

Supporting Information.

Methods. The degradation ratio of MFRs was calculated as following:

$$\text{Degradation ratio of MFRs} = 100 \times (W_1 - W_2)/W_1$$

Where W_1 and W_2 represented the mass of MFRs before and after the decomposition, respectively.

The concentration of degradation products in DMSO were quantified by NMR analysis using the internal standard (0.1g/mol fumaric acid). The degradation product (0.02g) was dissolved in 400 μL deuterium DMSO and 200 μL of internal standard was added before the NMR analysis. Specifically, by comparing their peak integrals to that of internal standard in the spectra, the masses of degradation products were calculated based on the equation 1:

$$w_{(x)} = P_{(std)} \times \frac{MW_{(x)}}{MW_{(std)}} \times \frac{nH_{(std)}}{nH_{(x)}} \times \frac{w_{(std)}}{P_{(x)}} \times \frac{I_{(x)}}{I_{(std)}} \quad (1)$$

where $w(x)$ and $w(std)$ were the weights of products and internal standard (g), respectively; $M_w(x)$ and $M_w(std)$ were the molecular weights of products and internal standard (g/mol), respectively; $P(x)$ and $P(std)$ were the purities of products and internal standard, respectively; $nH(x)$ and $nH(std)$ were the number of protons generating the selected signals for integration for products and internal standard, respectively; $I(x)$ and $I(std)$ were the integrals for the selected peaks of products and the internal standard.

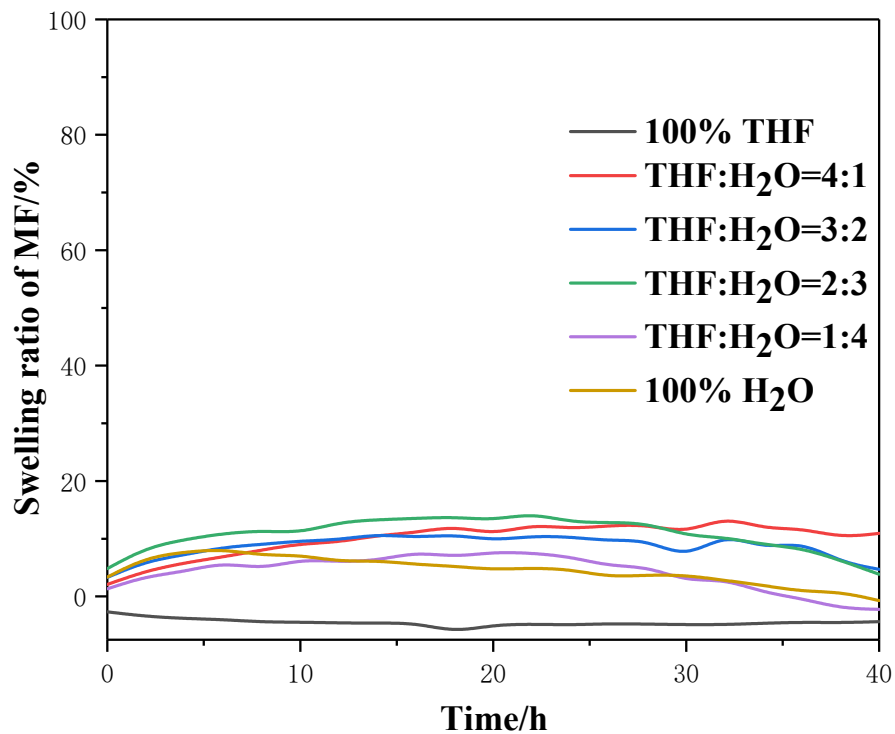


Figure S1. The swelling ratio of MFRs as a function of time in various THF-H₂O systems. (Swelling conditions: the Teflon-lined reactor, 100°C, MFRs: 10×10×3 mm³, 5g of THF-H₂O solvent, where 4:1, 3:2, 2:3 and 1:4 were the mass ratios of THF to H₂O, respectively)

The swelling ratio of MFRs was calculated as following:

$$\text{The swelling ratio} = 100 \times (G_2 - G_1) / G_1;$$

Where G_1 and G_2 represented the masses before and after the swelling.

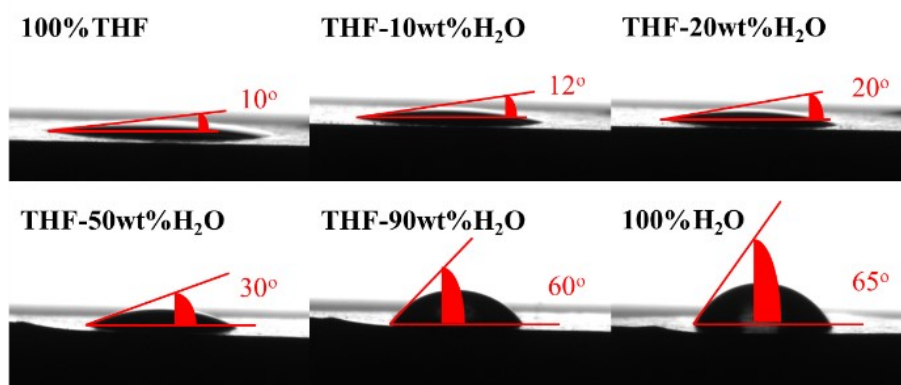


Figure S2. Contact angles of different solvent systems on the surface of MFRs.

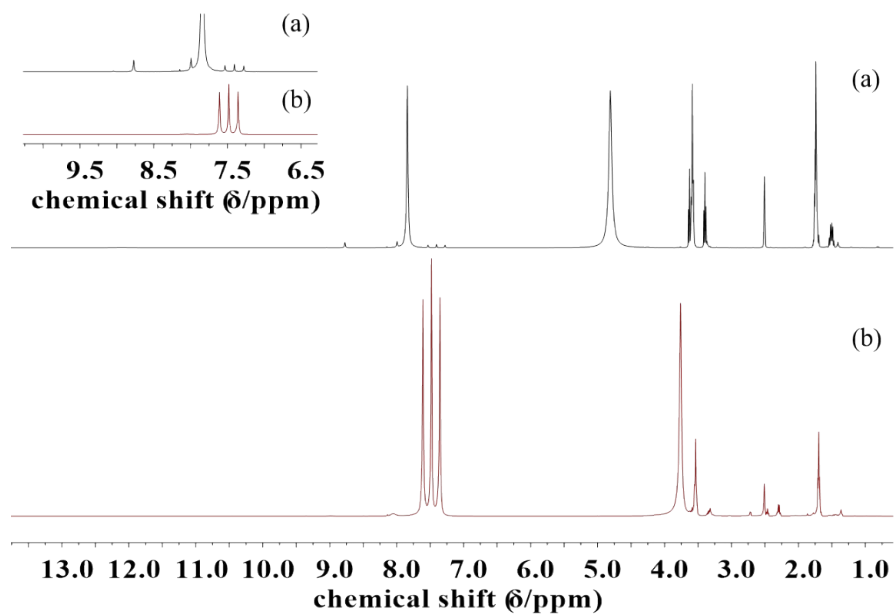


Figure S3. ¹H -NMR spectra of the decomposed products of MFRs before (a) and after (b) adding NH₄Cl solvent (The upper left corner is a partial enlargement of the figure) (Reaction conditions: the Teflon-lined reactor, 180 °C, 12 h, HCl-THF- 10wt.%H₂O system). The samples were prepared in DMSO-d₆.

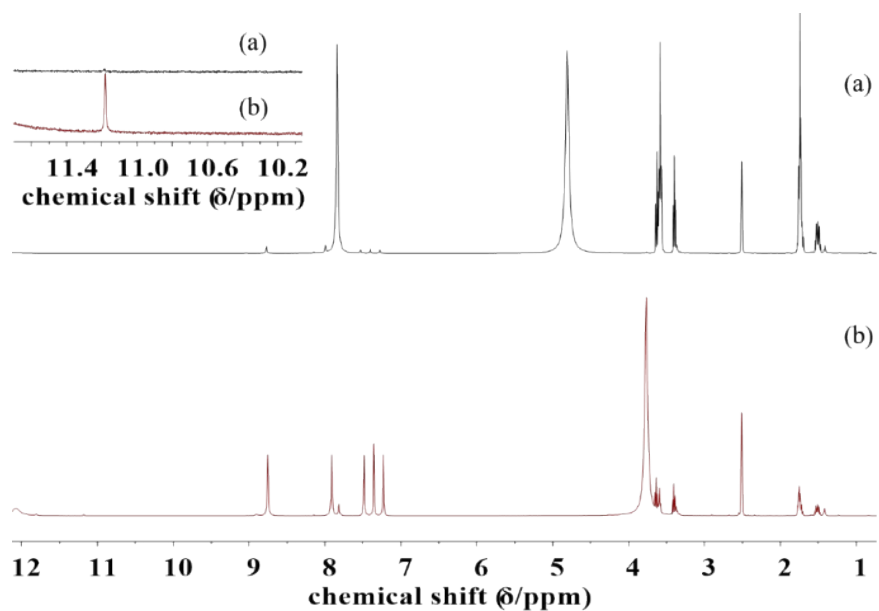


Figure S4. ¹H -NMR spectra of the decomposed products of melamine after degradation for 2h (a) and 6 h (b). (The upper left corner is a partial enlargement of the figure) (Reaction conditions: the Teflon-lined reactor, 180 °C, 0.3 g of melamine, HCl-THF-10wt.%H₂O system). The samples were prepared in DMSO- d₆ before NMR analysis.

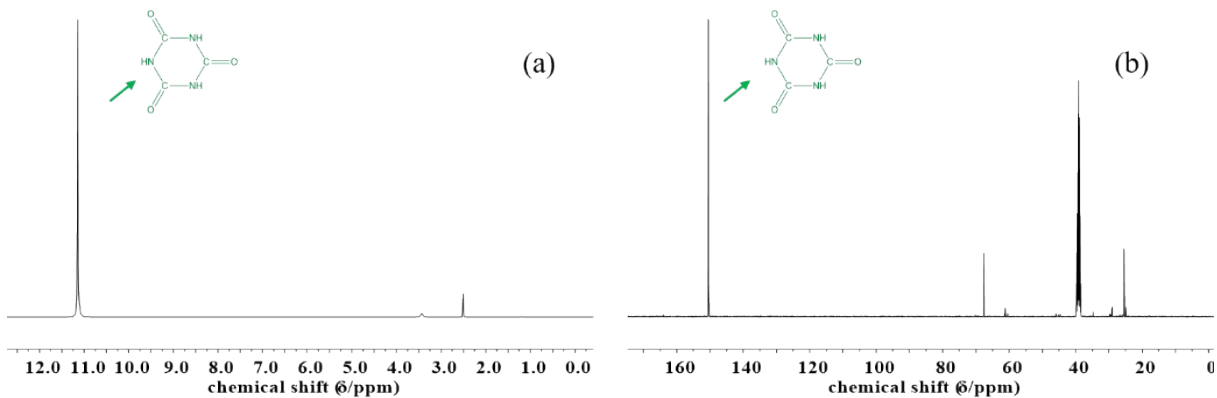


Figure S5. ^1H -NMR (a) and ^{13}C -NMR (b) spectra of cyanuric acid. (Reaction conditions: the Teflon-lined reactor, 200 °C, 12h, 0.3g of cyanuric acid, the MSA-THF-10wt% H_2O system).

The samples were prepared in DMSO-d_6 before NMR analysis. Cyanuric acid was unstable in the degradation system at 200°C.

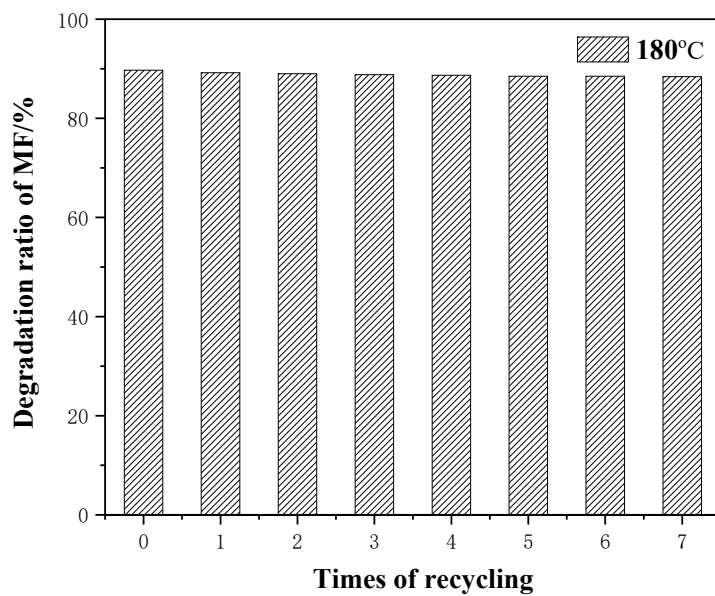


Figure S6. Reusability of the THF-H₂O system for the degradation of MFRs (Reaction conditions: the Teflon-lined reactor, 100 °C, 12 h, MFRs: 10×10×3 mm³, the THF- 10 wt% H₂O system).

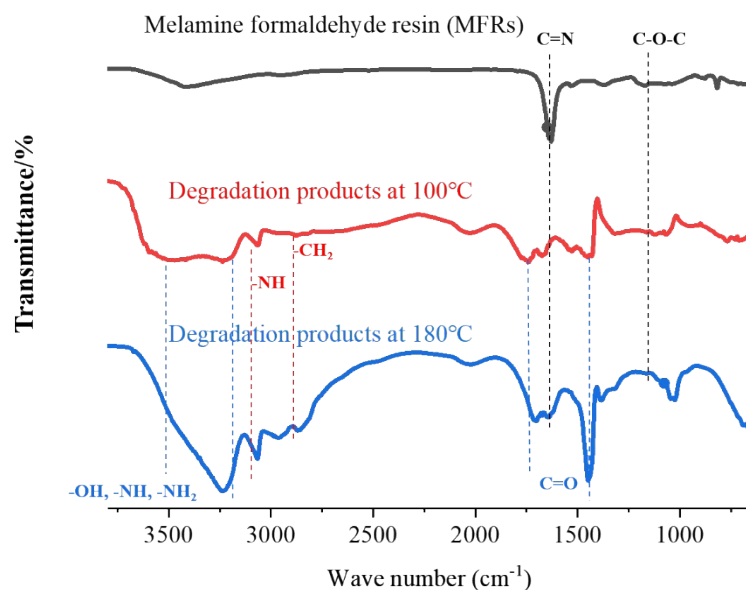


Figure S7. IR spectra of degradation products of MFRs at different temperatures (Reaction conditions: the Teflon-lined reactor, 12 h, MFRs ($10 \times 10 \times 3 \text{ mm}^3$), the THF-10wt% H_2O system).

The vibration of the original CNAR in MFRs disappeared after degradation at $180 \text{ }^\circ\text{C}$. Meanwhile, the remarkable reduction in the peak intensity for C=N bond at 1631 cm^{-1} suggested the transformation of ring structure. Correspondingly, the peak appeared at 1448 cm^{-1} and 1770 cm^{-1} indicated the formation of C=O bond. Compared with the IR spectrum of standard cyanuric acid, it was found that cyanuric acid was formed after MFRs was degradation at $180 \text{ }^\circ\text{C}$. The peaks between $2800 \sim 3000 \text{ cm}^{-1}$ suggested the $-\text{CH}_2$ groups, and the peak of $-\text{NH}$ at 3069 cm^{-1} was evident, and the enhanced peaks in the range of $3200 \sim 3400 \text{ cm}^{-1}$ implied the presence of OH, NH and NH_2 groups.

In contrast, the CNAR of MFRs did not change significantly after degradation at $100 \text{ }^\circ\text{C}$. The peak at 1610 cm^{-1} for the C=N bond still existed. This result indicated that the C-N bond with its C atom on the CNAR and its N atom outside the ring was difficult to break. And the peaks at 895 cm^{-1} and 1510 cm^{-1} also proved that the CNAR remained almost unchanged at $100 \text{ }^\circ\text{C}$.

Interestingly, compared with the raw MFRs materials, the peak intensity of the C-O-C bond at 1170 cm^{-1} obviously disappeared, indicating that the cleavage of the C-O bond was easier than the C-N bonds.

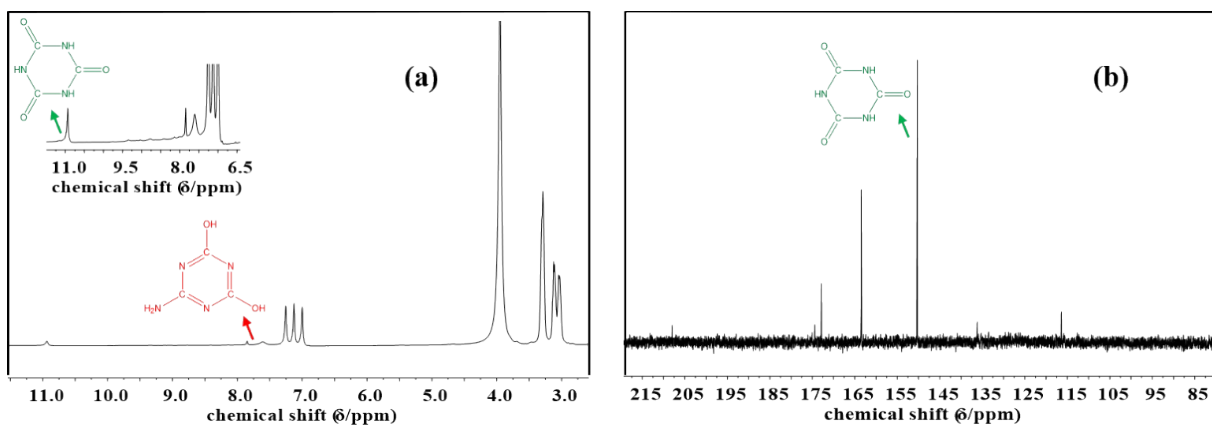


Figure S8. Reaction condition: ^1H -NMR spectrum(a) (The upper left corner is a partial enlargement of the figure), ^{13}C -NMR spectrum(b), Samples were prepared in DMSO-d_6 . The decomposed products of MFRs (the Teflon-lined reactor, 180°C , 12h, the HCl-butyrolactone-10wt% H_2O system).

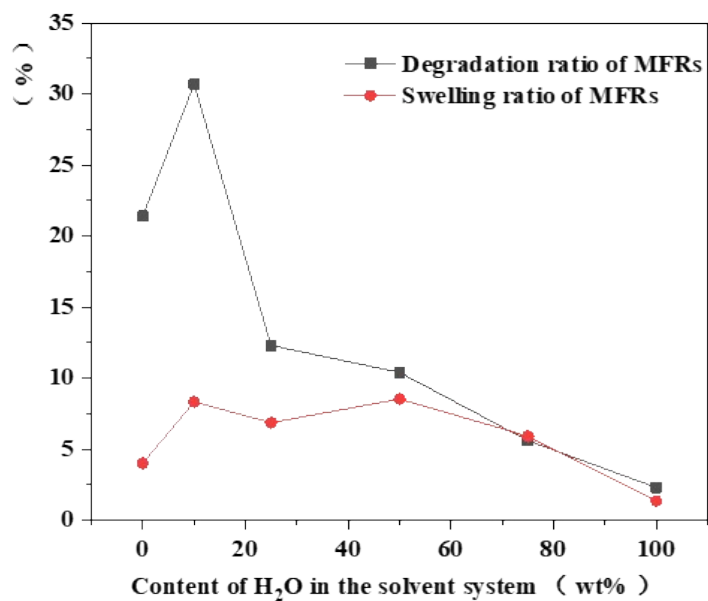


Figure S9. The relationship between swelling of the solvent systems and degradation ratio of MFRs. (Reaction condition: the Teflon-lined reactor, 100 °C, 6 h, MFRs (10×10×3 mm³), 5g of THF/H₂O solvent)

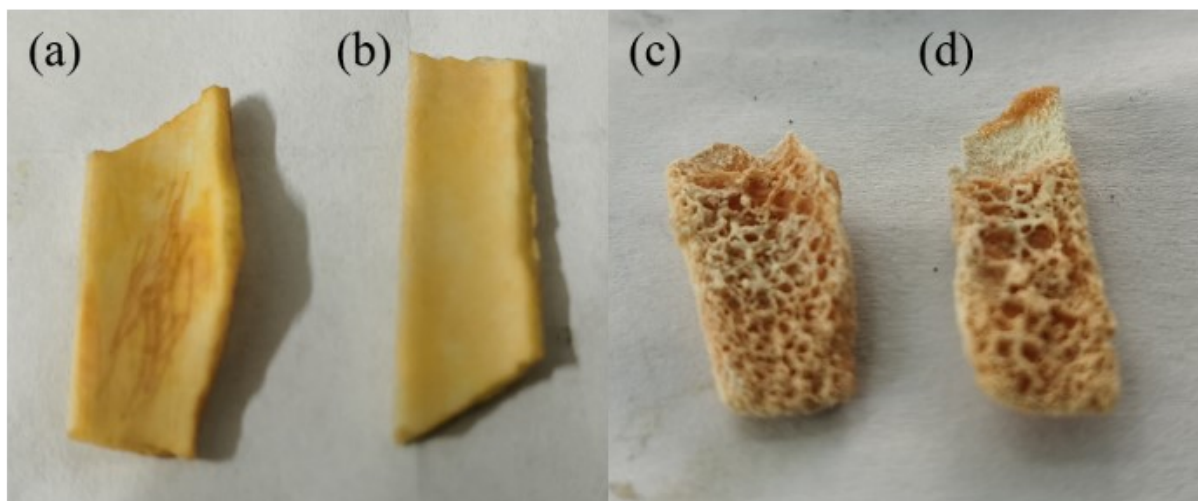


Figure S10. MFRs with rough surface (a) and smooth surface (b) (Reaction conditions: the teflon-lined reactor, the THF-10wt% H₂O system, 50 °C, 4 h); MFRs with rough surface (c) and smooth surface (d) (Reaction conditions: the Teflon-lined reactor, the MSA-THF-10wt%H₂O system, 100°C, 2 h).

To identify whether the degradation occurred during the swelling process or not, an experiment was designed. MFRs was pre-swelled in the THF-H₂O system at 50°C for 12 h and 24 h, respectively. Then, the two swollen resin samples after drying were analyzed by IR spectroscopy (Fig.S11 in ESI), and compared with the IR result of original resin; while the two solutions left were characterized by NMR (Fig.S12 in ESI).

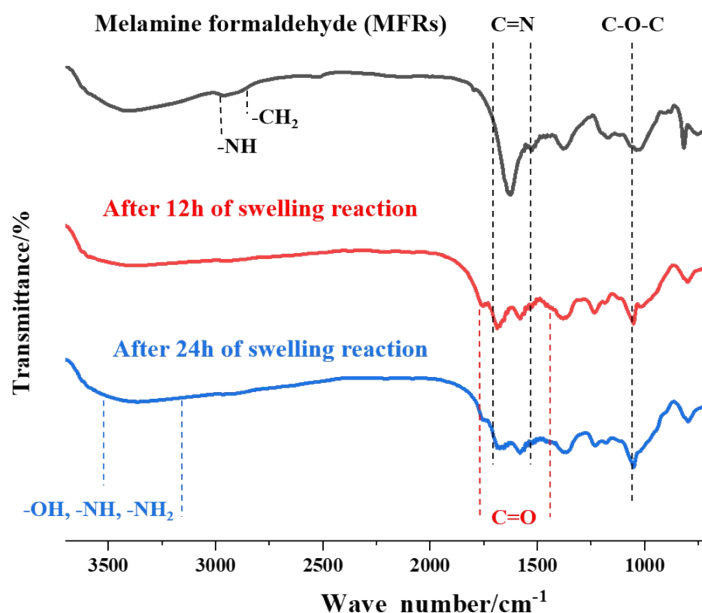


Figure S11. IR spectra of MFRs under different swelling time (swelling conditions: the Teflon-lined reactor, 50°C, MFRs (10×10×3 mm³), the THF-10wt% H₂O system).

The remarkable peak for C=N bond at 1631 cm⁻¹ suggested the CNAR structure (Fig.S11 in ESI). After swelling for 12 h, the peak intensity of C=N bond was partially weakened, meanwhile, two new peaks appeared at 1448 cm⁻¹ and 1770 cm⁻¹, respectively, which can be assigned to the C=O bond. The formation of C=O bond indicated that the structure of the ring has changed. After swelling for 24 h, the peak intensity of C=O bond was similar to that after swelling for 12 h. This

result indicated that the transformation of structure in the resin happened during the swelling process, and this kind of structural changes was limited.

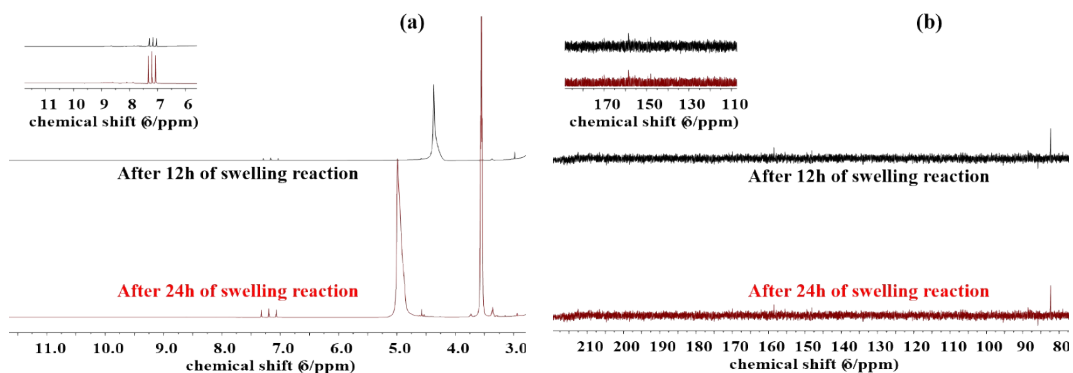


Figure S12. ^1H -NMR (a) and ^{13}C -NMR (b) spectra of the solution under different swelling time (swelling conditions: the Teflon-lined reactor, 50°C , MFRs ($10\times 10\times 3\text{ mm}^3$), the THF-10wt% H_2O system).

For the two swelling solutions, the appearance of three characteristic peaks (7~8 ppm) for ammonium ion (NH_4^+) in the ^1H -NMR spectra indicated that the $-\text{NH}_2$ outside of the CNAR was replaced by $-\text{OH}$ (Fig.S12a in ESI). This result was in good agreement with the finding in IR analysis (the formation of new $\text{C}=\text{O}$ bond), both of which indicated the occurrence of structural transformation.

Noticeably, after swelling for 24 h, the amount of NH_4^+ was increased (see the upper left corner of Fig. S12a). The signal at 11.2 ppm for cyanuric acid (the degradation product) and the signal at 8.1 ppm for ammelide (the intermediate product) were absent in both solutions. The absence of cyanuric acid and ammelide was also supported by the ^{13}C -NMR analysis. As shown in Fig. S12b, there existed no obvious signal peaks around 150~170 ppm.

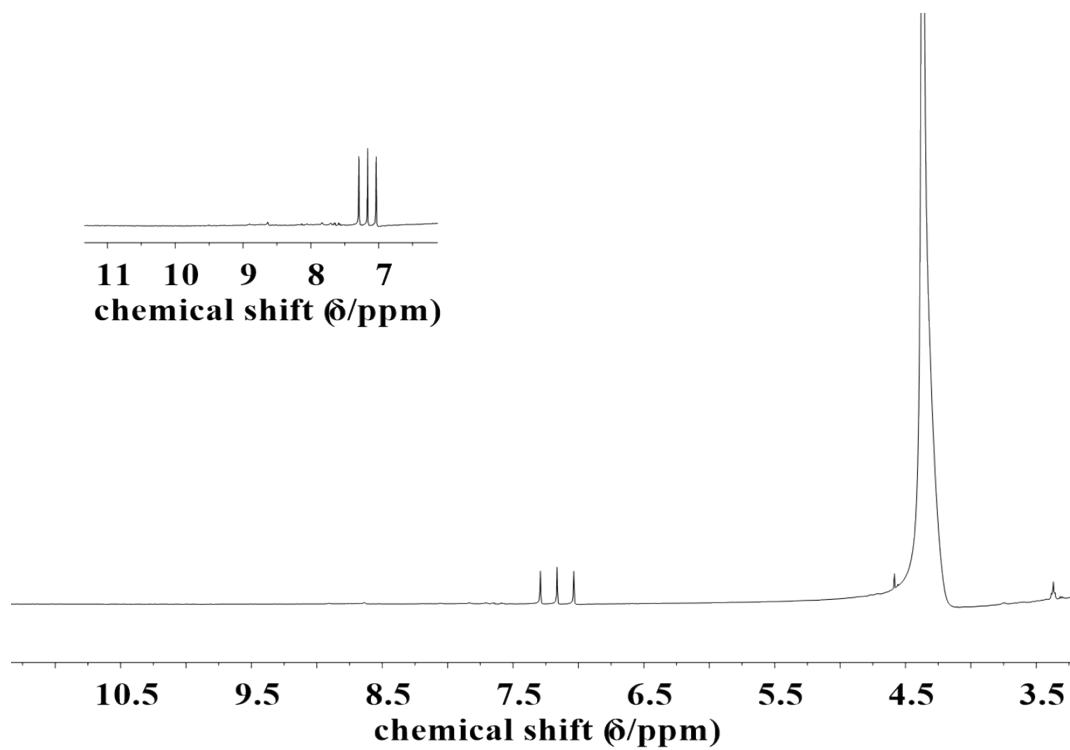


Figure S13. The reaction solution after degradation was collected and analyzed by NMR.

(Reaction condition: the Teflon-lined reactor, 180°C, 12h, the MSA-THF-10wt% H₂O system).

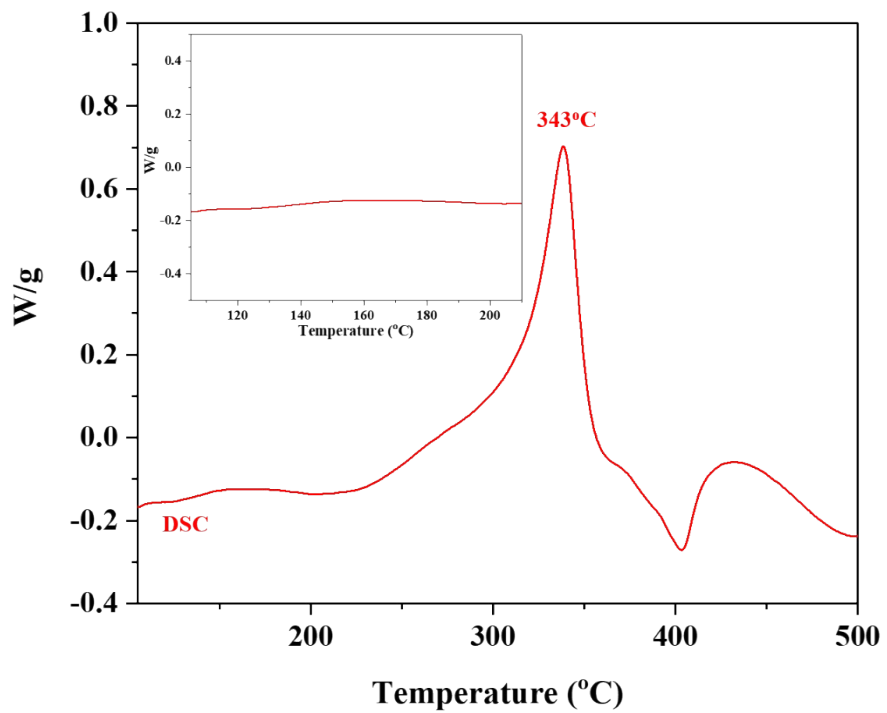


Figure S14. DSC analysis curves of MFRs.

Table S1. The pressures of the H₂O-THF solutions at different temperatures. ^a

Solvent	Temp/°C						
	50°C	100°C	120°C	140°C	160°C	180°C	200°C
THF	0.02	0.18	0.35	0.59	0.91	1.35	1.72
THF-5wt%H ₂ O	0.02	0.22	0.43	0.68	1.05	1.62	1.94
THF-10wt%H ₂ O	0.02	0.24	0.44	0.76	1.22	1.82	2.51
THF-20wt%H ₂ O	0.01	0.23	0.45	0.78	1.25	1.94	2.84
THF-25wt%H ₂ O	0.01	0.22	0.44	0.75	1.23	1.94	2.70
THF-50wt%H ₂ O	0.03	0.22	0.40	0.59	0.74	1.46	1.93
THF-75wt%H ₂ O	0.03	0.20	0.30	0.39	0.63	0.89	1.41
H ₂ O	0	0.06	0.13	0.29	0.53	0.90	1.37

(^a: Reaction condition: Teflon-lined reactor.)

Table S2. The boiling points for the H₂O-THF solutions with varied H₂O/THF ratios. ^a

Entry	Solvent	Boiling Point/°C
1	THF	66.8
2	THF-5wt%H ₂ O	64.3
3	THF-10wt%H ₂ O	62.1
4	THF-20wt%H ₂ O	59.5
5	THF-25wt%H ₂ O	58.7
6	THF-50wt%H ₂ O	61.2
7	THF-75wt%H ₂ O	62.5
8	H ₂ O	96.8

(^a: Round bottom flask, oil bath heat.)

Table S3. Elemental Analysis of MFRs in different acidic systems.

Sample	Protonic acid	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)
MFRs ^a		32.33	4.92	29.31	33.24	0
MFRs ^b	MSA	28.15	4.34	37.86	29.37	0.0021
MFRs ^c	H ₂ SO ₄	32.36	4.99	29.14	33.31	0

(^a: Fresh MFRs without any treatment, ^{b, c}: Reaction condition: Teflon-lined reactor, 80°C, 10h, in each run: the mass ratio of catalyst and solvent in the 5g catalytic system is 1:4, and the mass ratio of H₂O and THF in the solvent is 1:9)