Electronic Supplementary Material (ESI) for Polymer Chemistry.

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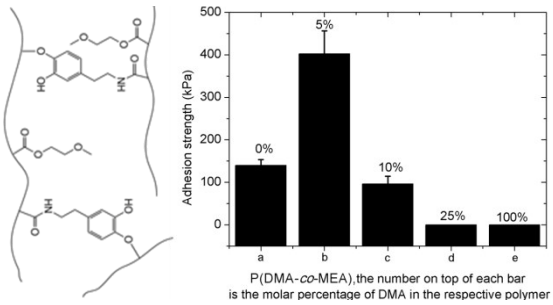

Catechol-containing polymers with a crosslinked structure were obtained by free radical polymerization. Optimal adhesion properties were obtained at a catechol composition of 5 mol%.

Electronic Supplementary Information

Effect of molecular composition and crosslinking on adhesion of a bio-inspired adhesive

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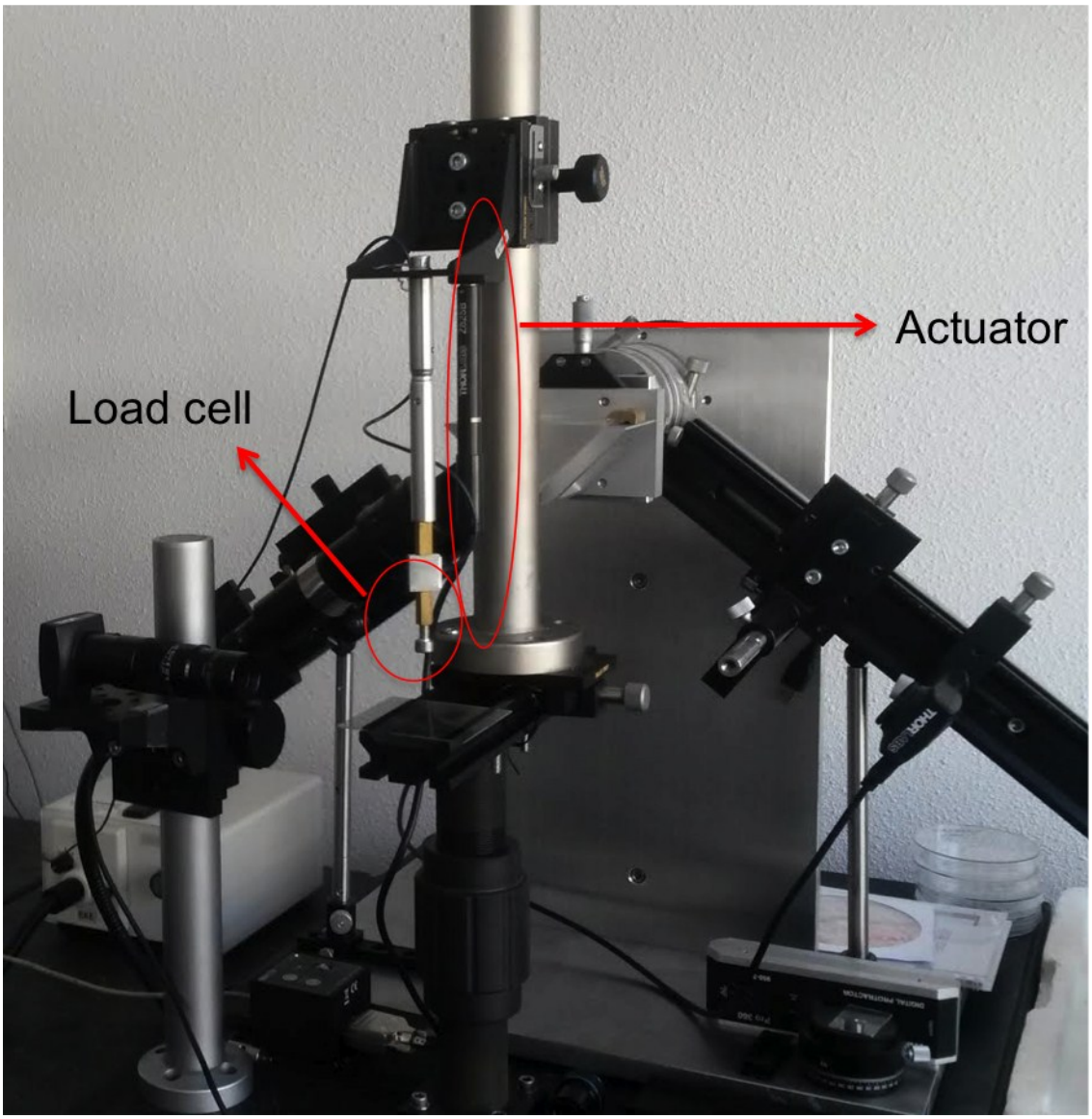


Figure S1. Picture of setup for indentation adhesion test

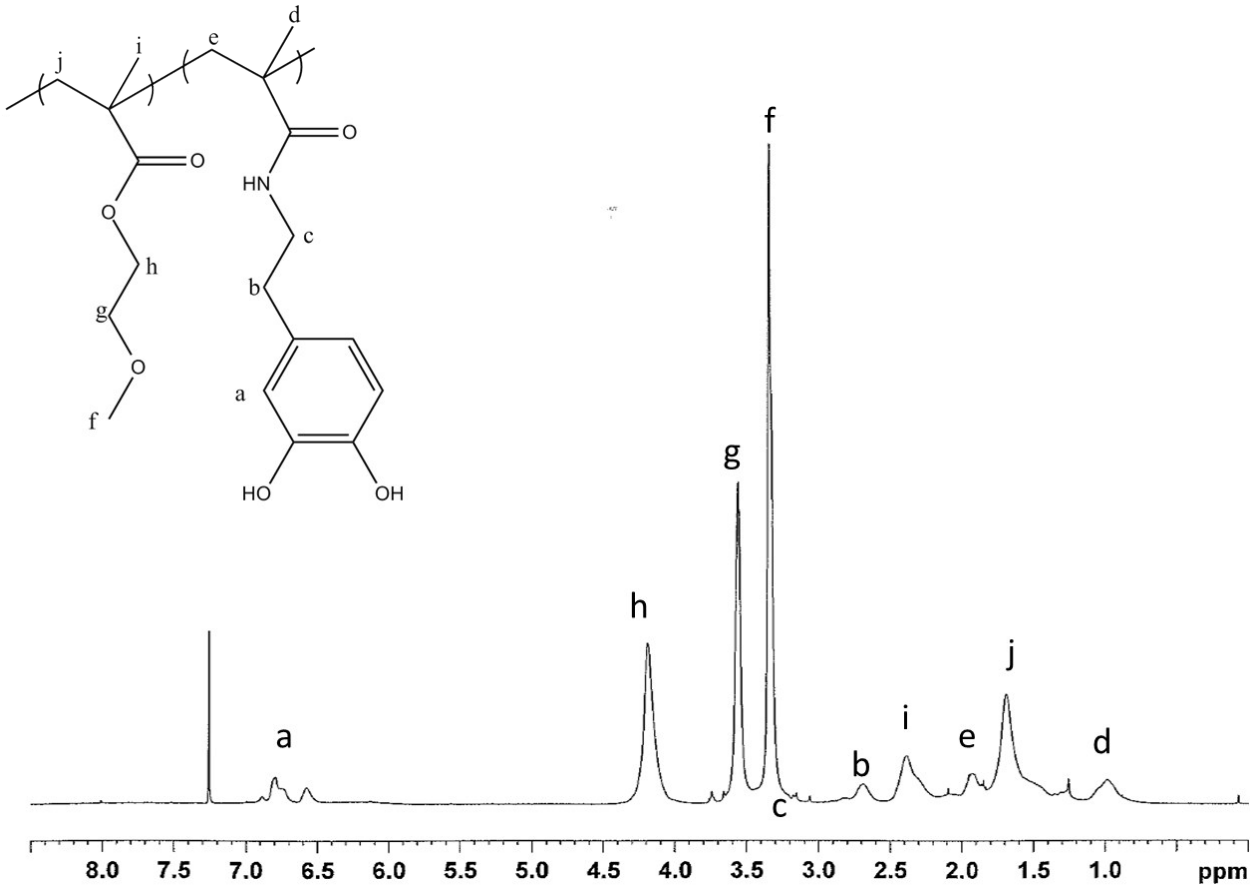


Figure S2. ^{1}H NMR spectra of poly($DMA_{0.10}$-*co*-$MEA_{0.90}$) in $CDCl_3$

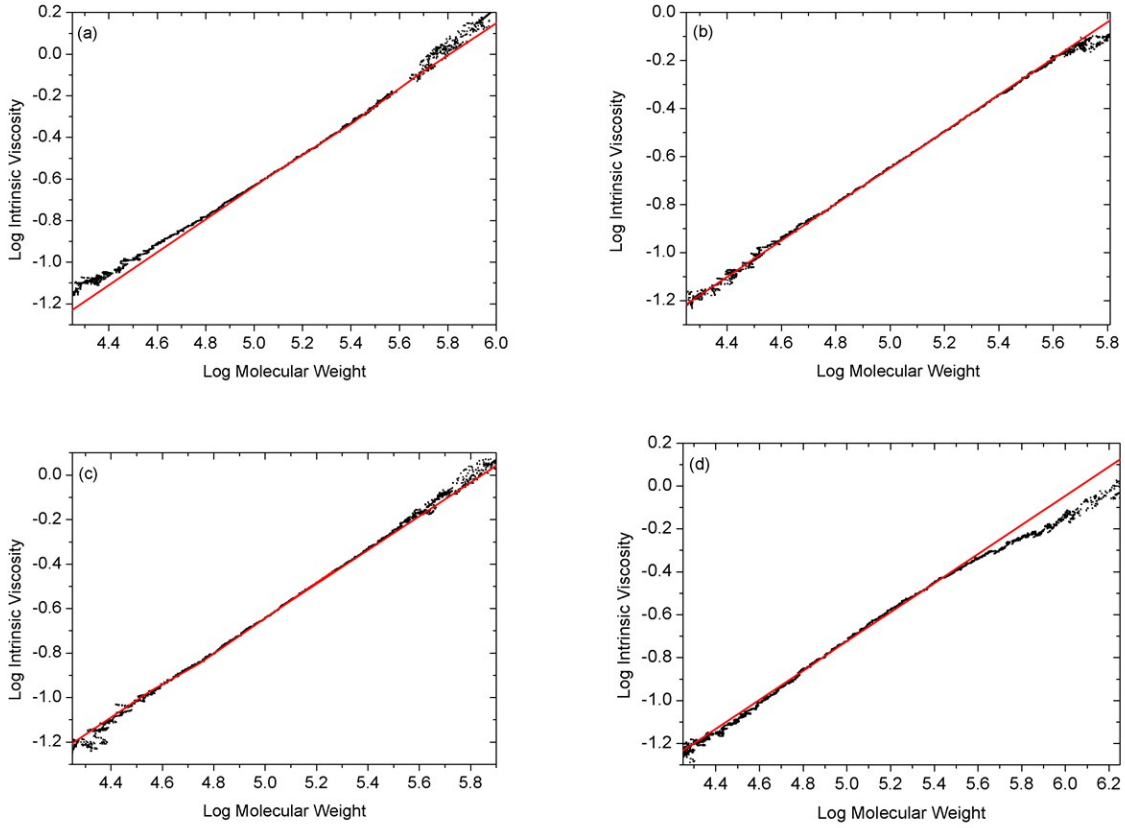
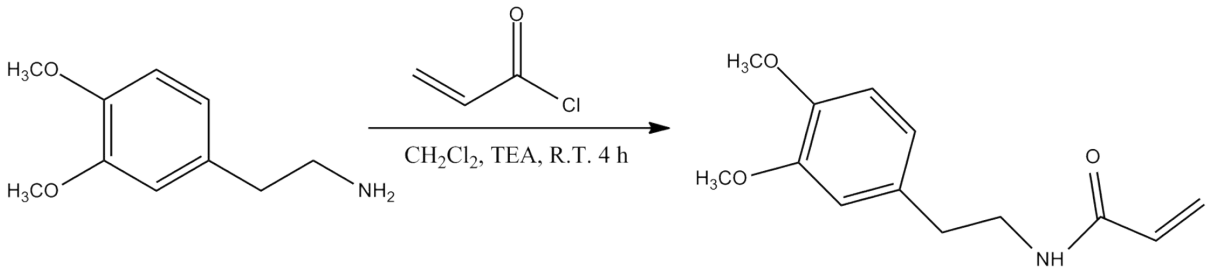


Figure S3. SEC-MALLS data of four polymers: intrinsic viscosity as a function of molecular weight on log-log scale. (a) PMEA; (b) poly($DMA_{0.05}$-*co*-$MEA_{0.95}$); (c) poly($DMA_{0.10}$-*co*-$MEA_{0.90}$); (d) poly($DMA_{0.25}$-*co*-$MEA_{0.75}$); (e) PDMA

ESI 1. Synthesis of N-(3,4-Dimethoxyphenethyl)acrylamide

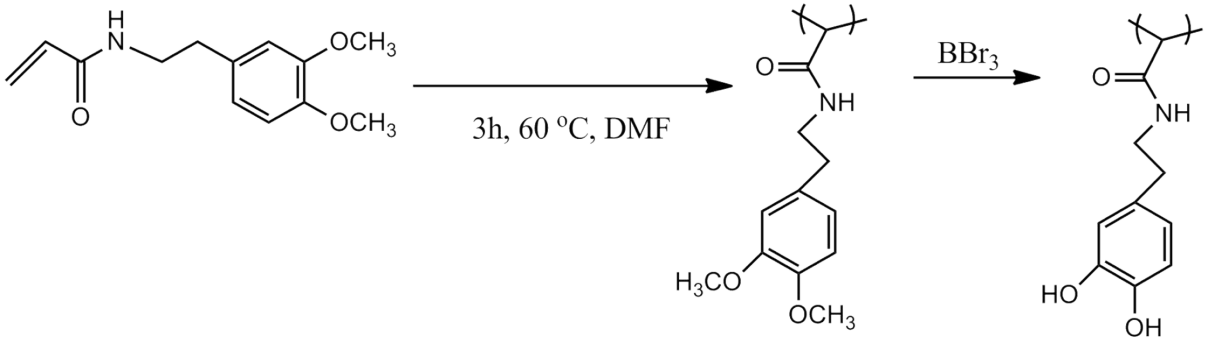
N-(3,4-Dimethoxyphenethyl)acrylamide (NDMA) was synthesized by reaction of 3,4-dimethoxyphenethyl amine with acryloyl chloride in dichloromethane at room temperature, see Scheme S1. 7 ml of 3,4-dimethoxyphenethyl amine in 70 ml of anhydrous dichloromethane (CH_2Cl_2) was added to a 250 ml three neck round bottom flask. The solution was bubbled with nitrogen under continuous stirring for 30 min at 0 °C. Afterwards, 6.92 ml of triethylamine (TEA) was added to the reaction mixture, followed by dropwise addition of 4.01 ml acryloyl chloride in 40 ml anhydrous dichloromethane at 0 °C. The reaction mixture was stirred overnight under continuous N_2 bubbling at room temperature. After the reaction, the reaction mixture was washed with 40 ml of 0.1 M HCl solution, 0.1 M Na_2CO_3 solution and three times with brine solution. The obtained yellowish solution was dried over Mg_2SO_4 and CH_2Cl_2 was removed by rotary evaporation. The obtained sample was dried in a vacuum oven overnight at room temperature.



Scheme S1. Synthesis of N-(3,4-Dimethoxyphenethyl)acrylamide (NDMA)

ESI 2. Synthesis of poly(N-(3,4-dimethoxyphenethyl)acrylamide) P(NDMA)

Homopolymer of N-(3,4-dimethoxyphenethyl)acrylamide was synthesized by free radical polymerization in dimethylformamide (DMF) at 60 °C using 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator (Scheme S2). 3.6911 g NDMA, 34.8 mg of AIBN in 20 ml DMF were added to a 50 ml three-neck round bottom flask, after which N_2 was bubbled through for 30 min. The reaction mixture was allowed to heat to 60 °C and was kept at this temperature for 3 h. The resulting mixture was diluted with 5 ml CH_2Cl_2, and precipitated into 300 ml cold diethyl ether. The precipitated fractions were collected and redissolved into 50 ml CH_2Cl_2, followed by precipitation into 500 ml cold diethyl ether. The precipitates were collected and dried under vacuum at room temperature.



Scheme S2. Synthesis of *poly(N-(3,4-dihydroxyphenethyl)acrylamide)*

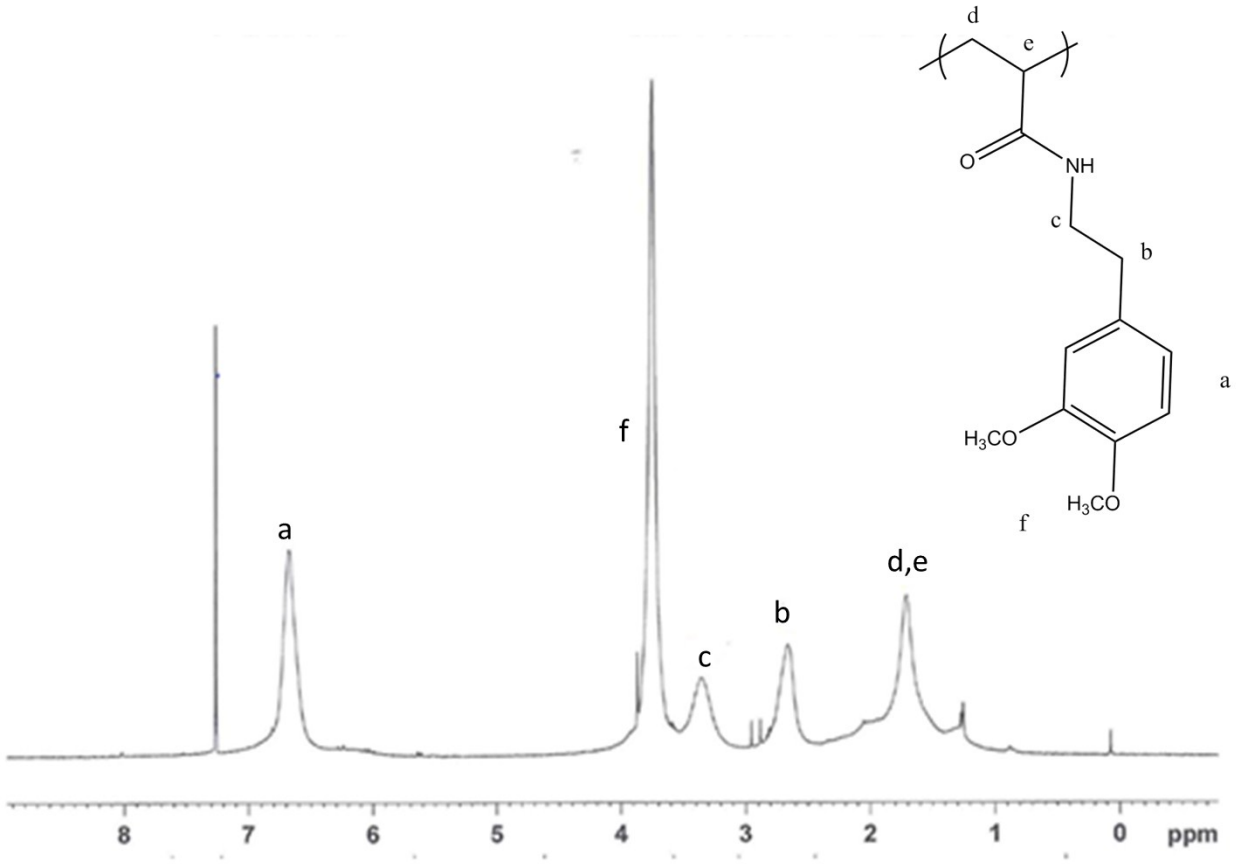


Figure S4. ^{1}H NMR spectra of poly(N-(3,4-dimethoxyphenethyl)acrylamide) in $CDCl_3$

ESI 3. Synthesis of linear PDMA (l-PDMA)

1.3 g PNDMA in 110 ml CH_2Cl_2 was added to a 250 ml three-neck round bottom flask at -65 °C under continuous stirring and nitrogen bubbling (Scheme S2). 18 ml 1M BBr_3 in DCM was added to the solution in a dropwise fashion. After that, the reaction mixture was slowly warmed to room temperature and stirred overnight. After the reaction, an orange slurry was formed. The slurry was added to 400 ml Milli-Q water at 4 °C under continuous stirring for 20 min. The reaction mixture was filtered and light yellow solids were obtained. The obtained solids were dried in a vacuum oven at room temperature.

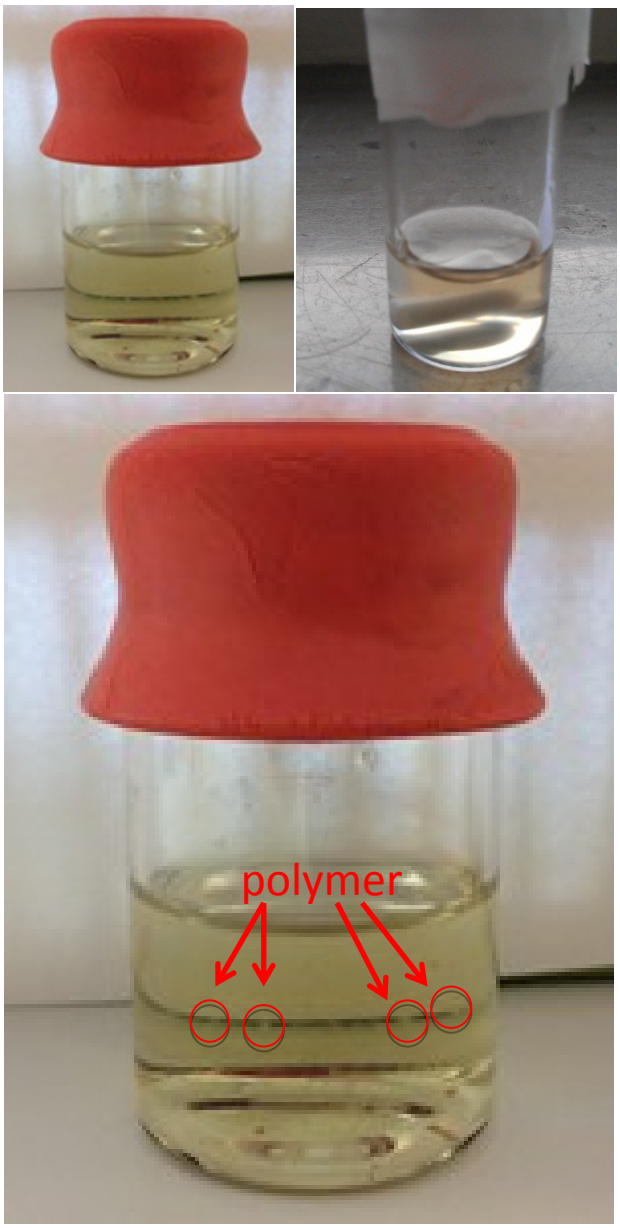


Figure S5. Pictures of l-PDMA (top left) and PDMA (top right) and enlarged picture of PDMA (bottom) in 0.1 mM NaOH solution kept under the protection of nitrogen

Table S1. Thickness of polymer films as determined by optical microscopy. The standard deviation of the thickness of each sample is based on three measurements at different locations in the same film.

Polymer	Thickness (μm)
PMEA	121.3±1.7
P($DMA_{0.05}$-*co*$MEA_{0.95}$)	101.1±1.8
P($DMA_{0.10}$-*co*-$MEA_{0.90}$)	115.6±2.5
P($DMA_{0.25}$-*co*-$MEA_{0.75}$)	79.1±3.9
PDMA	128.4±1.4