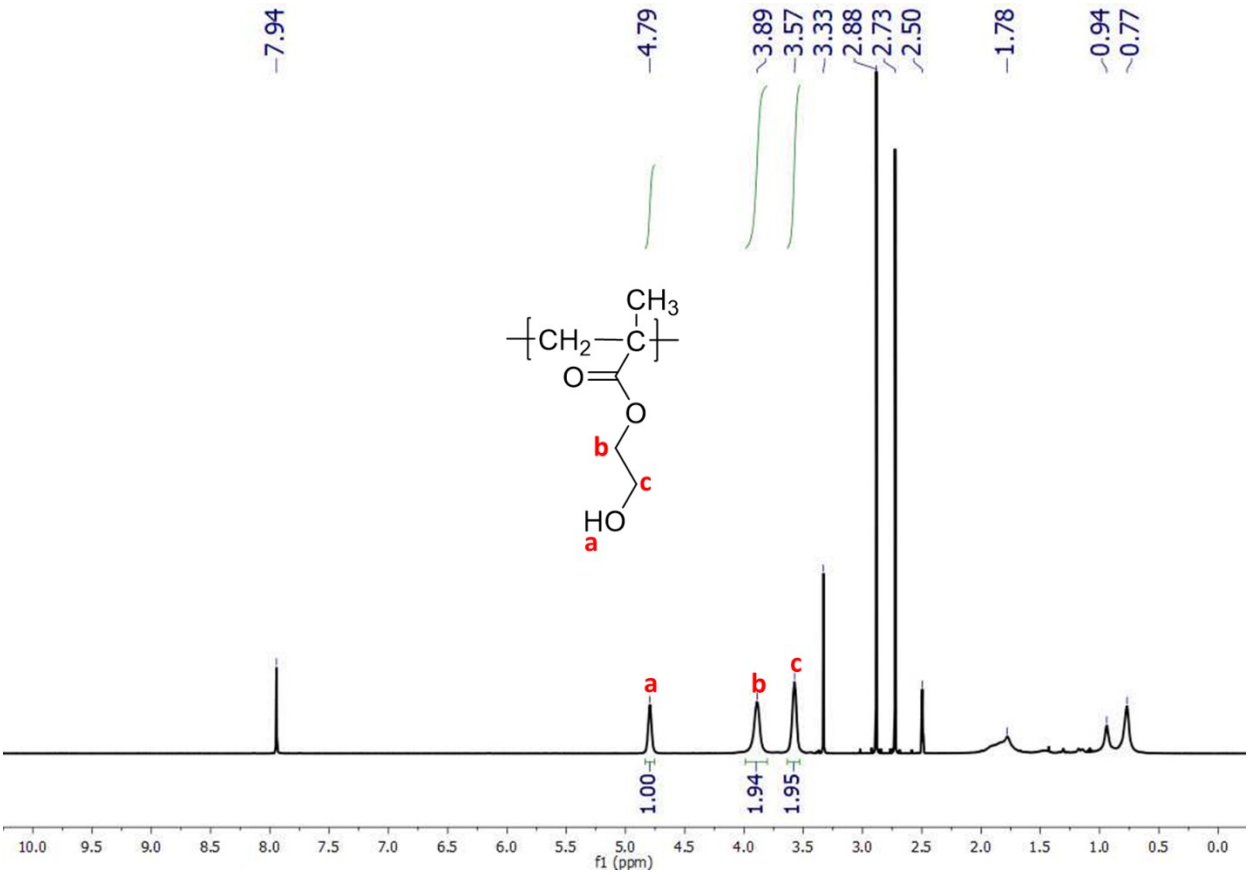

Figure S4 ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(HEMA).

3.2. NMR spectra of p(HEMA-co-SHAM$_{10}$)

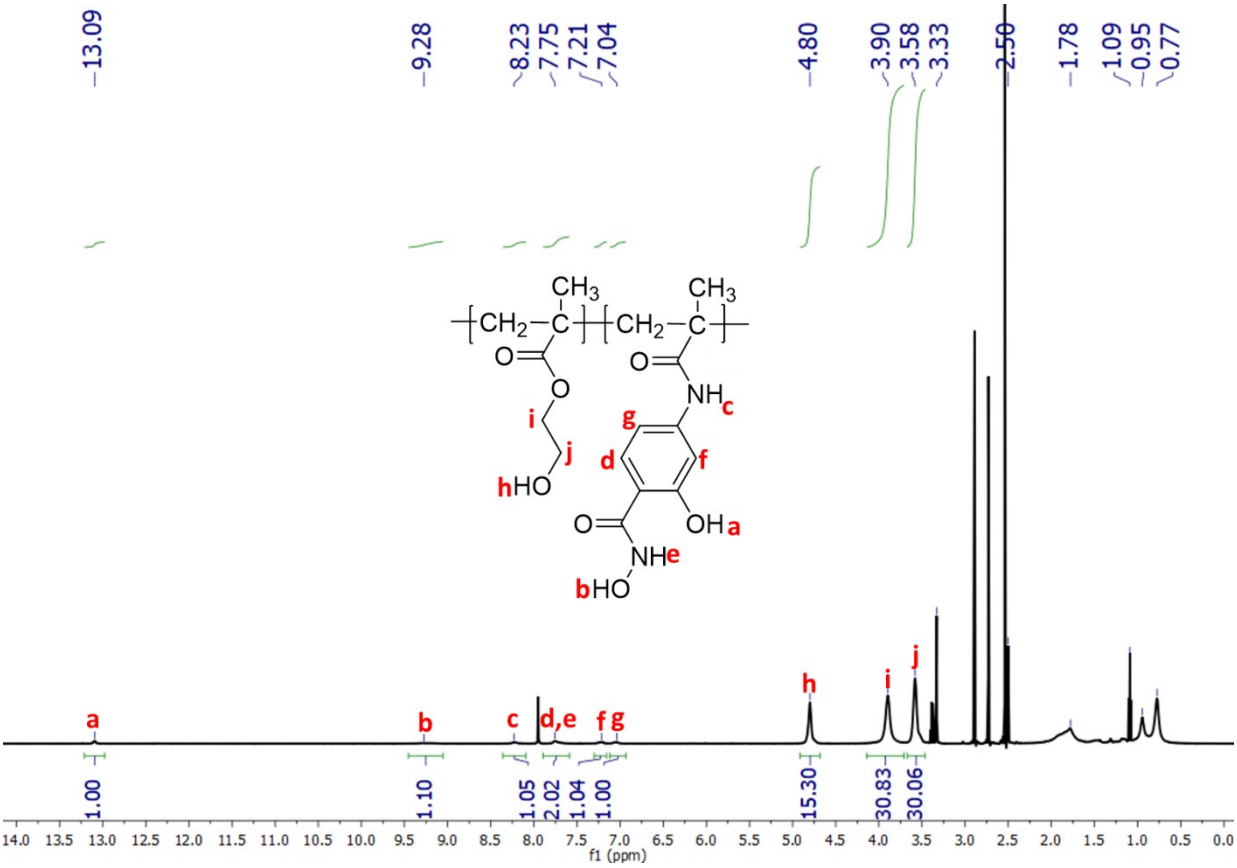

Figure S5. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(HEMA-co-SHAM$_{10}$).

3.3. NMR spectra of p(HEMA-co-SHAM$_{50}$)

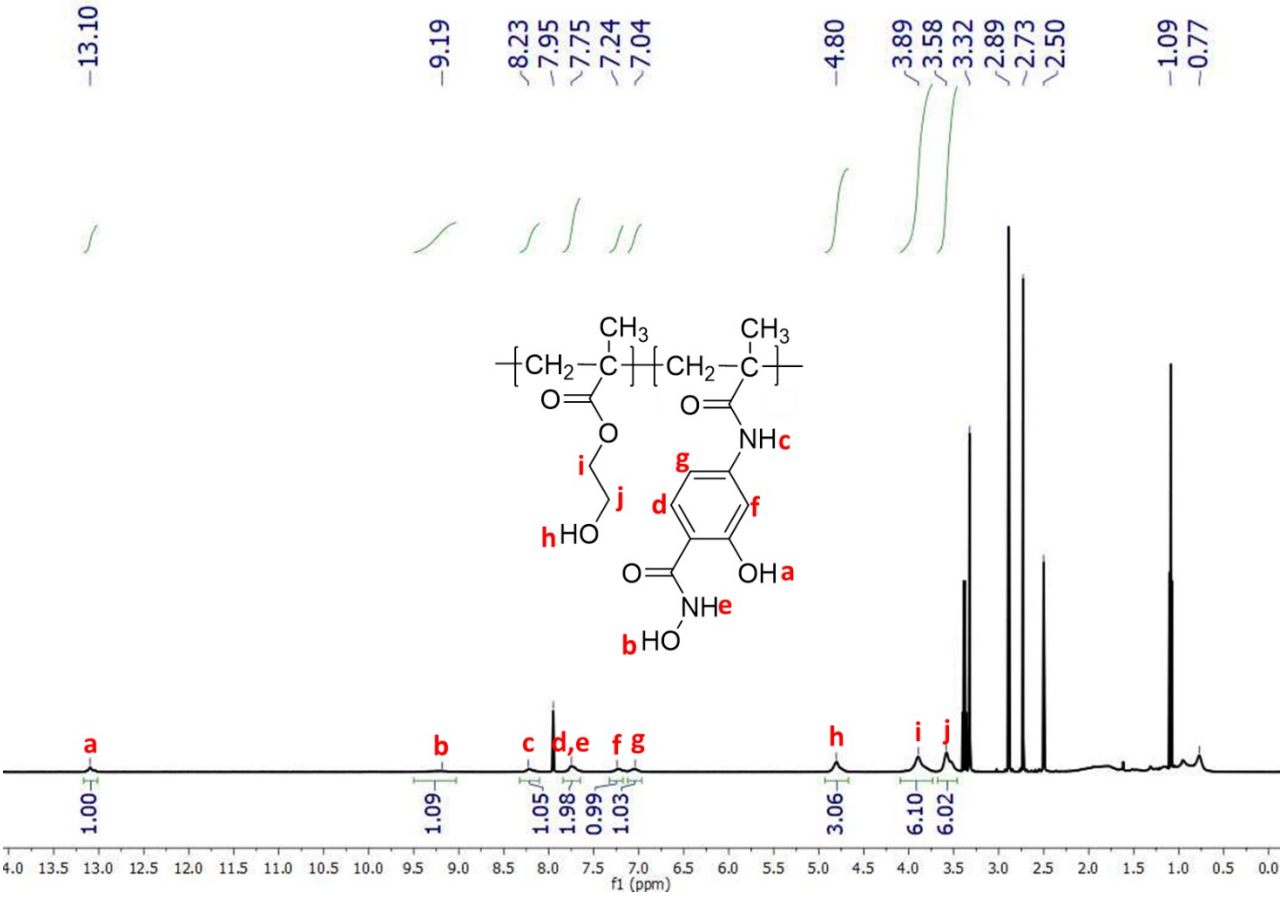

Figure S6. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(HEMA-co-SHAM$_{50}$).

3.4. NMR spectra of p(MEA)

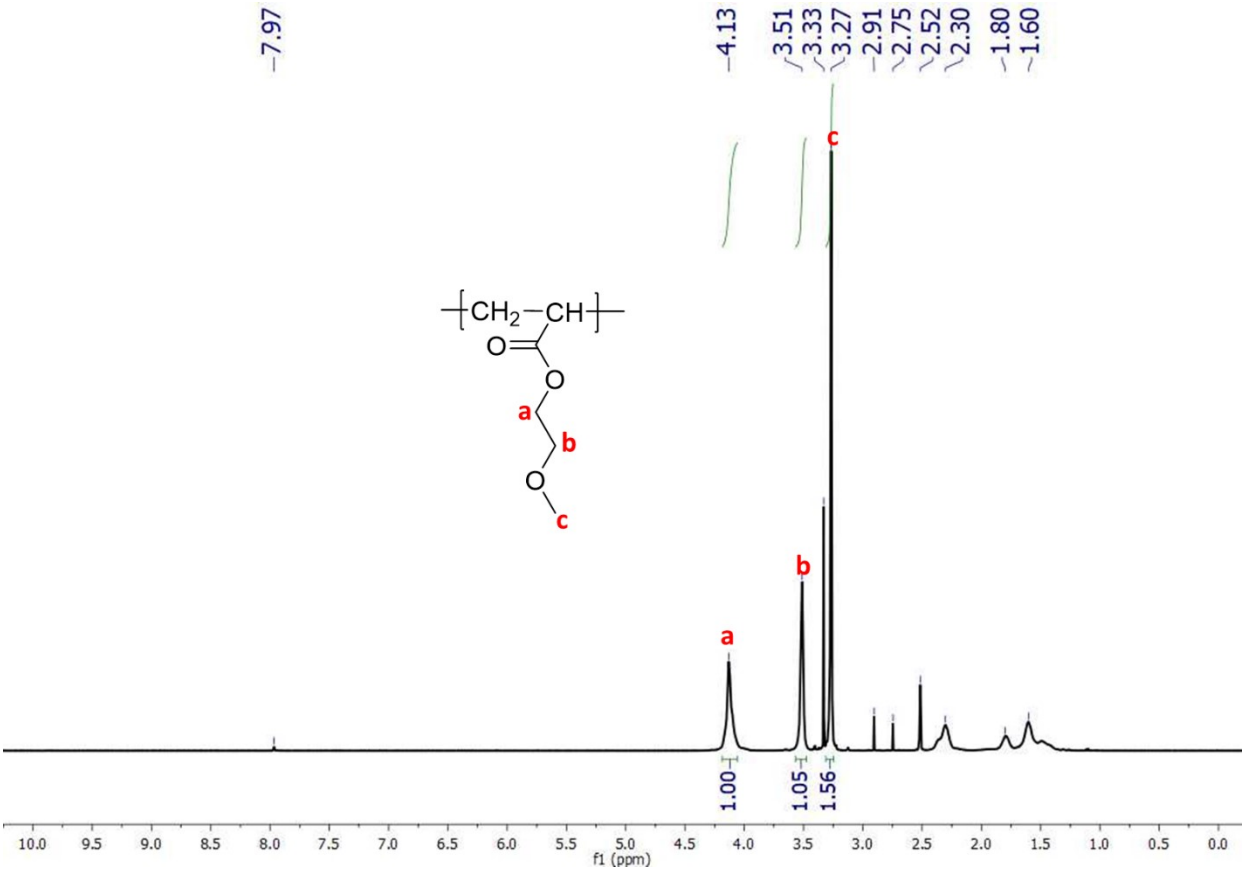

Figure S7. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(MEA).

3.5. NMR spectra of p(MEA-co-SHAM$_{10}$).

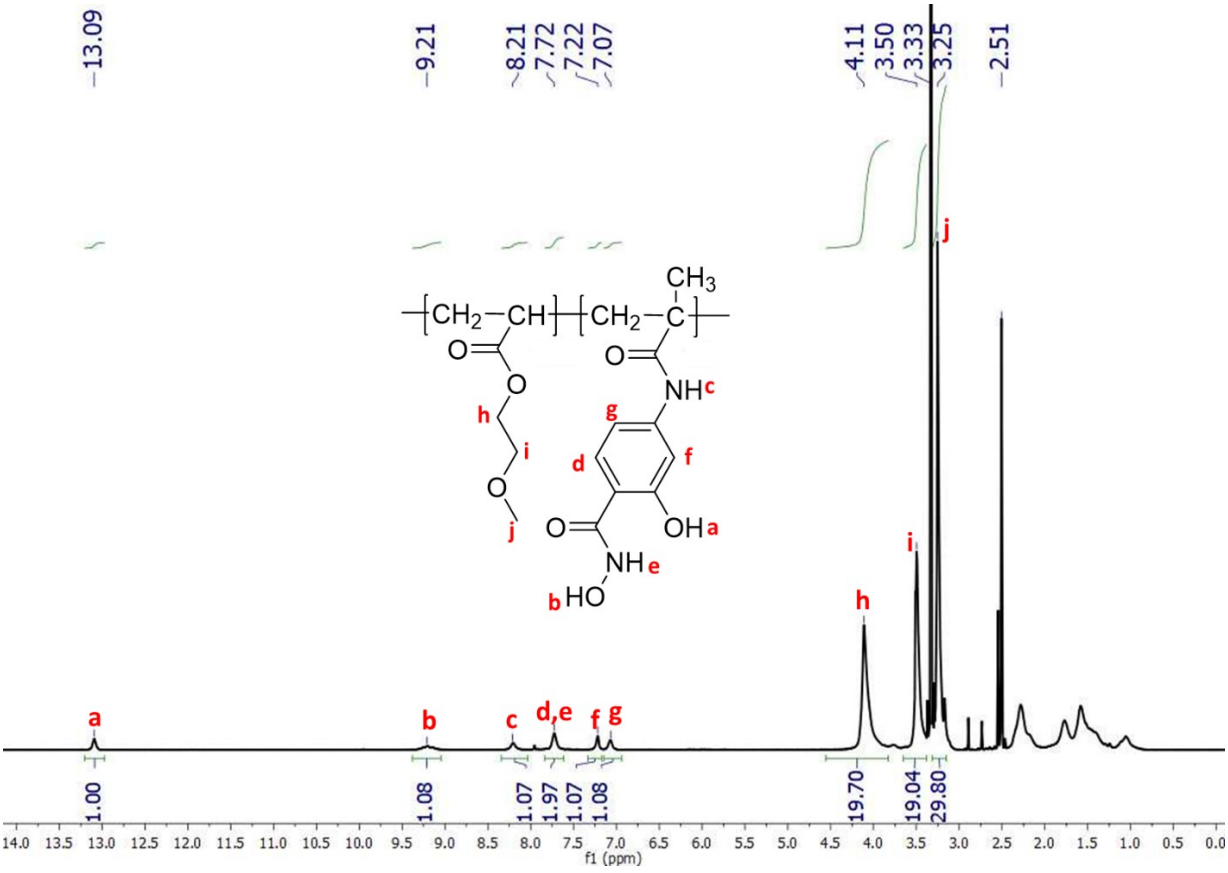

Figure S8. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(MEA-co-SHAM$_{10}$).

3.6. NMR spectra of p(MEA-co-SHAM$_{50}$)

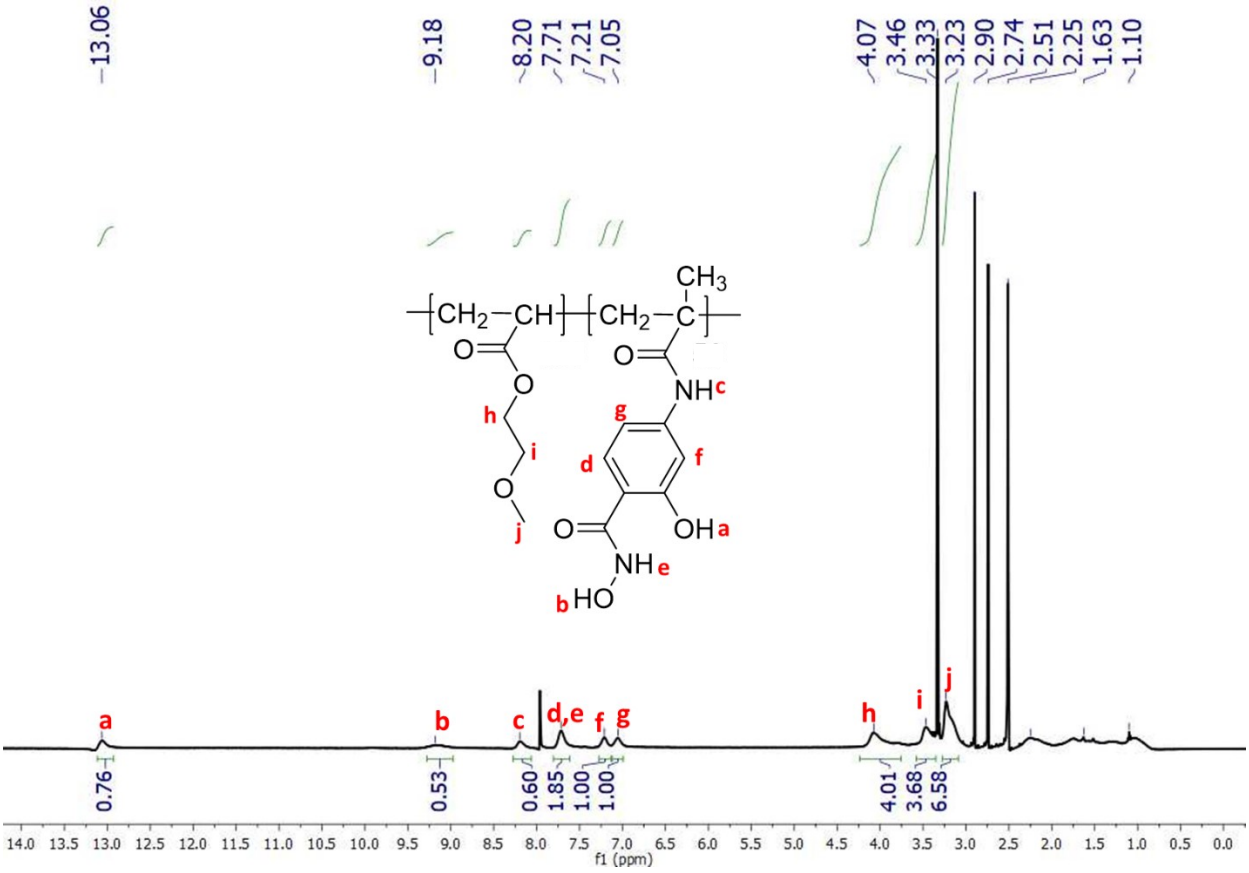

Figure S9. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(MEA-co-SHAM$_{50}$).

3.7. NMR spectra of p(HEMA-co-catechol$_{10}$)

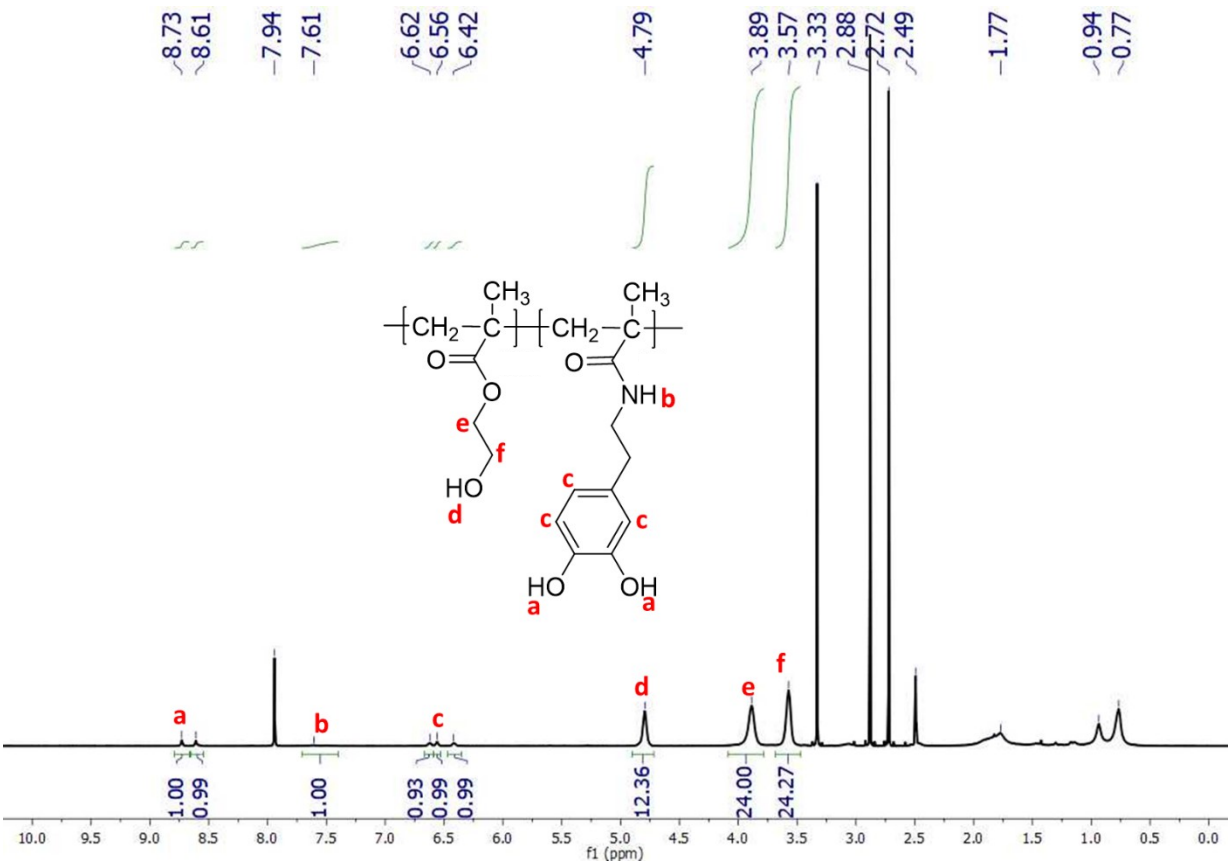

Figure S10. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(HEMA-co-catechol$_{10}$).

3.8. NMR spectra of p(MEA-co-catechol$_{10}$).

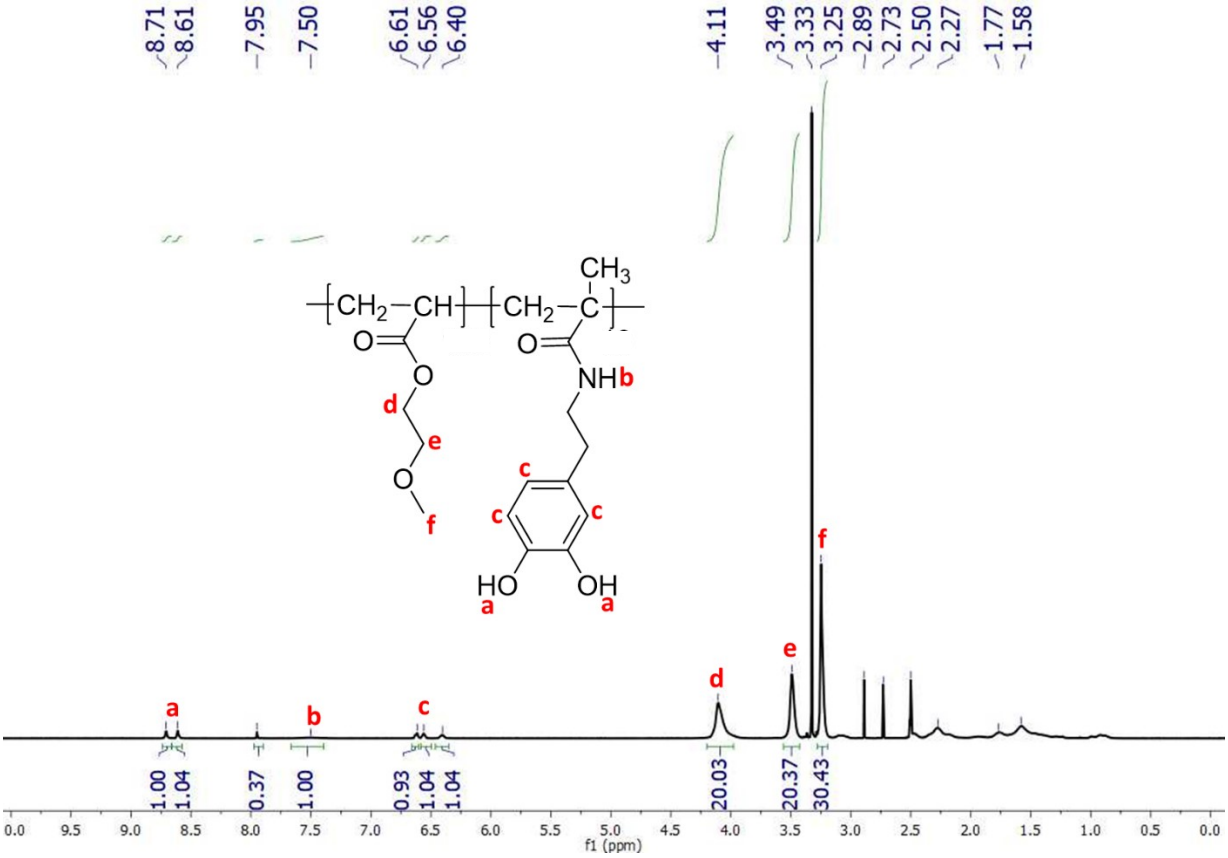

Figure S11. ^{1}H NMR (500 MHz, DMSO-d6) spectra of p(MEA-co-catechol$_{10}$).

4. GPC analysis of polymers

Table S1. Molecular weights of adhesive polymers

Polymer	M_n (g/mol)	M_w (g/mol)	PDI
p(HEMA)	5.49×10^5	2.86×10^6	5.20
p(HEMA-co-SHAM$_{10}$)	3.25×10^5	1.46×10^6	4.47
p(HEMA-co-SHAM$_{50}$)	4.54×10^5	1.40×10^6	3.09
p(MEA)	1.94×10^4	6.25×10^4	3.23
p(MEA-co-SHAM$_{10}$)	4.75×10^6	3.62×10^7	7.63
p(MEA-co-SHAM$_{50}$)	1.27×10^5	5.90×10^5	4.64
p(HEMA-co-catechol$_{10}$)	4.77×10^5	5.10×10^6	10.68
p(MEA-co- catechol $_{10}$)	1.99×10^4	1.94×10^5	9.74

5. ATR-FTIR analysis of dry adhesive

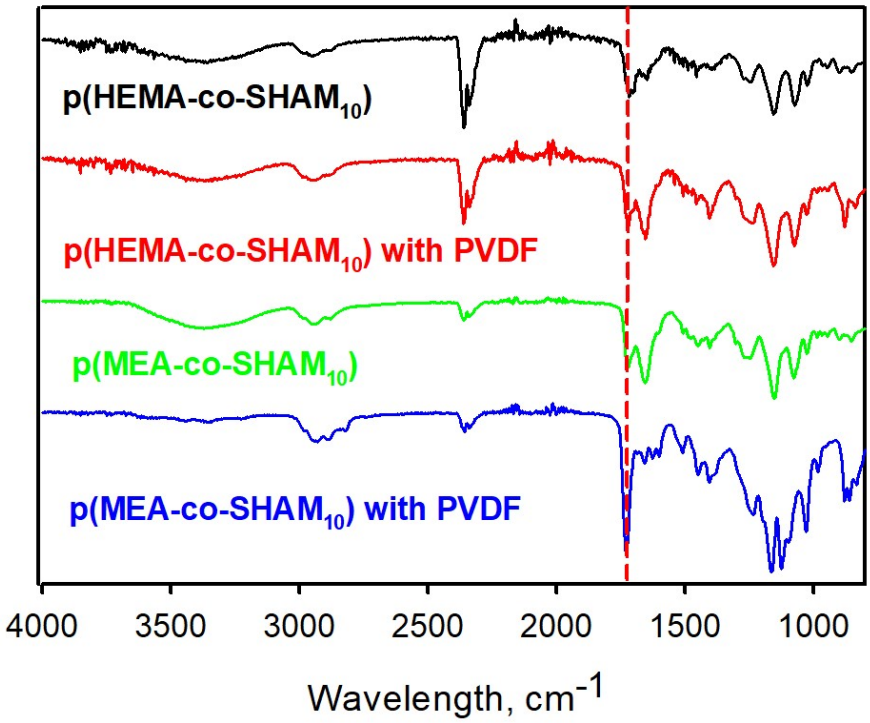

Figure S12. ATR-FTIR spectra of p(HEMA-co-$SHAM_{10}$) and p(MEA-co-$SHAM_{10}$) with and without addition of PVDF in the range of 4000 – 450 cm^{-1}. All the polymer contained 10 mol% SHAM. These adhesives were prepared by maintaining a copolymer-to-PVDF weight ratio of 85:15.

6. Lap shear adhesion test results

6.1. Lap shear test of MEA-based adhesives with different substrates

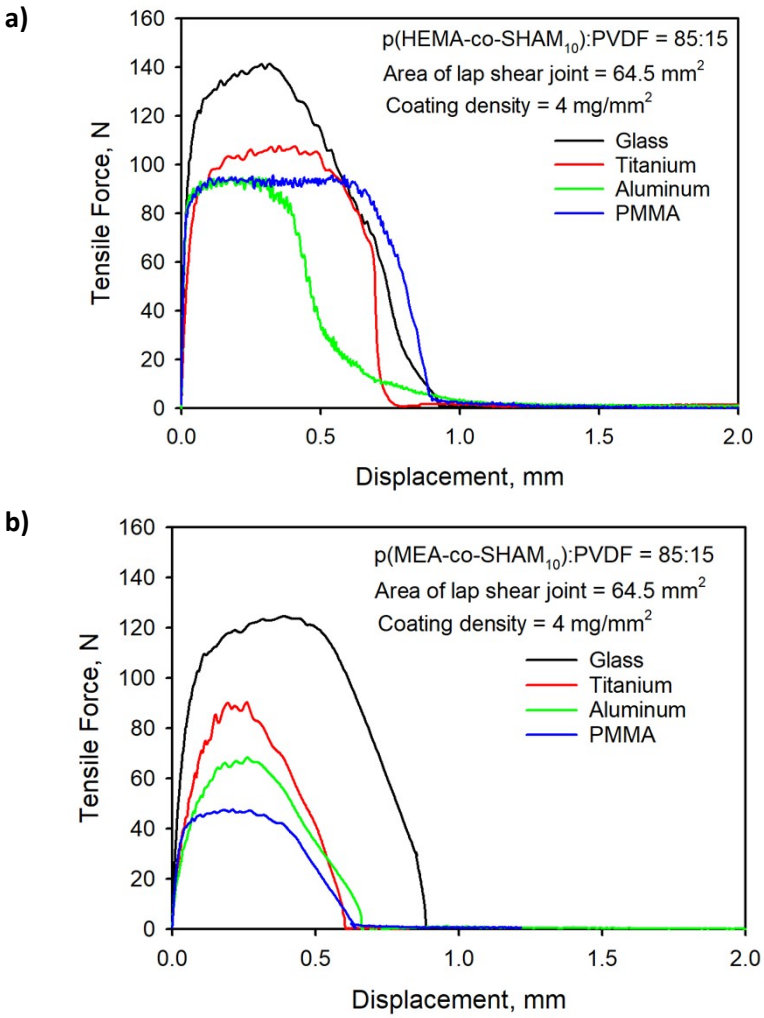

Figure S13. Lap shear curve for (a) p(HEMA-co-SHAM$_{10}$) and (b) p(MEA-co-SHAM$_{10}$) tested with different substrates. The adhesives were prepared by maintaining a copolymer to PVDF weight ratio of 85:15 with an area of joint overlap of 64.5 mm^2 and a coating density of 4 mg/cm^2. (n = 3)

6.2. Image of substrates after lap shear adhesion test

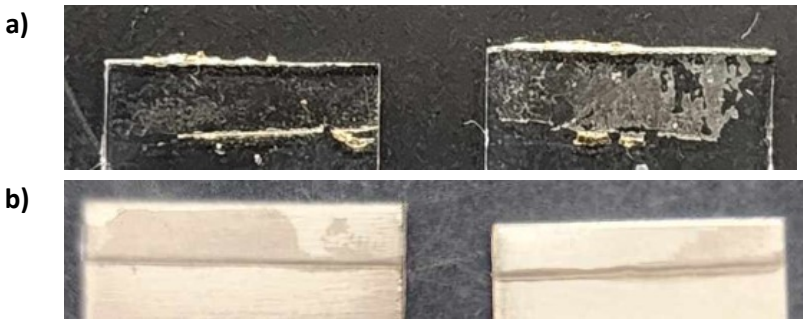

Figure S14. Image of (a) glass and (b) titanium substrates after performing the lap shear adhesion test tested with p(HEMA-co-$SHAM_{10}$). The adhesives were prepared by maintaining a copolymer to PVDF weight ratio of 85:15 with an area of joint overlap of 64.5 mm^2 and a coating density of 4 mg/cm^2.

6.3. Effect of coating density

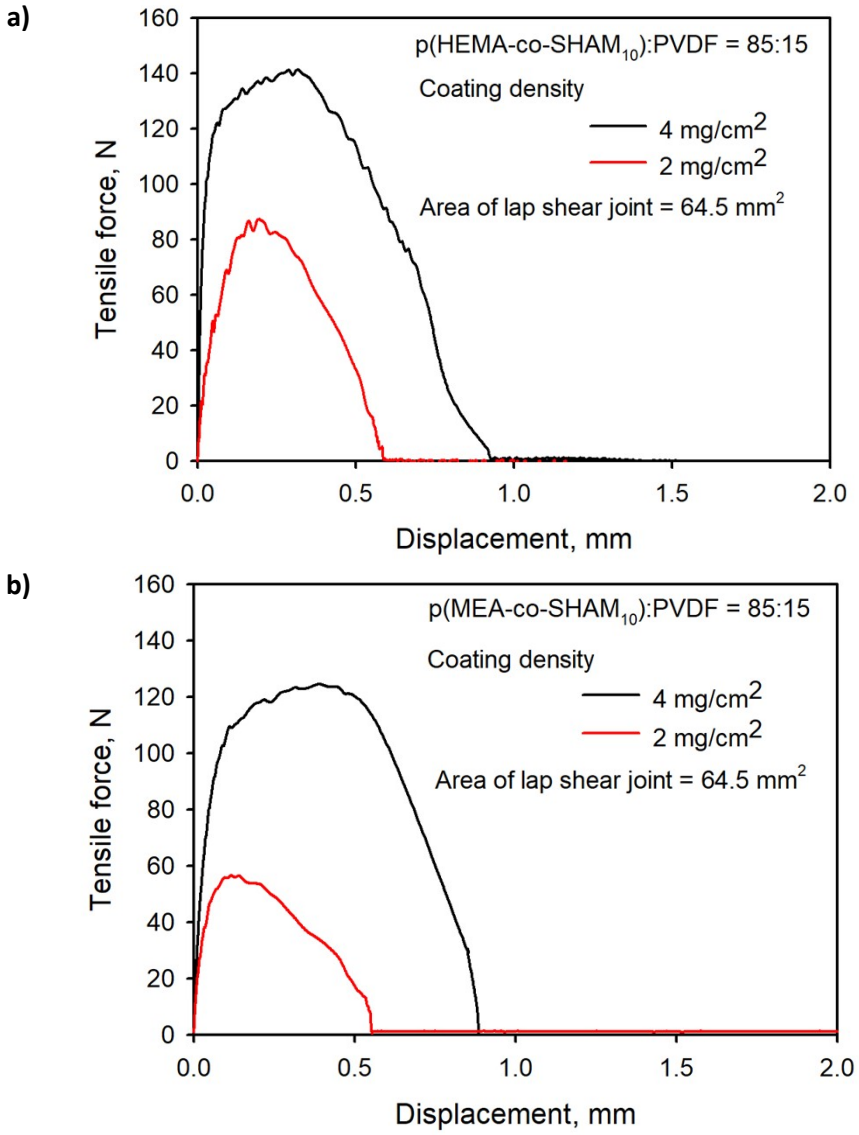

Figure S15. Lap shear curves of (a) p(HEMA-co-SHAM$_{10}$) and (b) p(MEA-co-SHAM$_{10}$) tested with different coating density. The adhesives were prepared by maintaining a copolymer to PVDF weight ratio of 85:15 with an area of joint overlap of 64.5 mm^2. Glass was used as the test substrate.

6.4. Effect of the area of lap shear joint (HEMA-based adhesive)

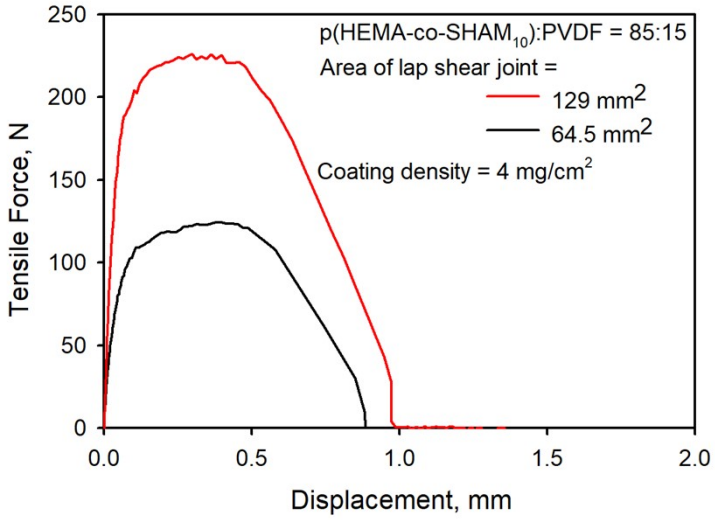

Figure S16. Lap shear curve of the adhesives prepared with p(HEMA-co-$SHAM_{10}$) tested with adhesive joints with different overlapped area. The adhesives were prepared by maintaining a copolymer to PVDF weight ratio of 85:15 with a coating density of 4 mg/cm^2. Glass surfaces were used as the test substrate.

6.5. Effect of copolymer to PVDF weight ratio

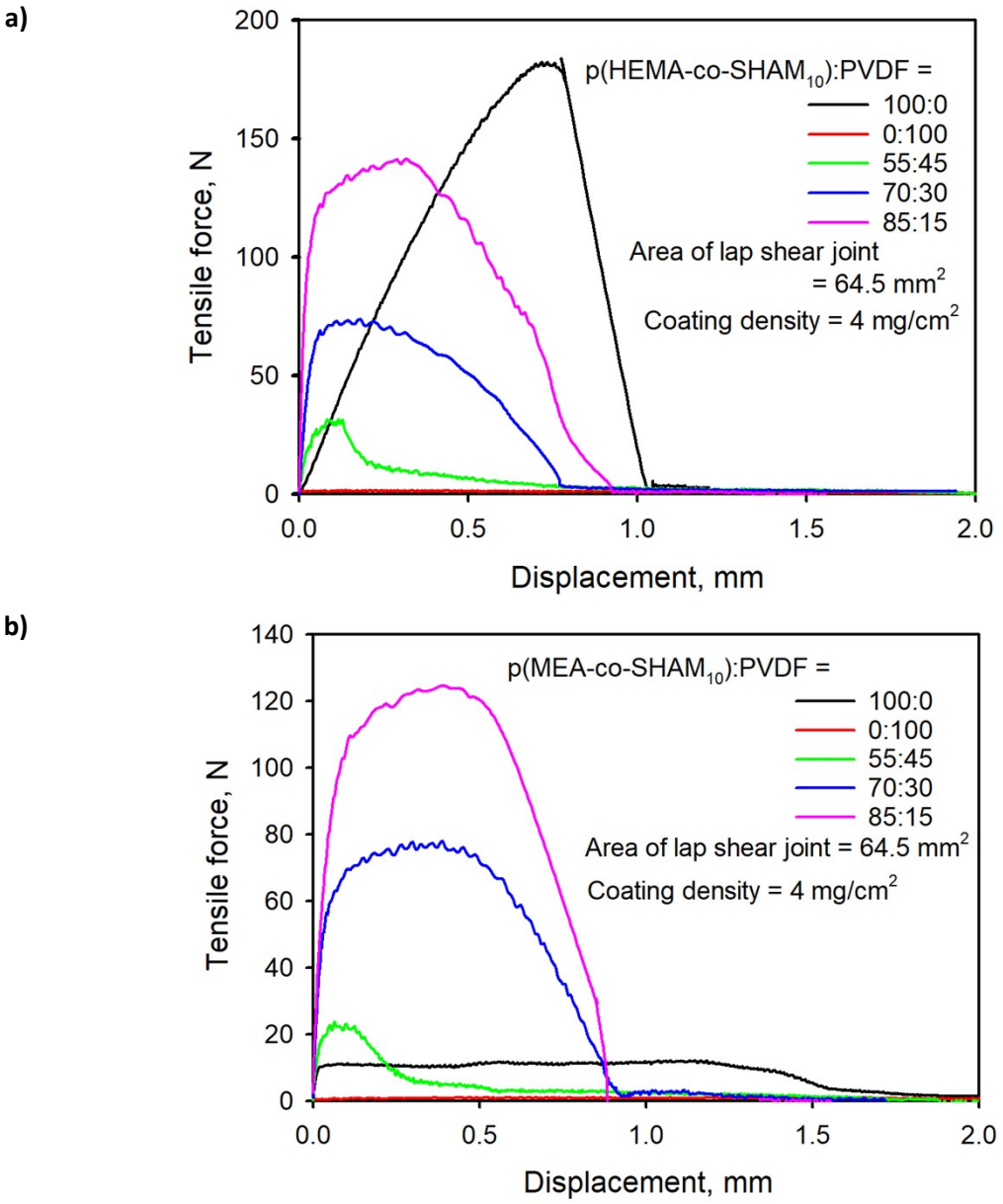

Figure S17. Lap shear curve of the adhesives prepared with (a) p(HEMA-co-$SHAM_{10}$) and (b) p(MEA-co-$SHAM_{10}$) with different copolymer to PVDF weight ratios. The adhesives were prepared with an overlapped area of 64.5 mm^2 and a coating density of 4 mg/cm^2. Glass surfaces were used as the test substrate.

6.6. Effect of mol% of SHAM on S_{adh}

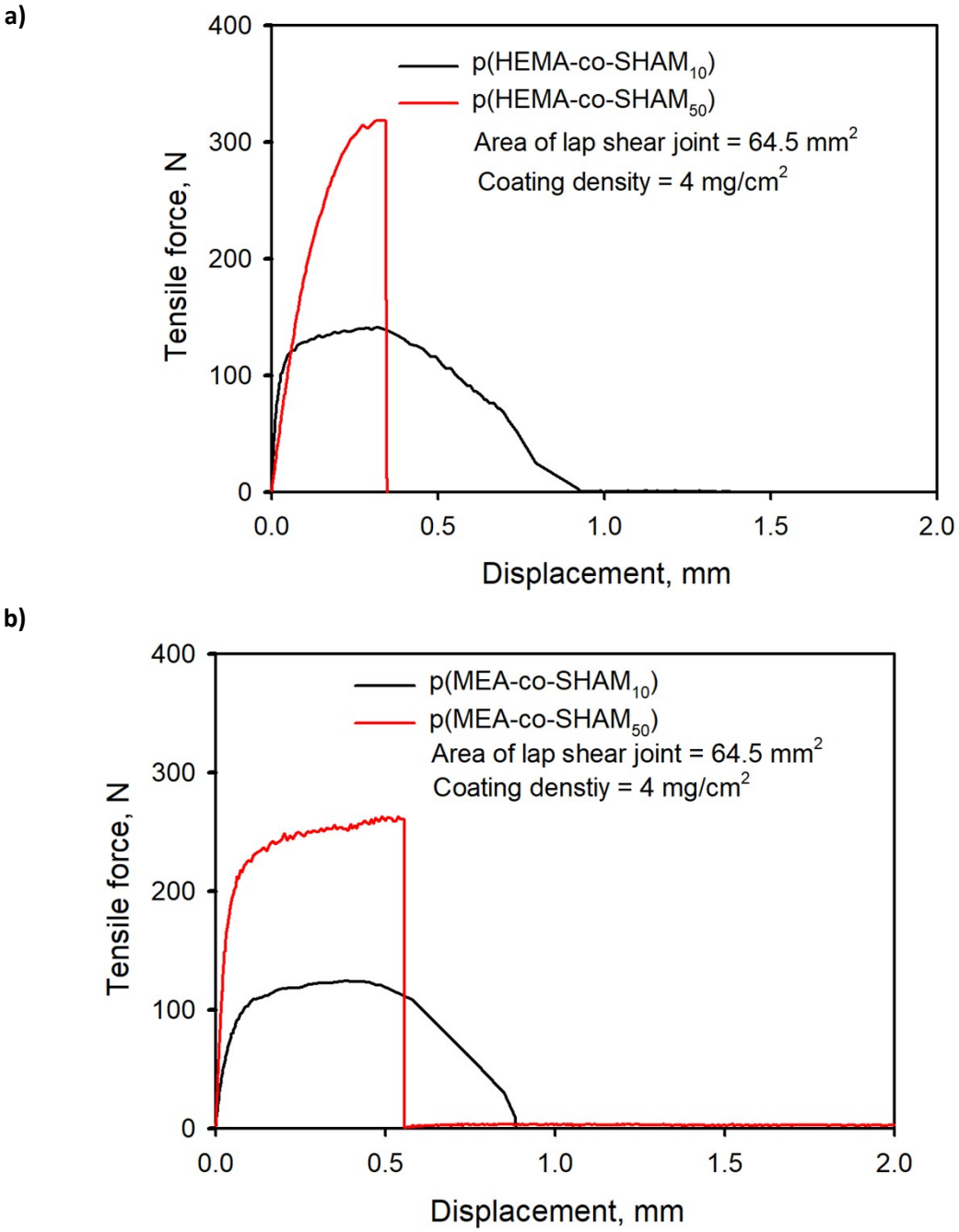

Figure S18. Lap shear curve of the adhesives prepared (a) p(HEMA-co-$SHAM_{10}$) and (b) p(MEA-co-$SHAM_{10}$) containing different mol% SHAM. Adhesives were tested at a copolymer to PVDF weight ratio of 85:15, with an overlapped area of 64.5 mm^2 and a coating density of 4 mg/cm^2.

6.7. Comparison of SHAM-based adhesive with commercial epoxy

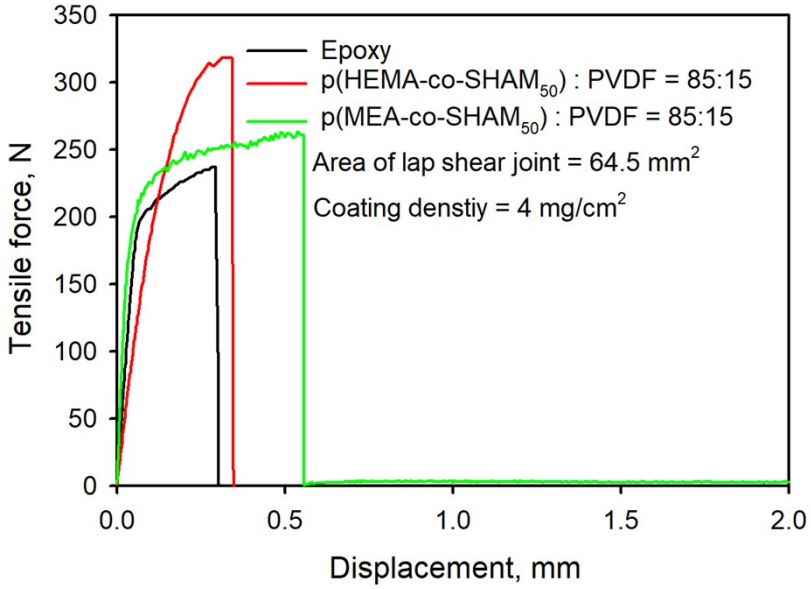

Figure S19. Lap shear curve of of epoxy, p(HEMA-co-$SHAM_{50}$), and p(MEA-co-$SHAM_{50}$). Adhesive contained a copolymer to PVDF weight ratio of 85:15, with an overlapped area of 64.5 mm^2 and a coating density of 4 mg/cm^2.

6.8. Supplementary video related information

The supplementary **Video S1** captured the tackiness of SHAM-based adhesive. The precursor solution containing a mixture of p(HEMA-co-$SHAM_{10}$) and PVDF (85:15 weight ratio) was coated onto the surface of a 100-g, stainless steel weight with a surface area of 258 mm^2 and a coating density of 4 mg/cm^2. Then, a glass substrate was attached to the adhesive-coated surface to create an adhesive interface (**Figure S19**). The adhesive joint was weighted down by another 100-g weight for ~10 seconds to bond the glass with the weight and the assembly was lifted.

Figure S20. Photograph showing adhesively bonded glass and weight used for demonstrating the tackiness of the adhesive. The adhesive was prepared with p(HEMA-co-$SHAM_{10}$) and PVDF mixture with a copolymer to PVDF weight ratio of 85:15, an overlapped area of 258 mm^2 and a coating density of 4 mg/cm^2.

7. Aging analysis of prepared adhesives

7.1. 5-day aging analysis of SHAM-based adhesive

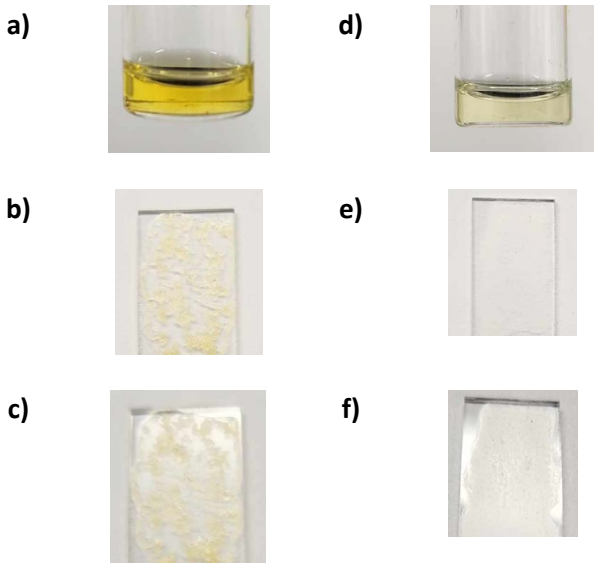

Figure S21: Qualitative analysis of (a-c) p(HEMA-co-SHAM$_{10}$)- and (d-f) p(MEA-co-SHAM$_{10}$)-based adhesive that contained a copolymer to PVDF weight ratio of 85:15. Photographs of (a,d) adhesive precursor solution, (b,e) dried adhesive on glass surface, and (c,f) adhesive coating after 5 days.

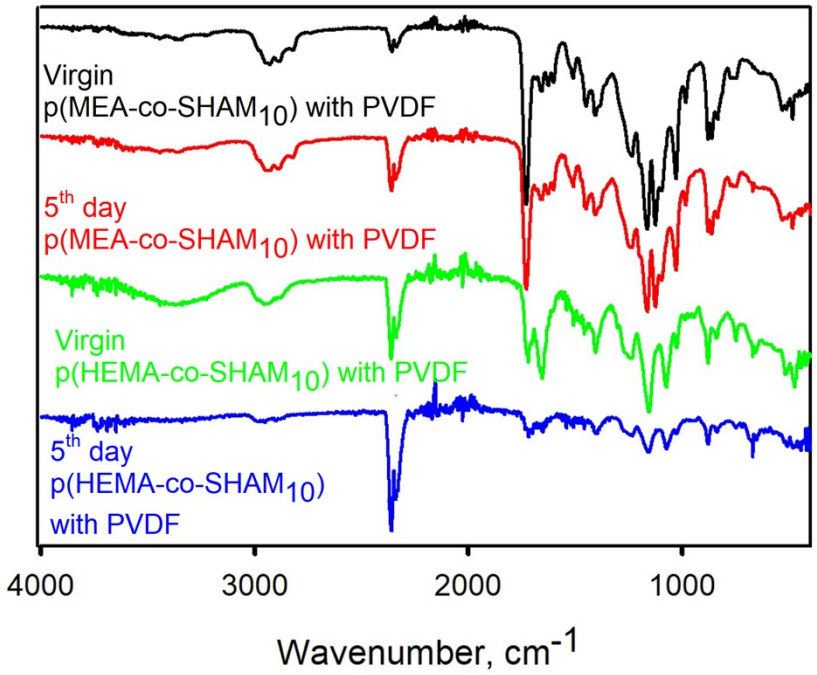

Figure S22. ATR-FTIR spectra of adhesives prepared with PVDF by maintaining a copolymer to PVDF weight ratio of 85:15. Adhesive precursor mixture was drop-coated onto a glass slide and exposed to normal room conditions (Temperature ≈21.5° C, Humidity ≈ 20%) for 5 days. The spectra were collected before and after 5 days for comparison.

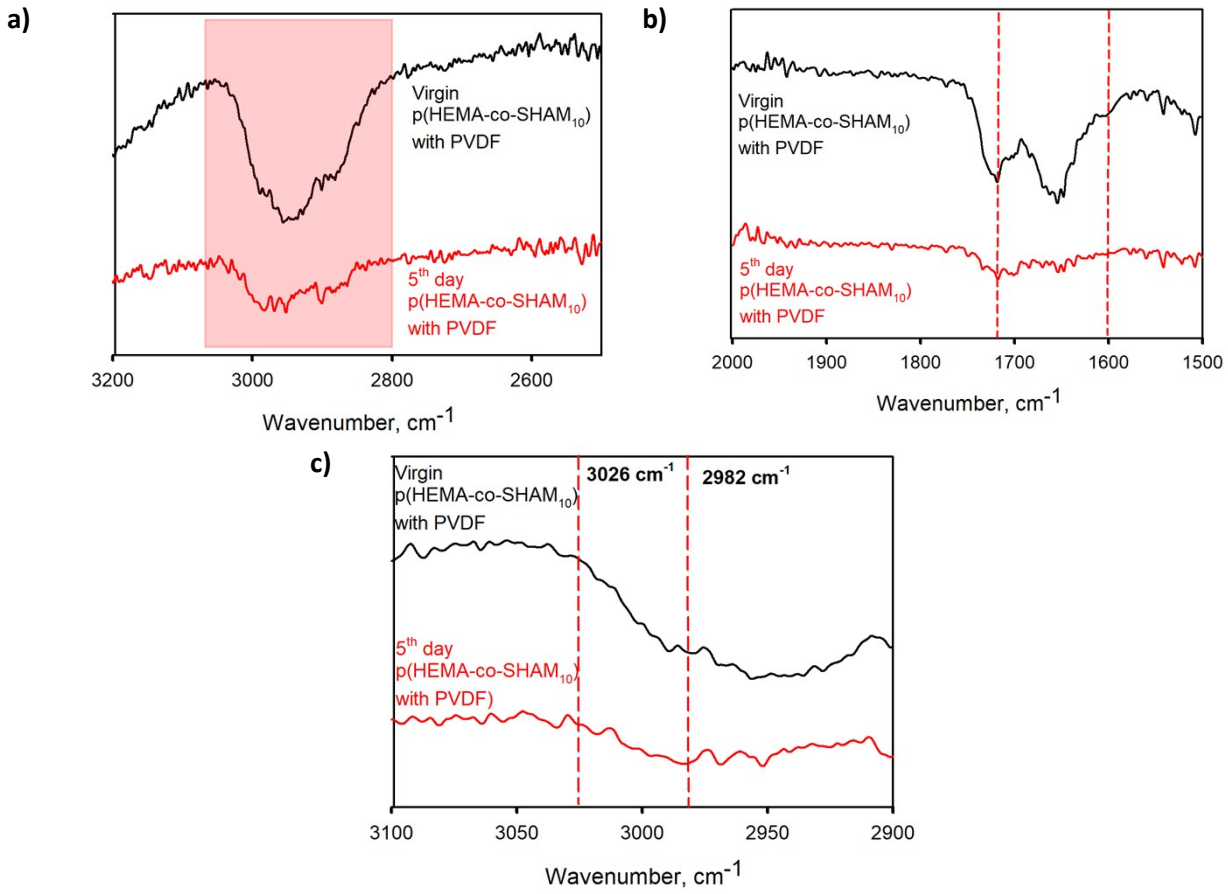

Figure S23. ATR-FTIR spectra of p(HEMA-co-SHAM$_{10}$) with a copolymer to PVDF weight ratio of 85:15, showing a) C-H stretching region of 2800 – 3063 cm^{-1} (red boxed region) in the range of 3200 – 2500 cm^{-1}, b) peaks associated with C=O and C=C (red dashed line at 1720 – 1730 cm^{-1} and around 1600 cm^{-1}) in the range of 2000 -1500 cm^{-1}, respectively, and c) peaks associated with PVDF (red dashed lines) in the range of 3100 – 2900 cm^{-1}.

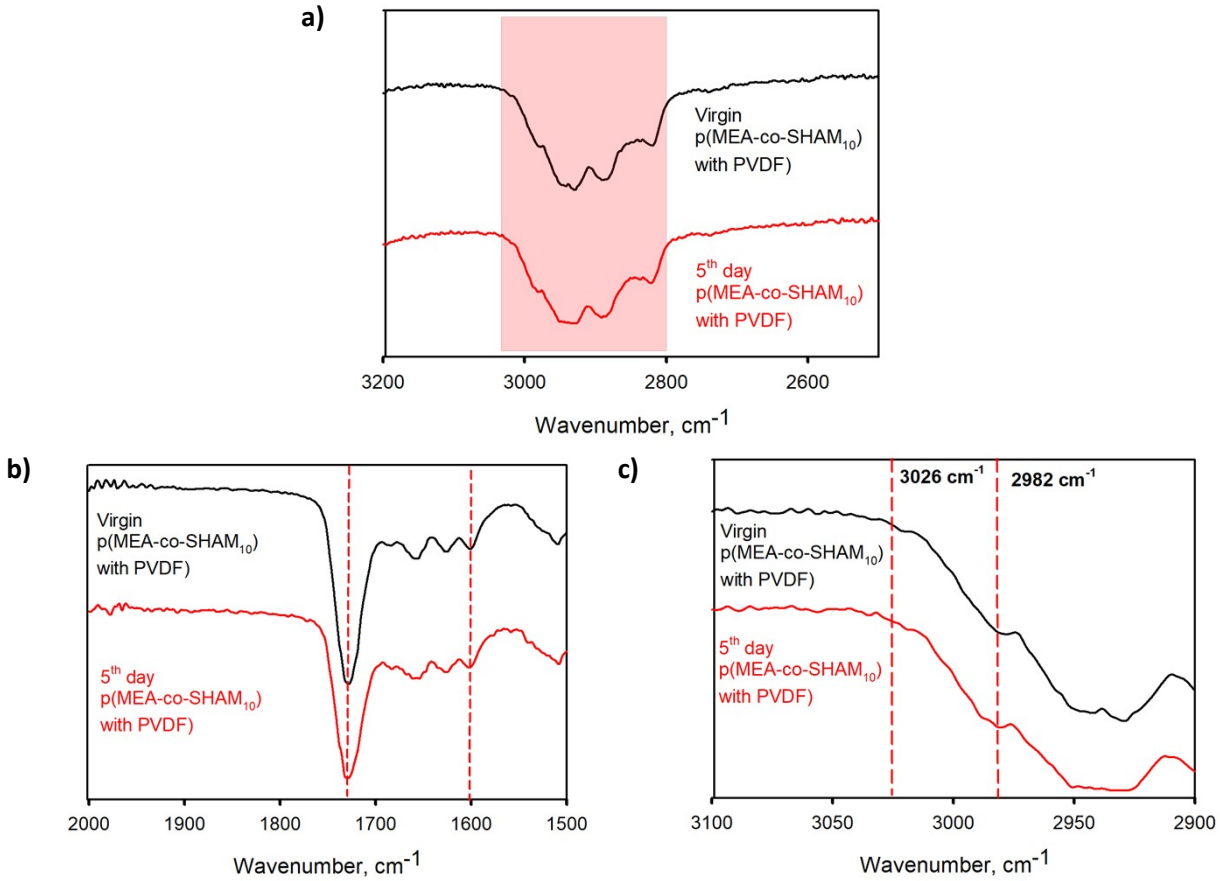

Figure S24. ATR-FTIR spectra of p(MEA-co-SHAM$_{10}$) with a copolymer to PVDF weight ratio of 85:15, showing a) C-H stretching region (red boxed region, at 2800 – 3063 cm^{-1}) in the range of 3200 – 2500 cm^{-1}, b) peaks associated with C=O and C=C (red dashed line, at 1720 – 1730 cm^{-1} and around 1600 cm^{-1}) in the range of 2000 -1500 cm^{-1}, respectively, and c) peaks associated with PVDF (red dashed lines) in the range of 3100 – 2900 cm^{-1}.