

Supporting Information for

**Changing Polymer Catechol Content to Generate Adhesives for High versus  
Low Energy Surfaces**

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**Synthesis and Characterization of Poly(catechol-MMA-OEG).**

**Table S1.** Characterization data for poly(catechol-MMA-OEG) terpolymers synthesized.

**Figure S1.** Statistical analysis of adhesive bonding strengths on aluminum and Teflon.

**Figure S2.** Solvent effects of adhesion of poly(catechol-MMA-OEG) on aluminum.

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**Table S2.** Lap shear adhesion force-vs-extension curves average FWHM.

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**Figure S6.** Shear modulus of polymers with varying catechol content.

**Figure S7.** Failure modes on substrates before iodine staining.

## Synthesis and Characterization

### *Monomer Influences on Polymer Synthesis*

The same batch of dopamine methacrylamide (DMA) was used for most of the final family of polymers to avoid batch-to-batch variation as much as possible. The 41 mol% and 51 mol% catechol polymers were from a different batch of DMA than the others used in this study, which may be a potential reason for slight variations of those two polymers with adhesion testing on aluminum and Teflon. Batch-to-batch variation also affected the polymer synthesis. This phenomenon was evidenced by the altered final incorporations compared to the initial feed ratios of the monomers outlined in Table S1. Extensive analysis of the DMA with NMR, mass spectrometry (MS), infrared (IR) spectroscopy, and UV-visible spectroscopy showed that some DMA was dimerized through borate protecting two catechol groups. Batches of DMA that were able to be polymerized and yielded the best adhesion strengths contained about 7.5-11.5% of the boron-containing dimer. This composition was determined by NMR spectra integration of the doublet at 6.33 ppm. Mass spectrometry also suggested the presence of DMA molecules that were protected by a single borate, creating a boronate ester derivative. The variations from batch-to-batch in amounts of dimer, borate-protected DMA, and unprotected DMA likely affected polymer reproducibility and caused the differences in resulting polymers. That said, the 41 mol% and 51 mol% catechol polymers were still used for this study. The adhesion strengths of these polymers followed the same trends and were not substantially higher or lower than the other similar incorporations.

To achieve a family of eight polymers with consistent OEG incorporation, a 33 mol% OEG monomer feed yielded the best results for targeting this incorporation. The differences in molar feed ratio to final polymer composition was likely due to the differences in kinetics of

polymerization of the three different monomers polymerized together. Table S1 shows this 33 mol% feed was maintained for all final polymers used in this study. The catechol content ranged from 0 to 51 mol% after altering feed ratios of the DMA and OEG monomers during synthesis. A copolymer with 55 mol% catechol and 45 mol% OEG was not used due to solubility issues.

#### *Solubility of Poly(Catechol-MMA-OEG)*

For early polymer batches, solubility was limited for higher incorporations of DMA, even with several different solvents and lower concentrations. Polymers with 30-40 mol% catechol incorporation precipitated out of solution before setting up adhesion tests, and higher percentages were completely insoluble. Initial DSC testing was performed with these polymers to confirm a statistical terpolymer microstructure rather than a block configuration induced by polymerization kinetics. The presence of two separate glass transition temperatures ( $T_g$ ) would have been indicative of a block microstructure, which would contribute to poor solubility of the polymer. The DSC experiments did not show multiple thermal events, so the polymers were assumed to have a statistical terpolymer configuration. The poor solubilities could likely be attributed to the Trommsdorff effect: high viscosity during synthesis decreased the rate of diffusion for monomers, causing high conversion by autoacceleration.<sup>1,2</sup> In addition to insolubility, this effect can be justified by the low monomer concentration determined from  $^1\text{H}$  NMR before polymer purification and the high, bimodal molecular weight distributions ( $\bar{M}$ ) detected by GPC.<sup>2</sup> This effect was noted by gelation of the polymerization solution during synthesis within a few hours of initiation. To resolve this issue, concentration during synthesis was decreased (i.e., more solvent was added) so that the solutions would not gel during polymerization. Since molecular weight is also dependent upon concentration during synthesis, terpolymers with the highest

DMA incorporation were synthesized first to achieve a desirable molecular weight. Other syntheses were adjusted by adding more solvent and reducing concentration to achieve more comparable molecular weights.

#### *Molecular Weights of Poly(Catechol-MMA-OEG)*

Molecular weights of polymer chains can play a role in adhesion. Consequently, monomer concentrations and reaction times were adjusted for each feed ratio to maintain comparable molecular weights between the different polymers. Between influences of three different monomers, autoacceleration effects, solubility issues, and attaining final composition and molecular weight targets, it took over 90 syntheses to achieve a series of eight polymer samples similar enough to use for the following structure-function studies. The family of synthesized polymers had a weight-average molecular weight ( $M_w$ ) range between 13,000 - 59,000 g/mol (Table S1). Number-average molecular weights ( $M_n$ ) had a smaller range and remained more consistent between the polymers.

Lower molecular weights were observed with more catechol present. These polymers were not readily soluble in the tetrahydrofuran (THF) eluent used by the available GPC. Matrix-assisted laser desorption ionization (MALDI) MS was also attempted to confirm molecular weights, but the mixture of three different monomers into a single polymer chain made finding a suitable matrix difficult. However, solubility trends and an observed decrease in molecular weight with increased catechol are consistent with other catechol-containing methacrylate copolymers.<sup>3</sup> Additionally, a dispersity ( $\mathcal{D}$ ) of  $\sim 2$  is typical for free radical polymerizations, but higher catechol content contributed to higher  $\mathcal{D}$ , which can be attributed to the radical scavenging effect of catechols.<sup>3</sup> These similarities suggest that higher catechol content polymers

are likely crosslinked in nature, which could have occurred through reaction of catechol radicals and propagating radicals from a different polymer chain. Prior literature has shown that higher DMA content correlates with more crosslinking in the polymers, but the overall number of branches in the polymer is low.<sup>3</sup> While branching may influence adhesion, the lower concentrations used for adhesion studies may account for this effect.

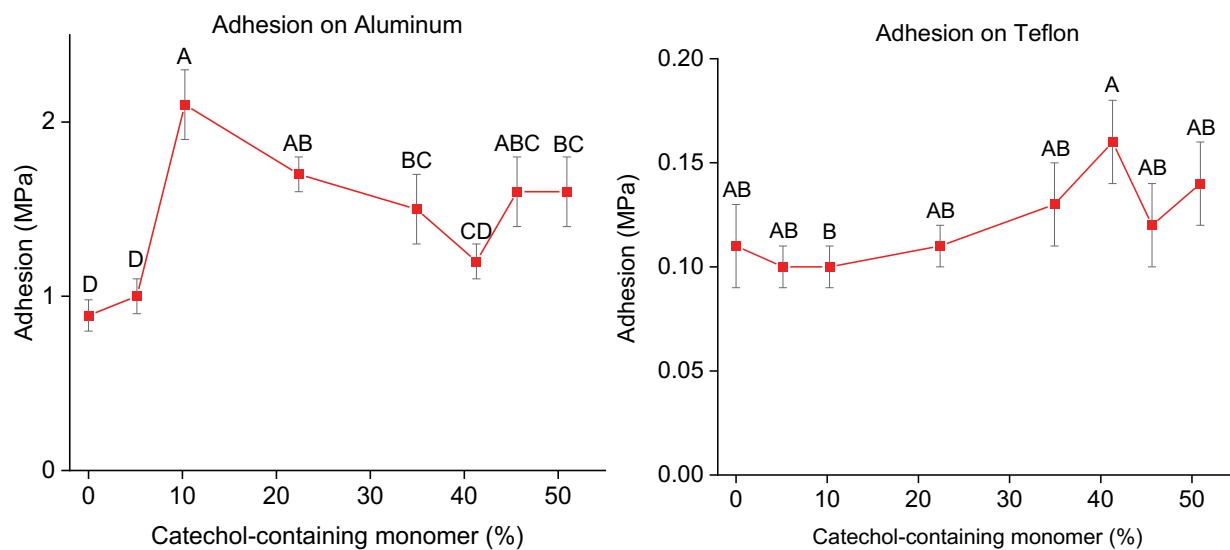
## References

- (1) O'Shaughnessy, B.; Yu, J. Autoacceleration in Free Radical Polymerization. 1. Conversion. *Macromolecules* **1994**, *27*, 5067–5078.
- (2) O'Shaughnessy, B.; Yu, J. Autoacceleration in Free Radical Polymerization. 2. Molecular Weight Distributions. *Macromolecules* **1994**, *27*, 5079–5085.
- (3) Yang, J.; Keijsers, J.; van Heek, M.; Stuiver, A.; Cohen Stuart, M. A.; Kamperman, M. The Effect of Molecular Composition and Crosslinking on Adhesion of a Bio-Inspired Adhesive. *Polym. Chem.* **2015**, *6* (16), 3121–3130.

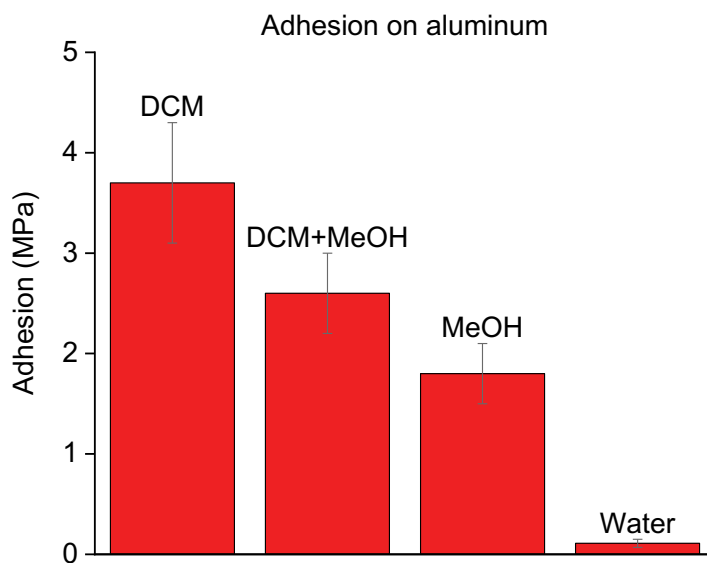
**Table S1:** Characterization data for poly(catechol-MMA-OEG) terpolymers synthesized

Feed (mol%)			Incorporation (mol%)			M <sub>n</sub>	M <sub>w</sub>	Dispersity
Catechol	MMA	OEG	Catechol	MMA	OEG	(g/mol) <sup>a</sup>	(g/mol) <sup>b</sup>	(Đ)
0	67	33	0	53	47	24,700	46,100	1.9
5	62	33	5	51	44	26,100	59,000	2.3
10	56	34	10	46	43	12,100	36,400	3.0
20	47	33	22	31	46	10,900	30,600	2.8
34	32	34	35	21	44	6,680	15,300	2.3
40	27	33	41	14	45	8,250	18,000	2.2
40	27	33	46	9	46	10,900	21,700	2.0
50	17	33	51	6	44	7,700	13,000	1.7

<sup>a</sup>Number-average molecular weight, <sup>b</sup>Weight-average molecular weight

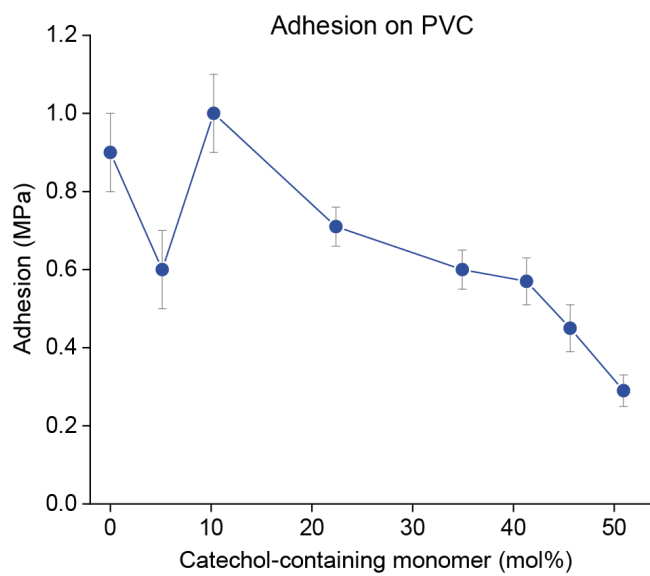


**Figure S1:** Adhesive bonding strengths on aluminum and Teflon. Adhesion data are represented by the mean  $\pm$  90% confidence intervals. ANOVA and Tukey's *post hoc* tests were performed to determine significant differences in the adhesion strengths. Means that do not share a letter are significantly different.



**Figure S2:** Adhesion of poly(catechol-MMA-OEG) with 10 mol% catechol on aluminum. Adhesion in methanol, methylene chloride (DCM), and a 1:1 combination of the two are shown with a concentration of 0.15 g/mL. The highest concentration achieved in water was 0.1 g/mL. Although DCM appears to give higher adhesion in this one case, not all polymers could dissolve into this solvent. Consequently, 1:1 DCM:MeOH and 0.1 g/mL were chosen for the structure-function studies.

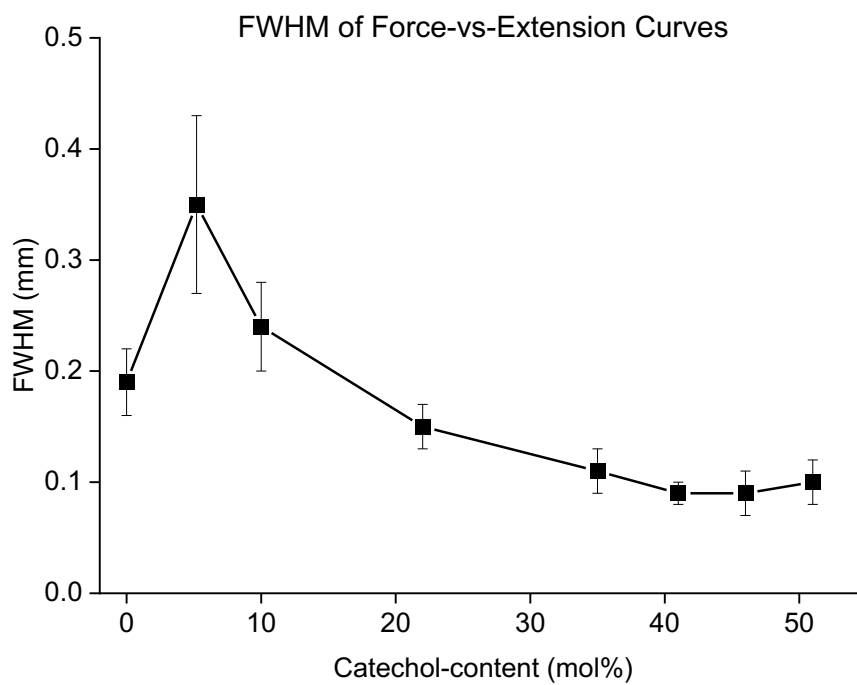




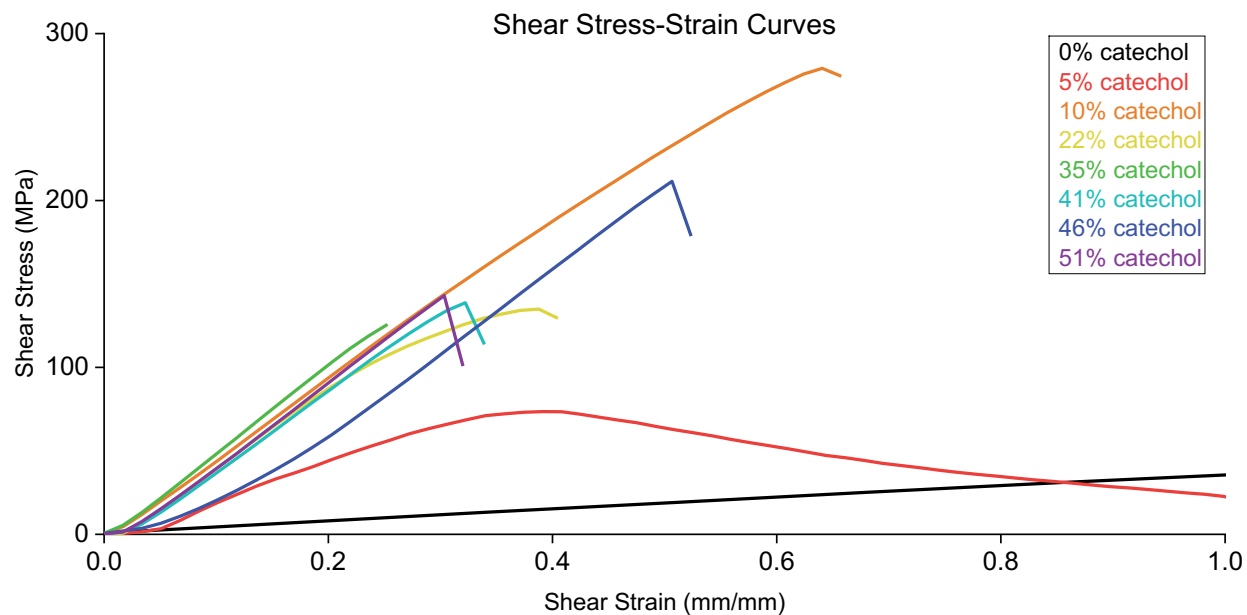
**Figure S3.** Adhesion of poly(catechol-MMA-OEG) on low energy PVC substrates.

Catechol Content (mol%)	FWHM
0%	$0.19 \pm 0.03$
5%	$0.35 \pm 0.08$
10%	$0.24 \pm 0.04$
22%	$0.15 \pm 0.02$
35%	$0.11 \pm 0.02$
41%	$0.09 \pm 0.01$
46%	$0.09 \pm 0.02$
51%	$0.1 \pm 0.02$

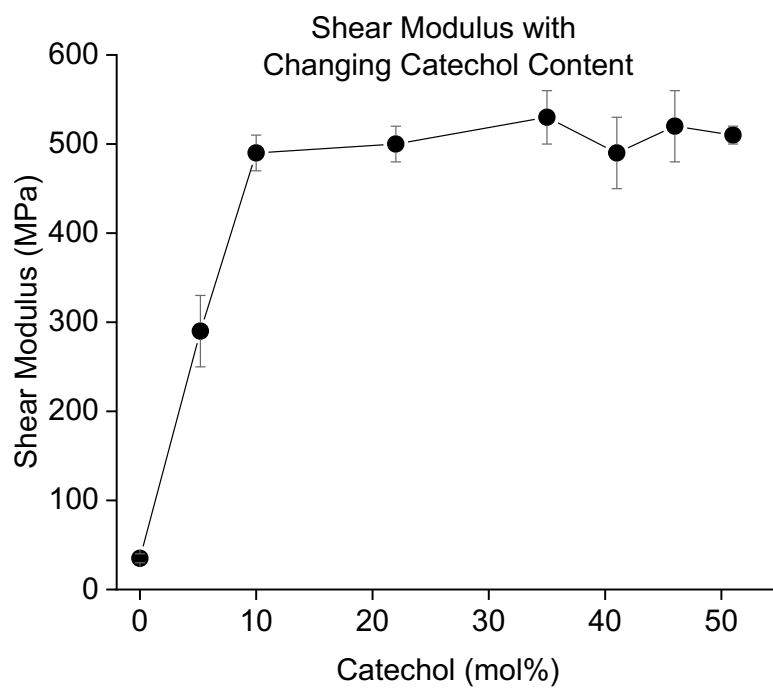
**Table S2:** Average full width at half maximum (FWHM) values of force-vs-extension curves from adhesion testing of the methacrylate terpolymers with varying catechol content on aluminum substrates.



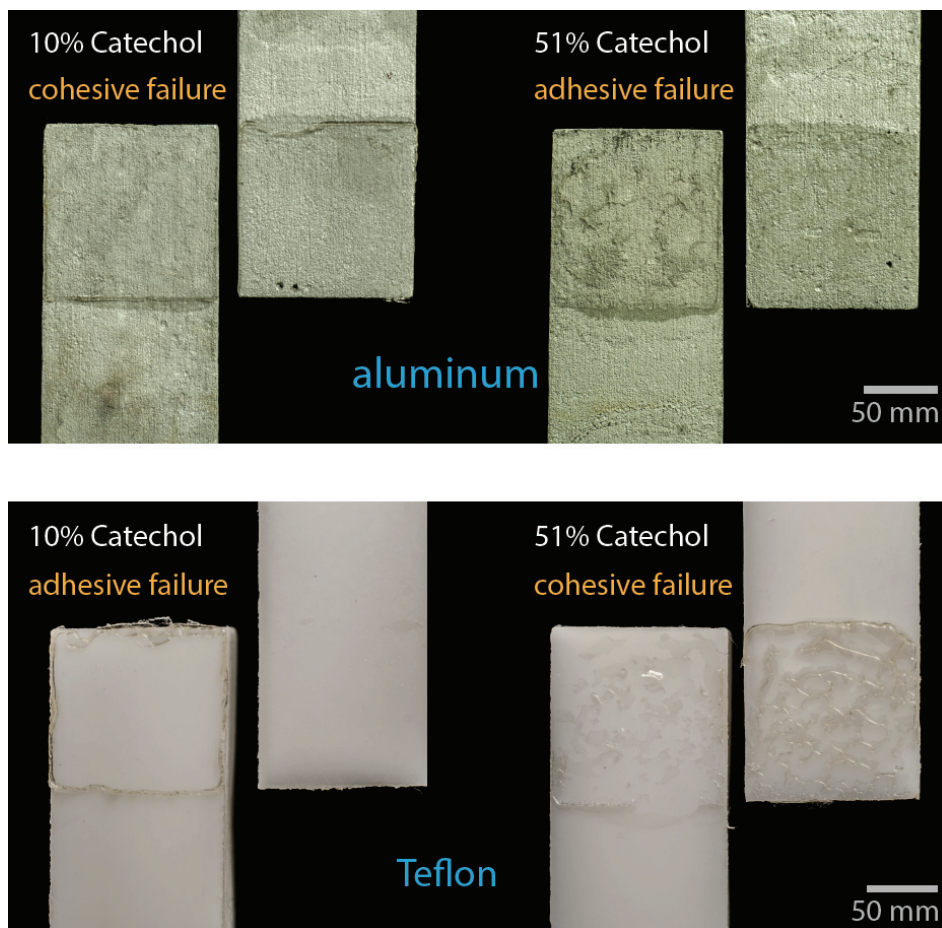
**Figure S4:** Average full width at half maximum (FWHM) values of force-vs-extension curves from adhesion testing of the methacrylate terpolymers with varying catechol content on aluminum substrates.



**Figure S5:** Shear stress-strain curves of terpolymers with increasing catechol content. Shear stress and shear strain was calculated from lap shear adhesion testing. Representative curves of each polymer are shown. The 0% catechol polymer (black) yields at a shear strain of 4.



**Figure S6:** Shear modulus of terpolymers with changing catechol content calculated from lap shear adhesion testing following an adaptation of methods outlined in ASTM D5656.



**Figure S7:** Aluminum and Teflon substrates after pulling apart for adhesion testing. Indications of failure modes can be seen in the four different cases. These same samples after staining with iodine are in Figure 5.