Facile Catalyst-free Synthesis, Exchanging, Hydrolysis of Acetal Motif for Dynamic Covalent Networks

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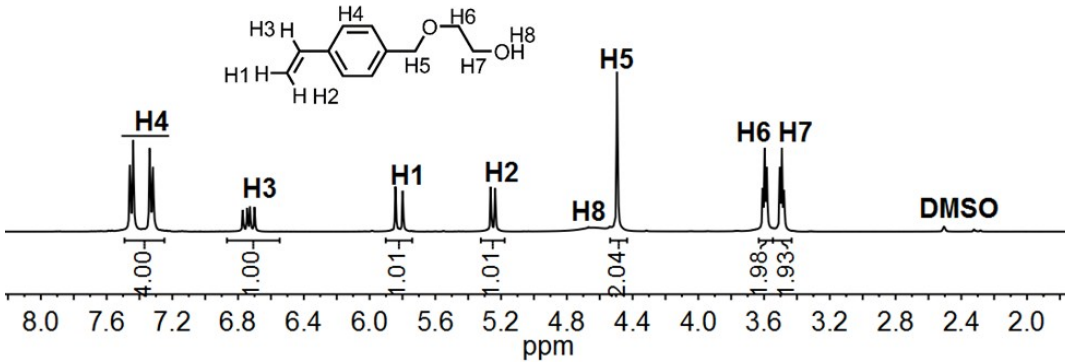

Fig. S1 [1]H NMR spectrum of 2-(4-vinyl-benzyloxy)-ethanol (**1**).

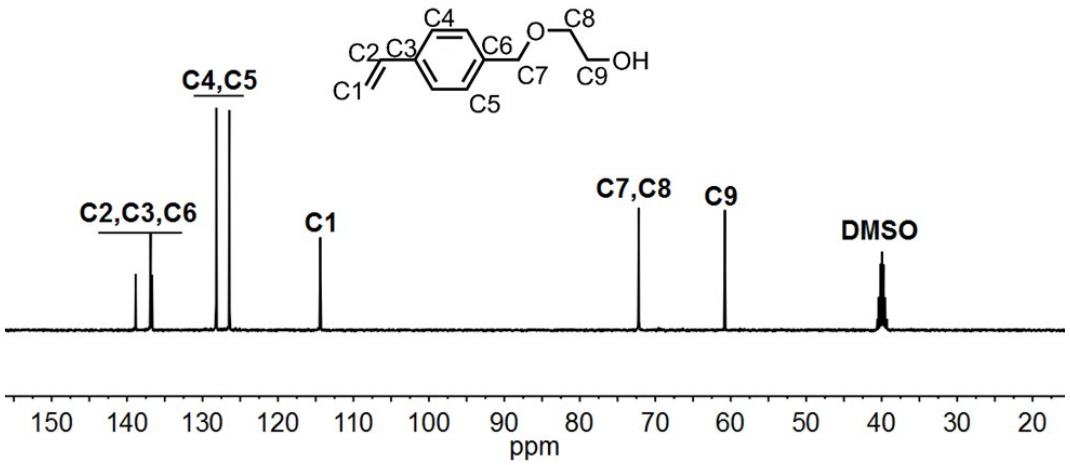

Fig. S2 [13]C NMR spectrum of 2-(4-vinyl-benzyloxy)-ethanol (**1**).

Calculated theoretical element contents for $C_{10}H_{14}O_2$ (%): C, 74.16; H, 7.86; O: 17.98.

Measured element contents for $C_{10}H_{14}O_2$ (%): C, 74.85, 74.76; H, 7.48, 8.16; O: 17.64, 18.09.

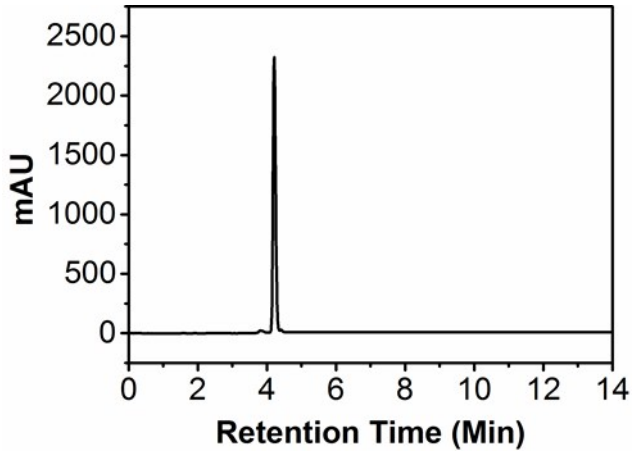

Fig. S3 HPLC spectrum of compound 1. Purity is 97.2%.

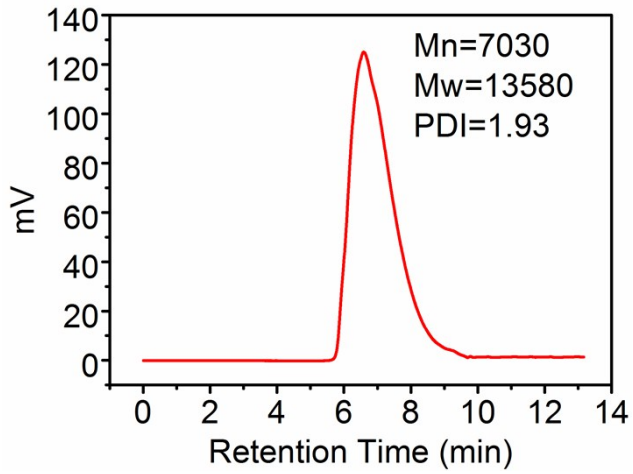

Fig. S4 GPC curves of PSS-OH in THF.

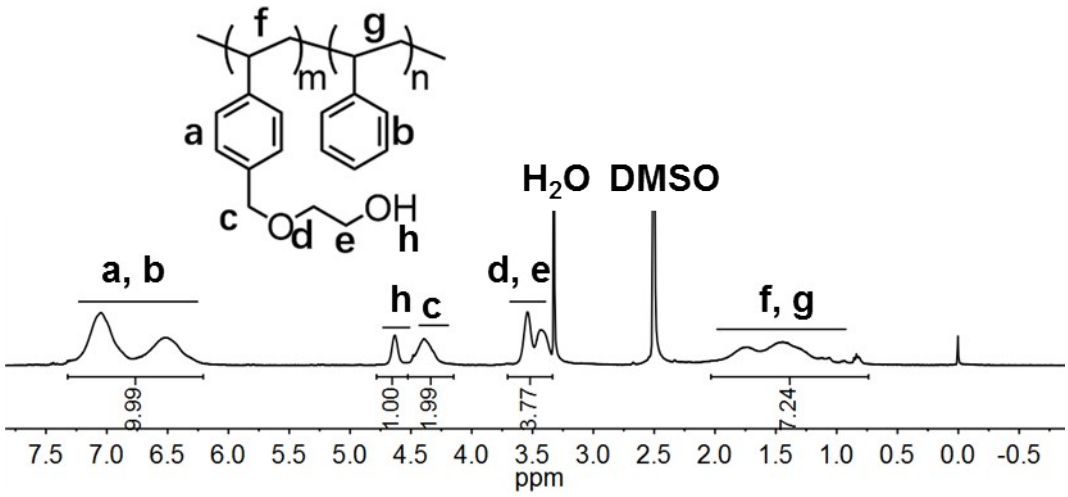

Fig. S5 ^{1}H NMR spectrum of poly (styrene-co-styrene-OH) (PSS-OH).

The molar proportion of **1** in PSS-OH was calculated from the integral area of protons c (1.99)

and protons a and b (9.99) in the ^{1}H NMR spectrum of PSS-OH (Fig. S5).

$$The\ molar\ proportion\ of\ 1 = \frac{1.99/2}{\frac{1.99}{2} + \frac{9.99 - 1.99 \times 2}{5}} \times 100\% = 45\%$$

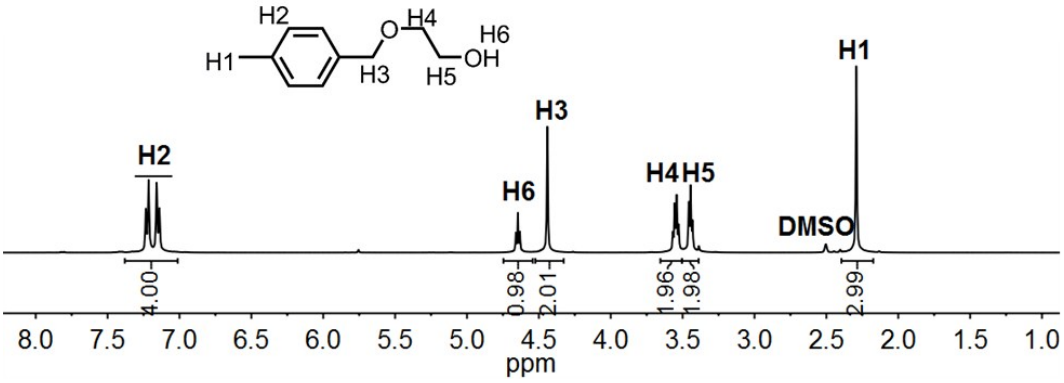

Fig. S6 ^{1}H NMR spectrum of 2-(4-methylbenzyloxy) ethanol (**2**).

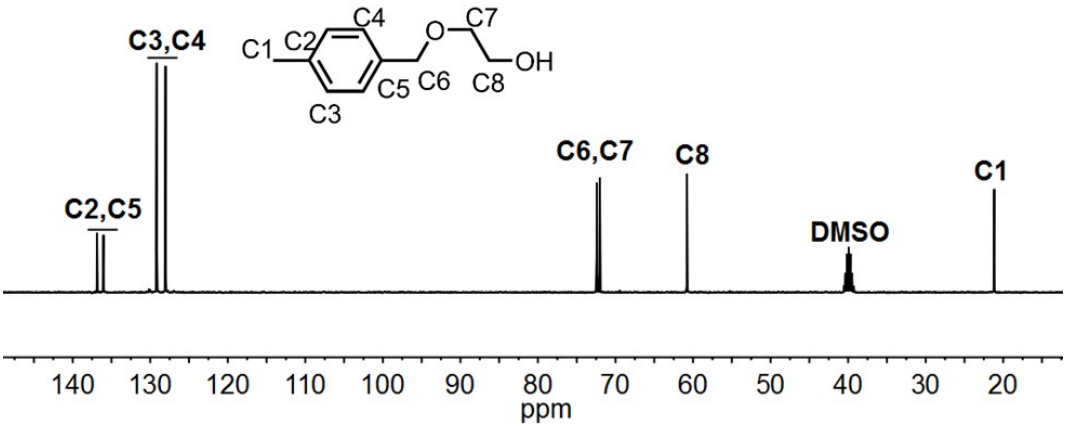

Fig. S7 ^{13}C NMR spectrum of 2-(4-methylbenzyloxy) ethanol (**2**).

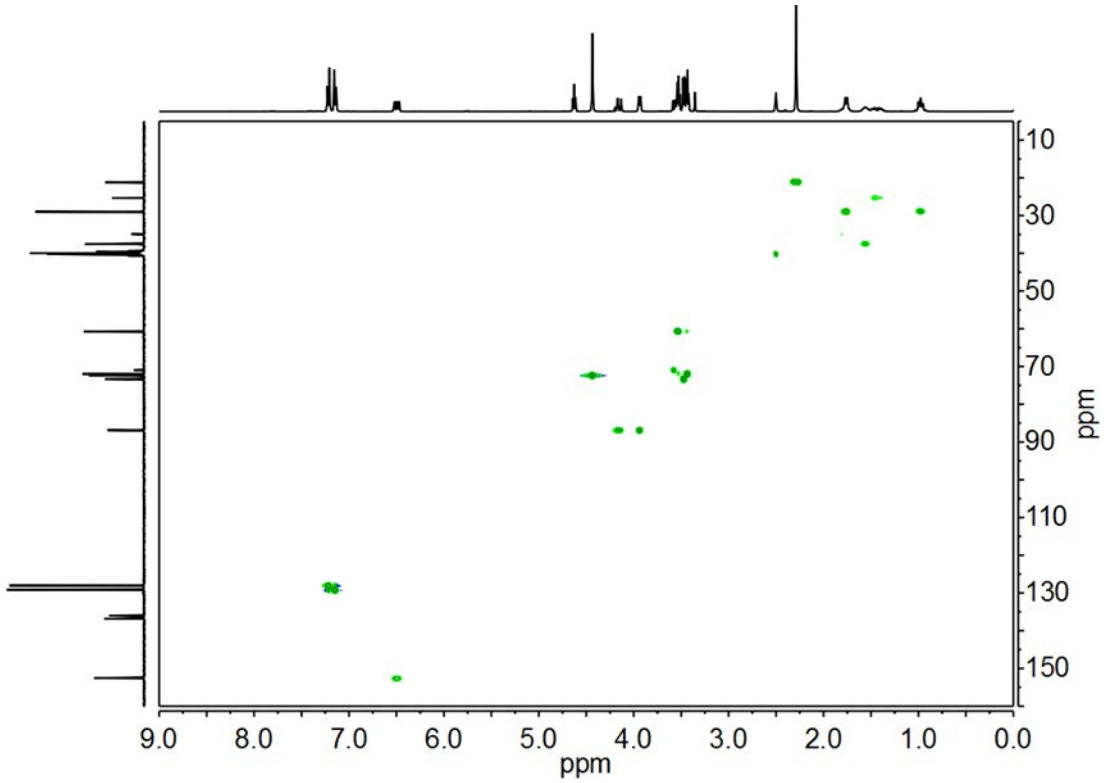

Fig. S8 ^{13}C-^{1}H-COSY HMQC of ac alcohol **2** and CVDE at 25 ºC.

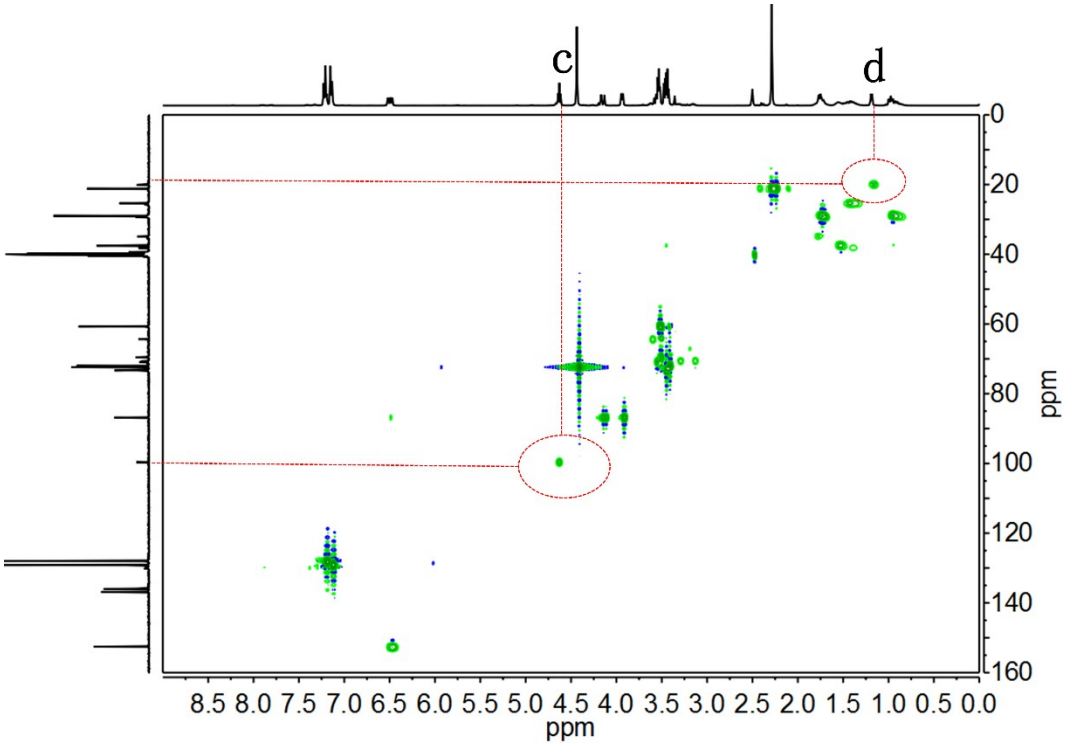

Fig. S9 ^{13}C-^{1}H-COSY HMQC of ac alcohol **2** and CVDE at 80 ºC.

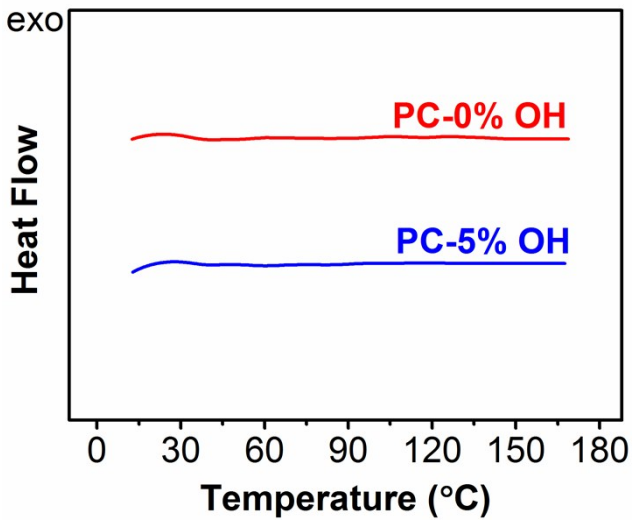

Fig. S10 Non-isothermal DSC curves of the acetal dynamic networks.

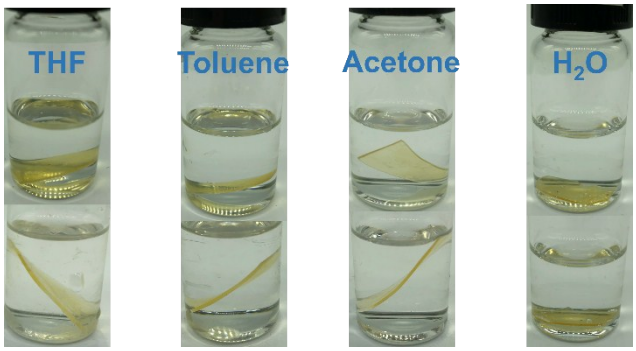

Fig. S11 The images of PC-5% OH before and after immersing in 40 °C THF, acetone, toluene for 12 h and H_2O for 2h.

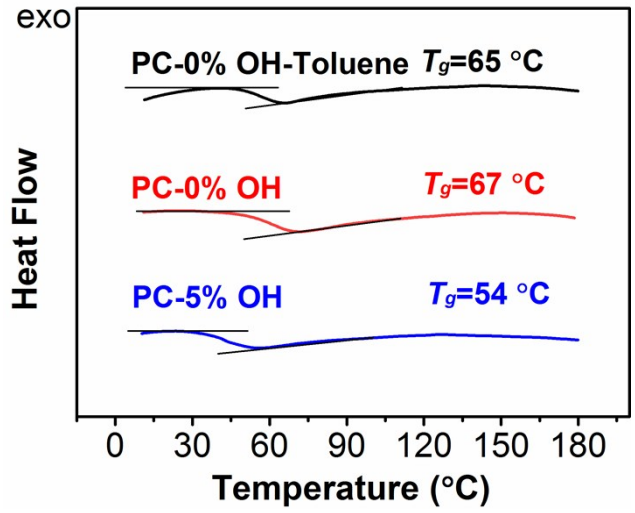

Fig. S12 DSC curves of the acetal dynamic networks PC-0% OH, PC-5% OH and PC-0% OH-Toluene (prepared with the help of toluene).

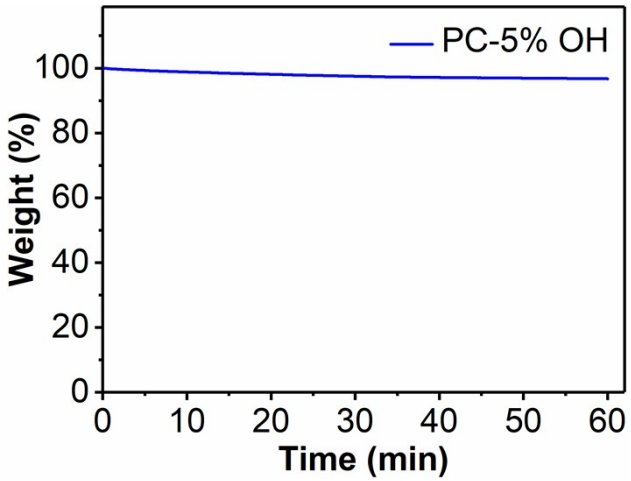

Fig. S13 Isothermal TGA curves of PC-5% OH at 180 °C under nitrogen.

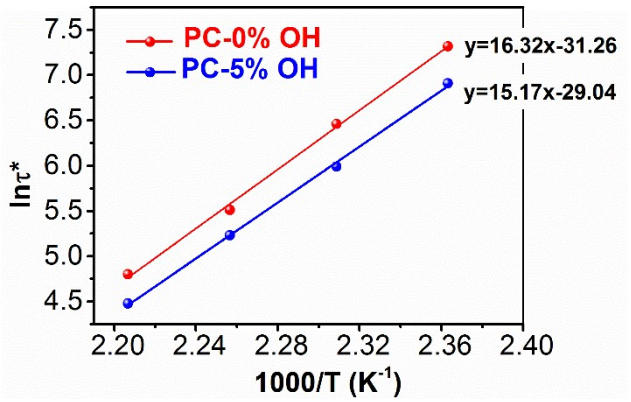

Fig. S14 Arrhenius plots of the measured relaxation times.

Calculation of topology-freezing temperatures (T_v) and activation energies (E_a) [1]

Topology-freezing temperatures (T_v) and activation energies (E_a) were determined using the methodology reported in literature[2]. The measured values of characteristic relaxation times (τ*s) were plotted versus 1000/T. The plots were fit to the Arrhenius law in equation (1)

$$\tau^*(T) = \tau_0^* e^{E_a/RT} \quad (1)$$

(R : universal gas constant; 8.314 J K^{-1} mol^{-1})

Equation (2) can be transformed to equation (2) (Fig. S9):

$$\ln \tau^*(T) = \ln \tau_0^* + {Ea}/{RT} \quad (2)$$

$$ln\tau^*(T) = 16.32 \times \frac{1000}{T} - 31.26 \quad (3)$$

PC-0% OH: E_a/R=16.32 E_a=136 kJ mol^{-1}

PC-5% OH: $ln\tau^*(T) = 15.17 \times \frac{1000}{T} - 29.04$ (4) $E_a/R=15.17$ $E_a=126$ kJ mol^{-1}

T_v is defined to be the temperature at which the material reaches a viscosity of 10^{12} Pa. The relation of the viscosity η and the τ^* is known as the Maxwell relation (equation (5)

$$\eta = G \times \tau^* = (E'/2(1+v)) \times \tau^* \quad (5)$$

(G : shear modulus, E' : storage modulus, v : Poisson's ratio)

Using the Poisson's ratio (v) of polystyrene (0.336),

$$\eta = 0.374 \times E' \times \tau^* \quad (6)$$

The storage modulus of PC-0% OH from 150 °C to 180 °C is 8.5 MPa, and that of PC-5% OH in the same temperature range is 7.1 MPa (Fig. 5). Because η is 10^{12} Pa at T_v, τ^*s at T_v of PC-0% OH and PC-5% OH are calculated to be 3.1×10^5 s and 3.8×10^5 s, respectively. Using these values and equation (3) and (4), T_v was computed to be 99 °C for PC-0% OH and 89 °C for PC-5% OH.

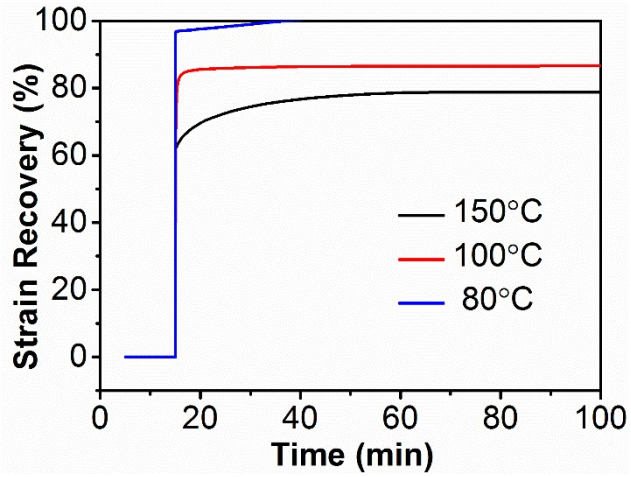

Fig. S15 Stain recovery as a function of time from creep tests for PC-5% OH under 0.2 MPa stress at different temperatures.

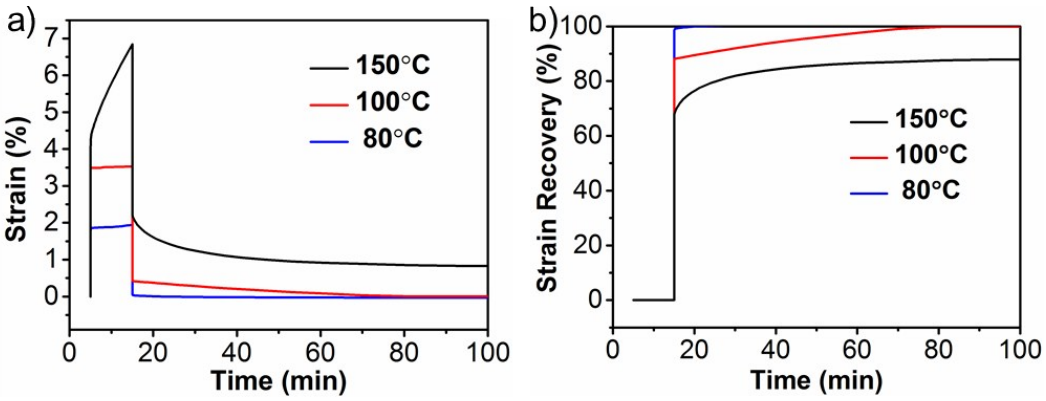

Fig. S16 a) Creep curves of PC-0% OH. b) Stain recovery as a function of time from creep tests for PC-0% OH under 0.2 MPa stress at different temperatures.

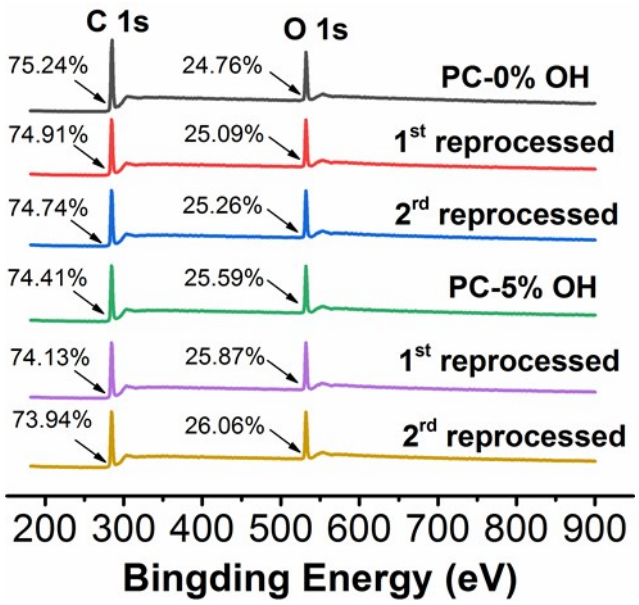

Fig. S17 XPS spectra of original and reprocessed samples.

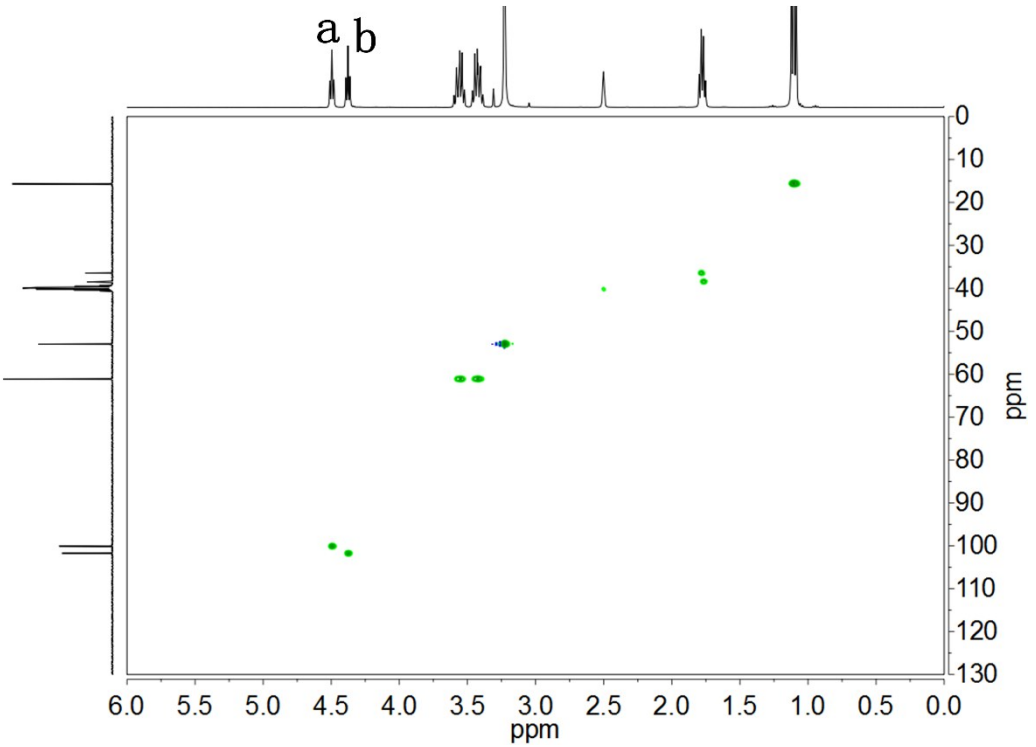

Fig. S18 ^{13}C-^{1}H-COSY HMQC of acetal **3** and **4** at 150 ºC for 0 min.

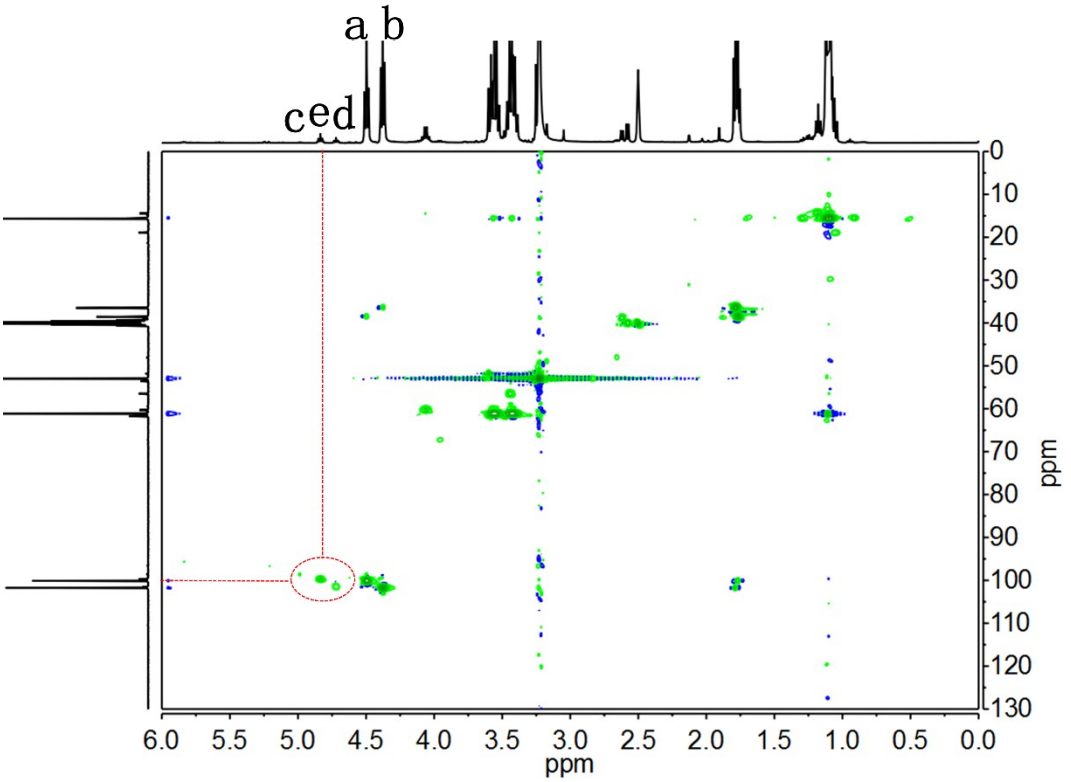

Fig. S19 ^{13}C-^{1}H-COSY HMQC of acetal **3** and **4** at 150 ºC for 8 h.

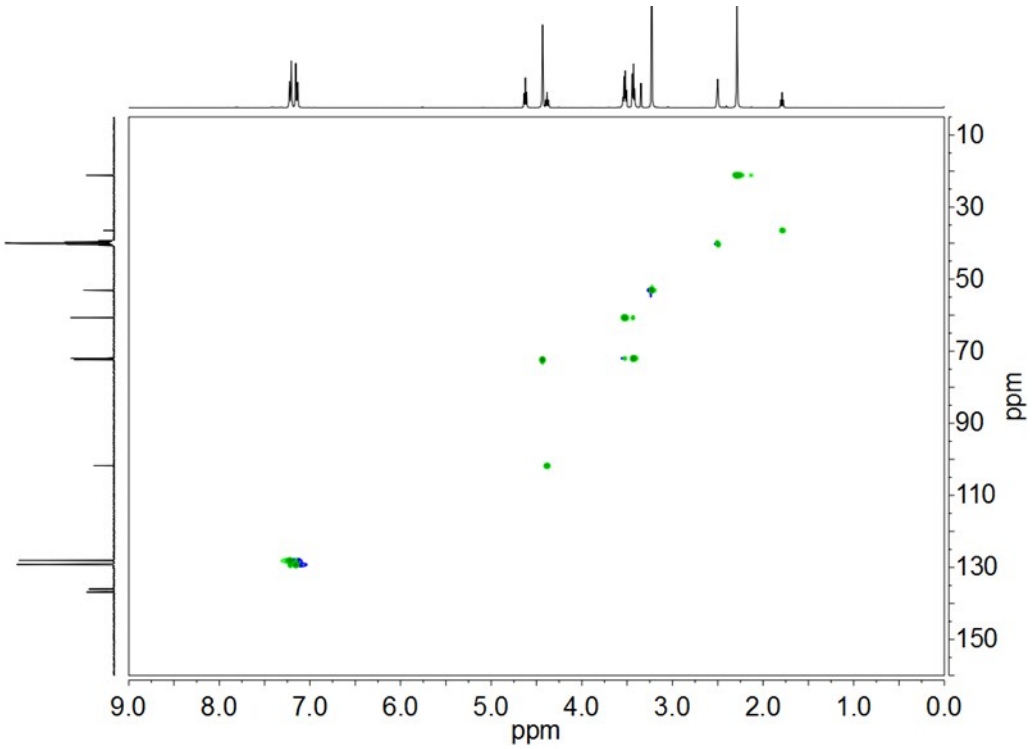

Fig. S20 ^{13}C-^{1}H-COSY HMQC of alcohol **2** and acetal **4** at 150 ºC for 0 min.

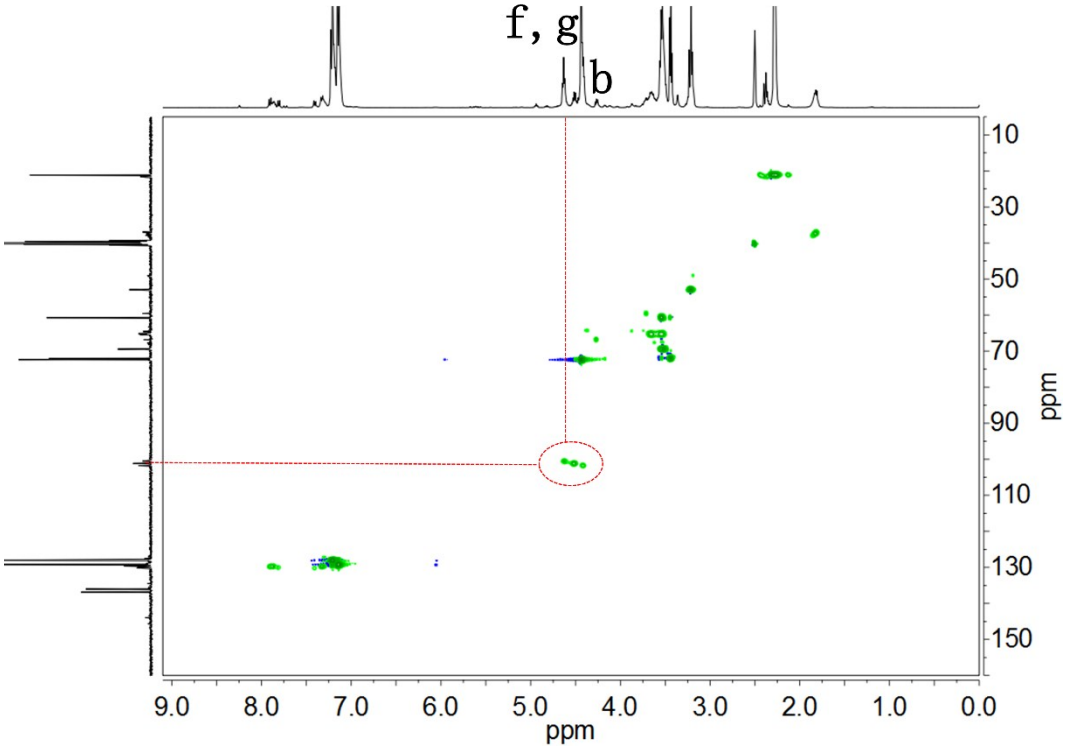

Fig. S21 ^{13}C-^{1}H-COSY HMQC of alcohol **2** and acetal **4** at 150 ºC for 8 h.

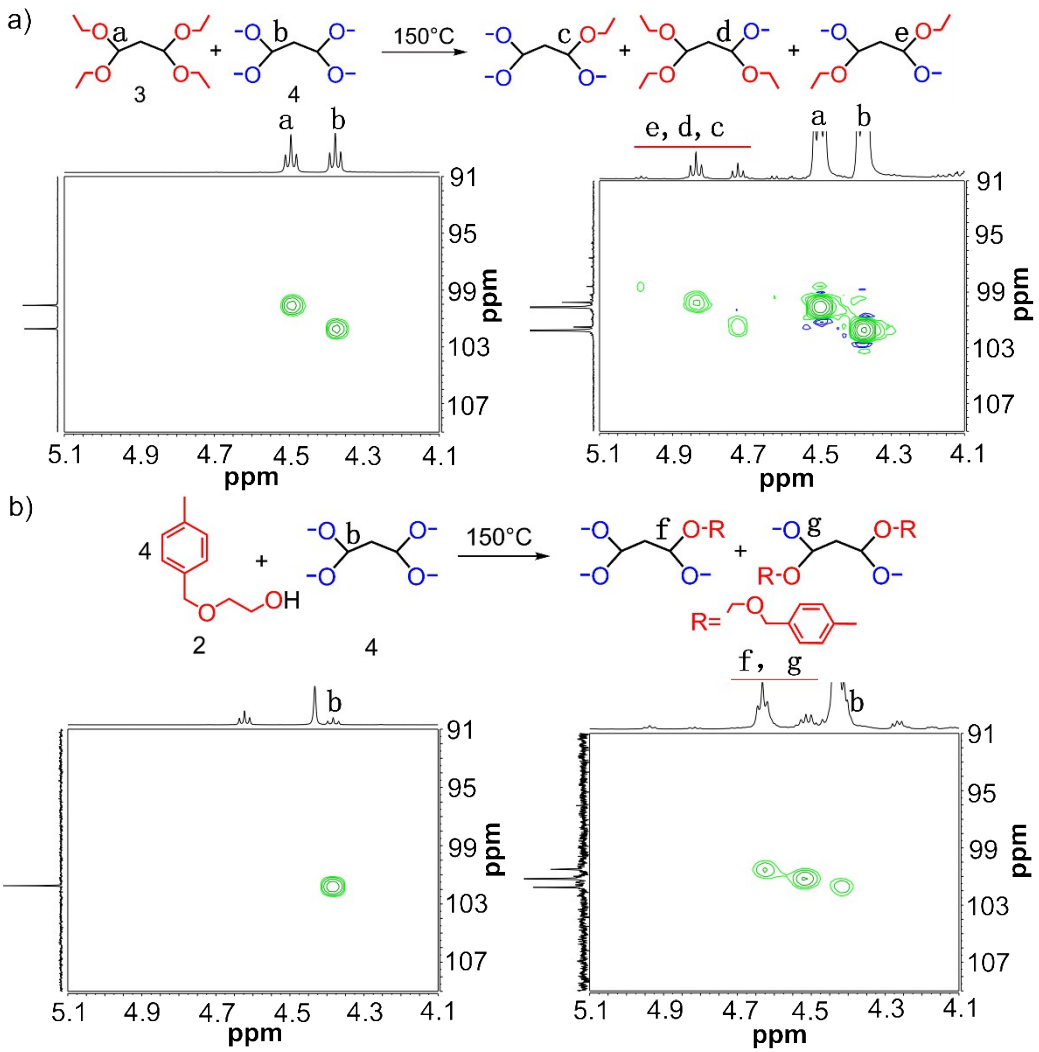

Fig. S22 Catalyst-free acetal exchange mechanism: a) metathesis of acetal and the ^{1}H NMR spectra of the reaction system at 150 ºC for different times; b) transacetalation and the ^{1}H NMR spectra of the reaction system at 150 ºC for different times.

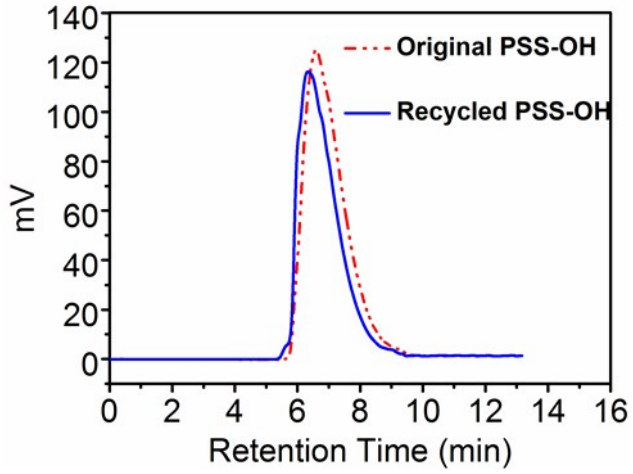

Fig. S23 GPC curves of recycled and original PSS-OH in THF.

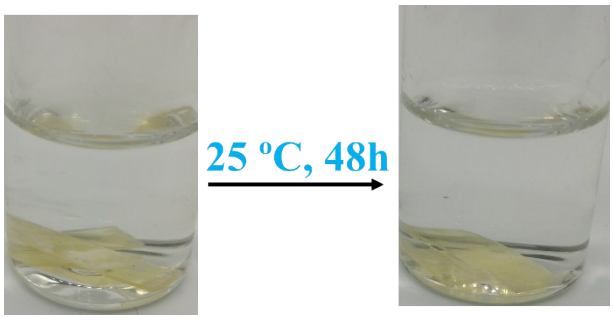

Fig. S24 The images of PC-0% OH before and after immersing in 25 °C water for 48 h.

Table S1. Swelling degree of PC-5% OH at 40 °C in THF, acetone, toluene for 12 h and H_2O for 2 h.

	m_0 (mg)	m_1 (mg)	Swelling degree (%)
THF	123.2	216.8	176
Toluene	83.6	133.7	160
Acetone	71.9	105.6	147
H_2O	83.7	90.4	108

Table S2. Gel content of the acetal networks.

	m_0 (mg)	m_1 (mg)	Gel content (%)
PC-0% OH	212.5	206.2	97
PC-5% OH	207.3	199.2	96

Table S3. Mechanical properties of the original and reprocessed acetal networks.

Sample		Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break(%)
PC-0% OH	original	33.3±2.1	1109±113	5.3±0.9
	1st reprocessed	32.0±1.2	1009±76	4.4±1.1
	2rd reprocessed	29.7±1.9	968±89	4.5±0.3
PC-5% OH	original	28.8±1.9	1046±54	4.4±0.7
	1st reprocessed	29.2±2.7	871±67	5.0±0.9
	2rd reprocessed	27.2±1.6	879±71	3.4±0.3

REFERENCES

1 Y. Nishimura, J. Chung, H. Muradyan and Z. Guan, *J. Am. Chem. Soc.*, 2017, **139**, 14881-14884.

2 M. Capelot, M. M. Unterlass, F. Tournilhac and L. Leibler, *ACS Macro Lett.*, 2012, **1**, 789-792.