Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Rational design of a biomimetic glue with tunable strength and ductility

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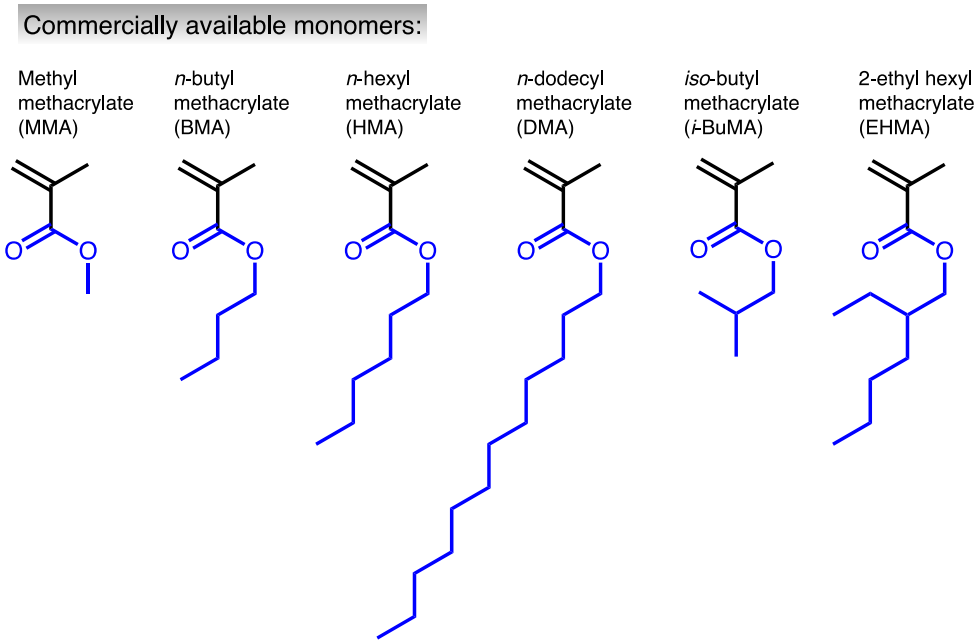
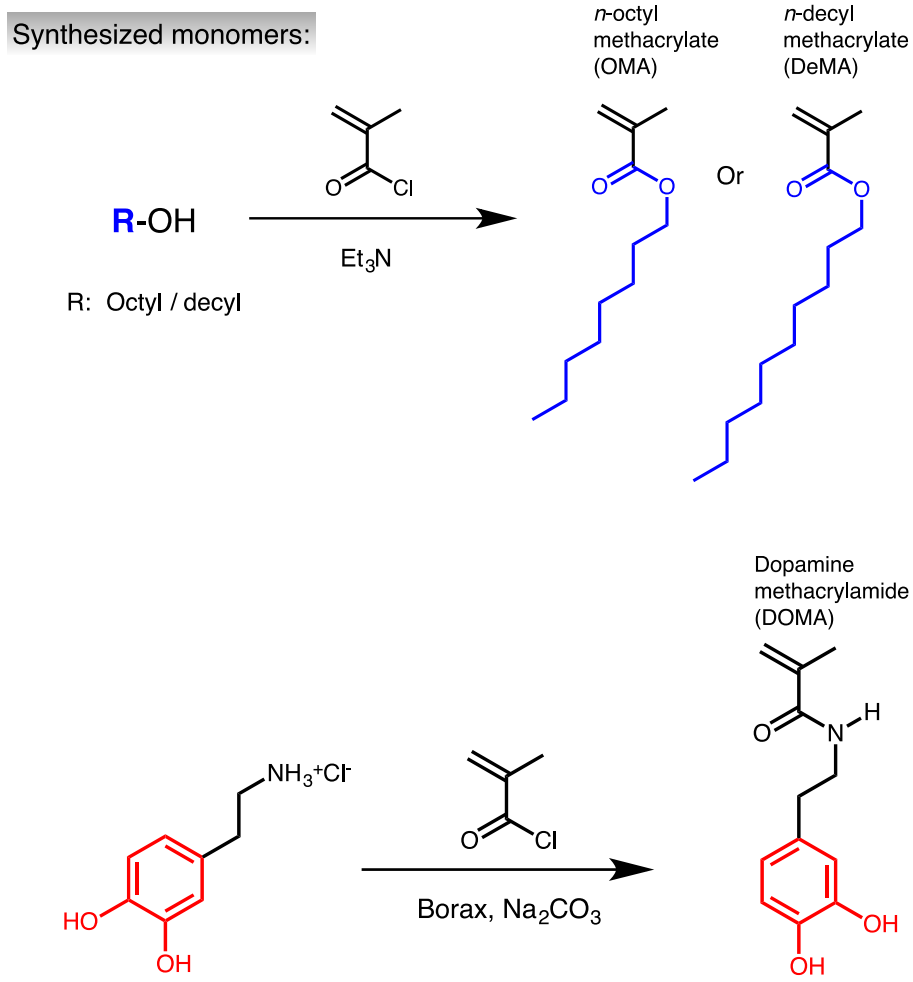
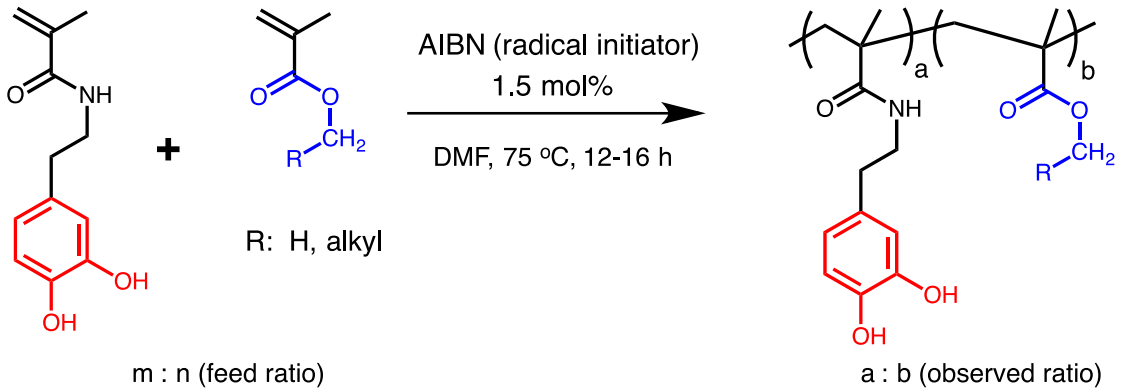


Figure S1: Chemical structures of commercially available methacrylate monomers used in the present study.



Scheme S1: Chemical structures of alkyl methacrylate and dopamine appended methacrylamide monomers synthesized in the present study. For detailed synthetic procedure and characterization, see ref. 24 and 44.



Scheme S2: Radical initiated random copolymerization of dopamine methacrylamide (DOMA) with various combinations and composition of alkyl methacrylates.

Polymer name	Feed (mol %)		Observed (mol %)		M_w [g/mol], (PDI)	Temperature of 10% decomposition (°C)	T_g (°C)
	DOMA	AMA	DOMA	AMA			
Poly **1** [DOMA-MMA]	16	84	12	88	24,000 (2.2)	349	124
Poly **2** [DOMA-BMA]	16	84	11	89	13,000 (1.5)	289	72
Poly **3** [DOMA-HMA]	20	80	12	88	14,000 (1.5)	320	36
Poly **4** [DOMA-OMA]	20	80	11	89	20,800 (1.7)	318	13
Poly **5** [DOMA-DeMA]	25	75	10	90	16,000 (1.5)	300	-41
Poly **6** [DOMA-DMA]	33	67	11	89	32,000 (1.6)	324	-56
Poly **7** [DOMA-iBuMA]	16	84	12	88	13,000 (1.4)	335	87
Poly **8** [DOMA-EHMA]	20	80	10	90	28,000 (1.9)	345	22

Table S1: Compositions and key parameters of different polymers with various alkyl chain lengths and branching. Observed molar ratio was estimated from ^{1}H NMR. Molecular weight (M_w) and polydispersity index (PDI; M_w/ M_n) was calculated from gel permeation chromatography (GPC) using polystyrene standards.

DOMA-OMA (Poly 4a-f) series:

Polymer code	Feed (mol %)		Observed (mol %)		M_w [g/mol], (PDI)	T_g (°C)
	DOMA	AMA	DOMA	AMA		
Poly **4a** (control)	0	100	0	100	22,000 (1.5)	-45
Poly **4b**	6	94	2	98	22,600 (1.6)	-38
Poly **4c**	13	87	7	93	23,000 (1.6)	-22
Poly **4d**	17	83	9	91	20,400 (1.6)	-4
Poly **4e**	20	80	11	89	20,800 (1.7)	13
Poly **4f**	33	67	16	84	13,000 (1.5)	36

Table S2: Series of DOMA-*co*-OMA (Poly 4a-f) copolymers containing *n*-octyl side chains. Variation of final DOMA content was achieved by changing monomer feed ratio. Molecular weight (M_w) and glass transition temperature (T_g) data have also been provided for each sample.

DOMA-EHMA (Poly 8a-g) series:

Polymer code	Feed (mol %)		Observed (mol %)		M_w [g/mol], (PDI)	T_g (°C)
	DOMA	AMA	DOMA	AMA		
Poly **8a** (control)	0	100	0	100	15,700 (1.4)	-2
Poly **8b**	6	94	1	99	22,500 (1.4)	2
Poly **8c**	11	89	3	97	23,200 (1.4)	6
Poly **8d**	14	86	6	94	20,600 (1.6)	12
Poly **8e**	17	83	8	92	20,600 (1.6)	16
Poly **8f**	20	80	10	90	28,000 (1.9)	22
Poly **8g**	25	75	15	85	14,200 (1.6)	30

Table S3: Series of DOMA-*co*-EHMA (Poly 8a-g) copolymers containing 2-ethyl hexyl side chains. Variation of final DOMA content was achieved by changing monomer feed ratio. Molecular weight (M_w) and glass transition temperature (T_g) data have also been provided for each sample.

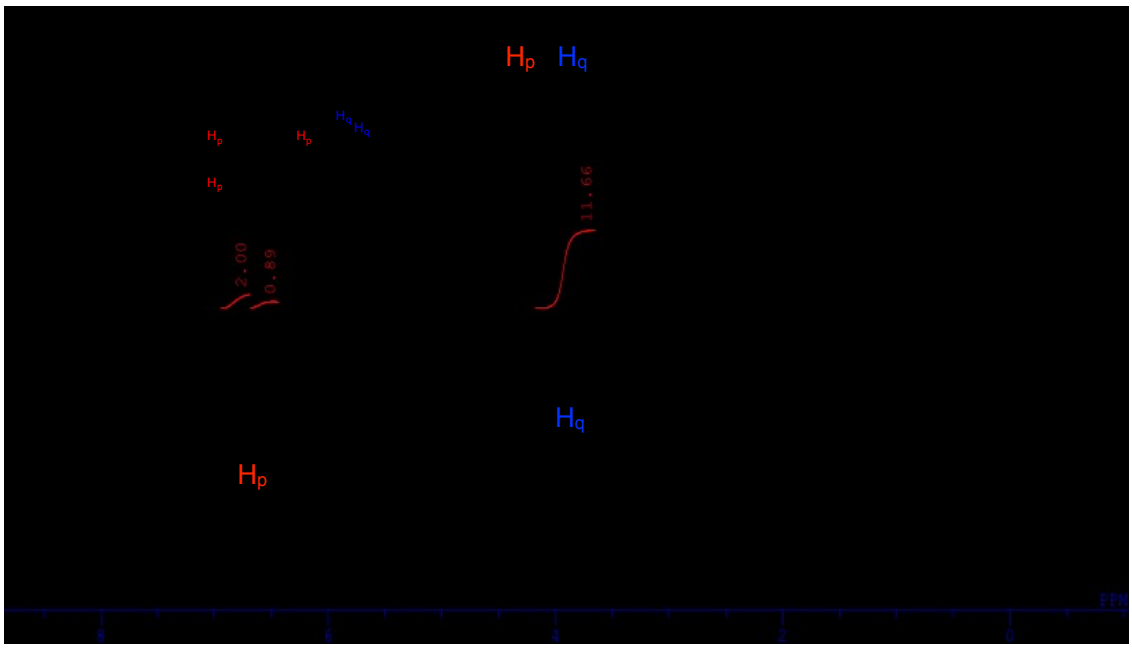


Figure S2: A typical ^{1}H NMR spectra of copolymers in $CDCl_3$ at 298K. The final molar ratio of DOMA unit and alkyl methacrylate units were estimated from integral ratio of peak around 6.5-7.0 ppm (aromatic protons) and 4.0 ppm ($–OCH_2-$), respectively.

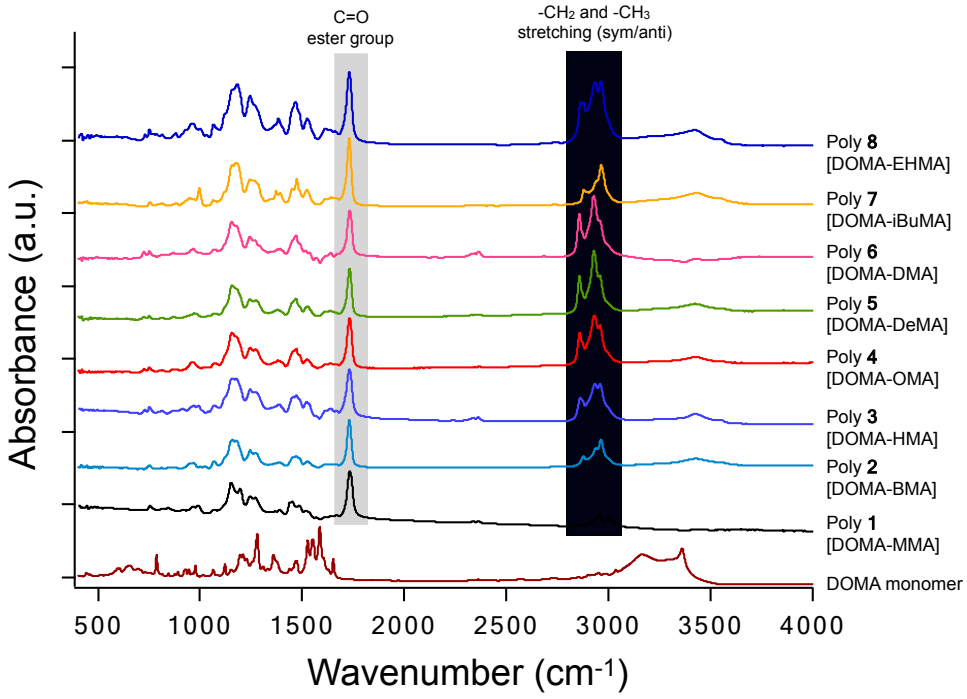


Figure S3: FT-IR comparison among DOMA monomer and copolymers in KBr pellet. For DOMA monomer, broad peak around 3000~3400 cm^{-1} is due to amide (N-H) and catechol (O-H) segments. The most characteristic peaks for all copolymers (poly 1-8) were from alkyl methacrylate units, major part of these polymers. Presence of typical alkyl $–CH_2–$ & $–CH_3$ stretchings (~2800-2950 cm^{-1}) and ester group (1750 cm^{-1}) was observed for all cases.

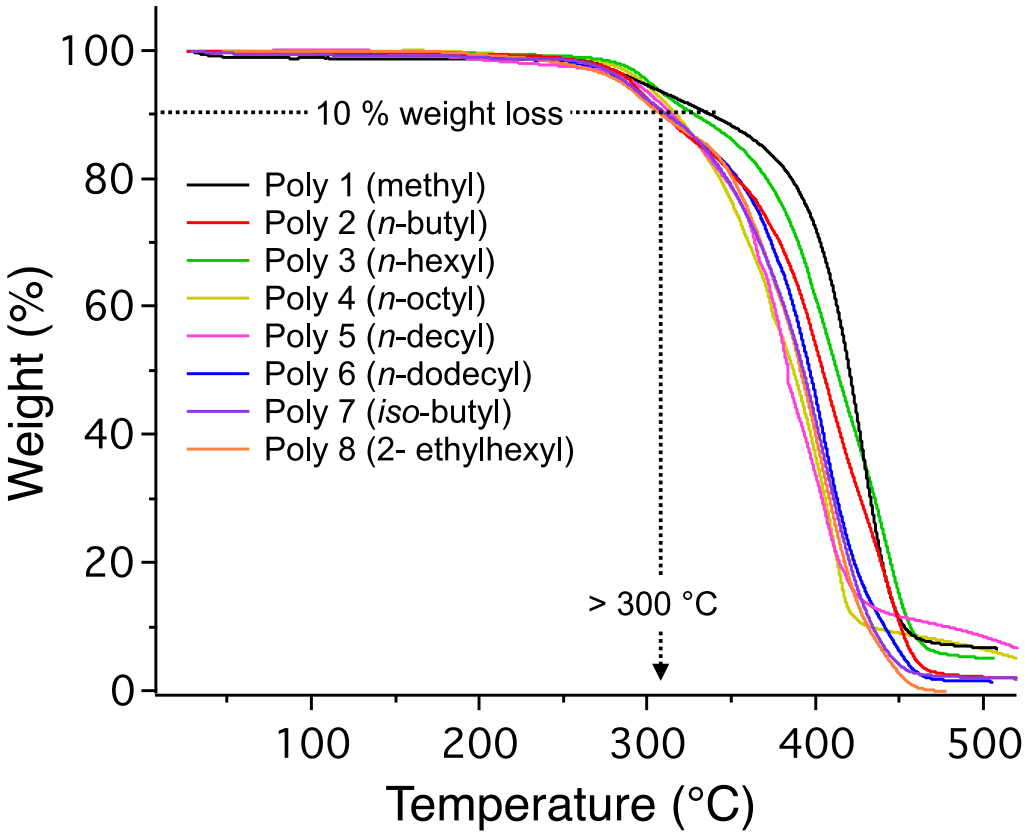


Figure S4: Thermo gravimetric analysis (TGA) plots of different copolymers. There was no decomposition or unusual peak below 200 °C, indicates absence of any residual solvent or small molecules. Only ~10 % weight loss was observed close to 300 °C most of the cases, implying good thermal stability. However, the polymers completely decomposed above 450 °C.

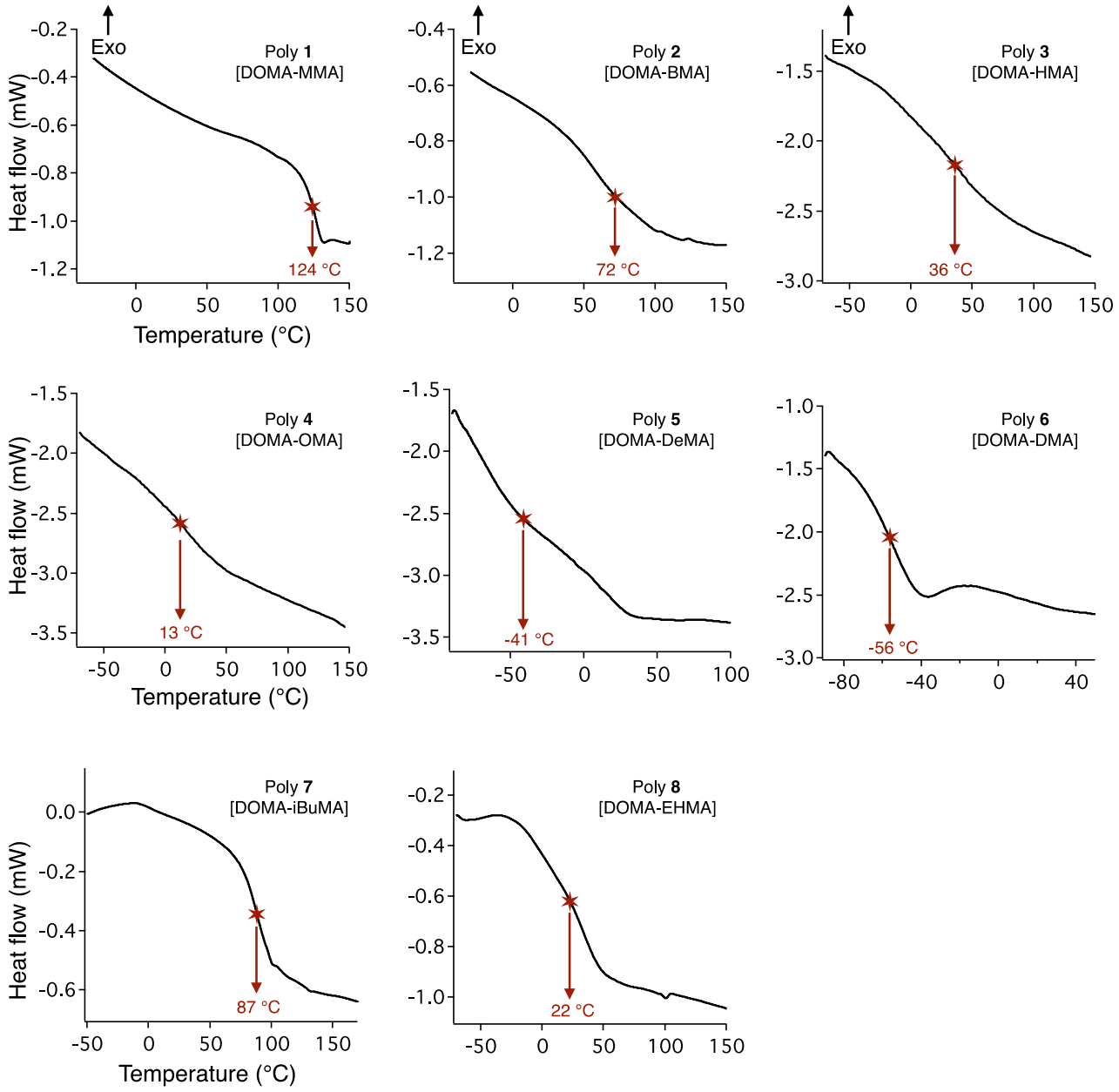


Figure S5: Differential scanning calorimetry (DSC) thermograms of different copolymers. There was significant variation of glass transition temperature (T_g) with alkyl chain length. For example, shorter chains like methyl and butyl copolymers (poly 1, 2) have T_g at 124 °C and 72 °C, respectively. On the other hand, very long chains like decyl or dodecyl (poly 5,6) exhibited T_g at very low temperature -41 °C and -56 °C, respectively. These informations were very useful to assess the chain mobility and related influence on bonding strength.

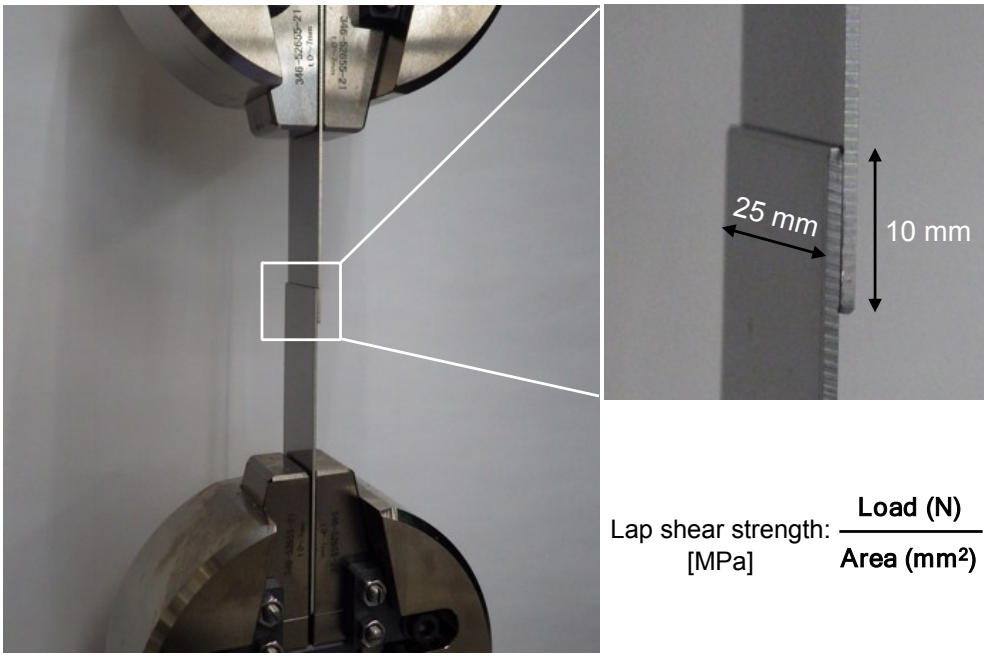


Figure S6: Photograph of a single-lap joint aluminum substrate, installed for lap-shear test. The trails were performed using 10,000 N load cell and crosshead speed of 2 $mm.min^{-1}$. Overlapped area for all measurements was maintained same (10 mm x 25 mm), and reported strength in MPa is highest load (N) gained divided by area (mm^2).

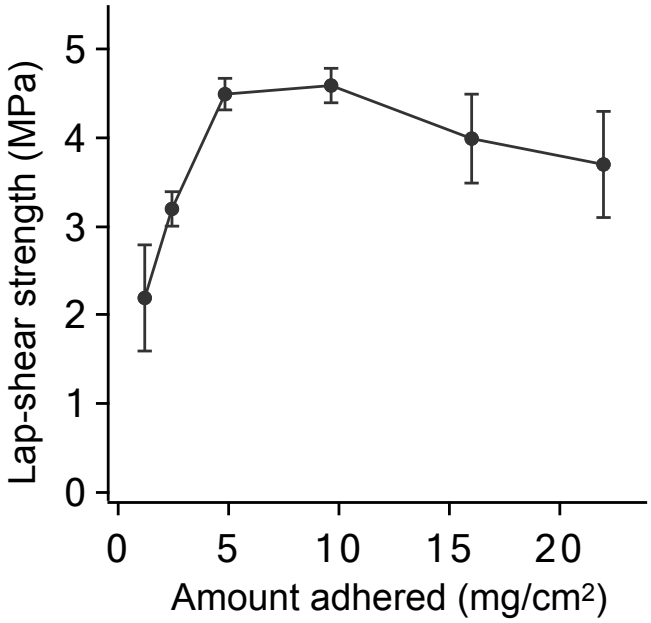


Figure S7: Dependence of bonding strength on amount adhered on the substrates. Substrate was aluminum and curing temperature was maintained at 70 °C for all cases.

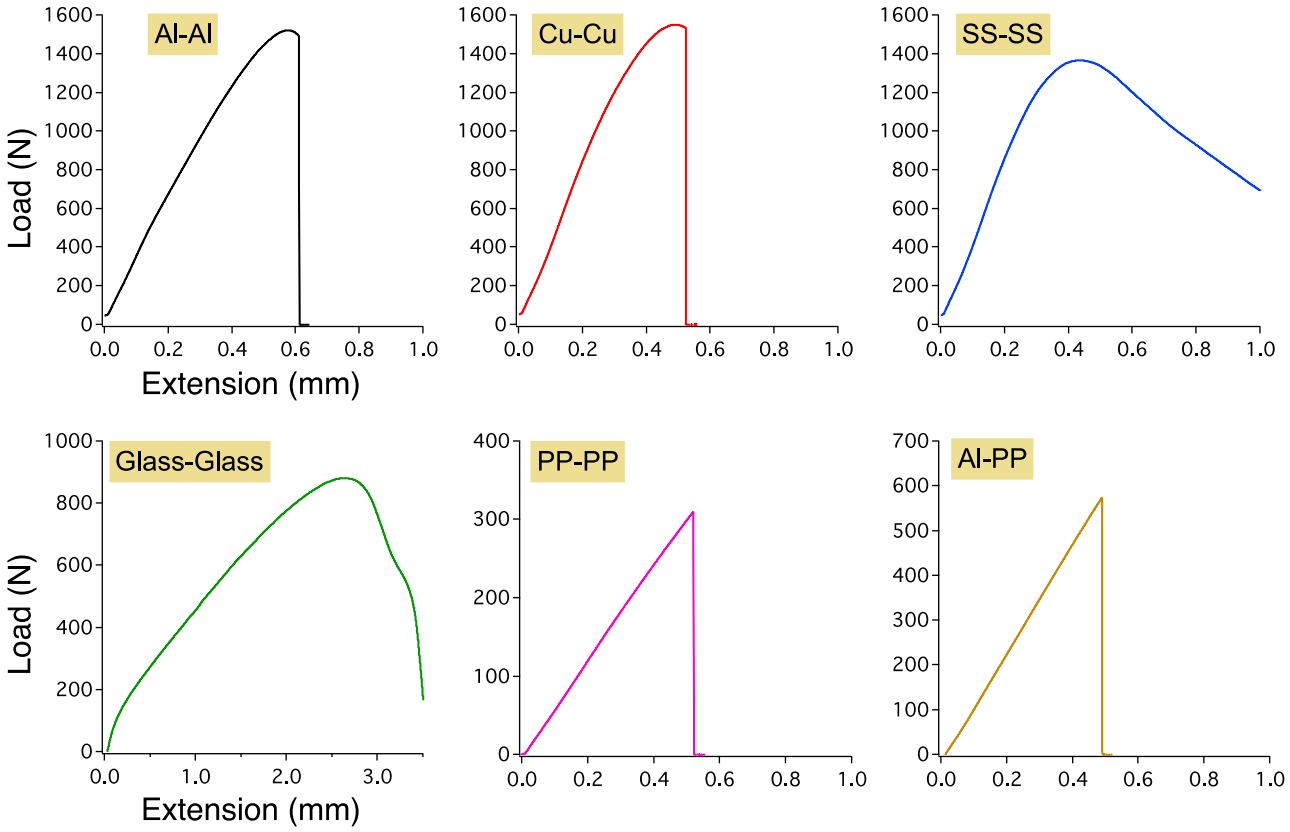


Figure S8: Raw profiles (load *vs* extension) of lap-shear test using different substrates under best molecular composition and formulation conditions achieved in the present study. Metal substrates (Al, Cu, SS) exhibited highest load in the range of 1400-1600 N when extension was close to 0.4-0.5 mm (5 % strain). Highest loading ability for glass substrate was ~ 900 N, but extension was much higher than metals (2.5 mm, 25 % strain). On the other hand, plastic substrates yielded lower strength than both metals/glass in both similar and dissimilar attachments. It was clear that, the bonding nature and performance depends on parameters including substrate modulus, substrate-adhesive interfacial interactions, and others under same formulation conditions.

	Adhesive name	Strength (MPa)	Reference
Commercial glues	Ethylcyanoacrylate (Krazy glue)	7 ± 1	R1
	Epoxy (Loctite quick-set)	18 ± 2	R2
	Poly(vinyl acetate) (Elmer's glue)	3.8 ± 0.6	R2
Mussel-mimetic glues	Poly[(3,4-dihydroxystyrene)-*co*-styrene]	11 ± 0.5	R2
	Poly(DOMA-*co*-MMA)	1.3 ± 0.6	R3
	Poly(DOMA-*co*-MMA-*co*-PEGMA)	3 ± 0.5	R3
	Poly[(3,4-dihydroxystyrene)-*co*-styrene-*co*-VMEG]	2.3 ± 0.5	R4
	U1444-DMPA-DA	5.2 ± 0.5	R5
	Poly(DOMA-*co*-EHMA)	6 ± 0.3	Present report

Dopamine methacrylamide (DOMA); poly (ethylene glycol) methyl ether methacrylate (PEGMA); 4-vinylbenzyl[methyltetra(ethylene glycol)] (VMEG);

Table S4: A summary of adhesive strength among present adhesive system, commercial glues and other DOPA-based synthetic polymer adhesives, reported earlier. Adhesive strength evaluated only by single-lap joint method and for metal substrates has been considered for this comparison, because bonding performance is often dependent on multiple factors, including evaluation method, formulation conditions, substrates, among others.

References:

R1. C. R. Matos-Pérez, J. D. White and J. J. Wilker, *J. Am. Chem. Soc.,* 2012, **134**, 9498-9505.

R2. H. J. Meredith, C. L. Jenkins and J. J. Wilker, *Adv. Funct. Mater.*, 2014, **24**, 3259-3267.

R3. H. J. Meredith and J. J. Wilker, *Adv. Funct. Mater.,* 2015, **25**, 5057-5065.

R4. C. R. Matos-Pérez and J. J. Wilker, *Macromolecules,* 2012, **45**, 6634-6639.

R5. P. Y. Sun, L. Y. Tian, Z. Zheng and X. L. Wang, *Acta. Polym. Sin.,* 2009, **1**, 803-808.