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Supporting Information

Preparation and Properties of Hyperbranched Polyurethane Acrylate Hard Coatings

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^{1}H NMR analysis

For the **Figure S1**, the peaks in the region between 5.2 to 6.5 ppm, corresponding to the alkene or acrylate protons at the periphery, clearly show that no double bonds are observed. The peak signals at 4.78 ppm and 4.58 ppm (c, a) can be attributed to the protons of -OH, and the proton signals at 3.55 ppm, 3.34 ppm (d, b) for -O-C<u>H</u>-, -O-C<u>H</u>$_2$- are observed, respectively. Also, the thioether hydrogen atoms (-C<u>H</u>$_2$-S-) appear at 2.63 ppm and 2.46 ppm (e, f). Moreover, the peaks at 1.96 ppm (g) and 4.42 ppm (h) are attributed to the protons in -CH$_2$-C<u>H</u>$_2$-CH$_2$- and -O-C<u>H</u>$_2$-, respectively, in TAC-MTGL. The peaks at 2.48 ppm (g) and 5.25 ppm (h) are attributed to the protons in -CH$_2$-C<u>H</u>$_2$-CO- and -N-C<u>H</u>$_2$-N-, respectively, in TAT-MTGL. The peaks at 2.49 ppm (g) and 4.00 ppm (h) are attributed to the protons in -CH$_2$-C<u>H</u>$_2$-CO- and -C-C<u>H</u>$_2$-COO-, respectively, in TMPTA-MTGL. Through the above analyses, it can be confirmed that TAC-MTGL, TAT-MTGL and TMPTA-MTGL have been successfully prepared, which is in accordance with previously reported literatures.[1,2]

The ^{1}H NMR spectra of HBPUA-TAC, HBPUA-TAT and HBPUA-TMPTA in $CDCl_3$ are shown in **Figure S2**. Clearly, several groups of characteristic peaks at 5.00-6.50ppm (s, u, t, b, a) would be observed in the spectra, indicating the existence of allyl and acrylate groups in HBPUA-TAC, HBPUA-TAT and HBPUA-TMPTA (the ratios between allyl groups and acrylate groups is 1:2). Moreover, some protons have a similar chemical shift due to the similar compositions and structures of three HBPUA oligomers. The peaks at 0.66-1.12 ppm (f, j, k) are attributed to the protons in -CH$_2$-C<u>H</u>$_3$ and -C-C<u>H</u>$_2$-C-, the peak at 1.42 ppm (e) is attributed to the protons in -C-C<u>H</u>$_2$-CH$_3$, and the peaks at 1.70-2.00 ppm (i, w) are attributed to the protons in -CONH-CH-C<u>H</u>$_2$-C- and -COO-CH$_2$-C<u>H</u>$_2$-CH$_2$-. Additionally, the peaks at 2.52-3.03 ppm (l, o, p)

are attributed to the protons in -C-C$\underline{H}_2$-NHCOO- and -C$\underline{H}_2$-S-, the peak at 3.31 ppm (d) is attributed to the protons in -O-C$\underline{H}_2$-C- and the peaks at 3.58-4.25 ppm (c, g, h, m, v) and 5.01 ppm (n) are attributed to the protons in CH_2=CH-C$\underline{H}_2$-O-, -C-C$\underline{H}_2$-O-CONH-, -O-CONH-C$\underline{H}$-CH_2- and -COO-C$\underline{H}_2$-CH_2-. Finally, the peak at 5.01 ppm (n) is attributed to the protons in -NHCOO-CH_2-C$\underline{H}$(CH_2-)-O-CONH-. The different chemical surroundings of the protons of -O-C$\underline{H}_2$- (HBPUA-TAC), -N-C$\underline{H}_2$-N- (HBPUA-TAT) and -COO-C$\underline{H}_2$- (HBPUA-TMPTA) form three diverse peak signals at 4.35 ppm, 5.32 ppm and 4.08 ppm for peak r, respectively, are shown in the spectra. Besides, other characteristic peaks, peak q of HBPUA-TAC and peaks x and y of HBPUA-TMPTA are also observed, which when combined with other analysis mentioned above (peak r) indicate that the hyperbranched cores of TAC-MTGL, TAT-MTGL and TMPTA-MTGL exist in the oligomers.

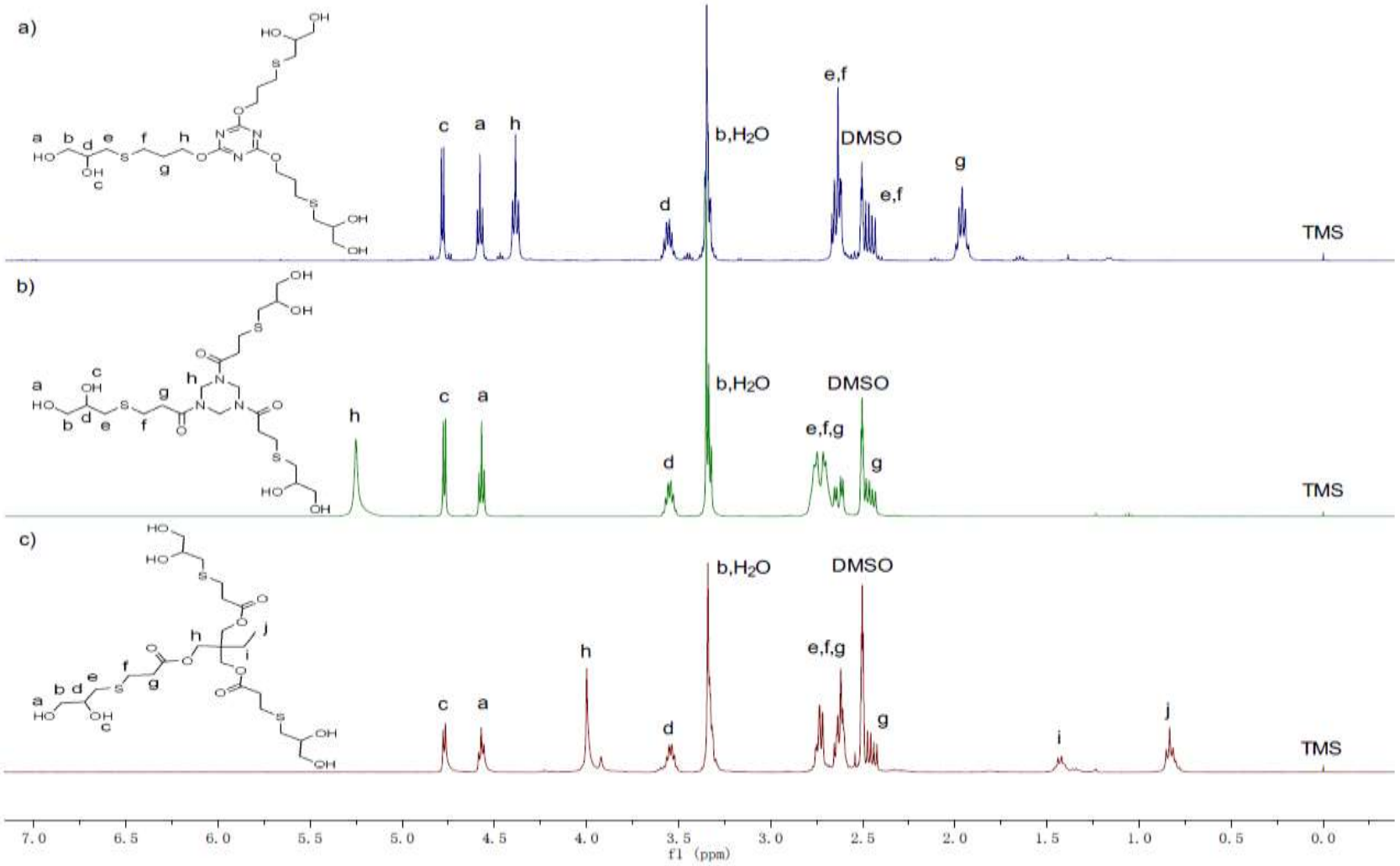

Figure S1. [1]H NMR spectra of a) TAC-MTGL, b) TAT-MTGL and c) TMPTA-MTGL.

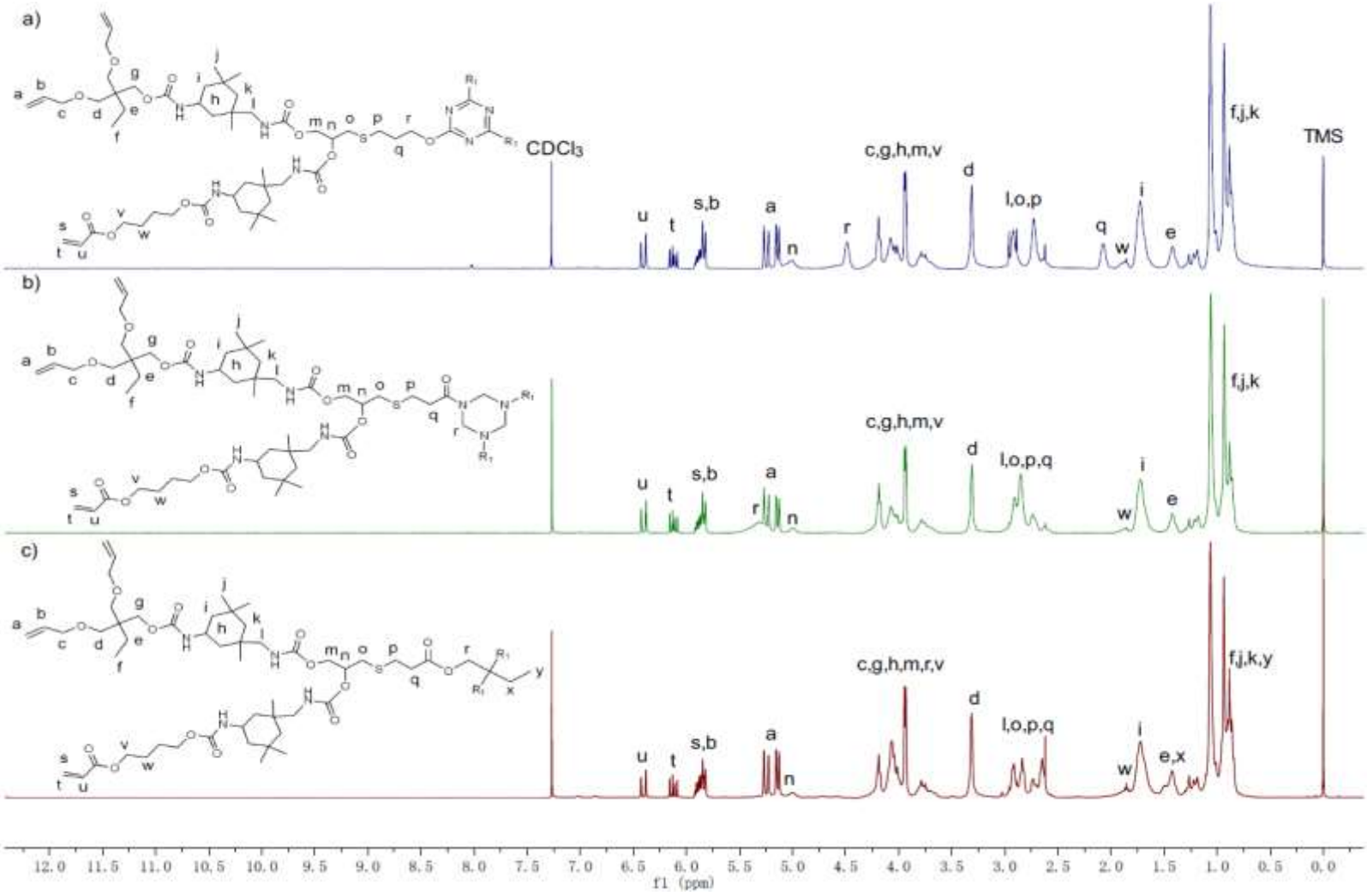

Figure S2. [1]H NMR spectra of a) HBPUA-TAC, b) HBPUA-TAT and c) HBPUA-TMPTA.

GPC analysis

The molecular weights and polydispersity (PDI) of HBPUA oligomers were analyzed by GPC in THF, using linear polystyrene standard. From **Figure S3**, there exist two peaks in each GPC curve, showing that oligomerization during the synthetic reaction was occurred due to the high reaction temperature. However, because of the self-inhibition in the allyl group, the oligomerization in HBPUA oligomers tends to form the dipolymer and tripolymer (**Figure S3**). The weight-average molecular weight (M_w) of HBPUA-TAC, HBPUA-TAT and HBPUA-TMPTA are 4298 g/mol, 5430 g/mol and 5531 g/mol, respectively, which are higher than the corresponding theoretical value (HBPUA-TAC: 2979 g/mol, HBPUA-TAT: 2979 g/mol and HBPUA-TMPTA: 3026 g/mol). Hence, the PDI of each oligomer shows high value because of the occurrence of oligomerization, even more than 1.60, indicating that the hyperbranched oligomers are obtained instead of the ideal dendrimer. The relatively low M_w of HBPUA-TAC can be attributed to the existence of the rigid core (triazine ring), which would constrain the chain motion resulting in the reduction of oligomerization.

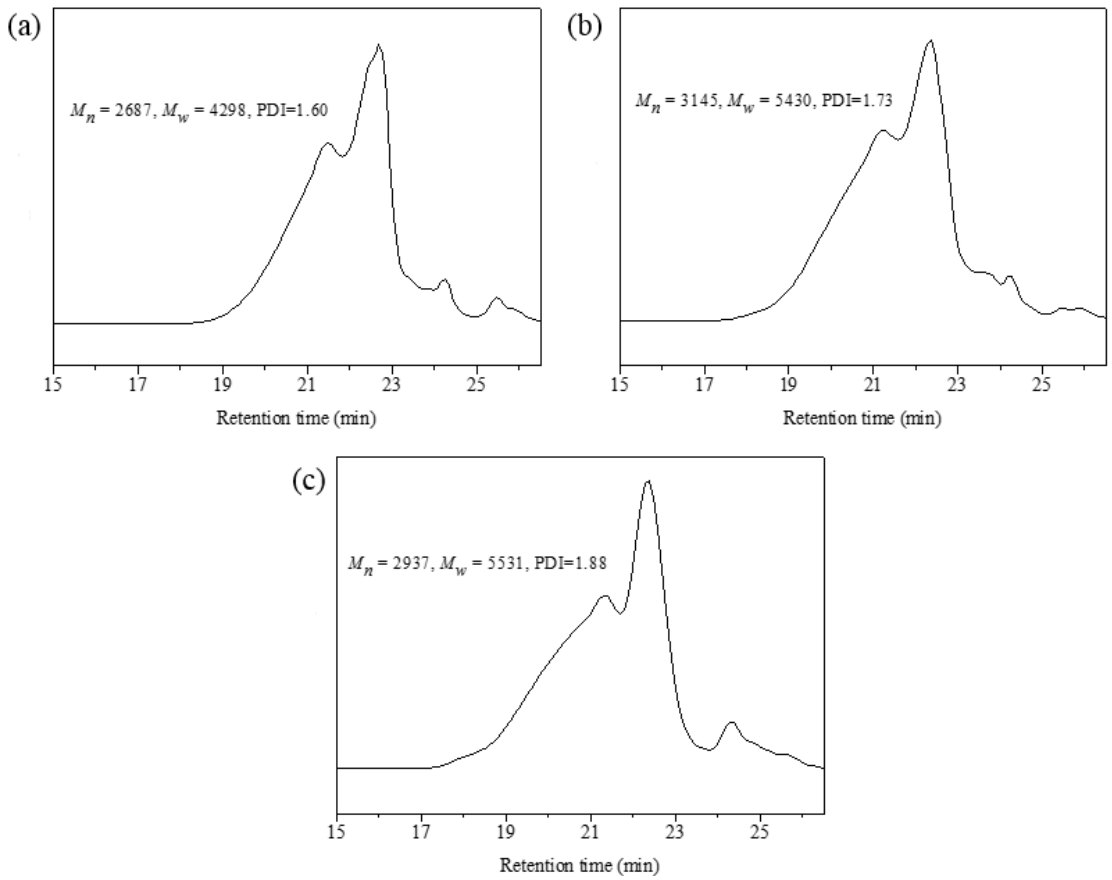

Figure S3. GPC curves of a) HBPUA-TAC, b) HBPUA-TAT and c) HBPUA-TMPTA.

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