SUPPLEMENTARY INFORMATION

FOR

A facile method to fabricate hybrid hydrogels with mechanical toughness using a novel multifunctional cross-linker

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Synthesis of the multifunctional cross-linker (AGE-M). To a 100ml glass reactor equipped with a stirrer and a heating jacket, are added 1g of melamine, 100ml of deionized water, and a predetermined amount of allyl glycidyl ether (AGE). The molar ratio of AGE to melamine is 3 to 18. The mixture is heated while stirring to 75^{o}C and kept at this temperature until the reaction is completed. The extent of reaction is followed by measuring the epoxy number with a dioxane solution of hydrochloric acid. The final products for the NMR characterizations are obtained by freeze drying the aqueous solution. The cross-linkers are labelled as AGEx-M where x is the molar ratio of AGE to melamine.

Calculation of the yield of AGE and melamine: The total mass of AGE and melamine added is m_1, the mass of the product after freeze dried is m_2, the yield of AGE and melamine is m_2/m_1*100%. Since AGE is easy to be removed under vacuum, the obtained product after freeze dried is exactly the pure cross-linker.

NMR characterizations: The products for the NMR characterizations are obtained by freeze drying the different aqueous solutions of the cross-linker. Then they are dissolved in D_2O and measurements are performed with a Varian Inova magnet operating at 600 MHz ($_1H$) at 25°C. As the allyl group doesn't participate in the ring-opening reaction, the protons on the allyl group can be used as an interior label. Thus, no external standard is added.

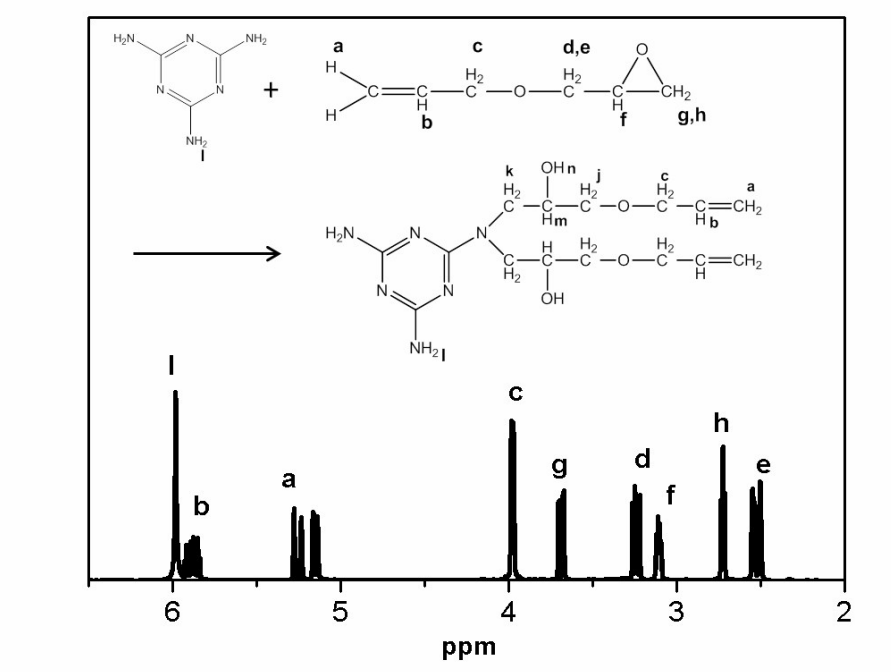


Fig.S1 1H-NMR spectrum of the unreacted mixtures of AGE and melamine

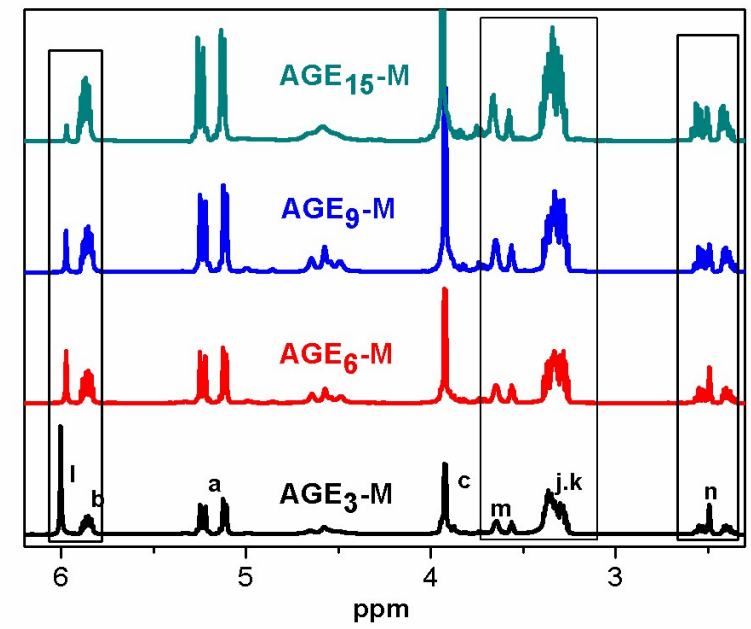
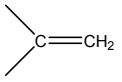
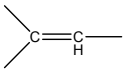
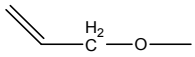
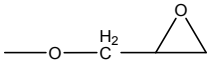
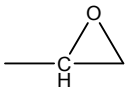
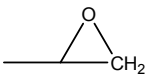
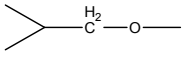
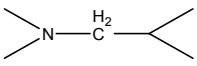
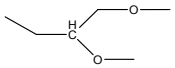


Fig.S2 1H-NMR spectra of the products prepared by different molar ratio of melamine to AGE

Table.S1 Chemical shifts for protons at structure elements in allyl glycidyl ether and reaction products of melamine with allyl glycidyl ether.

Structure Elements	Chemical Shift (δ ppm)
	5.3-5.1 (a)
	5.9-5.8 (b)
	4-3.9 (c)
	3.3-3.2 (d), 2.57-2.5 (e)
	3.15-3.05 (f)
	3.7-3.65 (g), 2.75-2.7 (h)
	3.45-3.2 (j)
	3.45-3.2 (k)
	3.7-3.5 (m)
—OH	2.6-2.3 (n)
—NH_2	6.0-5.9 (l)
—NH—	6.4-6.1

In the spectrum of the unreacted mixtures of melamine and allyl glycidyl ether, the signal at ca.6.0 ppm is due to all the amine protons. And there are 8 peaks existed in allyl glycidyl ether whose affiliations are listed in table S1. The protons in the methylene beside the epoxy group split into two peaks due to the conformational difference, one proton is close to the oxygen atom at the epoxy group and the signal moves to the low field at 3.3-3.2 ppm, while the other moves to high field to 2.57-2.5 ppm. Identically, the methylene in the epoxy group also breaks into two peaks as a result of the similar phenomenon. The spectra of the products in different ratios are shown in Fig.S2 , the broad peaks among 3.45-3.2 ppm are ascribed to the methylene protons in the structure of -N-CH_2-C- and -C-CH_2-O which have the same chemical shifts. The peaks m at 3.7-3.5 ppm split into two peaks due to chiral structures. From the spectra, we can find that the primary amino group decreases as the amount of AGE increases but doesn't vanish even at a excess ratio of 15. Generally, melamine is resistant against full substitution, it is hard to obtain even hexakis melamine despite the ease of reaction with formaldehyde which has been reported by Lubezak.[1] However, it is amazing that the second amino group whose chemical shift is 6.4-6.1 ppm doesn't exist in the spectrum even the amount of AGE is insufficient when the molar ratio is less than 6. This is perhaps the second amine group is more reactive to the epoxy group than the primary amine group in this system.

As the allyl group doesn't participate in the ring-opening reaction, the protons on the allyl group can be used as an interior label. Thus we calculate the peak areas ratio of protons in amine (l) and protons in double bonds (b) to investigate how many protons

in the amine group have been substituted by AGE. The results are listed in table S2. As a matter of course, the substitution ratio of protons in melamine increases with the augment of AGE's content. And the average number of protons grafted by AGE in one melamine monomer can also be figured out from which we can find that not all the AGE monomers are grafted to the nitrogen atoms. However, almost all the AGE is reacted completely since the conversion is quite high (above 96%), thus we can state that the rest AGE is reacted with the hydroxy group produced earlier by the reaction of amino and epoxy group which indicates a polyetherol chain is formed beside the nitrogen atom. Furthermore, the average number of the repeated units in one polyetherol chain is calculated from which we can find the value is also increased as the molar ratio of ingredients increases and about 2-3 within the ratio range. Nevertheless, we should note that these values are all averages and the products produced under different molar ratios are all mixtures.

Table.S2 Different values of the AGE-M produced under different molar ratios of melamine to AGE.

Sample name	Yield of melamine and AGE	Peak area ratio[a]	Conversion ratio[b] of protons	Average grafted number[c]	Average number of repeated units[d]
AGE_3-M	96.7%	1.43	28.5%	1.71	1.70
AGE_6-M	98.9%	0.5	50%	3	1.98
AGE_9-M	98.3%	0.23	69%	4	2.21
AGE_{12}-M	97.4%	0.12	76%	4.5	2.60
AGE_{15}-M	98.2%	0.04	90%	5.4	2.73
AGE_{18}-M	97.5%	0.02	94%	5.6	3.13

[a] Peak area ratio of l:b

[b] Conversion ratio of protons in melamine = (6/x-peak area ratio) / (6/x) *100%

[c] Average grafted number in one melamine monomer=6 * Conversion ratio

[d] Average number of repeated units in one oligomer = x* Yield of melamine and AGE / average grafted number

References

1. Lubczak, J., *Journal of applied polymer science* **65**: 2589-2602 (1997).