Supporting Information

Regioselective RAFT-HDA: a New Approach to Hyperbranched Polymers with Precise Topology Control

Jiayi Zhang[a,b], Ruyue Cao [a,b], Xiaowei Wang[a,b] Yixuan Wang[a,b] and Anchao Feng*[a,b]

a. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China.

b. Center of Advanced Elastomer Materials, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

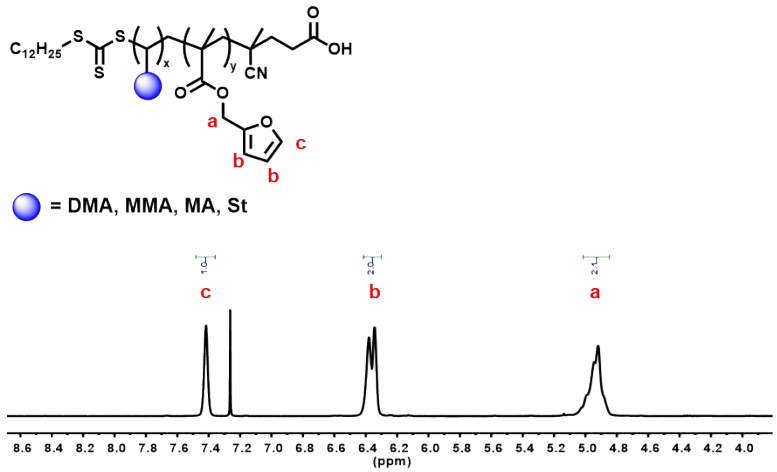

Fig. S1 ^{1}H NMR spectrum (DMSO) of the diene building block diene moiety.

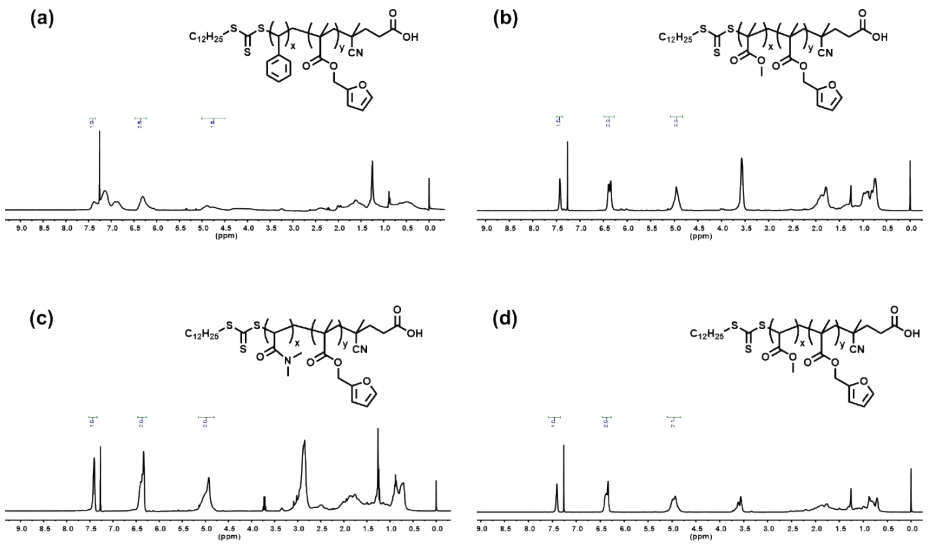

Fig.S2 The ^{1}H NMR spectrum (DMSO) of the diene building block: a)SF; b)MMF; c)DF; d)MF.

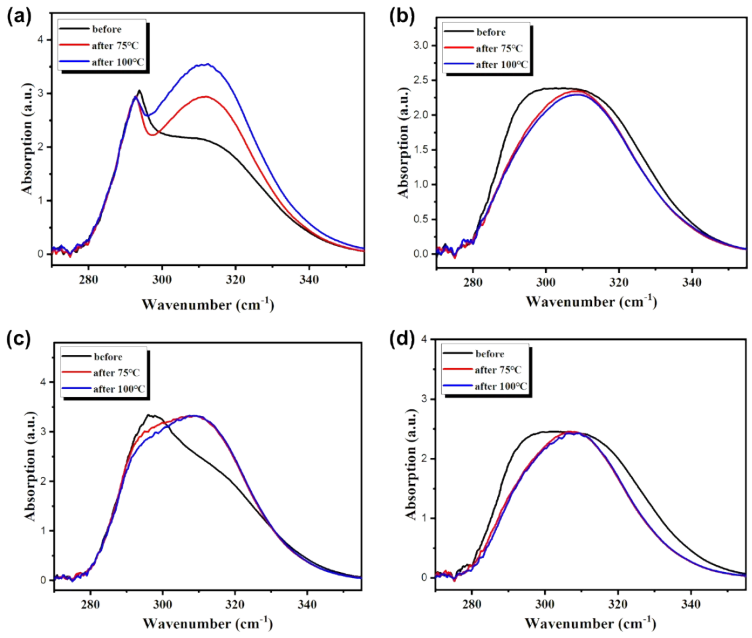

Fig. S3 Changes in the UV absorption spectra before the reaction (black), after the reaction at 75°C (red), and after the reaction at 100°C (blue): a) St-based polymer; b) MMA-based polymer; c) DMA-based polymer; d) MA-based polymer.

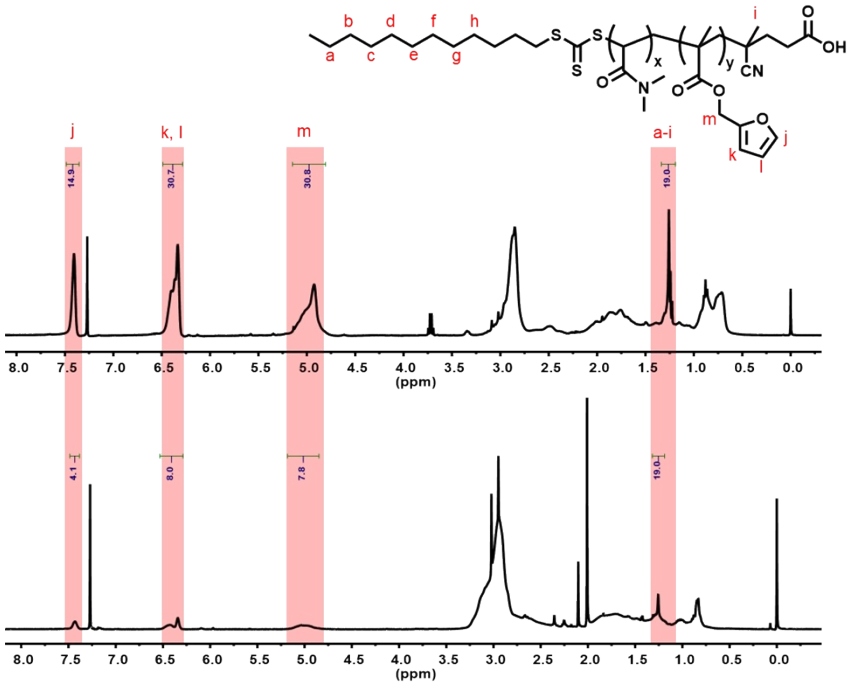

Fig. S4 The ^{1}H NMR spectrum (DMSO) of DF (top) and D-DF (bottom).

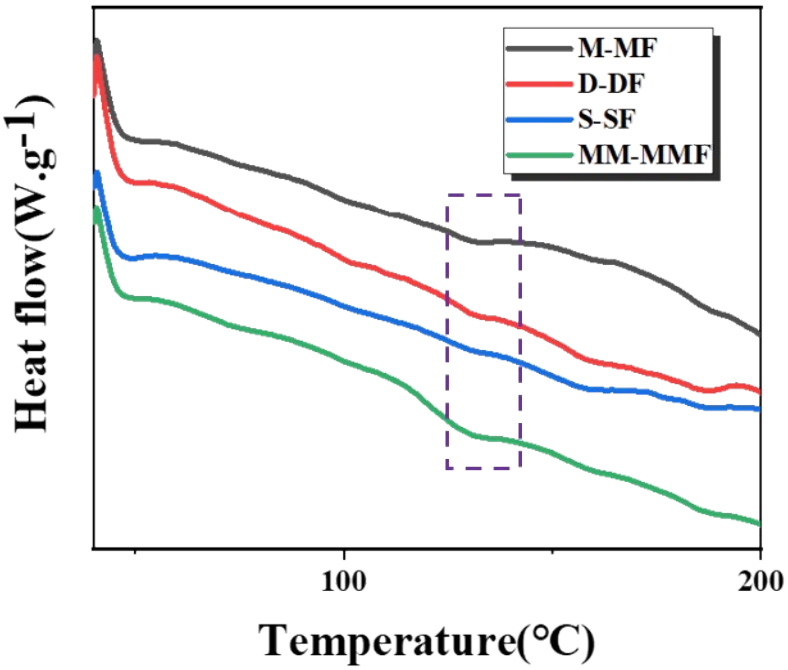

Fig. S5 DSC characterization results of four different monomer-based building blocks of D-DF, S-SF, M-MF and MM-MMF after HDA reaction.

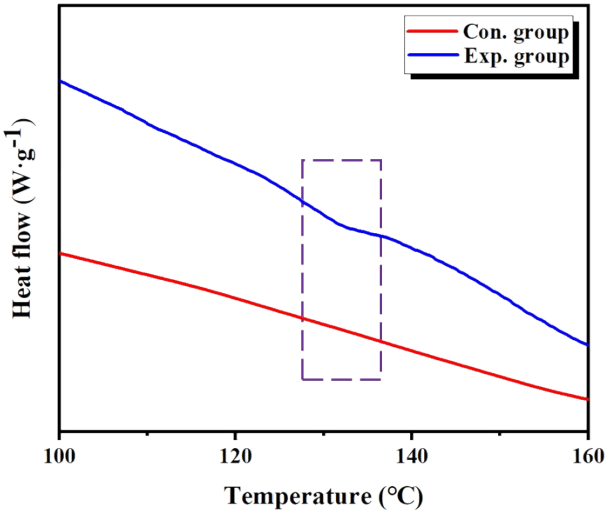

Fig. S6 The DSC results of the brush-type polymer (blue) and the control group (polymer without the HDA reaction) (red).

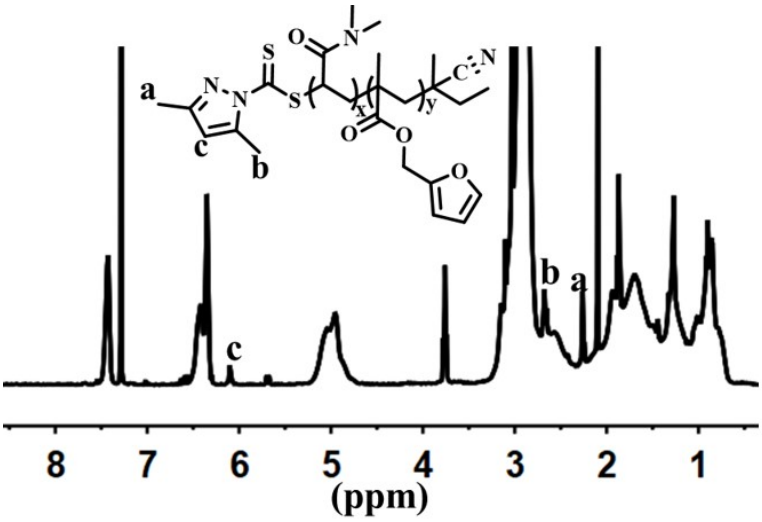

Fig. S7 ^{1}H NMR spectrum ($CDCl_3$) of the macromonomer AB_x.

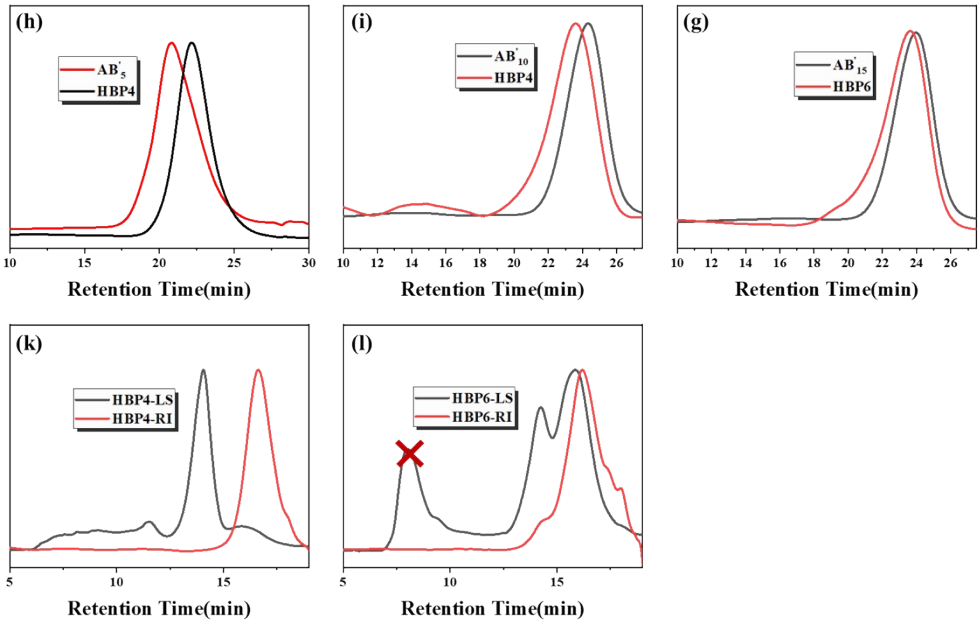

Fig. S8 GPC: (h-g) Comparison of relative molecular weight changes based on linear polystyrene standards before and after HDA reaction of AB'_5, AB'_{10} and AB'_{15} blocks; h) AB'_5 (black M_n = 6000, $Đ$ = 1.16), and HBP4 (red M_n = 8200 $Đ$ = 1.25); i) AB'_{10} (black M_n = 7000, $Đ$ = 1.14), and HBP5 (red M_n = 8683 $Đ$ = 1.29); g) AB'_{15} (black M_n = 8800, $Đ$ = 1.21), and HBP6 (red M_n = 10700 $Đ$ = 1.31). GPC-MALLS: (k-l) HBP4 and HBP6 absolute molecular weight characterization results; k) HBP4 by LS detector (black M_n = 413400 $Đ$ = 9.75), and by RI detector (red M_n = 8200 $Đ$ = 1.25); l) HBP6 by LS detector (black M_n = 73400 $Đ$ = 7.41), and by RI detector (red M_n = 10700 $Đ$ = 1.31).

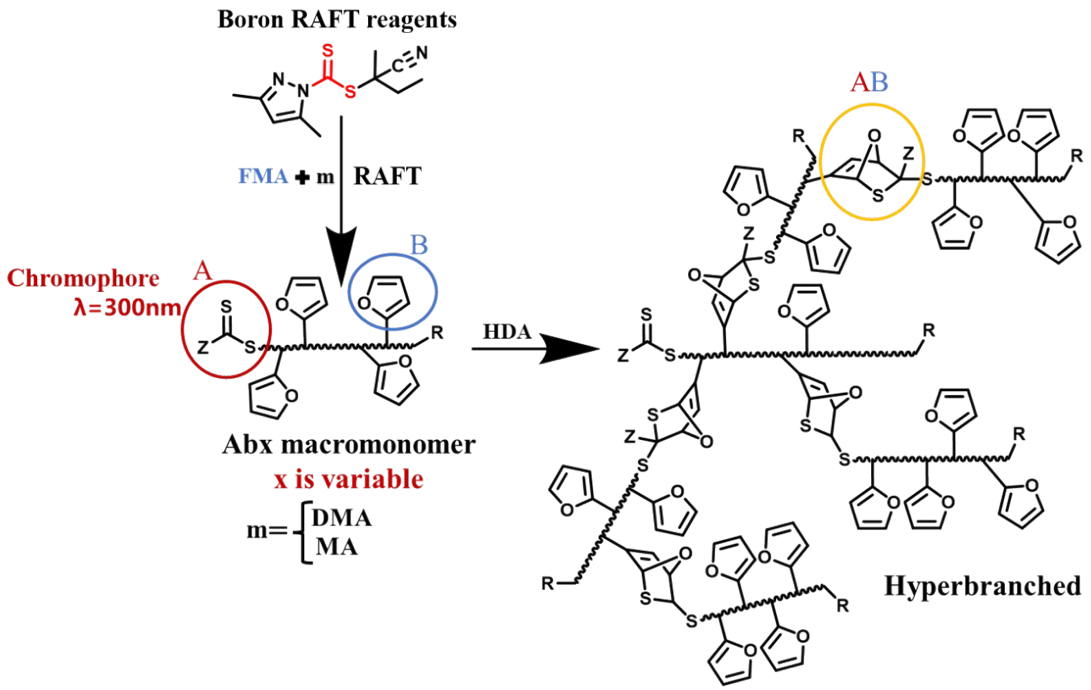

Fig. S9 The schematic diagram of the UV testing principle for AB_x and hyperbranched polymers.

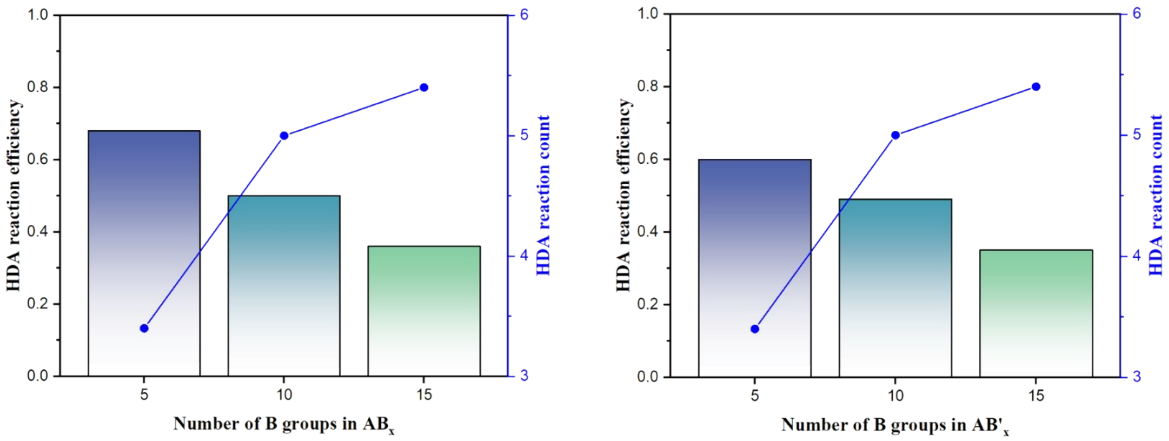

Fig. S10 HDA reaction efficiency (bar chart) and the absolute number of functional groups undergoing the HDA reaction (line chart) for AB_x macromonomers with different functionalities. (a) AB_x obtained from the copolymerization of DMA and FMA; (b) AB'_x obtained from the copolymerization of MA and FMA.

Table S1. Summarized data on brush-like polymers after HDA reaction.

Blocks	r(furan/ dithioesters)	$[F]_0$ (mol.ML^{-1})	$[S]_0$ (mol.ML^{-1})	T(°C)	M_n [b]	$Đ$ [b]
M-MF1	1	10^{-5}	10^{-5}	60	-	-
M-MF2					156700	1.14
D-DF1					14300	1.15
D-DF2					163300	1.09
MM-MMF1					799000	1.03
MM-MMF2					747700	1.04
S-SF1					25000	1.01
S-SF2					24400	1.02

r = reactivity ratio, M_n = number-average molecular weight, $Đ$ = dispersity index, 'b' obtained from GPC.

Table S2. Temperature probes for the synthesis of Ab_x macromonomers.

Blocks	CTA	T(°C)	Time (h)	M_n [a]	M_n [b]	$Đ$ [b]
$P(DMA_{30}$-co-$FMA_5)$	CDPC	75	1	21500	22100	1.42
$P(DMA_{30}$-co-$FMA_5)$		100	1	1000	3000	1.16
$P(DMA_{30}$-co-$FMA_5)$		100	2	1800	4700	1.15
$P(DMA_{30}$-co-$FMA_5)$		100	4	2200	5000	1.18
$P(DMA_{30}$-co-$FMA_5)$		100	6	3200	4600	1.04

M_n = number-average molecular weight, $Đ$ = dispersity index, 'a' obtained from NMR, and 'b' obtained from GPC.

Table S3. Summarized data on AB_x and AB'_x building blocks.

Blocks	f	M/f (g.mol^{-1})	DP^n	M_n [a]	M_n [b]	$Đ$ [b]
$P(DMA_{50}$-co-$FMA_5)$ (AB_5)	5	1336	51	5400	5700	1.40
$P(DMA_{50}$-co-$FMA_{10})$ (AB_{10})	10	761	62	6900	7200	1.30
$P(DMA_{50}$-co-$FMA_{15})$ (AB_{15})	15	474	58	6600	6800	1.50
$P(MA_{50}$-co-$FMA_5)$ (AB'_5)	5	1449	53	5800	6000	1.16
$P(MA_{50}$-co-$FMA_{10})$ (AB'_{10})	10	762	60	6900	7000	1.14
$P(MA_{55}$-co-$FMA_{15})$ (AB'_{15})	15	586	69	8200	8800	1.21

f= Specifically refers to the number of functional groups required for the HDA reaction, M = relative molecular mass, DP = degree of polymerization, M_n = number-average molecular weight, $Đ$ = dispersity index, 'a' obtained from NMR, and 'b' obtained from GPC.