

Support Information for RSC Advances

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-ethanediamine and 1,8-octanediamine, 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:

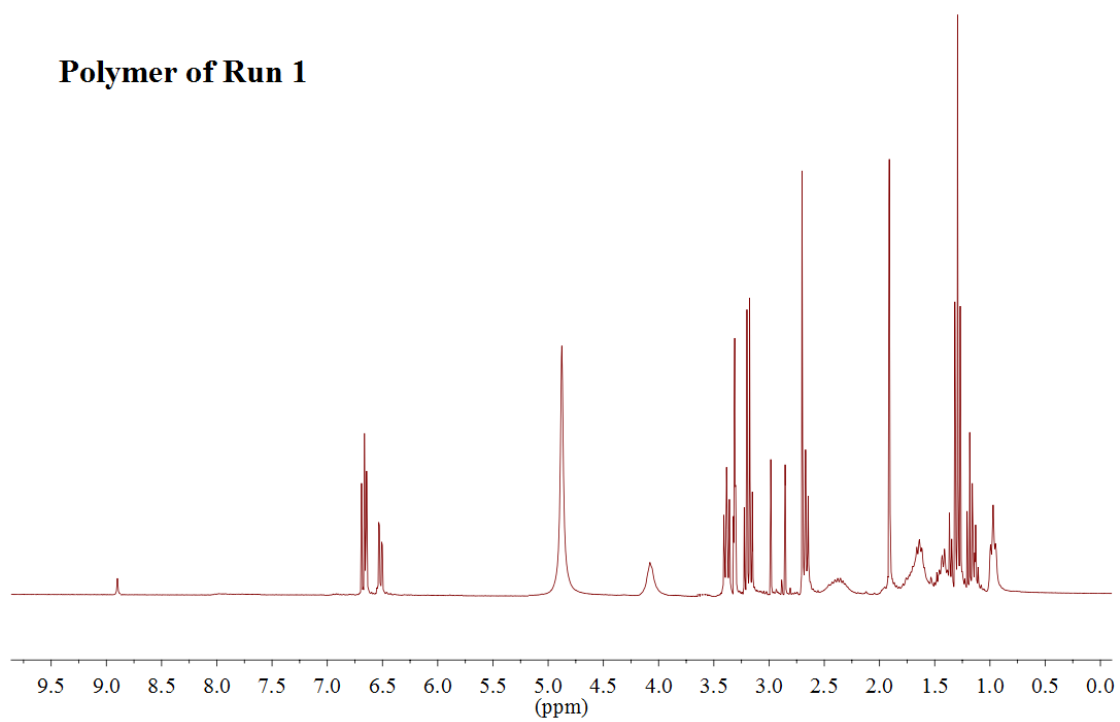
The four terpolymers were synthesized by the similar method, only with different feed

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.

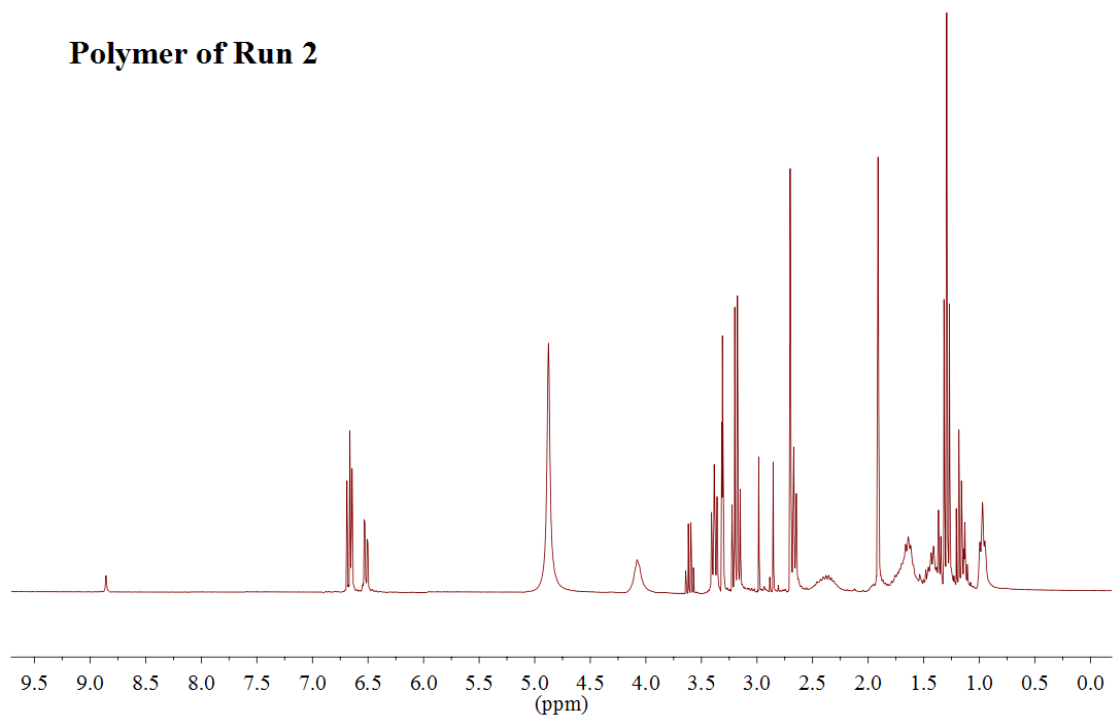
The ^1H NMR spectroscopy of the terpolymer in run 3 (300 MHz, $\text{CD}_3\text{OD}/\text{TMS}$): δ 11.5 (-COOH), 8.8 (-CONH-), 6.8-6.5 ($\text{C}_6\text{H}_3(\text{OH})_2$ -), 4.0 (-COOCH₂-), 3.3-2.5 (Ar-CH₂CH₂-NH-), 1.8-0.9 (the protons in the backbone and CH₃CH₂CH₂CH₂O-). The four synthesized terpolymers 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):

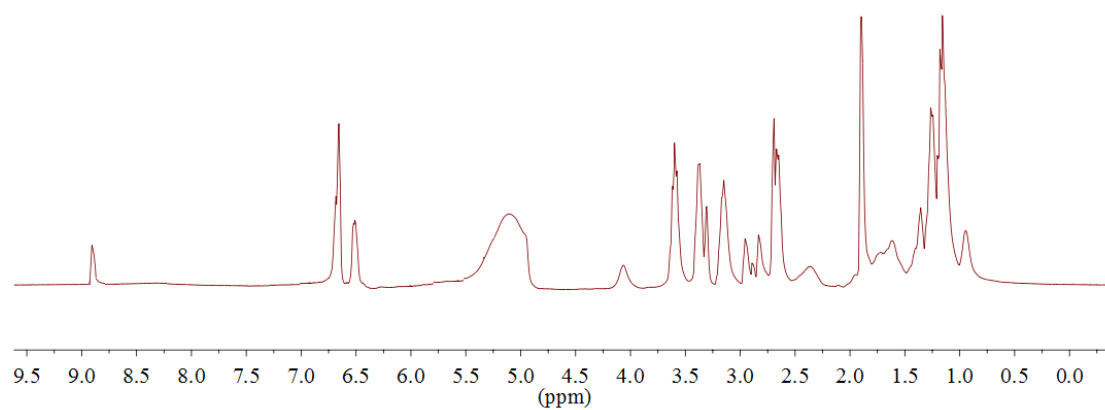
Polymer of Run 1



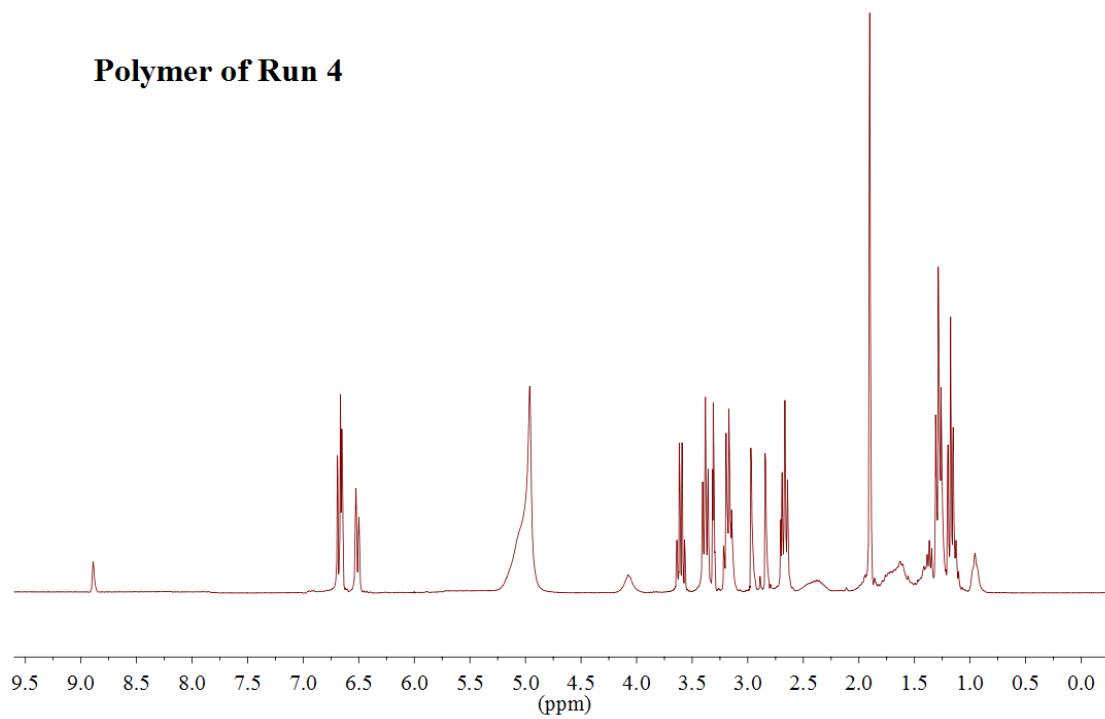
Polymer of Run 2



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]

	The non-neutralized polymer			The neutralized polymer			
	%C	%H	%N	%C	%H	%N	diamine
Run 1	59.5	7.0	2.3	59.1	8.3	13.5	(by ED)
				61.9	8.9	12.1	(by BD)
				66.0	9.8	10.0	(by OD)
Run 2	60.7	7.0	3.1	60.3	8.0	12.1	(by ED)
				63.5	7.1	11.2	(by BD)
				65.9	9.4	9.4	(by OD)
Run 3	61.8	7.0	3.8	61.4	7.8	10.5	(by ED)
				63.1	8.2	9.8	(by BD)
				65.7	8.9	8.7	(by OD)
Run 4	62.5	7.0	4.3	62.1	7.6	9.9	(by ED)
				63.4	8.0	9.3	(by BD)
				65.6	8.6	8.4	(by OD)

[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 (from 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.

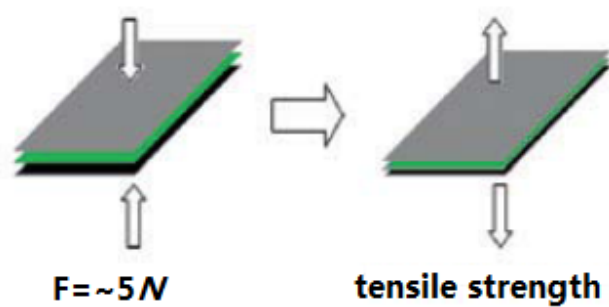


Figure S1. The samples preparation procedures before using

References used in supporting information:

1. Lee, H.; Lee, B. P.; Messersmith, P. B. *nature* **2007**, 448, 338.