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Underwater bonding strength of marine mussel-inspired polymers containing DOPA-like units with amino groups

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Materials:

N-(3,4-dimethylphenethyl) methacrylamide (DMA) was synthesized according the literature. [1] Acrylic acid, butyl acrylate, dimethylformamide and ethanol were purchased from Guangzhou chemical reagent factory. Azodiisobutyronitrile and the three diamines, 1,4-butanediamine, 1,2-ethanediame and 1,8-octanediame, were purchased from Aladdin chemical reagent company. Acrylic acid, butyl acrylate and dimethylformamide were distilled before use. Azodiisobutyronitrile was purified by crystallization from ethanol. All other reagents were used as received.

Synthesis of the terpolymers:

The four terpolymers were synthesized by the similar method, only with different feed
ratio. To illustrate our synthetic procedure for these terpolymers, we detail here the
synthetic method for run 1 (Table 1). DMA (0.4260 g), acrylic acid (0.4163 g) and butyl
acrylate (0.2954 g) were put into an ampoule, followed by azodiisobutyronitrile (0.0100
g). Then, dimethylformamide (DMF, 5.0 mL) was added. The mixture was degassed by
three freeze-pump-thaw cycles, sealed under argon, and heated to 70°C for 24 hrs. White
semi-solid product was obtained by precipitation from ethanol/water (3:1) three times and
dried in a vacuum oven at 60 °C for 24 hrs. The yield is about 75%. The products
obtained through such method were used in the tensile strength test under dry
environment. The products used for tensile strength test under wet environment were
precipitated from ethanol/water (3:1) containing diamine [the diamines used in this paper
were 1,2-ethanediamine (ED), 1,4-butanediamine (BD) and 1,8-octanediamine (OD) and
the amount of the diamine was almost ten times to AA (molar ratio)] first and
subsequently precipitated from ethanol/water (3:1) three times. The other experiments,
from run 2 to 4, were carried out through the similar method with different feed ratio.

The 1H NMR spectroscopy of the terpolymer in run 3 (300 MHz, CD3OD/TMS): δ
11.5 (−COOH), 8.8 (−CONH−), 6.8–6.5 (C6H3(OH)2−), 4.0 (−COOC2H5), 3.3–2.5
(Ar−CH2CH2−NH−), 1.8–0.9 (the protons in the backbone and CH2CH2CH2CH2O−). The
four synthesized terpolymers have similar 1H NMR spectroscopies except the integral
area of each peak.

The 1H NMR spectra of these copolymers are given below (the proton signal of
carboxyl group is omitted in the spectrum):
Polymer of Run 1

Polymer of Run 2
Polymer of Run 3

Polymer of Run 4
**Elementary analysis of the synthesized polymers (non-neutralized and neutralized by diamines):**

Table S1 Elementary analysis for the as-synthesized polymers and their neutralized form[^a]

<table>
<thead>
<tr>
<th></th>
<th>The non-neutralized polymer</th>
<th>The neutralized polymer</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
</tr>
<tr>
<td><strong>Run 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>59.5</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run 2</strong></td>
<td>60.7</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run 3</strong></td>
<td>61.8</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run 4</strong></td>
<td>62.5</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

[^a]: the elemental analysis was performed on Elementar Vario EL.
The data of elementary analysis for the synthesized polymers are compiled into Table S1. The content of element nitrogen increases along with the increase of DMA content (form polymer Run 1 to Run 4) because the element nitrogen is only existent in DMA segment. The content of element nitrogen is less than 5% in non-neutralized form. When the as-synthesized polymers are neutralized by diamine (such as by ED, BD or OD), the content of element nitrogen increases suddenly, in the range of 8.4~13.5.

**Samples preparation for tensile strength test:**

The samples for tensile strength test were fabricated as follows. For dry adhesion tests, the terpolymer (20 mg) was dissolved into 1.0 mL of ethanol, and the solution was dropped on a smooth bone chip surface (0.5 cm × 0.5 cm). When the ethanol on the chip was almost evaporated, another same size bone chip was put on the top of it and the two-chips were pressed together with a force about 5 N for one minute. Finally, the two bone chips were apart by tensile forces perpendicular to the adhesive interface at the speed of 5 mm/min (Figure S1). As for the tensile strength test under wet environment, the samples preparation procedures were exactly the same, except for the two bone chips environment (the samples were tested underwater) and the terpolymers, the terpolymers used here neutralized by diamine.
Figure S1. The samples preparation procedures before using

References used in supporting information: