Long-subchain Janus-dendritic Copolymers from Local-confined Click Reaction and Generation-dependent Micro-phase Separation

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Element analysis for different Janus-dendritic PSt/PtBA copolymers

As for J-(PSt)¹-N₃/(PtBA)¹-N₃, nitrogen element comes from α , ω -diazido tetra(ethylene glycol) and the introduced azido groups at the end. Theoretical weight percent of nitrogen was estimated to be 1.80 % based on molecular weight of *alkynyl*-(PSt-Br)₂ and *alkynyl*-(PtBA-Br)₂, roughly consistent with experimental result. As for J-(PSt)¹-N₃/(PtBA)²-Br, the introduction of more PtBA units induced the increase of oxygen element and the presence of bromo group at the ends of PtBA half-dedrons and caused the decrease of nitrogen element. The variation of element amount with the growth of Janus-dendritic copolymers verified the changes in the copolymer composition and the end groups.

 Table S1. Variation of element amount for different Janus-dendritic PSt/PtBA

 copolymers by element analysis technique

Janus-dendritic copolymer	C %	Н%	O %	N %
J-(PSt) ¹ -N ₃ /(PtBA) ¹ -N ₃	75.73	7.750	14.91	1.610
J-(PSt) ¹ -N ₃ /(PtBA) ² -Br	70.00	8.824	20.42	0.756
J-(PSt) ² -N ₃ /(PtBA) ² -N ₃	75.07	8.457	14.93	1.543
J-(PSt) ² -N ₃ /(PtBA) ³ -Br	68.89	11.44	18.80	0.870

GPC traces of J-(PSt)²-N₃/(PtBA)³-Br and J-(PSt)³-N₃/(PtBA)⁴-Br

The crude products of J-(PSt)²-N₃/(PtBA)³-Br was quite broad in molecular weight distribution, due to the presence of unreacted macromonomers and un-expected by-products from coupling reaction between bromo groups of *alkynyl*-(PtBA-Br)₂. Therefore, precipitation fraction should be utilized with THF as the good solvent and MeOH/water (20:1, v/v) as the poor solvent.



Figure S1. GPC traces of J-(PSt)²-N₃/(PtBA)³-Br (A) and J-(PSt)³-N₃/(PtBA)⁴-Br (B).

The synthesis of J-(PSt)³-N₃/(PtBA)⁴-Br was even tried from click reaction between J-(PSt)³-N₃/(PtBA)³-N₃ and *alkynyl*-(PtBA-Br)₂, but the molecular weight distribution is too broad as shown in Figure S1B. It should be caused by the too large fraction of J-(PSt)³-N₃/(PtBA)³-N₃ unimer in acetone.

GPC diagrams of J-(PSt)¹/(PtBA)¹, J-(PSt)²/(PtBA)² and J-(PSt)³/(PtBA)³ from MALLS detector

GPC measurement with MALLS detector can offer the absolute molecular weight of different copolymers. The diagrams of J-(PSt)¹/(PtBA)¹, J-(PSt)²/(PtBA)² and J-(PSt)³/(PtBA)³ from MALLS detector are shown in Figure S2 and indicate the increase in the absolute molecular weight with the generation.



Figure S2. MALLS-GPC diagrams of J-(PSt)¹/(PtBA)¹, J-(PSt)²/(PtBA)² and J-

 $(PSt)^{3}/(PtBA)^{3}$.

LLS study of J-(PSt)³/(PtBA)³ in DMF

To confirm that long-chain Janus-dendritic PSt/PtBA copolymers were molecularly dissolved in DMF, SLS and DLS were used. As shown in Figure S3, hydrodynamic radius of J-(PSt)³/(PtBA)³ is as low as 2 nm and apparent weight-average molecular weight by SLS is 55000 g mol⁻¹.



Figure S3. Hydrodynamic radius distribution (A) and Zimm plot (B) of J-(PSt)³/(PtBA)³

in DMF.

¹H-NMR analysis of Janus-dendritic copolymer through the whole generation

¹H-NMR analysis was used to monitor the change in chemical structure of Janusdendritic copolymer through the whole synthesis from the beginning of J-(PSt)¹-Br/(PtBA)¹-Br to the last of J-(PSt)³-Br/(PtBA)³-Br. The spectra are demonstrated in Figure S4. Signal f includes the methyl protons from tBA units and the backbone protons from both PtBA and PSt. Signal g represents the phenyl protons from PSt. The variation in their relative intensity with the growth of Janus-dendritic copolymers is clearly observed in the figures. The integral ratio of signal f to signal g, as well as the ratio of other characteristic signals, is summarized in Table S2.





Figure S4. ¹H-NMR spectra of Janus-dendritic copolymers.

	FTIR data	¹ H NMR data	
	A ₁₇₂₅ /A ₆₉₉	f:g	a:b:c:d:e
J-(PSt) ¹ -Br/(PtBA) ¹ -Br	-	3.5	2:12:2:2:2
J-(PSt) ¹ -N ₃ /(PtBA) ¹ -N ₃	-	3.5	4:12:0:2:2
J-(PSt) ¹ -N ₃ /(PtBA) ² -Br	5.2	9.5	6:12:0:6:2
J-(PSt) ² -Br/(PtBA) ² -Br	1.7	3.5	4:12:4:6:6
J-(PSt) ² -N ₃ /(PtBA) ² -N ₃	-	3.5	8:12:0:6:6
J-(PSt) ² -N ₃ /(PtBA) ³ -Br	3.6	7.3	12:12:0:14:6
J-(PSt) ³ -Br/(PtBA) ³ -Br	1.4	3.6	8:12:8:14:14

Table S2. Relative ratio of characteristic signals for FTIR and ¹H NMR analysis

Microphase separation evolution of J-(PSt)³-Br/(PtBA)³-Br with time.

The films of J-(PSt)³/(PtBA)³ were annealed in chloroform vapor for different durations.

At 4 h, J-(PSt)³/(PtBA)³ exhibited lamellar-like morphology with regular height distribution (Figure S5A). At 8 h, dune-like morphology with irregular height distribution was observed (Figure S5B). Isolated domains appeared at 12 h and their heights seemed remaining polydispersed. Finally at 24 h, the domains turn small and narrowly distributed while the height distribution was a little regular.



Figure S5. AFM images following the evolution of microphase separation of J-

(PSt)³/(PtBA)³ (A: 4 h, B: 8 h, C: 12 h, D: 24 h).

Micellar aggregations of Janus-dendritic copolymer

TEM characterization was carried out to determine the size of the micelles of Janusdendritic copolymer with different generations. The corresponding TEM images are shown in Figure S6.





(PSt)²/(PtBA)² (B) and J-(PSt)³/(PtBA)³ (C).