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Electronic Supplementary Information

Solid-phase esterification between poly(vinyl alcohol) and malonic acid and its function in toughening hydrogels

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Supplementary Figures

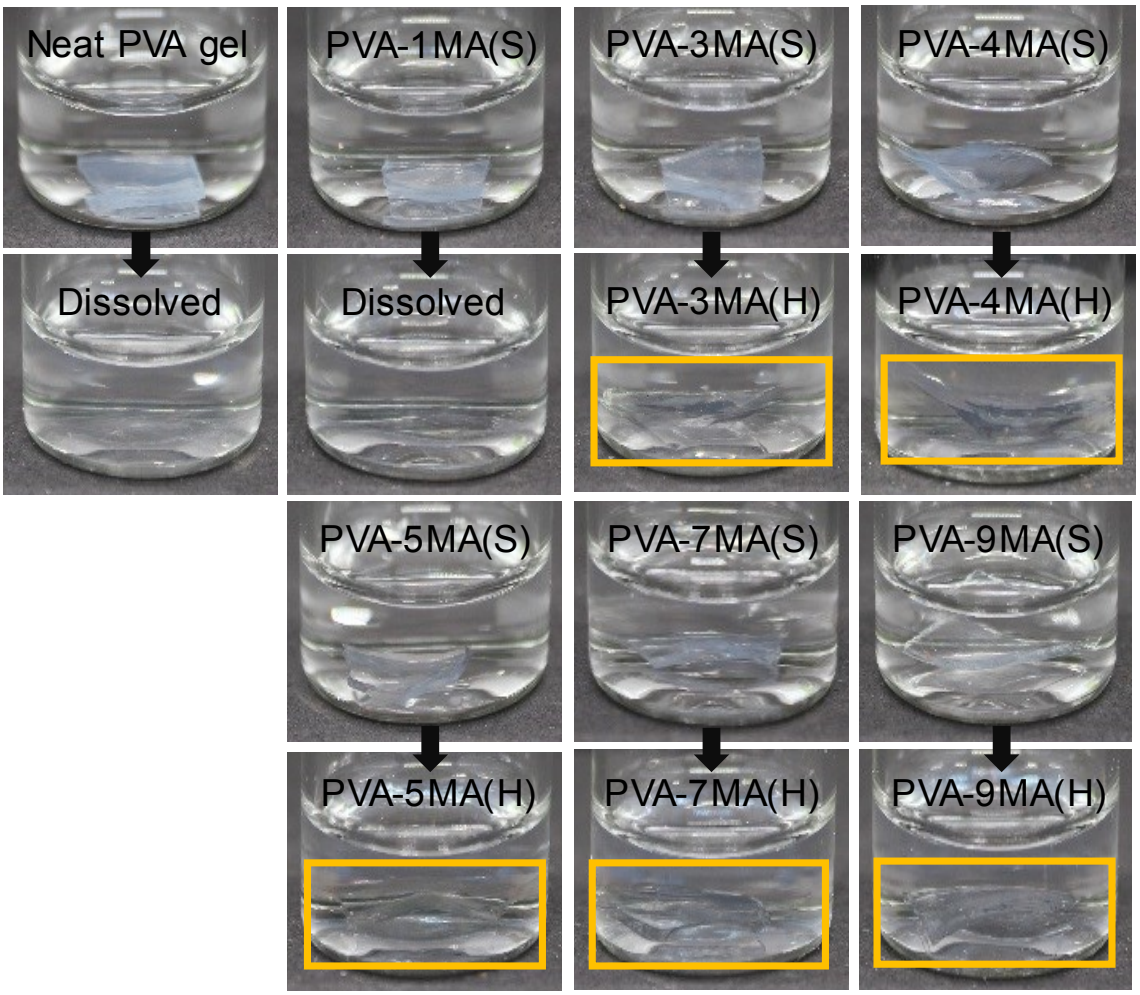

Fig. S1 Photographs showing the state of the PVA-*x*MA(S) hydrogels with varying MA content after being heated in deionized water at 95 °C for more than 20 h.

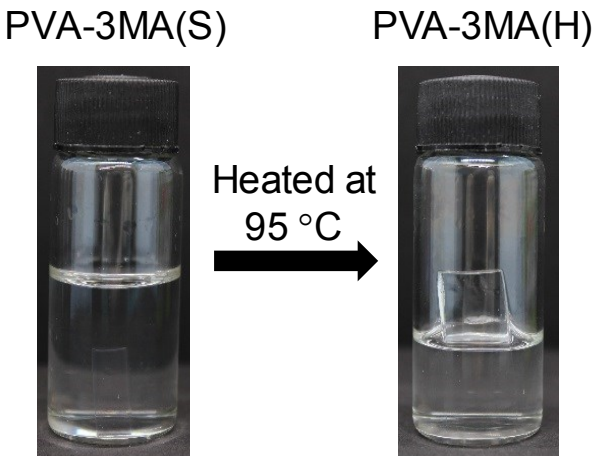

Fig. S2 Photographs showing the state of the PVA-3MA(S) hydrogel after being heated in a 5 mol L^{-1} NaSCN aqueous solution at 95 °C for more than 20 h.

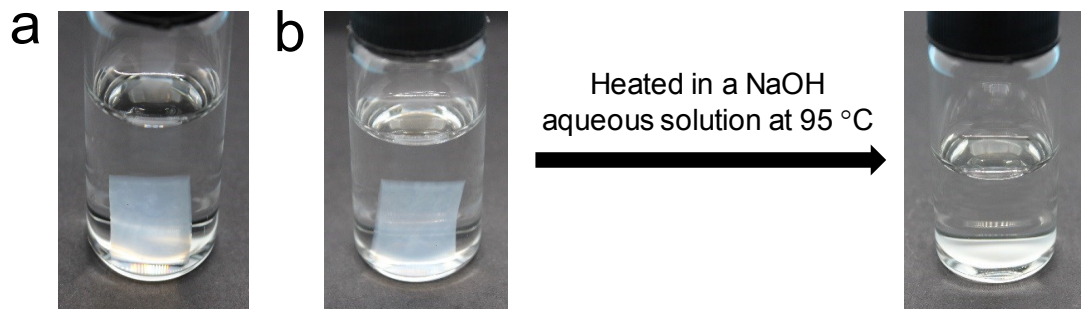

Fig. S3 (a) A photograph of the AP-PVA-7MA hydrogel in deionized water. (b) Photographs showing the state the PVA-7MA(S) hydrogel in deionized water and the PVA-7MA(S) hydrogel after being heated in a 0.2 mol L^{-1} NaOH aqueous solution at 95 °C.

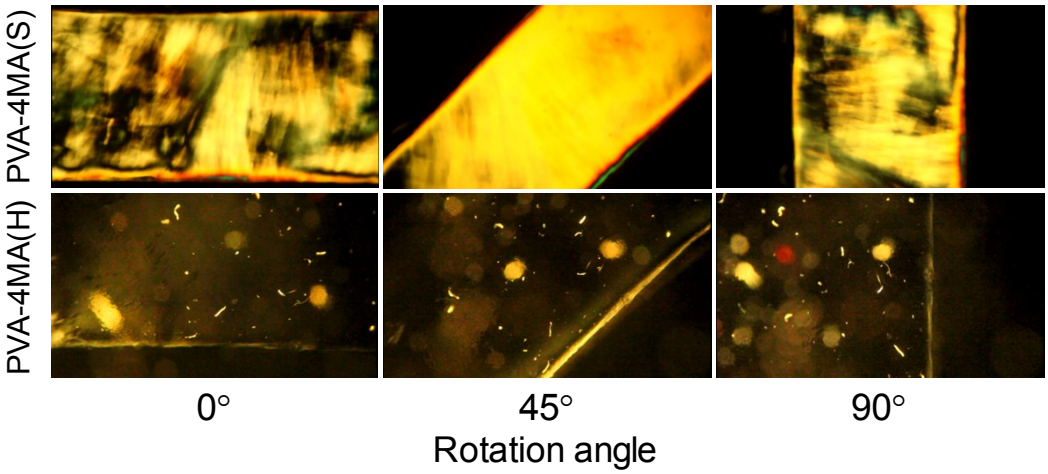

Fig. S4 Polarized optical microscopic (POM) images of the PVA-4MA(S) and PVA-4MA(H) hydrogels at the rotation angle of 0, 45, and 90°.

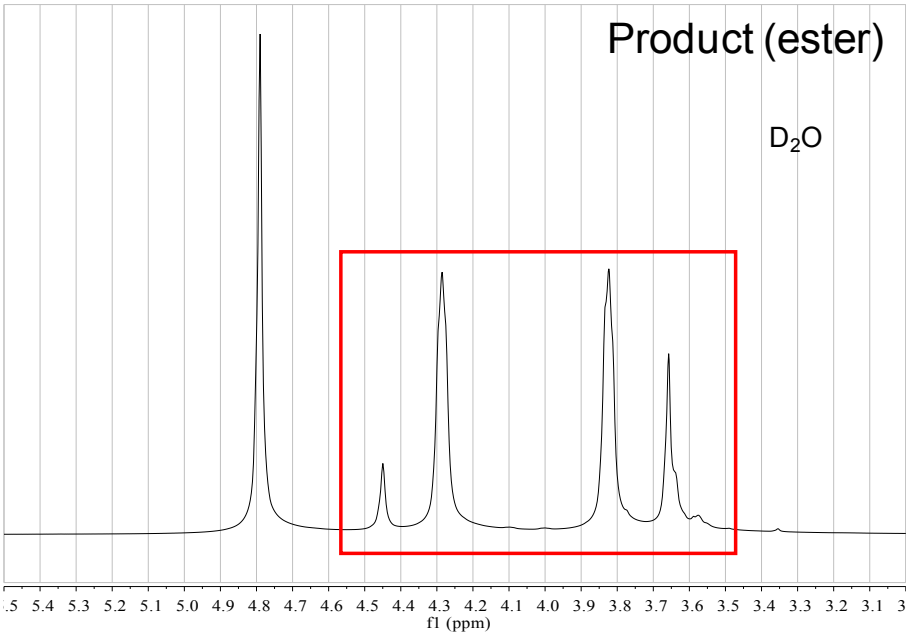

Fig. S5 ^{1}H-NMR spectrum of the separated esterification products between MA and ethylene glycol in D_2O at 298 K (400 MHz).

Supplementary Tables

Table S1 Water contents of the PVA-*x*MA(S) and PVA-*x*MA(H) hydrogels.

Hydrogel Code	H_2O (wt%)
PVA-0MA(S)	61.6 ± 0.2
PVA-1MA(S)	62.6 ± 0.4
PVA-3MA(S)	53.4 ± 0.7
PVA-4MA(S)	50.3 ± 0.3
PVA-5MA(S)	43.0 ± 0.6
PVA-7MA(S)	36.0 ± 0.7
PVA-9MA(S)	35.2 ± 0.4
PVA-3MA(H)	80.8 ± 0.3
PVA-4MA(H)	74.8 ± 1.1
PVA-5MA(H)	70.6 ± 0.5
PVA-7MA(H)	63.7 ± 0.4
PVA-9MA(H)	56.6 ± 1.2

Table S2 Values of the cross-linking density (ν_e) of the PVA-*x*MA(H) hydrogels at the temperature of 298 K.

Sample	ν_e (mol m^{-3})		
	0.01 rad s^{-1}	1 rad s^{-1}	100 rad s^{-1}
PVA-4MA(H)	172	183	190
PVA-5MA(H)	293	315	337
PVA-7MA(H)	338	359	416
PVA-9MA(H)	396	484	517

Supplementary Movies

Movie S1 A movie showing the PVA-4MA(S) hydrogel observed by POM at different rotation angles.

Movie S2 A movie showing the PVA-4MA(H) hydrogel observed by POM at different rotation angles.

Movie S3 A movie showing the load-bearing ability of the healed PVA-7MA(S) hydrogel.

Movie S4 A movie showing the tensile mechanical test of the healed PVA-7MA(S) hydrogel.