Electronic Supporting Information (ESI)

Non-Swellable Self-Healing Polymer under Seawater with Long-Term Stability

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Scheme S1 Synthetic scheme of catechol-containing polymer.

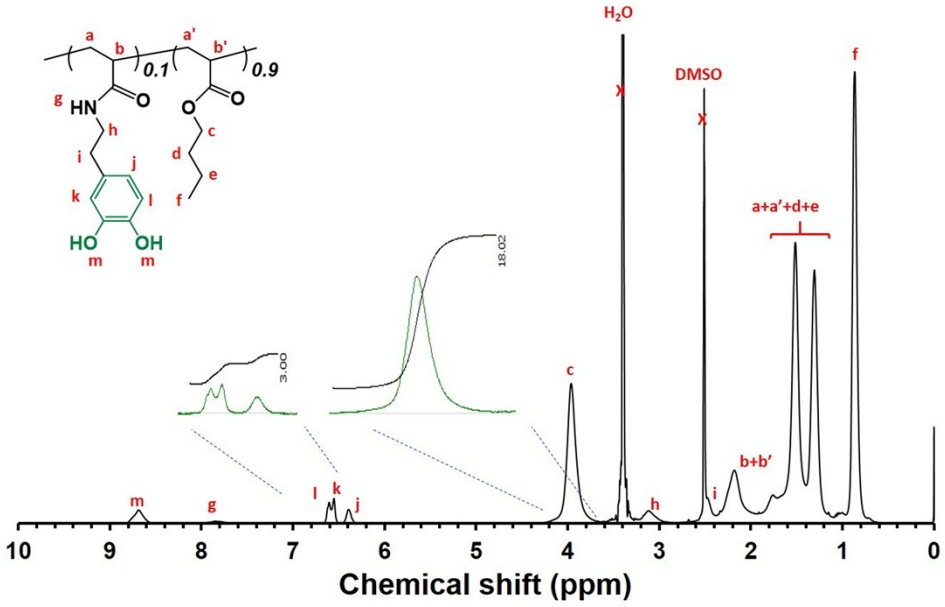

Fig. S1 ^{1}H NMR spectrum of P(DA-*co*-BA). The DA:BA molar ratio for P(DA-*co*-BA) was calculated to be 1:9 using the integration of 6.62–6.40 ppm (3H in DA) and 3.97 ppm (2H in BA).

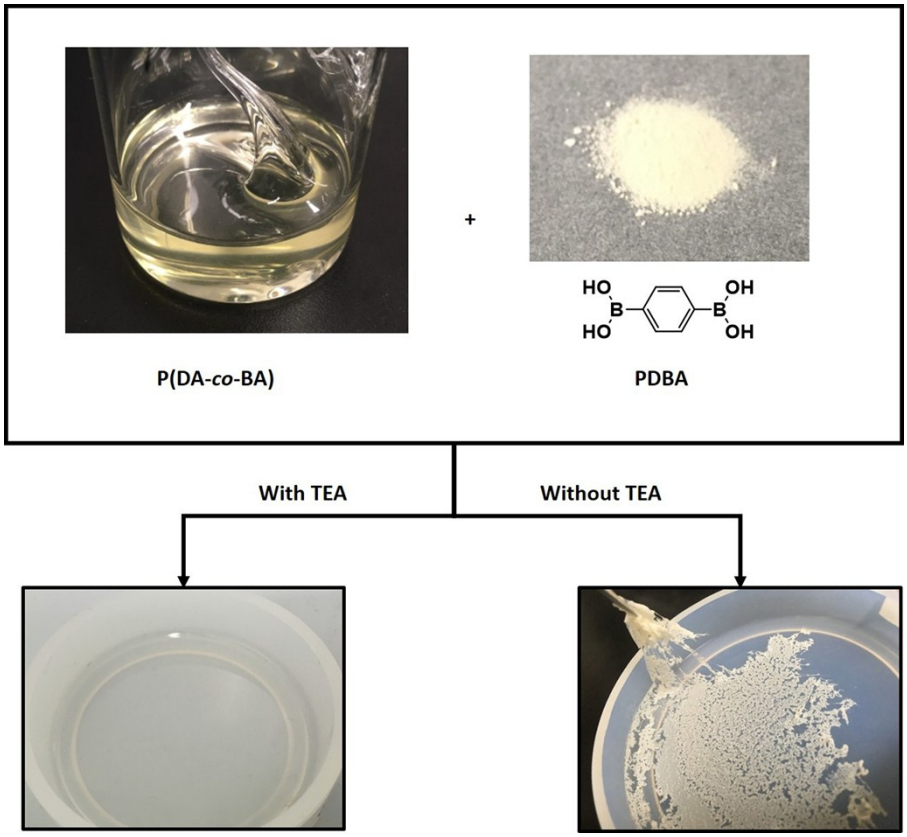

Fig. S2 For the preparation of P-PDBA films, the solution of liquid-like P(DA-*co*-BA) in chloroform was mixed with the solution of PDBA in methanol. With the addition of TEA into the mixture of P(DA-*co*-BA) and PDBA, a tough and highly transparent P-PDBA film was obtained. However, without the addition of TE
A, robust films could not be obtained.

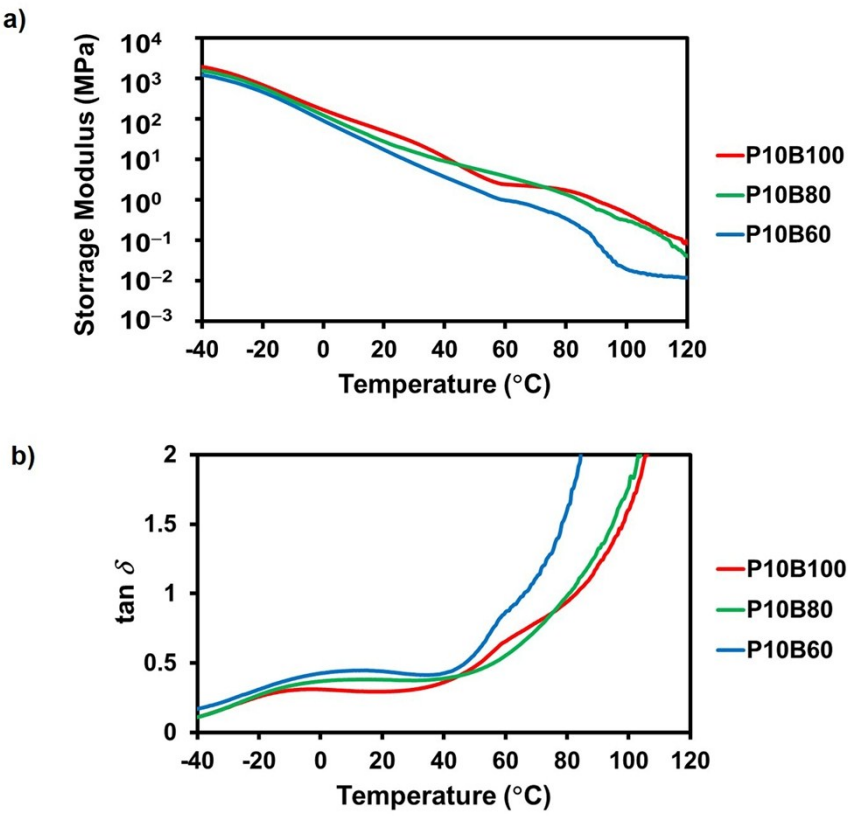

Fig. S3 DMA results of P-PDBA polymers. As the feed ratio of PDBA was increased, the relative height of tan δ at around −10 °C was decreased indicating the higher cross-linking density.

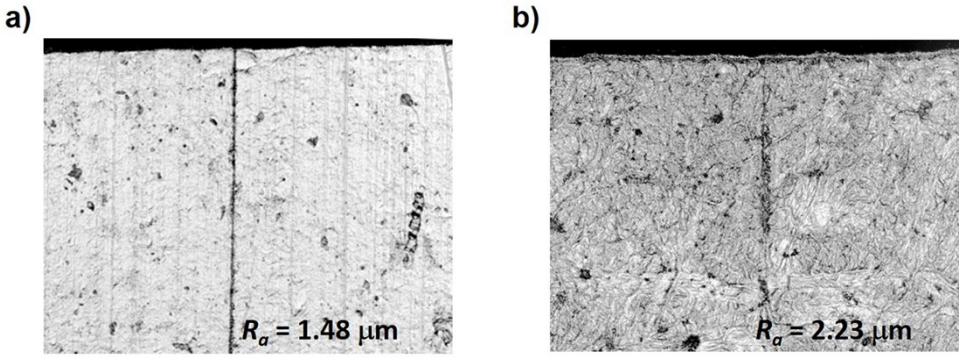

Fig. S4 Laser scanning microscopy images of P-PDBA 100%. Cut scar of (a) before self-healing, and (b) after self-healed under seawater for 3 days. Inset values are the mean roughness (R_a).

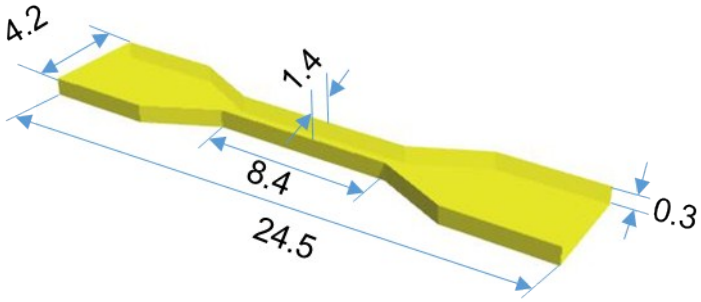

Fig. S5 Dimensions of the dumbbell shaped sample.

Table S1 The composition of the artificial seawater[S1]

Compound	Concentration [g L^{-1}]
NaCl	23.93
Na_2SO_4	4.01
KCl	0.68
$NaHCO_3$	0.2
KBr	0.1
H_3BO_3	0.026
NaF	0.003
$MgCl_2$	5.07
$CaCl_2$	1.14
$SrCl_2/6H_2O$	0.02

Table S2 Results of self-healing test

sample	Healing Condition	Young's modulus [MPa][a)]	Break strength [MPa]	Strain at break [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]	Healing efficiency [%][c)]
P-PDBA 100%	Original	2.3 ± 0.3	2.8 ± 0.2	5.1 ± 0.4	10.6 ± 1.4	-
	1 day in seawater	2.0 ± 0.2	2.0 ± 0.1	1.6 ± 0.1	2.0 ± 0.2	19 ± 1.5
	2 days in seawater	2.2 ± 0.3	1.9 ± 0.3	1.7 + 0.5	2.2 ± 0.8	21 ± 8
	3 days in seawater	2.1 ± 0.1	2.6 ± 0.2	4.7 ± 1.1	9.6 ± 2.8	91 ± 27
	3 days in desiccator[d)]	2.4 ± 0.8	0.8 ± 0.1	0.3 ± 0.1	0.2 ± 0.0	1.5 ± 0.5
P-Ca^{2+} 100%	Original	0.6 ± 0.01	2.3 ± 0.1	4.5 ± 0.5	5.4 ± 0.8	-
	3 days in seawater	1.2 ± 0.1	0.4 ± 0.04	0.4 ± 0.05	0.1 ± 0.02	1.8 ± 0.3

[a)] Calculated from the initial slope of stress strain curves. [b)] Integration of the area under the stress-strain curves. [c)] Quantified by percent recovery of toughness. [d)] The relative humidity of desiccator was less than 20%.

Table S3 Results of swelling ratio

Sample	Seawater pH 8.3[a)]	Seawater pH 7.0[b)]	Seawater pH 4.0[b)]	DI water
P-PDBA 100%	1.9 wt%	2.3 wt%	2.6 wt%	20 wt%
P-Ca^{2+} 100%	18 wt%	14 wt%	13 wt%	135 %

[a)] The pH of the artificial seawater was pH was 8.3. [b)] Acidic seawater (pH 7.0 and 4.0) was prepared by adding (HCl aqueous solution, 1N) to the pH 8.3 artificial seawater.

Table S4 The results of mechanical properties of swollen and dried state of network polymers (after 3 days immersion in seawater)

sample	Period	Young's modulus [MPa][a)]	Break strength [MPa]	Strain at break [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]
P-PDBA 100%	Original	2.3 ± 0.3	2.8 ± 0.2	5.1 ± 0.4	10.6 ± 1.4
	without dry	0.8 ± 0.2	0.6 ± 0.1	5.2 ± 0.5	2.0 ± 0.1
	after dry	2.1 ± 0.5	2.8 ± 0.2	5.4 ± 0.7	11.9 ± 0.8
P-Ca^{2+} 100%	Original	0.6 ± 0.01	2.3 ± 0.1	4.5 ± 0.5	5.4 ± 0.8
	without dry	0.5 ± 0.1	0.5 ± 0.1	1.6 ± 0.1	0.5 ± 0.1
	after dry	1.8 ± 0.8	1.2 ± 0.1	0.9 ± 0.1	0.8 ± 0.2

[a)] Calculated from the initial slope of stress strain curves. [b)] Integration of the area under the stress-strain curves.

Table S5 The results of mechanical stability test under seawater

sample	Period	Young's modulus [MPa][a)]	Break strength [MPa]	Strain at break [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]
P-PDBA 100%	Original	2.3 ± 0.3	2.8 ± 0.2	5.1 ± 0.4	10.6 ± 1.4
	1 month	2.1 ± 0.4	2.8 ± 0.1	5.5 ± 0.8	11.2 ± 1.7
P-Ca^{2+} 100%	Original	0.6 ± 0.01	2.3 ± 0.1	4.5 ± 0.5	5.4 ± 0.8
	1 month	4.4 ± 1.2	1.8 ± 0.1	0.8 ± 0.1	0.9 ± 0.1

[a)] Calculated from the initial slope of stress strain curves. [b)] Integration of the area under the stress-strain curves.

References

(1) Kester, D. R.; Duedall, I. W.; Connors, D. N; Pytkowicz, R. M.; Preparation of Artificial Seawater. *Limnology & Oceanography* 1967, **12**, 176-179.