Electronic Supporting Information (ESI)

Polymers with Autonomous Self-Healing Ability and Remarkable Reprocessability under Ambient Humidity Conditions

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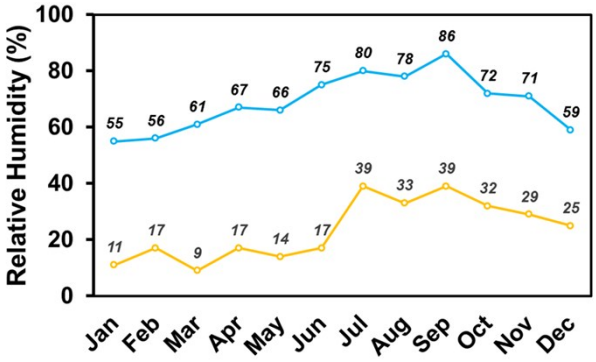

Fig. S1 The data of relative humidity of Tokyo, Japan in 2017. The monthly average relative humidity (Blue line). The lowest relative humidity of each month (Orange line). (Data source: Japan Meteorological Agency)

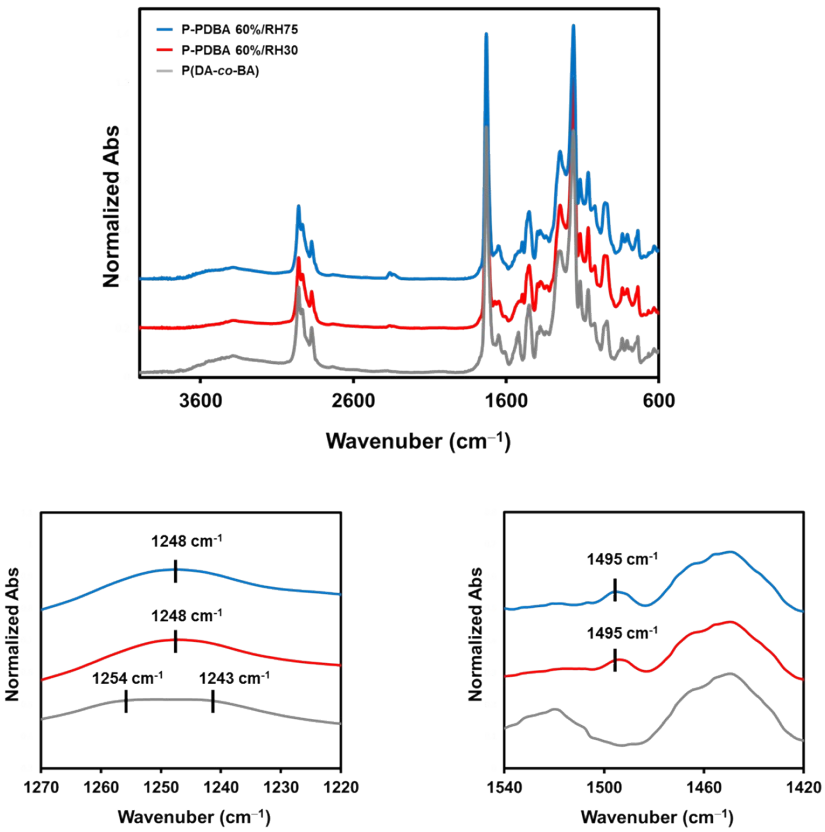

Fig. S2 ATR-FTIR spectra of P-PDBA 60% (blue: P-PDBA 60%/RH75, red: P-PDBA 60%/RH30) and P(DA-*co*-BA) (gray).

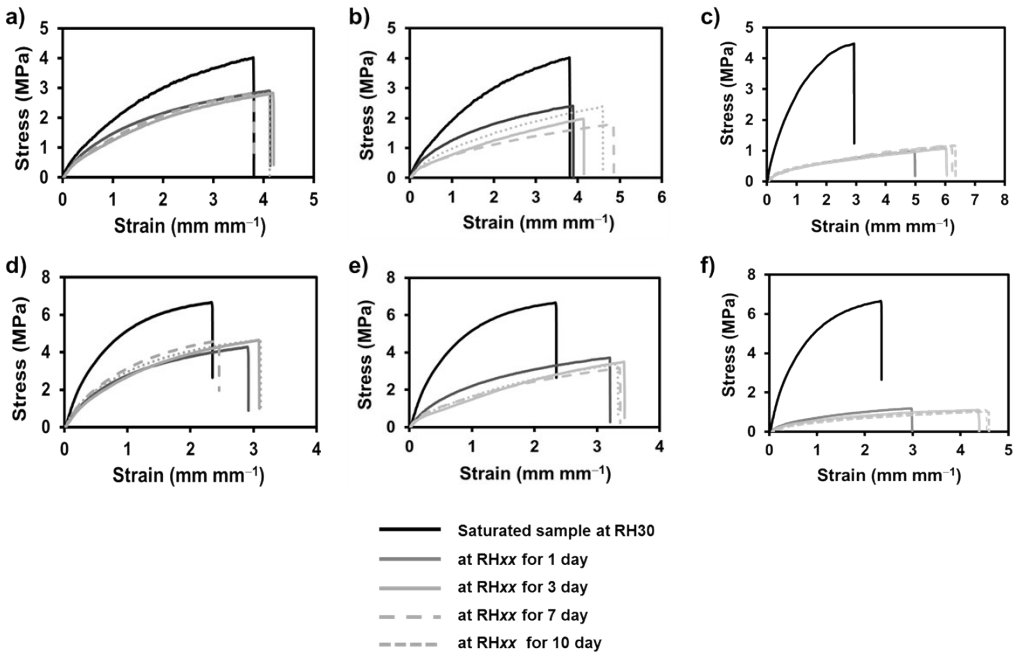

Fig. S3 Humidity dependent mechanical properties. Each sample was kept under ambient humidity conditions. P-PDBA 60% under (a) RH55, (b) RH75, and (c) RH90. P-PDBA 100% under (d) RH55, (e) RH75, and (f) RH90.

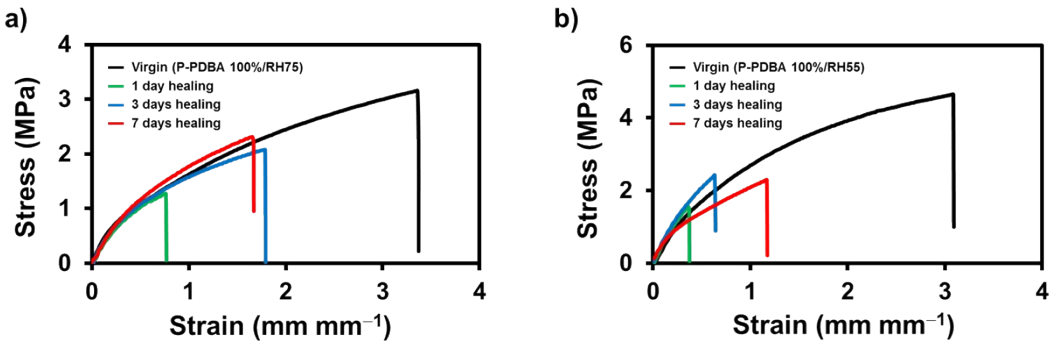

Fig. S4 Self-healing abilities of P-PDBA 100% under (a) RH75 and (b) RH55, together with the curve of virgin samples saturated under each humidity.

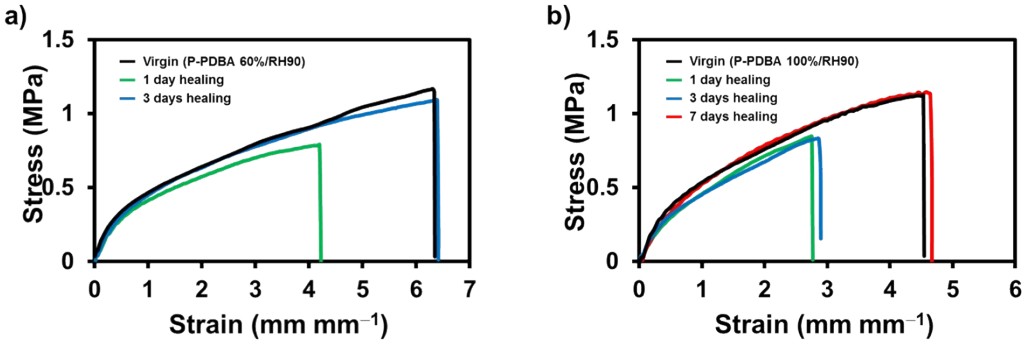

Fig. S5 Self-healing abilities of (a) P-PDBA 60% and (b) P-PDBA 100% under RH90, together with the curve of virgin samples saturated underRH90.

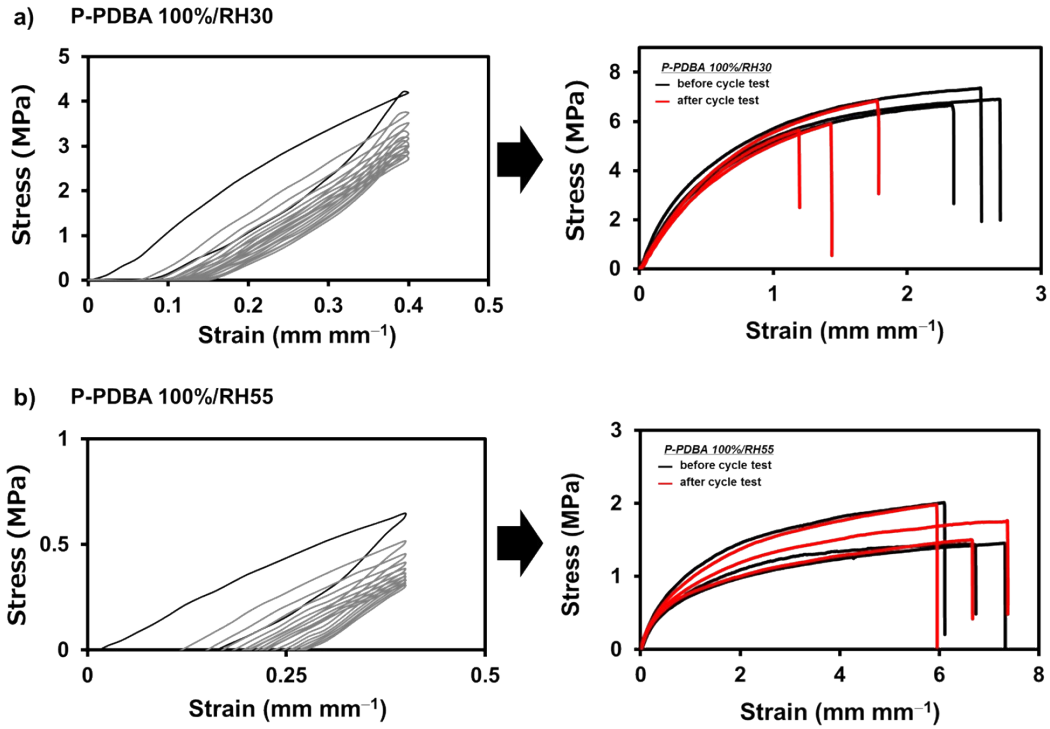

Fig. S6 Tensile properties of P-PDBA 100% after ten times loading-unloading cycles. The results of cyclic tests and tensile tests (a) under RH30 with P-PDBA 100%/RH30, (b) under RH55 with P-PDBA 100%/RH55.

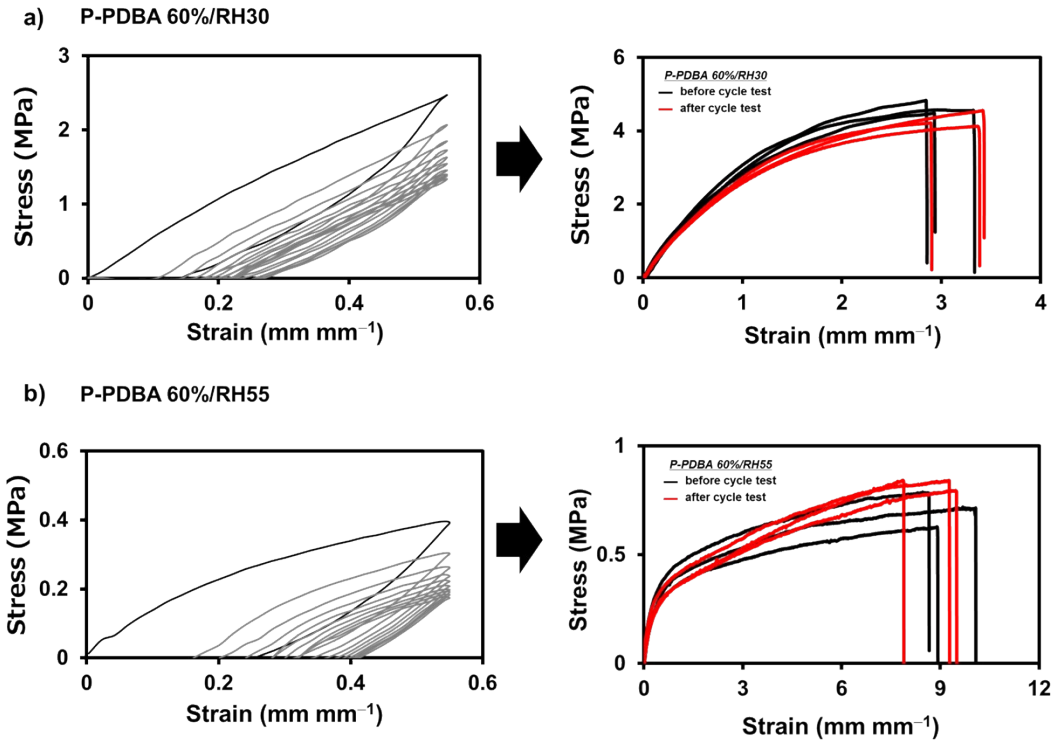

Fig. S7 Tensile properties of P-PDBA 60% after ten times loading-unloading cycles. The results of cyclic tests and tensile tests (a) under RH30 with P-PDBA 60/RH30, (b) under RH55 with P-PDBA 60%/RH55.

Unlike the results of P-PDBA 100%/RH30 (Figure S6a), there were no differences in mechanical properties between the virgin and fatigue accumulated P-PDBA 60%/RH30 even under dry conditions (Figure S7a). These results suggest that the reversible hydrogen bond interactions contribute to the energy dissipation under external stress in P-PDBA 60%/RH30, which results in the mechanical property retention without breaking tetrahedral boronate ester bonds under dry conditions. In case of P-PDBA 60%/RH55, malleability was observed which caused by network rearrangement via rapid transesterification between dynamic bonds (Figure S7b).

Table S1 Swelling behavior of P-PDBA polymers under various wet conditions.a

sample	Condition	Satd. swelling ratio (wt%)[a)]
P-PDBA 60%	RH55	0.05 ± 0.0
	RH75	0.61 ± 0.1
	RH90	2.40 ± 0.1
P-PDBA 100%	RH55	0.26 ± 0.1
	RH75	0.73 ± 0.2
	RH90	3.31 ± 0.1
	Underwater	~20[b)]

[a)] Swelling ratio was saturated in one day. [b)] Swelling ratio was saturated in 2 weeks.

Table S2 Humidity dependent mechanical properties under 55% relative humidity

sample	Saturated time	Young's modulus [MPa][a)]	Fracture stress [MPa]	Fracture strain [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]
P-PDBA 60%	Dried sample[c)]	4.1 ± 0.3	4.6 ± 0.2	3.0 ± 0.3	10.3 ± 0.2
	1 d	1.8 ± 0.1	2.9 ± 0.0	4.3 + 0.3	8.7 ± 0.7
	3 d	1.4 ± 0.1	2.8 ± 0.0	3.9 ± 0.3	7.2 ± 0.5
	7 d	1.7 ± 0.3	2.8 ± 0.2	4.0 ± 0.9	7.6 ± 2.2
	10 d	1.5 ± 0.2	2.9 ± 0.0	3.9 ± 0.2	7.2 ± 0.4
P-PDBA 100%	Dried sample[c)]	13.1 ± 2.4	6.7 ± 0.1	2.3 ± 0.3	13.3 ± 1.9
	1 d	4.6 ± 0.1	4.4 ± 0.2	3.4 ± 0.6	10.7 ± 2.7
	3 d	5.3 ± 0.7	4.7 ± 0.4	2.8 ± 0.5	8.8 ± 2.4
	7 d	5.7 ± 0.3	5.1 ± 0.4	3.3 ± 0.7	11.9 ± 3.8
	10 d	4.9 ± 1.2	4.4 ± 0.2	3.0 ± 0.1	9.1 ± 1.0

[a)] Calculated from stress at a small strain (< 10%). [b)] Integration of the area under the stress-strain curves. [c)] Samples were kept in desiccator more than 3 d.

Table S3 Humidity dependent mechanical properties under 75% relative humidity

sample	Saturated time	Young's modulus [MPa][a)]	Fracture stress [MPa]	Fracture strain [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]
P-PDBA 60%	Dried sample[c)]	4.1 ± 0.3	4.6 ± 0.2	3.0 ± 0.3	10.3 ± 0.2
	1 d	4.1 ± 0.3	4.6 ± 0.2	3.0 ± 0.3	6.9 ± 0.7
	3 d	1.3 ± 0.3	2.3 ± 0.1	4.3 + 0.6	5.8 ± 2.5
	7 d	0.8 ± 0.2	2.2 ± 0.3	4.2 ± 1.1	5.3 ± 0.5
	10 d	0.7 ± 0.4	1.8 ± 0.1	4.5 ± 0.8	6.8 ± 0.6
P-PDBA 100%	Dried sample[c)]	13.1 ± 2.4	6.7 ± 0.1	2.3 ± 0.3	13.3 ± 1.9
	1 d	3.5 ± 0.7	3.6 ± 0.3	3.3 ± 0.1	8.3 ± 0.7
	3 d	2.2 ± 1.0	3.5 ± 0.1	3.5 ± 0.6	7.8 ± 1.3
	7 d	2.5 ± 0.6	3.3 ± 0.4	3.5 ± 0.2	7.5 ± 0.7
	10 d	2.2 ± 0.9	3.3 ± 0.4	3.6 ± 0.3	7.8 ± 1.5

[a)] Calculated from stress at a small strain (< 10%). [b)] Integration of the area under the stress-strain curves. [c)] Samples were kept in desiccator more than 3 d.

Table S4 Results of self-healing tests under 55% relative humidity

sample	Healing time	Young's modulus [MPa][a)]	Fracture stress [MPa]	Fracture strain [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]	Healing efficiency [%][c)]
P-PDBA 60%	Saturated sample[d)]	1.5 ± 0.1	2.8 ± 0.0	3.9 ± 0.1	7.3 ± 0.2	-
	1 d	2.1 ± 0.4	1.5 ± 0.5	0.8 + 0.2	0.8 ± 0.5	10.9 ± 7.0
	3 d	1.2 ± 0.2	1.0 ± 0.0	0.9 ± 0.2	0.5 ± 0.1	7.3 ± 1.5
	7 d	1.0 ± 0.1	1.7 ± 0.1	2.1 ± 0.3	2.2 ± 0.4	30.0 ± 5.7
P-PDBA 100%	Saturated sample[a)]	5.3 ± 0.4	4.7 ± 0.4	3.0 ± 0.3	9.9 ± 1.7	-
	1 d	5.1 ± 0.8	1.5 ± 0.4	0.4 ± 0.1	0.3 ± 0.2	3.3 ± 1.9
	3 d	5.3 ± 0.7	2.3 ± 0.6	0.7 ± 0.3	1.0 ± 0.6	10.6 ± 6.5
	7 d	3.2 ± 0.9	2.0 ± 0.5	1.0 ± 0.2	1.3 ± 0.6	11.5 ± 5.3

[a)] Calculated from stress at a small strain (< 10%).[b)] Integration of the area under the stress-strain curves. [c)] Quantified by percent recovery of toughness. [d)] Samples saturated under 55% of humidity were used for healing tests.

Table S5 Results of self-healing tests under 75% relative humidity

sample	Healing time	Young's modulus [MPa][a)]	Fracture stress [MPa]	Fracture strain [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]	Healing efficiency [%][c)]
P-PDBA 60%	Saturated sample[a)]	0.8 ± 0.1	2.1 ± 0.2	4.5 ± 0.3	6.0 ± 0.8	-
	1 d	0.9 ± 0.2	1.2 ± 0.1	1.4 + 0.2	1.2 ± 0.2	19.2 ± 3.3
	3 d	0.6 ± 0.1	1.7 ± 0.1	4.9 ± 0.3	5.7 ± 0.8	96.1 ± 14.3
	7 d	0.7 ± 0.2	1.8 ± 0.1	5.0 ± 0.3	5.9 ± 0.5	98.7 ± 8.3
P-PDBA 100%	Saturated sample[a)]	2.3 ± 0.2	3.4 ± 0.1	3.5 ± 0.1	7.7 ± 0.2	-
	1 d	2.6 ± 0.2	1.2 ± 0.2	0.6 ± 0.2	0.5 ± 0.2	6.3 ± 2.8
	3 d	2.2 ± 0.4	2.0 ± 0.1	2.0 ± 0.4	2.6 ± 0.5	34.2 ± 6.1
	7 d	2.1 ± 1.0	2.1 ± 0.3	2.0 ± 0.5	2.6 ± 0.3	31.1 ± 5.9

[a)] Calculated from stress at a small strain (< 10%).[b)] Integration of the area under the stress-strain curves. [c)] Quantified by percent recovery of toughness. [d)] Samples saturated under 75% of humidity were used for healing tests.

Table S6 Results of self-healing tests under 75% relative humidity at different waiting time

sample	Conditions	Young's modulus [MPa][a)]	Fracture stress [MPa]	Fracture strain [mm mm^{-1}]	Toughness [MJ m^{-3}] [b)]	Healing efficiency [%][c)]
	Saturated sample[d)]	0.8 ± 0.1	2.1 ± 0.2	4.5 ± 0.3	6.0 ± 0.8	-
P-PDBA 60%	no waiting	0.6 ± 0.1	1.7 ± 0.1	4.9 ± 0.3	5.7 ± 0.8	96.1 ± 14.3
	24 h waiting	0.5 ± 0.1	1.8 ± 0.2	5.0 ± 0.1	6.0 ± 0.6	100 ± 10.2

[a)] Calculated from stress at a small strain (< 10%).[b)] Integration of the area under the stress-strain curves. [c)] Quantified by percent recovery of toughness. [d)] Samples saturated under 75% humidity were used for healing tests.