Supporting Information

Accessing the Next Generation of Synthetic Mussel-Glue Polymers via Mussel-Inspired Polymerization

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1 Materials

Oxone® (monopersulfate compound), 2-iodobenzoic acid, 2,6-di-tertbutyl-4-methylphenol (BHT, < 99%), 2,2’-(diethylenedioxy)-diethanethiol (95%), dithranol, sodium tetrafluoro acetate and tributyl phosphine were purchased from Sigma Aldrich® Chemie GmbH (Seelze, Germany) and bisphenol A, bisphenol Z, 1,4-bismercaptobenzene (98%) from TCI (Tokyo, Japan). Deuterated dimethyl sulfoxide (DMSO-d6) was obtained from deuteron (Kastellaun, Germany). N-Methyl-2-pyrrolidon (NMP peptide grade, free amines < 10 ppm) was purchased from Iris Biotech GmbH (Marktredwitz, Germany), tetrahydrofuran (LC-MS grade) and acetonitrile (LC-MS grade) were obtained from VWR® chemicals (Dresden, Germany) and formic acid (LC-MS grade) from Merck KGaA (Darmstadt, Germany).

Iodoxybenzoic acid (IBX) was synthesized according to the procedure described by Frigerio et al.[1] CAUTION! IBX was found to be explosive under heating > 200 °C or impact.[2]

Milli-Q water was produced using SG LaboStar® TM 1-UV system from SG water (Hamburg, Germany). As ion exchanger, Evoqua Water Technologies Polisher HP2 module was inserted. Electric conductivity of Milli-Q water was 0.055 µS cm⁻¹.

2 Instrumentation

Ultra-performance liquid chromatography with electron spray ionization mass spectrometry (UPLC-ESI-MS) was carried out on an ACQUITY-UPLC® H-Class CM Core System of Waters GmbH (Eschborn, Germany). Detection was done utilizing an ACQUITY-UPLC® photo diode array (PDA)-detector (wavelength range 190-500 nm) and an ACQUITY-UPLC® QDa mass detector with ESI-ionization. For analysis Waters software Empower™3 was used. Separation was conducted with ACQUITY-UPLC® BEH C18 VanGuard™ precolumn (110 Å, 1.7 µm, 5 × 21 mm ID) and an ACQUITY-UPLC® BEH C18-column (110 Å, 1.7 µm, 5×21 mm ID) from Waters. As mobile phase, mixtures of solvent A (Milli-Q water with 0.1% FA, v/v) and solvent B (acetonitrile with 0.1%FA, v/v) were used with 0.5 mL min⁻¹ flow rates.

Gel permeation chromatography (GPC) was carried out on an Eco-SEC-System with UV and RI-detection (HLC-8320 GPC) from Tosoh (Griesheim, Germany). As solvent tetrahydrofuran (THF, HiPerSolv CHROMANORM® for HPLC) from VWR® Chemicals (Dresden, Germany) was used and SDV columns (1000 Å 5 µm, 100000 Å 5 µm and 1000000 Å 5 µm) from PSS (Mainz, Germany) were applied.

MALDI-TOF-MS/MS measurements were carried out on a MALDI-TOF/TOF 5800 system (AB Sciex, USA). As matrix a mixture of 1:1 dithranol (20 mg mL⁻¹) and NaTFA (5 mg mL⁻¹) in THF was used.

Nuclear magnetic resonance spectroscopy (NMR) was performed on an Avance II 500 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany).

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Brucker Vertex 70v FT-IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany).

Thermo gravimetric analysis (TGA) was carried out on a TGA/SDTA851e system (Mettler Toledo, USA).

Differential scanning calorimetry (DSC) measurements were performed on DSC822e Differential Scanning Calorimeter (Mettler Toledo, USA).

Shear tests have been carried out with a Texture Analyzer Ta.XT.plus100C (Stable Micro Systems, Godalming, United Kingdom) with a 100 kg force cell. Also, a Zwick 1446 System (ZwickRoell GmbH & Co. KG, Ulm, Germany) was used if mentioned in the experimental description.

For shear test sample preparation, a manual hydraulic press with a west 6100+ temperature controller from Specac Ltd Science and Innovation Centre (Orpington, United Kingdom) was utilized.

Scanning electron microscope (SEM) imaging was carried out with a TM-1000 tabletop microscope (Hitachi, Japan).
3 Methods

3.1 General polymerization procedure

Unless otherwise described, polymerization was carried out for 15 min at room temperature with NMP as solvent. For this the bisquinone was solved in NMP (22.6 g/L), the solution was stirred and one equivalent of the dithiol was added. The dark reaction mixture brightened up during the reaction time and after 15 min a pale-yellow solution was obtained.

3.2 Sample preparation for GPC analysis

The dried polymer solid was solved in THF and filtered through 0.2 µm PTFE filter. 1.5 mL of the filtrated solution were transferred into glass vials and mixed with 7.5 µL of BHT-standard (50 mg/mL solution in THF). If a reducing step was carried out, additionally tributyl phosphine (7.5 µL) was added to the prepared solutions.

4 Monomer synthesis

4.1 Synthesis of bisquinone A (BQA)

Bisphenol A (5.0 g, 20 mmol) was dissolved in 200 mL methanol. The solution was mixed with IBX (18.5 g, 66 mmol) and the mixture was stirred for 15 min at room temperature. Formation of a red solid was observed. Subsequently, the mixture was cooled in an ice bath for 10 min, the red solid was filtrated off and was washed with cold methanol. The red solid was redissolved in chloroform. After filtration, the organic solvent was removed under reduced pressure to obtain a red solid in 5.2 g yield (92%).

NMR spectra are shown in Figure S 1 and Figure S 2.

\[ {^1}\text{H-NMR (500 MHz, DMSO-d}_6\text{)}: \delta [\text{ppm}] \; 7.07 (dd, J = 10.3, 2.4 Hz, 1H), 6.40 – 6.34 (m, 2H), 1.43 (s, 3H). \]

\[ {^{13}}\text{C-NMR (126 MHz, DMSO-d}_6\text{)}: \delta [\text{ppm}] \; 179.72, 179.61, 155.77, 139.90, 130.09, 126.26, 43.71, 24.16. \]

FT-IR: 2985 (w), 1686 (m), 1664 (s), 1622 (s), 1564 (m), 1543 (w), 1404 (m), 1285 (m), 1232 (w), 1178 (w), 1147 (w), 1128 (w), 1038 (w), 915 (w), 878 (w), 816 (m), 682 (w), 647 (w), 616 (w).
Figure S1. $^1$H-NMR of bisquinone A in DMSO-d$_6$.

Figure S2. $^{13}$C-NMR of bisquinone A in DMSO-d$_6$. 
4.2 Synthesis of bisquinone Z (BQZ)

Bisphenol Z (6.0 g, 20 mmol) was dissolved in 200 mL methanol. The solution was mixed with IBX (18.5 g, 66 mmol) and the mixture was stirred for 15 min at room temperature. Formation of a dark solid was observed. Subsequently, the mixture was cooled in an ice bath for 10 min, the dark solid was filtrated and washed with cold methanol. The dark solid was redissolved in chloroform. After filtration, the organic solvent was removed under reduced pressure and a brown solid is obtained in 4.9 g yield (74%).

NMR spectra are shown in Figure S 3 and Figure S 4.

$^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$[ppm] 7.13 (dd, $J = 10.4$, 2.4 Hz, 1H), 6.46 (d, $J = 1.9$ Hz, 1H), 6.37 – 6.33 (m, 1H), 2.00 – 1.92 (m, 2H), 1.48 (dd, $J = 30.0$, 4.3 Hz, 3H).

$^{13}$C-NMR (126 MHz, DMSO-$d_6$): $\delta$[ppm] 179.76, 179.53, 153.43, 139.38, 130.06, 128.51, 46.95, 30.97, 25.18, 21.53.

FT-IR: 2978 (w), 2928 (w), 1684 (m), 1661 (s), 1622 (m), 1562 (m), 1465 (w), 1404 (m), 1281 (m), 1140 (m), 1032 (w), 891 (w), 830 (w), 818 (m), 800 (m), 766 (w), 726 (w), 692 (w), 646 (m), 613 (m).

Figure S 3. $^1$H-NMR of bisquinone Z in DMSO-$d_6$. 
Figure S4. $^{13}$C-NMR of bisquinone Z in DMSO-d$_6$. 
5 Experiments

5.1 Color gradient during the BQA/EDET polymerization

![Color gradient images](image)

Figure S5. Color in the polymerization reaction of BQA with EDET indicates the consumption of the BQ-species.

5.2 BQA/EDET polymerization in different solvents

Polymerization of BQA and EDET was carried out as described in 3.1 by changing the solvents to NMP, DMSO, methanol, chloroform, tetrahydrofuran, ethanol, ethyl acetate, dimethyl formamide and acetone. After 15 min reaction time, the reaction mixtures were transferred to centrifuge tubes and the solvents were removed by lyophilization. The residues were redissolved in 10 mL THF to be analyzed by GPC.

![GPC chromatogram](image)

Figure S6. GPC chromatogram of the polymerization of BQA and EDET in different solvents. Polymerization mixtures were analyzed without previous precipitation. BHT was added as GPC-standard.
5.3 Kinetics and low molecular products of the BQA/EDET polymerization

Polymerization of BQA and EDET was carried out as described in 3.1. After defined times samples were taken from the reaction mixture, diluted in 80% acetonitrile and 20% water and analyzed using UPLC-ESI-MS (Figure S 7). Purity of BQA was verified by NMR prior to use for polymerization. The two peaks found in the zero sample UPLC chromatograms belong to the same BQA species and might potentially originate from different ion-adducts or non-covalent dimer formation as observed rather commonly e.g. in peptide samples.

Figure S 7. UPLC-ESI-MS analysis of polymerization kinetic after 0.5 min and 15 min reaction time compared to the chromatogram of the BQA monomer (0 min). Cyclic dimer (AA-BB)$_1$ with $m/z(-) = 437$ and cyclic tetramer (AA-BB)$_2$ with $m/z(-) = 875$ were found. Chromatogram at 280 nm. Solvent A: MQ-water, 0.1% FA, Solvent B: acetonitrile, 0.1% FA, gradient 10-90% B (4 min).
5.4 Precipitation procedure for p(BQA-EDET)

BQA and EDET were polymerized according to the procedure in paragraph 3.1. After polymerization, different precipitation methods were compared. For this 2.5 mL of the reaction mixture were added under stirring to the respective precipitation bath: A) Addition to 20 mL Milli-Q water and freeze drying of the mixture. B) Precipitation in 20 mL Milli-Q water, centrifugation for 20 min and 9000 min\(^{-1}\). C) Precipitation in a mixture of 60% methanol and 40% Milli-Q water followed by centrifugation for 20 min and 9000 min\(^{-1}\).

Figure S 8. THF-GPC data of precipitation experiments. Left: Comparison without precipitation (A) and precipitation in Milli-Q water (B). Right: Comparison without precipitation (A) and precipitation in 60% methanol and 40% Milli-Q water (C).

5.5 MALDI-TOF-MS/MS analysis of p(BQA-EDET)

Polymerization of BQA and EDET followed the procedure of section 3.1, but polymerization reaction was stopped after 5 min reaction time by precipitation. Polymer was redissolved in THF (2 mg/mL) and mixed with dithranol (20 mg/mL in THF) and sodium trifluoro acetate (5 mg/mL) in the ratio 1:1:1.

The cyclic hexamer (m/z (−) = 1337.34 was fragmented (Figure S 9) due to the high intensity in the parent MS spectra. The found fragments were listed in Table S 1 and Figure S 10 gives the assignable structures corresponding to the found fragment masses [m/z].

Figure S 9. MALDI-TOF-MS of the ion at m/z = 1337.34. m/z-differences of found signals are shown.
Table S 1. Comparison of found and calculated m/z values of the fragmentation of m/z = 1337.34 and the assignment of fragment numbers.

| m/z found | [M] calculated | [M+Na]^+ calculated | fragment |
|-----------|----------------|---------------------|----------|
| 429.20    | 406.14         | 429.13              | F 1      |
| 461.16    | 438.12         | 461.11              | F 2*     |
| 493.12    | 470.09         | 493.08              | F 3*     |
| 609.21    | 586.17         | 609.16              | F 4*     |
| 641.18    | 618.15         | 641.13              | F 5*     |
| 867.33    | 844.26         | 867.25              | F 6*     |
| 899.29    | 876.23         | 899.22              | F 7      |
| 1081.30   | 1058.28        | 1081.27             | F 8      |
| 1337.34   | 1314.35        | 1337.34             | F 0      |

*fragments strongly support the TCC structure element to be formed in the MiPoly.

Figure S 10. Assignment of the found fragment-Ions (F1-F8) and the initial structure (F0). All species were found as Na-adducts and for F2 and F7 also cyclic forms could be possible.
5.6 NMR analysis of p(BQA-EDET)

$^1$H-NMR of p(BQA-EDET) was carried out in DMSO-d$_6$. The $^1$H-NMR of p(BQA-EDET) confirms the ratio of BQA to EDET of 1:1 (Figure S 11).

Figure S 11. $^1$H-NMR in DMSO-D$_6$ of the p(BQA-EDET). The signals of BQA and EDET utilized for the calculation of the ratio are highlighted.
5.7 2D-NMR analysis of p(BQA-EDET)

2D-NMR of the p(BQA-EDET) was carried out in DMSO-d$_6$. The thiol-catechol-connectivity (TCC) in the backbone of p(BQA-EDET) could be confirmed with $^1$H-$^{13}$C-HSQC and $^1$H-$^{13}$C-HMBC (cf. Figure S 12). In $^1$H-$^{13}$C-HSQC the aliphatic (blue) C-atom couples with the proton signal at 3.43 ppm, while the aromatic (green) one is a quaternary C-atom, as it shows now $^1$H-$^{13}$C-HSQC coupling signal. In the $^1$H-$^{13}$C-HMBC spectra both, the aliphatic (blue) C-atom at 69.65 ppm as well as the quaternary C-atom at 120.46 ppm, couple with the purple protons of the aliphatic CH$_2$-group at 2.95 ppm.

![Figure S 12](image)

Figure S 12. Superimposed $^1$H-$^{13}$C-HSQC and $^1$H-$^{13}$C-HMBC spectra of p(BQA-EDET) in DMSO-d$_6$. The discussed $^1$H- and $^{13}$C-signals are highlighted.

In the polymerization via Michael-type addition of free thiols to quinone structures, different isomers are built. In NMR three different isomers are found. The substitution pattern of these isomers can be analyzed by $^1$H-$^1$H-NOESY. Afterwards the regioselectivity of the Michael-type addition in the polymerization process can be estimated by comparison of the integrals of the signal of the CH$_3$-groups of these isomers.

The $^1$H-$^1$H-NOESY spectrum (see Figure S 13) reveals a coupling between aromatic protons and the CH$_3$-groups of the bridge of the bicatecholic structure. Details are shown in Figure S 14. The CH$_3$-signal (blue) at 1.49 ppm couples with two proton signals (purple) at 6.61 and 6.45 ppm, whereby this structure can be assigned as the symmetric 5,5'-substituted isomers. The second CH$_3$-signal (green) at 1.59 ppm couples with four different protons (orange) at 6.39, 6.44, 6.77 and 6.85, which shows that these signals belong to the unsymmetrical 2,5'-substituted isomers.

Taking these results into account, the CH$_3$-signals can be assigned as follows: the signal at 1.49 ppm belongs to the symmetric 5,5'-isomer, the signal at 1.59 ppm belongs to the non-symmetric 2,5'-isomer and the signal at 1.71 belongs to the symmetric 2,2'-isomer and the ratio of these isomers is found to be 4.3 : 4.4 : 1.0, respectively. Based on this assignment, the analysis of the regioselectivity of the Michael-type addition leads to a 5'- to 2'-substitution patterns with the ratio of 2.4:1 (see Figure S 15).
Figure S 13. \textsuperscript{1}H-\textsuperscript{1}H-NOESY spectrum of p(BQA-EDET) in DMSO-$d_6$. 
Figure S 14. Excerpt from the $^1$H-$^1$H-NOESY spectrum of p(BQA-EDET) in DMSO-d$_6$. The discussed proton signals are highlighted.
Figure S 15. $^1$H-NMR spectrum of p(BQA-EDET) in DMSO-$d_6$. The CH$_3$-signals for the calculation of the ratio of the different isomers are integrated.
5.8 UV/vis kinetics of BQA/EDET polymerization

For direct kinetic measurements of the polymerization process with the UV/vis spectrometer, BQA (11.3 mg, 0.044 mmol) and EDET (7.5 µL, 0.044 mmol) were solved separately in 2.5 mL NMP. An aliquot (100 µL) of each solution was then further diluted in 1900 µL NMP. For the measurement, 1 mL of the bisquinone A solution and 1 mL of the EDET solution were mixed directly in the quartz cuvette. The time period between induction of the reaction and the start of the UV/vis measurement was about 5 seconds.

![UV/vis kinetic of a 100 times diluted polymerization mixture in NMP at 386 nm.](image)

**Figure S16.** UV/vis kinetic of a 100 times diluted polymerization mixture in NMP at 386 nm.
Polymerization of BQA and EDET was carried out as described in 3.1 with a solvent volume of 4 mL. Samples were withdrawn from the reaction mixture at different time points. 40 µL reaction mixture were diluted in 3 mL THF and directly analyzed by GPC. For selected samples the addition of tributyl phosphine (5 µL/mL) to the GPC samples prior to the measurements was investigated. The incubation time with tributyl phosphine was more than 15 h.

**Figure S 17.** GPC chromatogram of the polymerization of BQA and EDET. Samples were taken from the reaction mixture at defined time points and directly analyzed with GPC. BHT was added as internal standard.

**Figure S 18.** GPC chromatogram of the polymerization of BQA and EDET. Samples were withdrawn directly from the reaction mixture and the reducing agent tributyl phosphine was added to selected samples. BHT was added as internal standard.
5.10 Temperature dependency of MI-Poly

Polymerization of BQA and EDET was carried out as described in 3.1 but different temperatures (0°C, 20°C, 40°C, 60°C, 100°C, 140°C and 180°C) were utilized. Therefore, BQA (45.2 mg, 17.6 mmol) was solved in 2000 µL NMP and stirred at the defined temperature. Subsequently, EDET (30 µL, 17.6 mmol) was added and the mixture was stirred for 15 min. Reaction mixtures were precipitated in 16 mL 60% MeOH and centrifuged. The residues were dried and analyzed by GPC.

Figure S 19. Average molecular mass of p(BQA-EDET) polymerized at different temperatures (left) and corresponding chromatograms (right).

5.11 Influence of water on the BQA-EDET polymerization

Polymerization of BQA with EDET was carried out as described in section 3.1, but in a concentration of 11.3 mg/mL BQA and different proportions of water. The polymers were precipitated and analyzed with GPC.

Figure S 20. GPC-analysis of p(BQA-EDET) synthesized with different proportions of water in the reaction mixtures. Average molecular mass (left) and corresponding chromatograms (right).
5.12 GPC analysis of BQZ-BMT polymerization

Polymerization of BQZ with BMT was carried out as described in 3.1. Samples were withdrawn from the reaction mixture at different time points: 40 µL reaction mixture were diluted in 3 mL THF and directly analyzed by GPC.

Figure S 21. GPC chromatogram of the polymerization of BQZ and BMT. Samples were taken from the reaction mixture at defined time points and were directly analyzed by GPC.

5.13 Modularity of the MiPoly process

The bisquinone (BQA (2.00 g, 7.8 mmol) or BQZ (2.31 g, 7.8 mmol) was solved in 15 mL NMP, the solution was stirred and one equivalent of the dithiol (EDET (1337 µL, 7.8 mmol) or BMT (1.36 g, 7.8 mmol)) was added. Polymerization was carried out at room temperature for 15 min. Then the mixtures were precipitated in 160 mL 60% MeOH und 40% Milli-Q water. The residue was isolated, solved in acetone and precipitated in 160 mL Milli-Q water. The solid was separated and dried.

Figure S 22. Apparent average molecular weight ($M_a$) of the polymers $p$(BQA-EDET), $p$(BQA-BMT), $p$(BQZ-EDET) and $p$(BQZ-BMT) (left) and GPC curves (right). Analysis was carried out with THF-GPC.
5.14 Low molecular weight fractions in copolymerizations of BQA/EDET and BQZ/BMT

The GPC traces of p(BQA-EDET) and p(BQZ-BMT) from samples that have been directly withdrawn from the reaction mixture were compared. Figure S 23 shows that BQZ/BMT yields higher molecular masses while the BQA/EDET polymers have more prominent fractions of low molecular weight products. The traces were integrated (Figure S 24) and the proportion of the integral intensities of the low molecular products (area between 330 g/mol and 1300 g/mol) were calculated, resulting in 5% for the p(BQA-EDET) and 2% for p(BQZ-BMT).

Figure S 23. Comparison of the chromatograms of p(BQA-EDET) and p(BQZ-BMT). Samples were taken directly from the reaction mixture.

Figure S 24. Integration of the area of the chromatograms of p(BQA-EDET) (left) and p(BQZ-BMT) (right) between 330 and 1300 g/mol as well as from 1300 and 100000 g/mol (Signal at apparent 260 g/mol corresponds to the internal standard).
5.15 Thermal stability of the TCC-polymers

Figure S 25. TGA of p(BQA-EDET), p(BQA-BMT), p(BQZ-EDET) and p(BQZ-BMT). Applied heat rate 20 °C/min (20 °C-600 °C).
5.16 Thermal transitions by calorimetry

Figure S26. DSC-measurements of p(BQA-EDET), p(BQA-BMT), p(BQZ-EDET) and p(BQZ-BMT). Applied heat rate 10 °C/min (20 °C-200 °C). The second heating cycles are shown.
6 Macroscopic adhesion tests

Aluminum (5005 A, 100 mm × 25 mm × 1.5 mm) and poly(propylene) plates (Simona DWST, 100 mm × 25 mm × 3 mm) were cleaned with acetone and pre-treated with UV/Ozone for 30 min. Subsequently, an area of 25 mm × 10 mm of the test specimen was coated with a solution of the corresponding polymer in acetone (167 mg/mL). The solvent was evaporated at room temperature and the coated surfaces of two test specimen were combined. Curing was carried out in a “hot-melt”-like process in which the adhesive was cured for 15 min at 120 °C in a hot press, while applying 1000 kg weight for each test specimen. (These conditions were chosen to realize an application temperature above T_g to receive a homogenous and reproducible polymer adhesive layer. Therefore, the temperature has the biggest impact, as both remaining solvent and a curing temperature below T_g reduce the adhesive capabilities of the joint, if curing was carried out at 40 °C or 80 °C, respectively. The high pressure was not necessary, as comparable results were achieved, if the hot stage was just tightened by hand, without usage of the hydraulic press (see Table S2).) Afterwards the samples were cooled under pressure, removed from the hot press and could equilibrate overnight at r.t.. Force-extension-curves were measured in a shear arrangement with a velocity of 0.05 mm/s.

The adhesion strength was calculated by normalizing the maximum force of the force-extension-curve to the area of the adhesive overlap of the test specimen. A Grubbs test was performed on each series of measurements and outliers were not considered. Results are given as mean ± standard deviation. Statistical significance of the resulting data was calculated with the t-test (Student) considering a significance level of 99.9% (***) , 99% (**) or 95% (*).

Figure S 27. Force-extension-curves for the four different polymers on aluminum test specimen.
Figure S 28. Representative photographs of the fraction areas on aluminum after the shear test and SEM-images of the marked area (scale bar corresponds to 500 µm). Mainly cohesive failure was observed.
Figure S 29. Force-extension-curves for the four different polymers on poly(propylene) test specimen.
Figure S 30. Representative photographs of the fraction areas on poly(propylene) after the shear test and SEM-images of the marked area (scale bar corresponds to 1 mm). The observed surface was scratched to differentiate the coated surfaces (left images) from the non-coated one (right images). Mainly adhesive failure was observed.
Figure S 31. Photographs visualizing the failure process of the gluing on poly(propylene) substrates. The data set is provided as movie as well (see Supporting Video shear test PP.mp4)

Table S 2. Results of further investigations in lap-shear tests of BQA-EDET on aluminum substrates.

| curing time [min] | curing temperature [°C] | applied pressure [kg per lap joint] | adhesion strength [MPa] |
|-------------------|-------------------------|-------------------------------------|------------------------|
| 15                | 40                      | 1000                                | 0.5 ± 0.6              |
| 15                | 80                      | 1000                                | 1.0 ± 0.5              |
| 15                | 120                     | 1000                                | 2.5 ± 0.3              |
| 15                | 120                     | manually tightened                 | 2.4 ± 0.4              |
6.1 Comparison with benchmarks

Three different glues were used as benchmarks: A poly(vinylester) glue (Figure S 32), a 2-K-epoxide glue (Figure S 33) and a poly(cyanoacrylate) glue (Figure S 34).

Aluminum (5005 A, 100 mm × 25 mm × 1.5 mm) and poly(propylene) plates (Simona DWST, 100 mm × 25 mm × 3 mm) were cleaned with acetone and pre-treated with UV/Ozone for 30 min. Subsequently, an area of 25 mm × 10 mm of the test specimen were coated with the corresponding glue.

According to the procedure of the manufacturer, for the poly(vinylester) glue both test specimens were coated with a thin film, which was allowed to dry. Afterwards one sample was coated with an additional layer and both test specimen were combined. For the 2-K-Epoxid glue both glue components were mixed in the ratio 1:1. One test specimen was coated with this mixture and combined with the second plate. With the poly(cyanoacrylate) also one test specimen was coated and directly combined with the second plate.

All samples were pressed with 1000 kg for 5 min and could equilibrate overnight.

The aluminum samples glued with cyanoacrylate or 2-K-epoxide glue have been analyzed with a Zwick material testing system. All other samples have been tested with the Texture Analyzer. Force-extension-curves were measured in a shear arrangement with a velocity of 0.05 mm/s. The adhesion strength was calculated by normalizing the maximum force of the force-extension-curve to the area of the adhesive overlap of the test specimen.

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**Figure S 32.** Force-extension curves of poly(vinylester) glue on aluminum (left) and poly(propylene) (right).

**Figure S 33.** Force-extension curves of 2-K-epoxide glue on aluminum (left, measured on a Zwick system) and poly(propylene) (right). (The ends of the force-extension curves panel (left) correspond to the fracturing event).
Figure S 34. Force-extension curves of poly(cyanoacrylate) glue on aluminum (left, measured on a Zwick system) and poly(propylene) (right). (The ends of the force-extension curves panel (left) correspond to the fracturing event).
6.2 Adhesion tests of p(BQA-EDET) with different molecular weights

Glue application and curing were carried out as described in Section S6. For lap shear test of p(BQA-EDET) (4.0 kDa, A & 9.0 kDa, B & 15.9 kDa, C) the test specimen sizes were 80 mm × 20 mm × 1.5 mm for aluminum and 80 mm × 25 mm × 3 mm in the case of PP, with a coating area of 20 mm x 7 mm or 25 mm x 10 mm, respectively.

The p(BQA-EDET) with different molecular weights were synthesized by variation of the monomer concentration in the polymerization mixture and an adapted precipitation procedure yielding three different p(BQA-EDET) with apparent molecular weights of \( M_{w,app} = 4.0 \text{ kDa (D = 1.8), } M_{w,app} = 9.0 \text{ kDa (D = 1.6) and } M_{w,app} = 15.9 \text{ kDa (D = 2.6) (Figure S 35, left). As expected, the adhesive properties of these polymers on aluminum surfaces increased significantly from 0.8 ± 0.2 MPa for the low molecular mass product over 1.8 ± 0.2 MPa for the middle molecular weight polymer to 2.3 ± 0.5 MPa for the highest molecular weight compound (Figure S 35, right). As the failure of p(BQA-EDET) was always dominantly cohesive in nature, the strong positive effect of the increased molecular weight suggests an improved cohesion. Taking this into account, it is not surprising, that the effect on PP substrate gluing is less pronounced, as the limiting factor in these lap shear tests is mainly the adhesion capability of the utilized polymer. Thus, a significant improvement of the adhesive strength on increased molecular weight was only found for the comparison of A and C, meaning p(BQA-EDET) with the lowest molecular weight 4kDa with the highest molecular weight 15.9 kDa giving 0.9 ± 0.2 MPa and 1.2 ± 0.2 MPa, respectively (Figure S 35, right).

Figure S 35. Lap shear tests with p(BQA-EDET) with varying molecular masses. GPC chromatograms of the utilized p(BQA-EDET)-samples (left) and adhesive strength (right). A: \( M_{w,app} = 4.0 \text{ kDa, D = 1.8, } B: M_{w,app} = 9.0 \text{ kDa, D = 1.6 and } C: M_{w,app} = 15.9 \text{ kDa, D = 2.6. Statistical significance was calculated due to t-test (Student) with a significance level of 99.9% (** *), 99% (**) or 95% (*).}
6.3 Underwater adhesion tests of p(BQZ-EDET)

Wet gluing setup and soft curing procedure: For underwater adhesion tests the reported procedure of Wilker et al.[4] with an adapted curing protocol was utilized. Aluminum (5005 A, 800 mm × 20 mm × 1,5 mm) plates were cleaned with acetone and pre-treated with UV/Ozone for 30 min. Subsequently, one plate was submerged in Milli-Q water or a 599 mM NaCl-solution (sea water model) and an area of 20 mm × 10 mm of the test specimen was coated with 60 µL of a p(BQZ-EDET) solution in chloroform (750 mg/mL). A second plate was placed onto the coated surface and the gluing was burdened with ~350 g load. The adhesive was cured underwater for 3 days at 50 °C under load. The control experiment was carried out in dry conditions (non-wetted specimens, glue application in air) and for curing the samples were placed in a heating oven for 3 days at 50 °C.

The force-extension-curves of the data sets in Figure S 36 exhibited a large mean variation, indicating not optimal curing. Furthermore, the shape of the curves varies, where sharp rupture events refer to failure of stiff and brittle glues, while not-sharp fracture suggest a softer glue enabling partial shear flow before rupture. This could be due to residual solvents remaining in the adhesive layer, which acts as plasticizer. It is noteworthy, that the test series cured under sea water conditions show only sharp rupture events, while the greatest impact of remaining solvent seems to be found for the dry curing control experiments. This suggests that in this curing process water could be useful for the removal of the solvent and high ion strength even assists the glass formation of the adhesive layer.

Figure S 36. Lap shear tests with p(BQZ-EDET) after gluing and curing under water (left), under sea water model solution (middle) or under dry conditions (right).
SUPPORTING INFORMATION

7 References S.I.

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