

## Supporting Information

# Functional Highly Branched Polymers from Multicomponent Polymerization (MCP) Based on the ABC Type Passerini Reaction

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## Experiment Section

### Materials

Silica gel (200-300 mesh, Yantai Chem. Res. Inst.), sodium periodate (NaIO<sub>4</sub>, AR, Xi Long Chem. Co.), *trans*-cyclohexane-1,2-diol (Alfa Aesar, >98%), 1, 6-diisocyanohexane (Aldrich, >98%), hexanedioic acid (Sinopharm Chem. Reagent, >99.5%), 10-undecynoic acid (Alfa Aesar, >96%), 10-undecenoic acid (Alfa Aesar, >99%), phenylacetaldehyde (Alfa aesar, >95%) and methyl isocynoacetate (Alfa aesar, >95%) were used as received. All the solvents were purchased from commercial sources and further purified by conventional methods.

### Measurements

The number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostated at 35 °C, and THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was made against standard linear polystyrene

(PSt), the obtained datum was processed on professional software.

$^1\text{H}$  NMR (400 or 300 MHz) spectra were recorded in  $\text{CDCl}_3$  on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts.

### **Synthesis of Hexane-1, 6-dial**<sup>1</sup>

To a vigorously stirred suspension of silica gel (105 g, 1.75 mol) in  $\text{CH}_2\text{Cl}_2$  (500 mL) was added dropwise an aqueous solution of  $\text{NaIO}_4$  (0.65 M, 105 mL, 68.2 mmol). A solution of *trans*-cyclohexane-1, 2-diol (6.08 g, 52.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 mL) was then added, and the reaction was stirred for 24 h. The mixture was filtered on a sintered glass, and the silica gel was thoroughly washed with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the solvent afforded the title compound as a colorless oil. Yield: 75%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ = 9.78 ppm (t, 2H, CHO), 2.49 ppm (m, 4H,  $\text{CH}_2\text{CHO}$ ), 1.67 ppm (m, 4H,  $\text{CH}_2$ ).

### **General Procedure for the MCP**

The MCP was carried out in an airtight Schlenk flask. A typical procedure for the synthesis of HBP (Table 1, entry 3) is given below. Hexanedioic acid, 10-undecenoic acid, hexane-1, 6-dial, 1, 6-diisocyanohexane and THF were mixed and heated to 40 °C with stirring in a 25 mL Schlenk flask. Initially, the mixture is heterogeneous, and the solution turned clear after stirring for 0.5 h. An aliquot of mixture was taken out at a desired time to follow the polymerization kinetics by NMR. Finally, the reaction mixture was precipitated into diethyl ether after 48 h, and a white solid was obtained and dried under vacuum to determine the polymer yield.

When gelation occurred (Table 1, entry 1), the typical procedure is given below. Hex-

anedioic acid, hexane-1, 6-dial, 1, 6-diisocyanohexane and THF were mixed and heated to 40 °C with stirring in a 25 mL Schlenk flask. Initially, the mixture is heterogeneous, and the solution turned clear after stirring for 0.5 h. After 2 h, the stirring became quit slowly, and after 4 h, gelation occurred. The mixture was kept at this temperature for another 44 h. Finally, the gel was collected and dried under vacuum to get a yellow solid. The solubility of the gels in DMF, DMSO was tested both before and after being dried.

## Derivation of Formulas <sup>2</sup>

$N$  = the initial molar number of the dialdehyde ( $\mathbf{B}_2$ ) or the diisocyanide ( $\mathbf{C}_2$ )

When the molar ratio of  $\mathbf{A}_2/\mathbf{B}_2/\mathbf{C}_2/\mathbf{A}=x/1/1/y$

$xN$  = the initial molar number of the carboxylic diacid ( $\mathbf{A}_2$ )

$yN$  = the initial molar number of the mono-acid ( $\mathbf{A}$ )

The initial total molar number of molecules in the polymerization system:

$$N_0 = 2N + xN + yN = (2 + x + y)N \quad (1)$$

Define  $p$  = the fraction of acid groups being reacted at a given time  $t$

$N_t$  = the total number of remaining molecules at a given time  $t$

Assume that intramolecular cyclization as a competing and chain terminating process during propagation is absent. Then

$$p = \frac{\frac{3}{2}(N_0 - N_t)}{3(2x + y)N} \quad (2)$$

Combination of (1) and (2):

$$\frac{2(2x + y) \cdot p}{2 + x + y} = 1 - \frac{N_t}{N_0} \quad (3)$$

The number average degree of polymerization:

$$X_n = \frac{N_0}{N_t} \quad (4)$$

Combination of (3) and (4):

$$\frac{2(2x + y) \cdot p}{2 + x + y} = 1 - \frac{1}{X_n} \quad (5)$$

Assume that gelation occurs when  $X_n = \infty$ . Then the critical gelation condition is

$$\frac{2(2x + y) \cdot p}{2 + x + y} = 1 \quad (6)$$

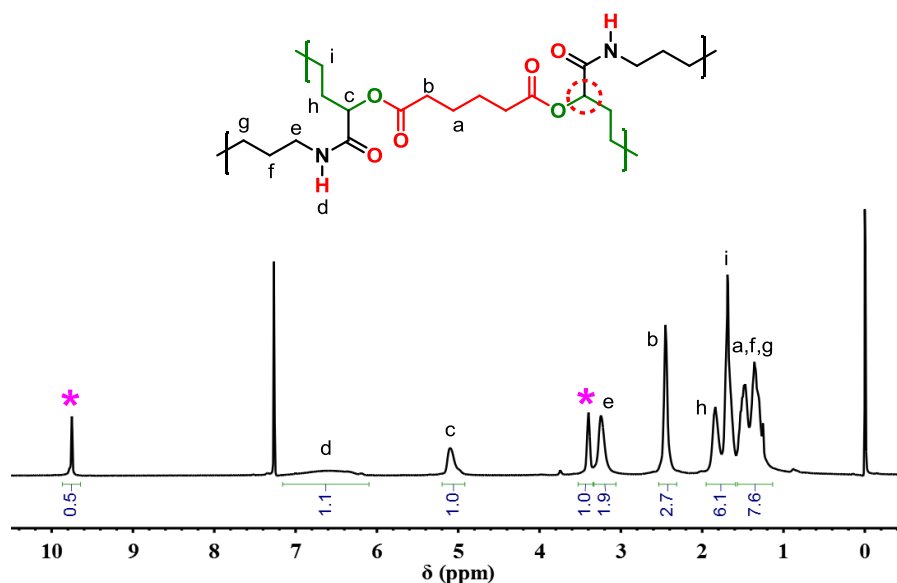
Assume  $p = 1$ . Then the critical gelation condition is

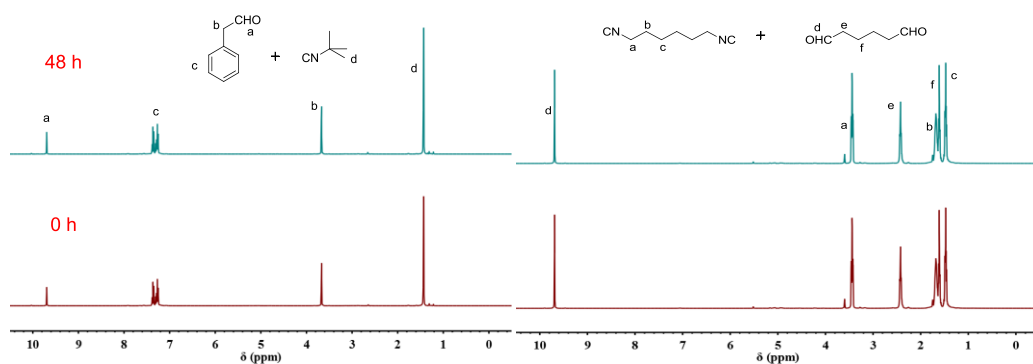
$$3x + y = 2 \quad (7)$$

**Table S1. Synthesis of functional HBPs with tunable DB and DF <sup>a</sup>**

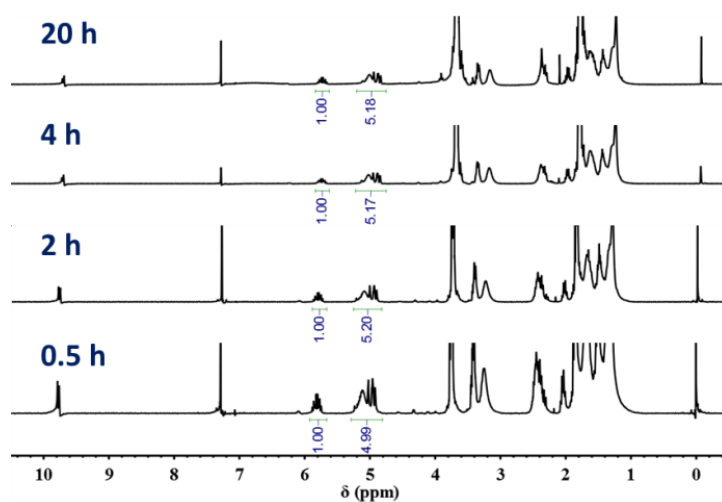
Entry	Ratio (A <sub>2</sub> /B <sub>2</sub> /C <sub>2</sub> /A) <sup>b</sup>	Mn(kDa)/PDI <sup>c</sup>	DB(%)/DF(%) <sup>d</sup>	Yield/% <sup>e</sup>
1 <sup>g</sup>	0.10/1.0/1.0/0.85	2.3/1.47	-	-
2 <sup>g</sup>	0.10/1.0/1.0/1.1	4.1/1.26	36/64	19 <sup>f</sup>
3	0.20/1.0/1.0/0.70	3.5/2.25	-	-
4	0.25/1.0/1.0/1.3	-	-	Gel
5	0.40/1.0/1.0/0.27	-	-	Gel
6	0.45/1.0/1.0/0	-	-	Gel
7	0.50/1.0/1.0/0	-	-	Gel
8	0.60/1.0/1.0/0	-	-	Gel

<sup>a</sup> Conducted in THF. <sup>b</sup> The concentration of diisocyanide or dialdehyde was 1.0 mol/L. <sup>c</sup> Measured by GPC in THF. <sup>d</sup> Determined by <sup>1</sup>H NMR spectra. <sup>e</sup> Determined after precipitation in ethyl ether and vacuum dryness (30 °C, 12 h). <sup>f</sup> The relatively low yields was due to the loss of oligomers during precipitation process. <sup>g</sup> The Mn of these two entries were characterized in-situ, and no polymers were obtained after precipitation because of the good solubility of oligomers in ethyl ether.

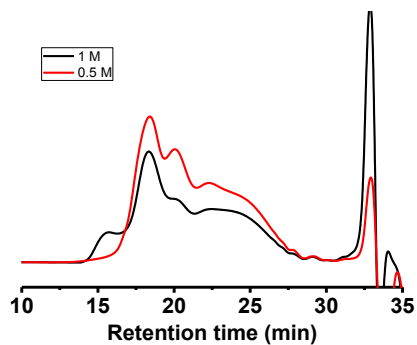
**Figure S1.** <sup>1</sup>H NMR spectrum of the HBP (Table 1, entry 2) obtained from the MCP of A<sub>2</sub>+B<sub>2</sub>+C<sub>2</sub> (0.41/1.0/1.0, [B<sub>2</sub>]=[C<sub>2</sub>]= 1.0 mol/L, THF).



**Figure S2.** Model reactions between isocyanides and aldehydes.

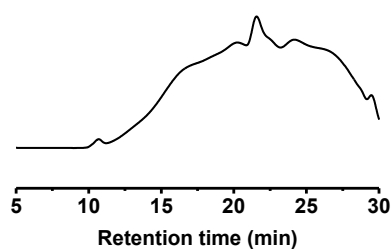
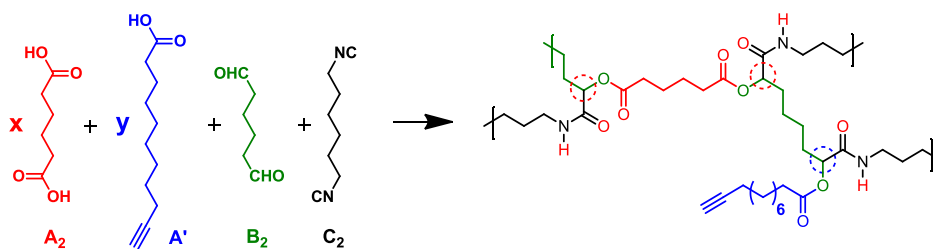


**Figure S3.** Time-dependent  $^1\text{H}$  NMR spectra of the MCP of  $\text{A}_2+\text{B}_2+\text{C}_2+\text{A}$  (molar ratio, 0.33/1.0/1.0/0.50) ( $[\text{B}_2]=[\text{C}_2]=1.0$  mol/L, THF).

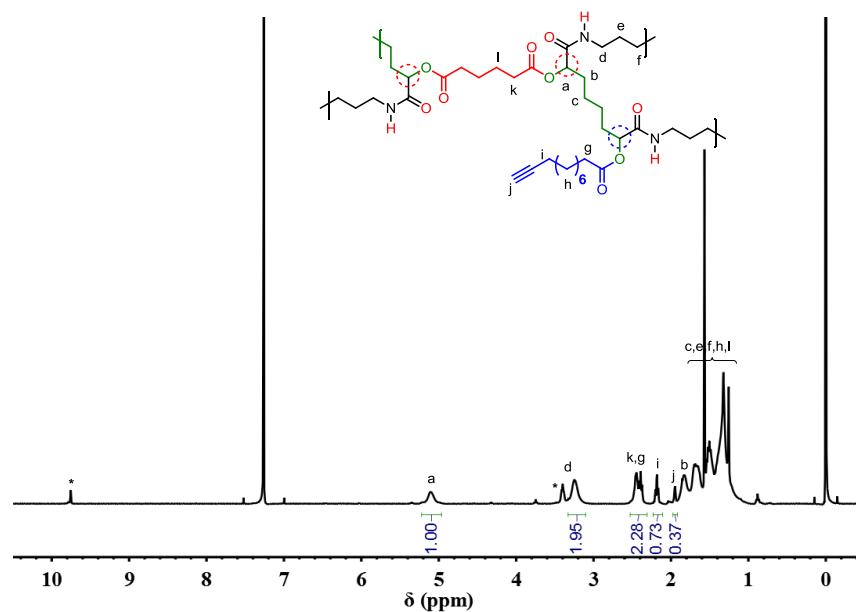


**Figure S4.** GPC traces of HBPs obtained from the MCP of  $\text{A}_2+\text{B}_2+\text{C}_2+\text{A}$  (0.33/1.0/1.0/0.50, THF) at two different concentrations of  $\text{C}_2$ .

**Scheme S1. Synthesis of HBPs from the MCP of  $A_2+B_2+C_2+A'$ .**

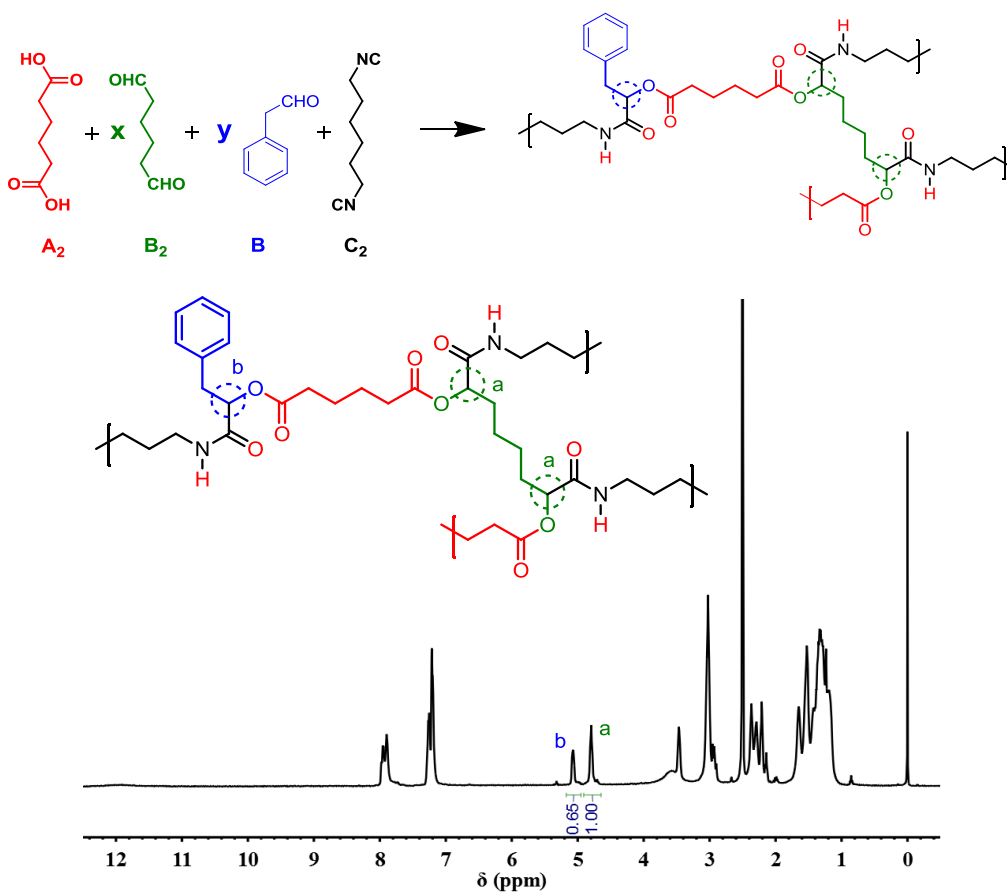


**Figure S5.** GPC traces of the HBP obtained from the MCP of  $A_2+B_2+C_2+A'$  (0.33/1.0/1.0/0.50,  $[B_2]=[C_2]=1.0$  mol/L, THF).



**Figure S6.**  $^1H$  NMR spectrum of the HBP obtained from the MCP of  $A_2+B_2+C_2+A'$  (0.33/1.0/1.0/0.50,  $[B_2]=[C_2]=1.0$  mol/L, THF). The DF =  $j/a = 37\%$  was determined by the integration ratio of the proton  $j$  at 1.9 ppm (functional alkynyl group) and the proton  $a$  (the sum of functional linkage and branching linkage). The DB =  $1 - DF = 63\%$ .

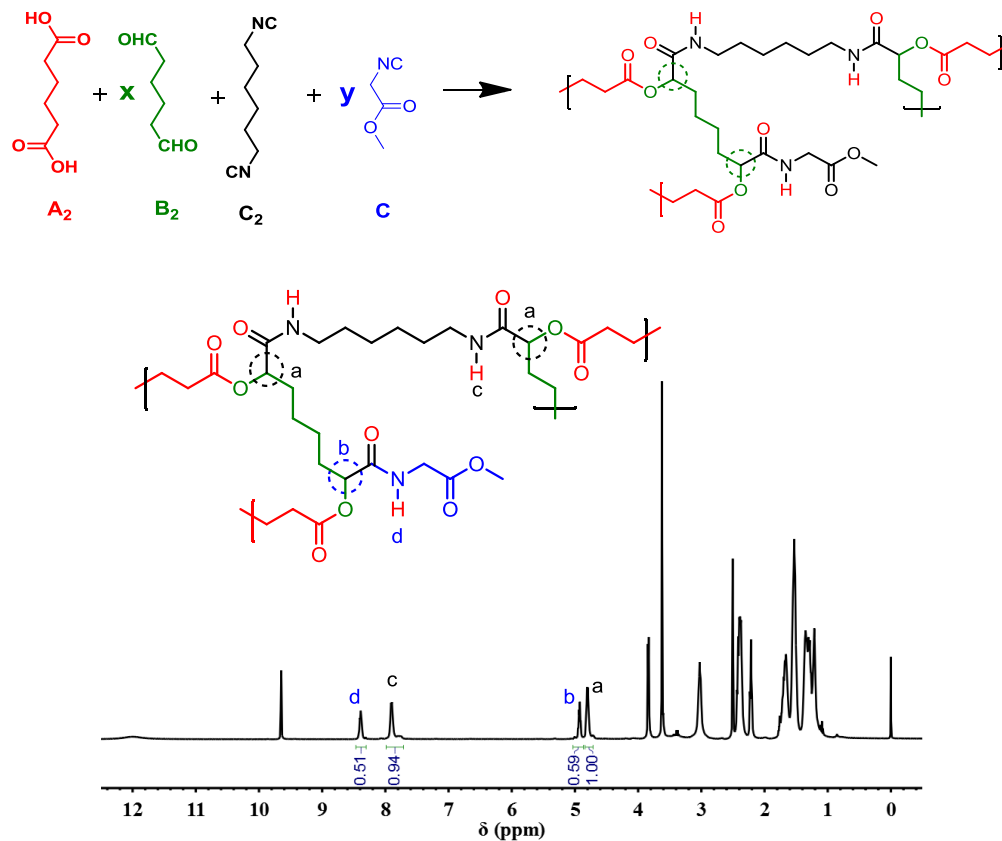
**Scheme S2. Synthesis of HBPs from the MCP of  $A_2+B_2+C_2+B$  (B represents phenylacetaldehyde).**



**Figure S7.**  $^1\text{H}$  NMR spectrum of the HBP ( $M_n = 16.6$  kDa,  $\text{PDI} = 1.80$ , measured by GPC in DMF) obtained from the MCP of  $A_2+B_2+C_2+B$  (1.0/0.33/1.0/0.50,  $[A_2]=[C_2]=1.0$  mol/L, THF). The  $\text{DB} = a/(a+b) = 61\%$  and  $\text{DF} = b/(a+b) = 39\%$  was determined by the integration ratio of proton  $a$  at 4.8 ppm (the branched structures) and the proton  $b$  at 4.9 ppm (the functional structures).



**Scheme S3. Synthesis of HBPs from the MCP of  $A_2+B_2+C_2+C$  (C represents methyl isocyanoacetate).**



**Figure S8.**  $^1\text{H}$  NMR spectrum of the HBP ( $M_n = 25.5$  kDa, PDI = 1.67, measured by GPC in DMF) obtained from the MCP of  $A_2+B_2+C_2+C$  (1.0/0.33/1.0/0.50,  $[A_2]=[B_2]=1.0$  mol/L, THF). The DB =  $a/(a+b) = 63\%$  and DF =  $b/(a+b) = 37\%$  was determined by the integration ratio of proton *a* at 4.8 ppm (the branched structures) and the proton *b* at 5.1 ppm (the functional structures). Moreover, the DB and DF calculated by the proton *c* and *d* gave similar results (DB = 65% and DF = 35%).

## References

1. S. Lopez, F. Fernandez-Trillo, P. Midon, L. Castedo, C. Saa, *J. Org. Chem.* 2005, **70**, 6346.
2. W. H. Carothers, *Trans. Faraday Soc.* 1936, **32**, 39.