Electronic Supporting Information

Preparation of hyperbranched polymers by oxa-Michael addition polymerization

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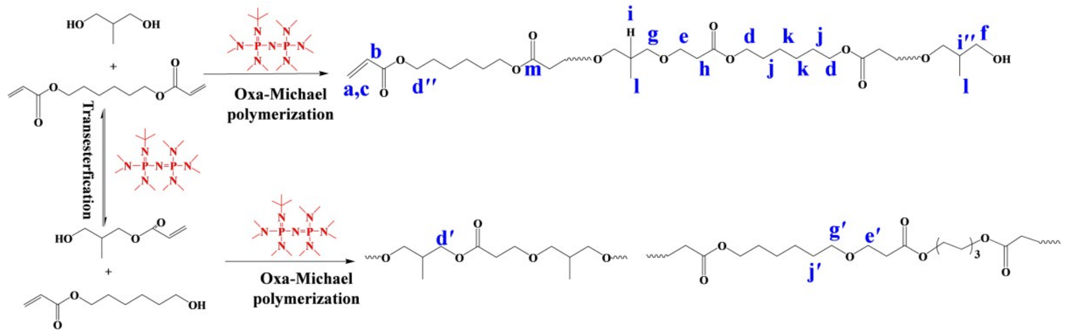


Scheme S1 Preparation of linear reference polymer via Michael addition polymerization of 2-methyl-1,3-propanediol (MPO) and 1,6-hexanediol diacrylate (HDDA).

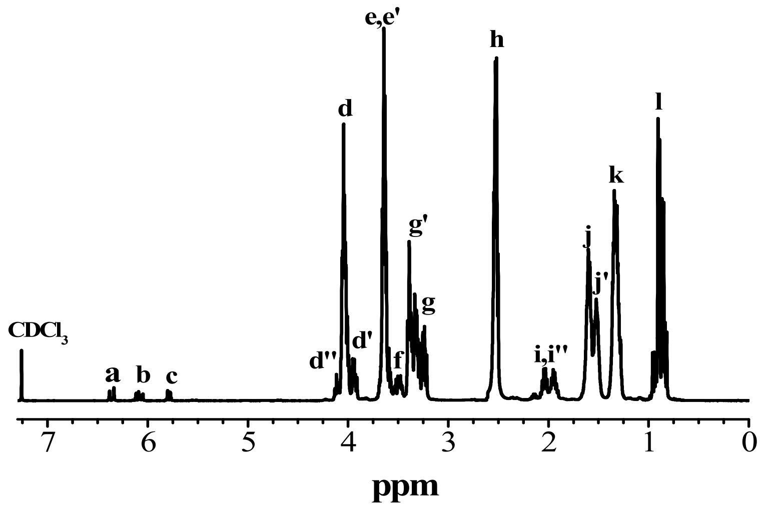


Figure S1 ^{1}H NMR spectrum of purified linear reference polymer obtained from *t*-BuP_2-catalyzed oxa-Michael addition polymerization of MPO and HDDA at 25 ^{o}C (in $CDCl_3$, 500 MHz).

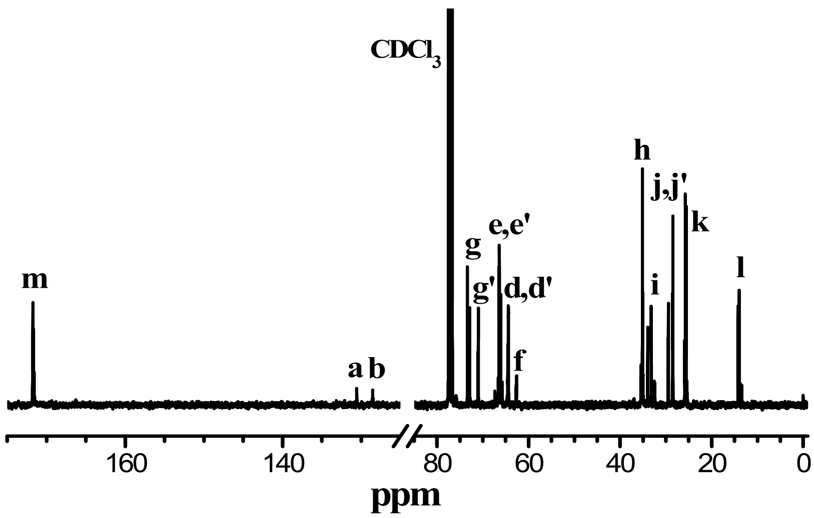


Figure S2 ^{13}C NMR spectrum of purified linear polymer prepared from *t*-BuP_2-catalyzed oxa-Michael addition polymerization of MPO and HDDA at 25 ^{o}C (in $CDCl_3$, 500 MHz).

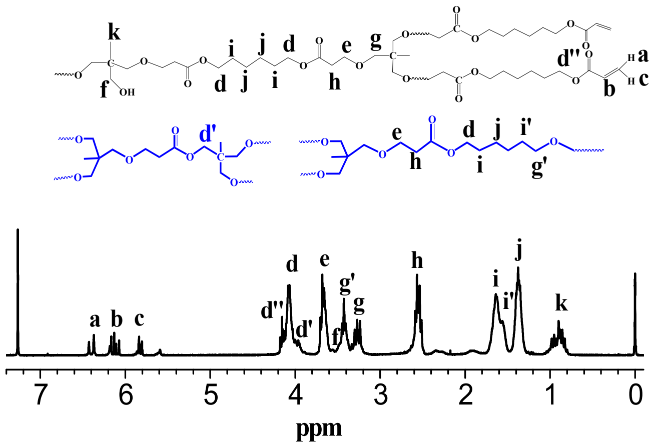


Figure S3 ^{1}H NMR spectrum of the purified hyperbranched polymers obtained from *t*-BuP$_2$-catalyzed oxa-Michael addition polymerization of TME and HDDA in DMF at 25 ^{o}C (in CDCl$_3$, 500 MHz).

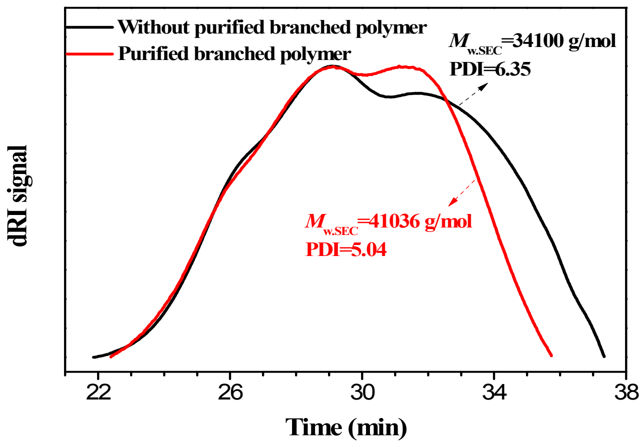
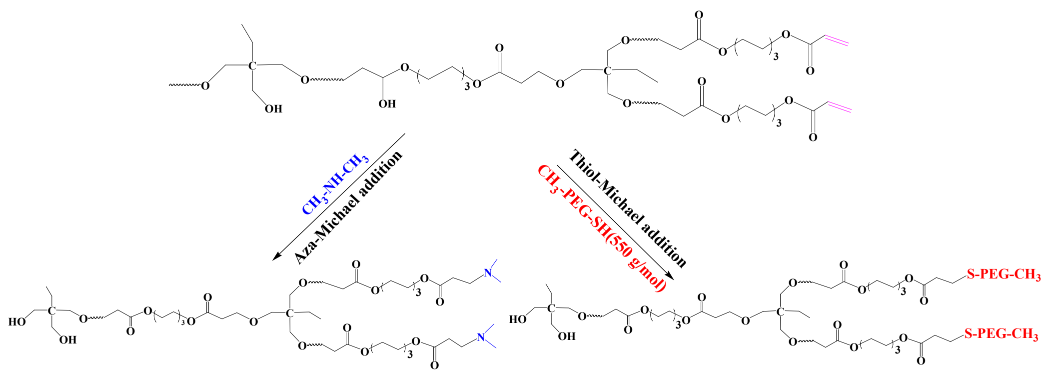


Figure S4 SEC curves of acrylic double bond terminated hyperbranched polymers before and after purification.



Scheme S2 The synthesis route of post-functionalized hyperbranched polymers via Michael addition reaction.

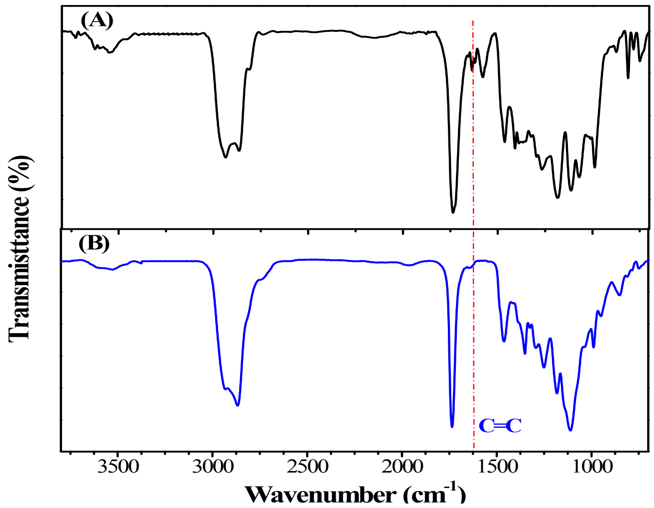


Figure S5 FTIR spectra of acrylic double bond terminated hyperbranched polymers before (A) and after (B) modification with mPEG-SH.

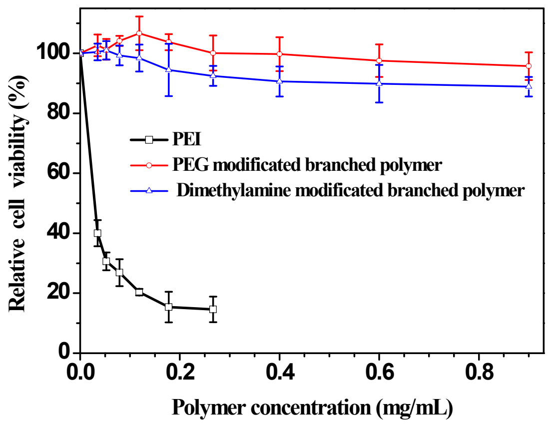


Figure S6 Cytotoxicity of the post-functionalized hyperbranched polymers in HepG2 cells.

Equation S1.

The ^{1}H NMR spectrum was used to calculate the transesterification of degree (DT) of branched (Figure 2A) polymers *via* the following equations:

Without transesterification reaction=S_d,

With transesterification reaction =$S_{d'}$,

DT(%)=$S_{d'}/(S_d+S_{d'})\times 100\%$.

$S_{d'}$ and S_d represent the peak areas of the related signals.

Equation S2.

The ^{1}H NMR spectrum was used to calculate the degree of branching (DB) of polymers *via* the following equations:

(1) **Without purified hyperbranched polymers:**

Linear units(L)= $S_f/2$

Terminal units(T)=$(S_{d''}/2)\times Conv._{\text{double bonds}}$

Dendritic units (D)=T

DB=(D+T)/(D+T+L)=$(S_{d''}\times Conv._{\text{double bonds}})/(S_{d''}\times Conv._{\text{double bonds}}+S_f/2)$

$S_{d''}$ and S_f represent the peak areas of the related signals (Figure 2A).

(2) **Purified hyperbranched polymers:**

Linear units(L)= $S_f/2$

Terminal units(T)=$S_{d''}/2$

Dendritic units (D)=T

DB=(D+T)/(D+T+L)=$S_{d''}/(S_{d''}+S_f/2)$

$S_{d''}$ and S_f represent the peak areas of the related signals (Figure 2A).