

SUPPORTING INFORMATION

for

Thermo- and Water-Induced Shape Memory Poly(vinyl alcohol) Supramolecular Network Crosslinked by Self-Complementary Quadruple Hydrogen Bonding

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The Verification of UPy Dimers. The UPy groups have the capacity for self-assembly by quadruple hydrogen bonding, which can be associated with a donor-donor-acceptor-acceptor (DDAA) array or a donor-acceptor-donor-acceptor (DADA) array.¹ The DDAA array is present as the keto tautomer of UPy dimers, whereas the DADA array is as the enol tautomer (**Figure 4Sa**).² To further prove the formation of UPy dimers in the PVA networks, ¹H NMR and FT-IR spectra were employed to identify the characteristic features of the tautomers. In the ¹H NMR spectrum of UPy-NCO in CDCl₃ (**Figure 4Sb**), the NH proton signals are found at 13.12, 11.88 and 10.20 ppm. These signals are indicative of extensive hydrogen bonding as the 4[1H]-pyrimidinone tautomer.³ The FT-IR spectrum of the keto form of the UPy dimers

shows a band at 1699 cm^{-1} that is characteristic of the carbonyl stretch of pyrimidine, which is absent in the enol tautomer.² Solid-state $^1\text{H-NMR}$ was performed on PVA-UPy-10% to determine the properties of the undissolved pure hydrogen-bonded polymer networks. In Figure 4Sc, proton resonances of NH overlap, and only two weak peaks are observed at 12.64 and 7.76 ppm. FT-IR spectroscopy is also sensitive at detecting changes in the hydrogen bonding of the UPy groups.² The ATR FT-IR spectra of PVA-UPy-10% is shown in Figure 4S c, and a band similar to the vibration of the UPy functional group can be observed in the keto form of UPy-NCO. For the pyrimidin-4-ol tautomer, there is a band at approximately 2500 cm^{-1} corresponding to the vibration of a hydrogen-bonded OH group.⁴ However, in Figure 2c there is an absence of this vibration, further indicating that the PVA-UPy-10% was present as the keto tautomer. Therefore, the UPy dimmers are formed in PVA-UPy-10% via quadruple hydrogen bonds in DDAA arrays, rather than DADA arrays, which is consistent with a prior report.⁵

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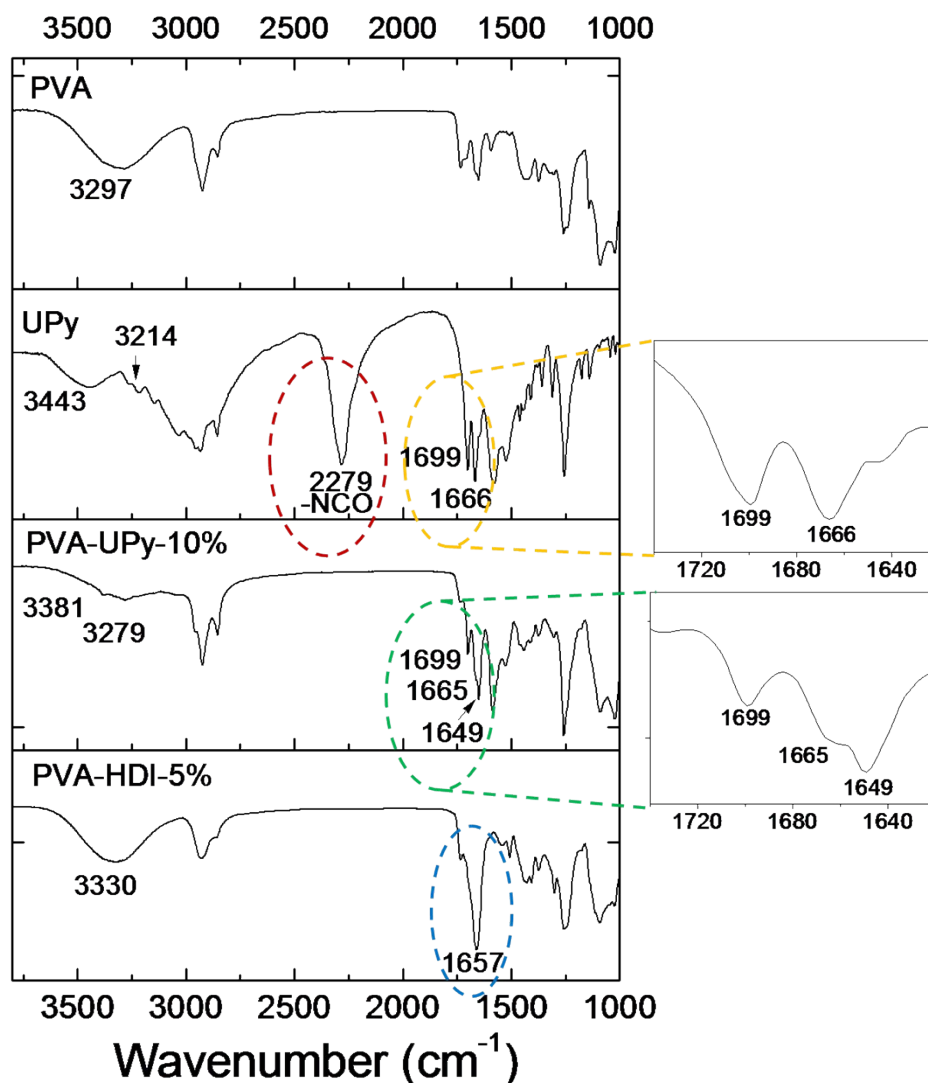


Figure S1 FT-IR spectra of polymer PVA-UPy- 10% and PVA-HDI-5%. For UPy, the peak at 2279 cm⁻¹ are corresponding to the isocyanate vibration (NCO), 1699 cm⁻¹ and 1666 cm⁻¹ corresponding to the carbonyl vibration (C=O) in pyrimidinone and urea respectively. In PVA-UPy- 10%, isocyanate vibration disappeared and a new peak at 1649 cm⁻¹ corresponding to the carbonyl vibration (C=O) in urethane appeared, which indicated the UPy successfully attached to PVA. In PVA-HDI-5%, the peak at 1657 cm⁻¹ corresponding to the carbonyl vibration (C=O) in urethane, also indicate the HDI successfully reacted with PVA.

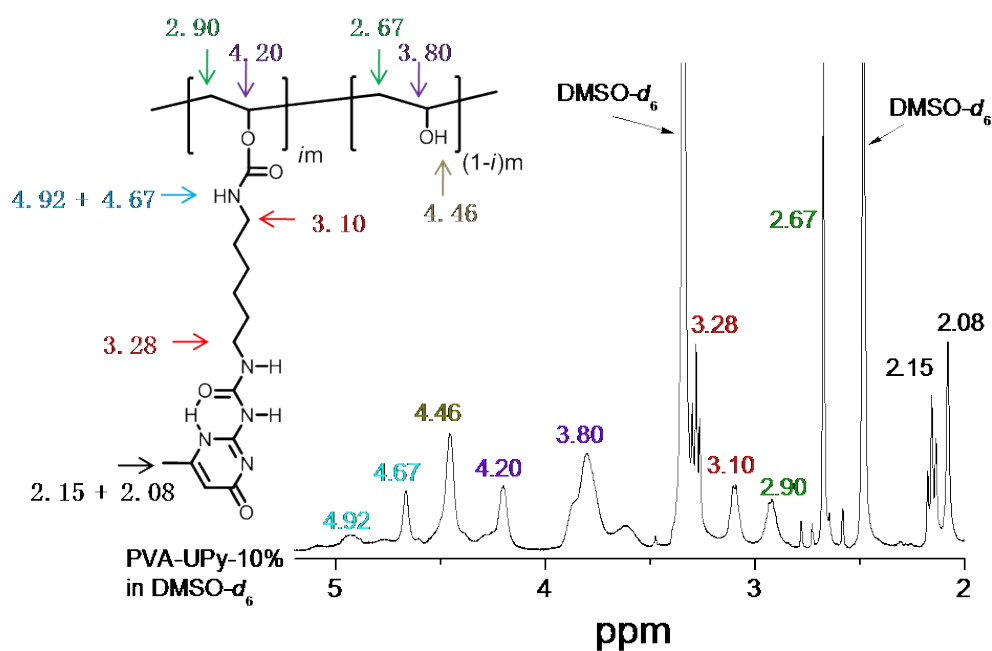
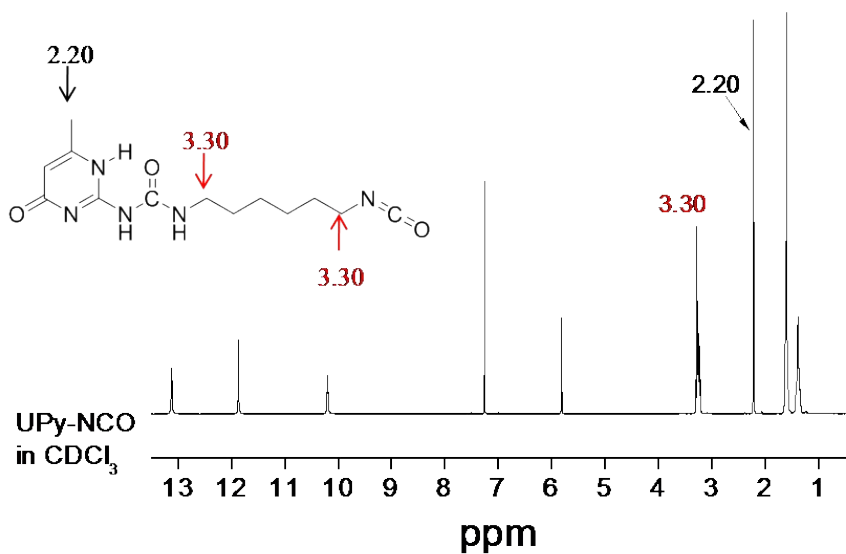


Figure S2 ^1H NMR spectra of UPy-NCO and PVA-UPy-10%. In UPy-NCO, the protons adjacent to the isocyanate (NCO) are at 3.30 ppm, while in PVA-UPy-10% that protons shift to 3.10 ppm indicating the formation of urethane. And two new peaks appeared at 4.92 and 4.67 ppm corresponding to the proton of urethane $[\text{NH}(\text{C}=\text{O})\text{O}]$. The formation of urethane proved UPy-NCO successfully reacted with the OH of PVA.

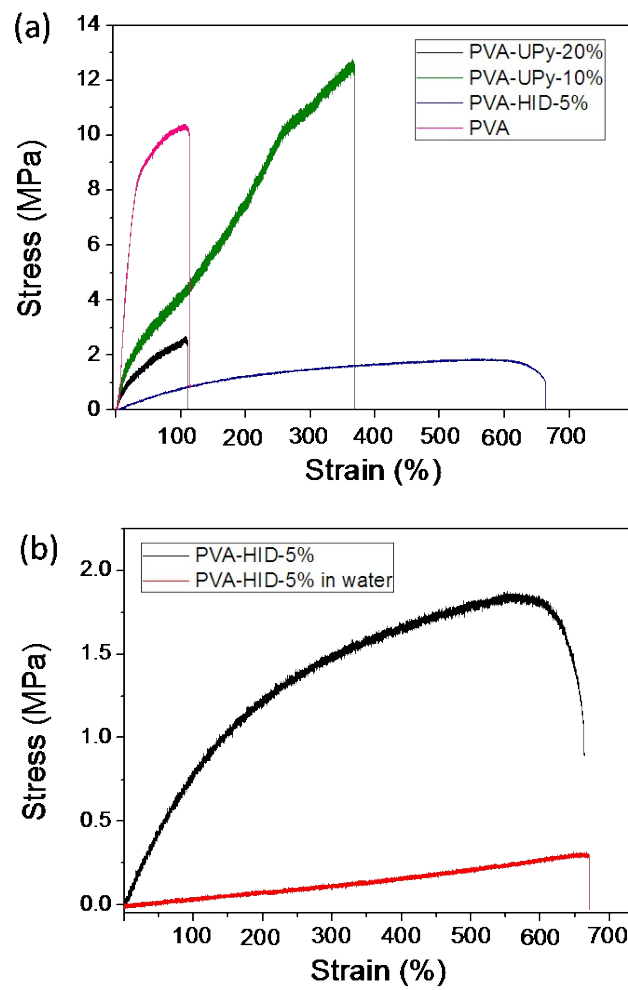


Figure S3 Tensile curves of (a) PVA crosslinked by HDI and UPy; (b) PVA-HDI-5% before and after absorbing water.

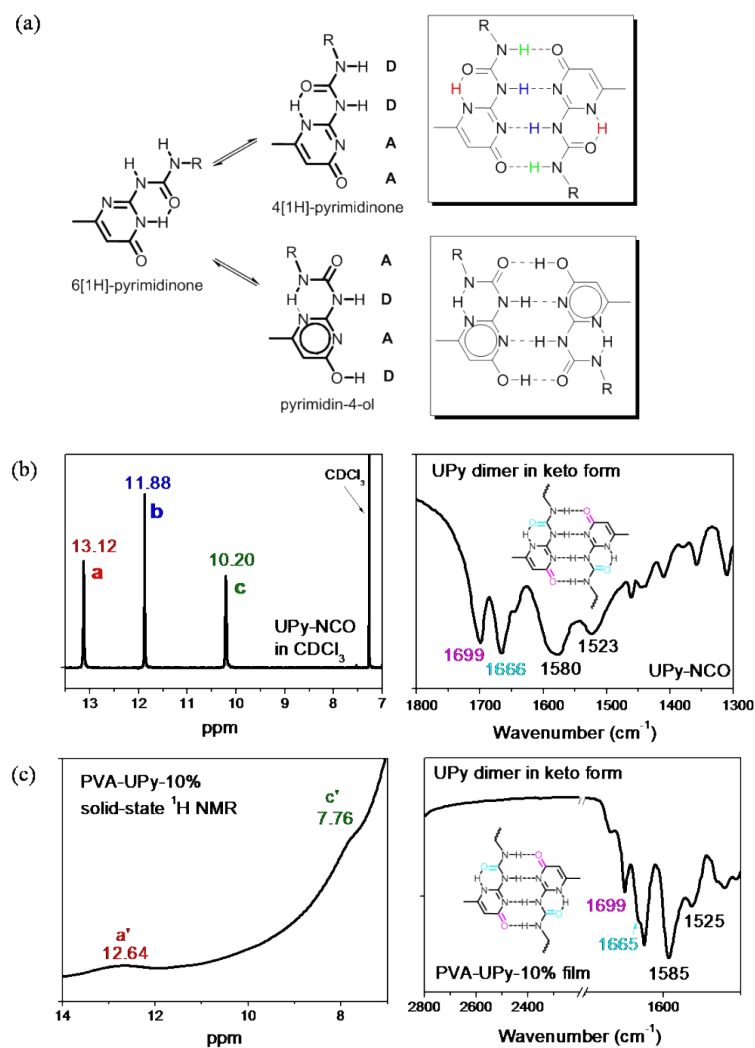


Figure S4. (a) Tautomeric forms of UPy groups, where 6[1H]-pyrimidinone can form a DDAA array as the 4[1H]-pyrimidinone tautomer, or it can assume the DADA configuration as the pyrimidin-4-ol tautomer.² (b) The ^1H NMR and FT-IR spectrum of UPy-NCO that indicates the UPy is dimerized as 4[1H]-pyrimidinone. (c) ^1H NMR of polymer PVA-UPy-10% in solid state and the FT-IR spectra of a PVA-UPy-10% film in dry state (the same as UPy-NCO), indicating that the UPy is also dimerized as 4[1H]-pyrimidinone.

Table S1 Swelling ratio and gel contents of polymer PVA-HDI-*i* and PVA-UPy-*i* in

NMP

Sample	Swelling Ratio (S_r , %)	Gel Contents (G_r , %)
PVA-HDI-5%	1376±45	95.2±1.3
PVA-HDI-10%	950±31	97.6±2.2
PVA-HDI-20%	475 ± 17	97.7 ± 3.7
PVA-UPy-5%	dissolved	dissolved
PVA-UPy-10%	dissolved	dissolved
PVA-UPy-20%	dissolved	dissolved

Table S2 Transition temperature of polymer PVA-HDI-*i* and PVA-UPy-*i* testing by DSC

Sample	The second heating	The second cooling
	T_g (°C)	T_g (°C)
PVA	47.1	46.5
PVA-HDI-5%	29.4	18.8
PVA-HDI-10%	23.5	11.8
PVA-HDI-20%	-0.5	-10.4
PVA-UPy-5%	39.2	38.6
PVA-UPy-10%	48.7	48.6
PVA-UPy-20%	69.3	60.5

Table S3 Shape fixing and recovery ratio of polymer PVA-HDI-*i* and PVA-UPy-*i* in hot air.

Sample	Shape Fixing Ratio (R_f , %)	Shape Recovery Ratio (R_r , %)
PVA	95	92
PVA-HDI-5%	98	98
PVA-HDI-10%	98	97.
PVA-HDI-20%	no	no
PVA-UPy-5%	no	no
PVA-UPy-10%	99	87
PVA-UPy-20%	98	89

Table S4 Shape recovery ratio of polymer PVA-HDI-*i* and PVA-UPy-*i* in water

Sample	Shape Recovery Ratio (R_r , %)
PVA-HDI-5%	96
PVA-HDI-10%	97
PVA-UPy-10%	98
PVA-UPy-20%	98