

Table S1 ^{13}C NMR chemical shifts of poly(4MP) and assignments.

Peak	Branched units	Assignment	Chemical shift (ppm)		Ref.
			This work	Literatures	
1	C, D	C5, D1	19.9	19.70, 19.9	[2], [3]
2	A, B	A1, A2, B1, B2	20.5	19.5-20.07	[4]
3	C	C1	20.7	20.1, 20.2-20.6	[2], [4]
4	E	E4	21.4	21.4	[9]
5	G	G1	22.7	22.4	[2]
6	E	E1	23.0-23.2	23.5	[2]
7	J	J1	23.6	23.21, 25.65, 23.5	[2], [4], [8]
8	J	J2	25.8	26.75, 25.8	[2], [8]
9	E	E2	25.9	25.8	[2]
10	C, G	C7, G5,	27.3	27.0, 27.24	[2], [4]
11	D, G	D4, G2	27.8	28.0, 27.2,	[2-4]
12	G, B, C	G4, B5, C2	28.2	28.1, 27.97	[2] [4]
13	A	A4	28.6	27.97	[4]
14	C, D	C4, D2	30.8	30.6, 30.38	[2], [8]
15	F	F1	31.6	31.29	[4]
16	A, B	A3, B3	33.2	33.38	[4]
17	H, I, J	I1, H1, J4	33.5	31.5, 33.62	[2], [5-7]
18	G	G6	35.7	34.7	[2]
19	D, G	D3, G7	37.5	37.5, 37.6, 37.45,	[2-4]
20	C	C6	38.2	37.77	[4]
21	F	F2	38.5	38.87	[5-7]
22	G	G3	39.4	39.2	[2]
23	H	H2	41.8-42.7	39-42	[1]
24	I	I2	43.4-44.1	42-44	[1]
25	J	J3	45.1	45.5	[2]
26	C	C3	45.3-45.4	46.2	[2]
27	A, B	A4, B4	45.9-46.1	45.0-47.5	[4]
28	E	E3	46.7-48.2	47.0-48.0	[2]

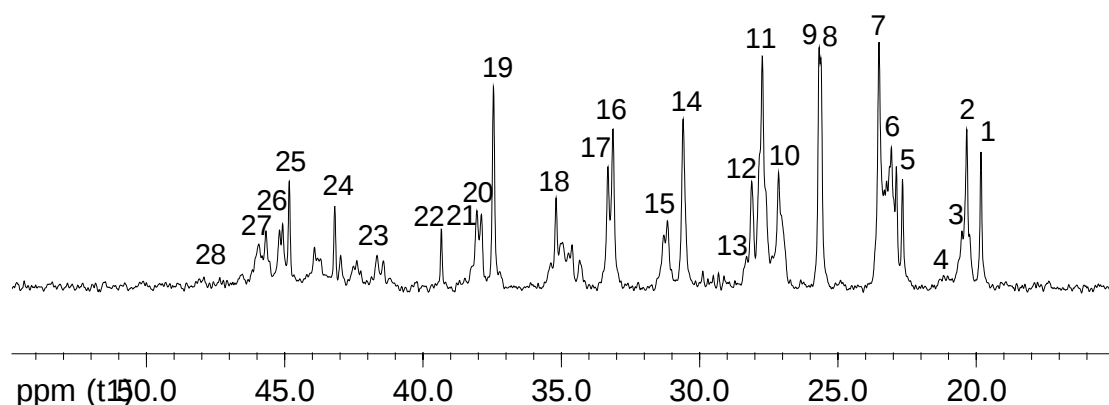
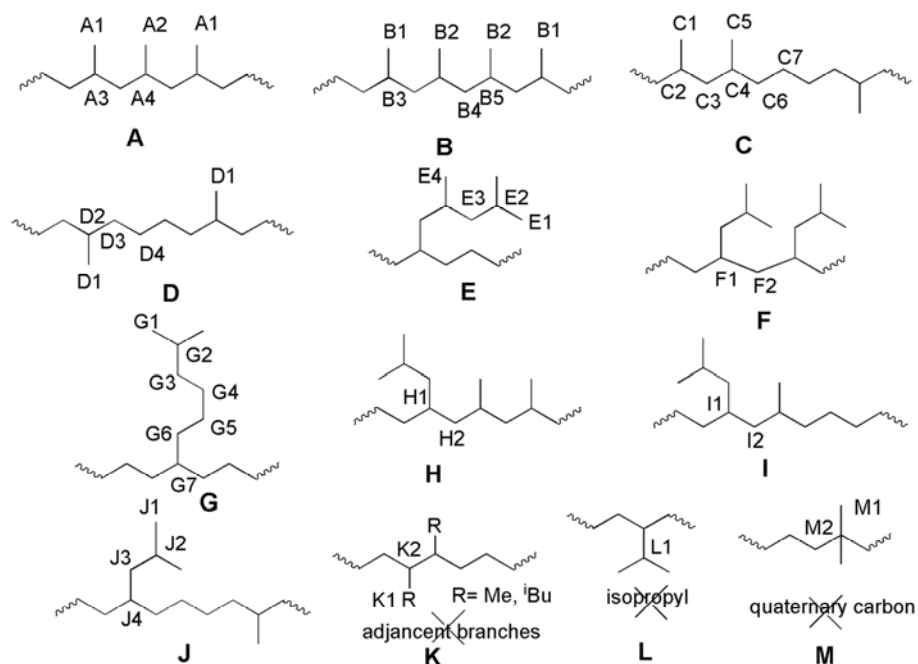


Fig. S1. ^{13}C NMR spectrum of poly(4MP) prepared by C1/DEACat 20 °C.

Branched units



References:

- (1) E. F. McCord, S. J. McLain, L. T. J. Nelson, S. D. Ittel, D. Tempel, C. M. Killian, L. K. Johnson and M. Brookhart, *Macromolecules*, 2007, **40**, 410-420.
- (2) E. F. McCord, S. J. McLain, L. T. J. Nelson, S. D. Arthur, E. B. Coughlin, S. D. Ittel, D. Tempel, L. K. Johnson, C. M. Killian and M. Brookhart, *Macromolecules*, 2001, **34**, 362-371.
- (3) G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*,

1999, **32**, 1620-1625.

- (4) G. B. Galland, L. P. Da Silva, M. L. Dias, G. L. Crossetti, C. M. Ziglio and C. A. L. Filgueiras, *J. Polym. Sci. Part A Polym. Chem.*, 2004, **42**, 2171-2178.
- (5) S. Losio, A. C. Boccia, L. Boggioni, M. C. Sacchi and D. R. Ferro, *Macromolecules*, 2009; **42**: 6964-6971.
- (6) S. Losio, A. C. Boccia and M. C. Sacchi, *Macromol. Chem. Phys.*, 2008, **209**, 1115-1128.
- (7) S. Losio, P. Stagnaro, T. Motta, M. C. Sacchi, F. Piemontesi and Galimberti M. *Macromolecules* 2008; **41**: 1104-1111.
- (8) F. A. Kunrath, F. F. Mota, O. L. Casagrande, R. S. Mauler and R. F. de Souza. *Macromol. Chem. Phys.* 2002, **203**, 2407-2411.
- (9) H. Gao, J. Pan, L. Guo, D. Xiao and Q. Wu, *Polymer*, 2011, **52**, 130-137.