Supplementary Information for

Investigation on the fluorescence-(stimulus-response) properties of linear and star PVBCz-*b*-PDMAEMA block copolymers synthesized via ATRP

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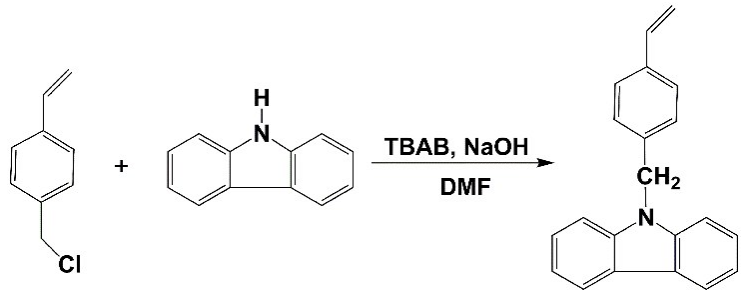
Synthetic procedures

Synthesis of monomer (VBCz)

VBCz was synthesized according to the reference[1]. A mixture of carbazole (5.00 g, 30.0 mmol), sodium hydroxide (1.20 g, 37.5 mmol) and tetra-*n*-butylammonium bromide (TBAB) (200 mg, 0.62 mmol) in DMF (100 mL) was stirred for 2 h. Then 1-(chloromethyl)-4-ethenyl-benzen (5.50 g, 36.0 mmol) was added dropwise, and the reaction mixture was continually stirred for 20 h at ambient temperature (scheme 1). The resulting mixture was precipitated in deionized water. The resultant white precipitate was filtered and dried under vacuum at 70°C. The crude product was purified by recrystallization from acetone to give 5.40 g of white crystals with a yield of 63.5%. ^{1}H-NMR(400 MHz, $CDCl_3$, δ, ppm): 5.18-5.20 (d, 1H, C**H**$_2$=C), 5.65 (s, 2H, N-C**H**$_2$), 5.71-5.76 (d, 1H, C**H**$_2$=C), 6.61-6.68 (m, 1H, CH$_2$=C**H**), 7.13-7.15 (d, 2H, Ar**H**), 7.21-7.64 (m, 8H, Ar**H**), 8.17-8.19 (d, 2H, Ar**H**). Anal.Calcd for $C_{21}H_{17}N$: C 89.01, H 6.05, N 4.94; Found: C 88.92, H 5.97, N 4.86.



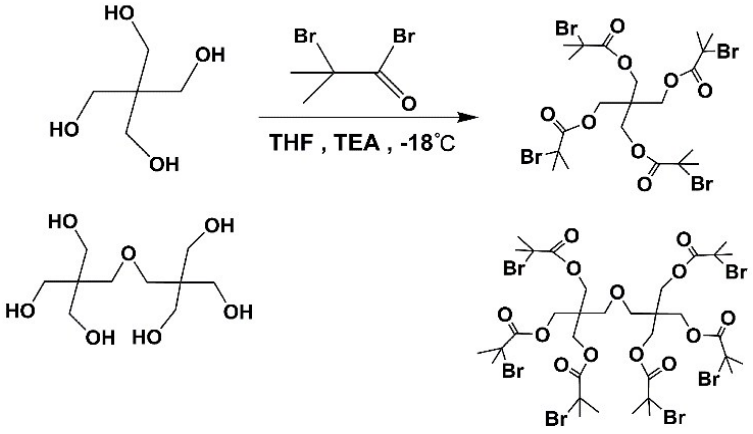
Scheme S1. Synthesis of the monomer (VBCz).

Synthesis of multi-functional initiators [2-4]

4-arm initiator Pentaerythritol (3.29g, 24.2mmol) (2.79, 50.0mmol), TEA (15.2mL, 108.7mmol) were added into a Schlenk flask along with anhydrous THF (100 mL) by syringe under argon. Cooling the mixture to -18 °C, and 2-Bromo-iso-butyryl bromide (BiBB) (13.5mL, 108.7mmol) dissolved in anhydrous THF (40 mL) was added dropwise (Scheme 1b). The reaction solution was subjected to continuous stirring for 24 h at room temperature and then diluted with CH_2Cl_2. The resulting organic extracts were washed twice with 200 mL HCl (2 M), twice with 200 mL saturated $NaHCO_3$, and twice with 200mL saturated NaCl in turn. The solution was then dried with anhydrous $MgSO_4$. (Scheme 2). The resultant mixture was filtered, concentrated, recrystallized from hot methanol and filtered to afford 11.5g (yield: 65%) of 4-arm initiator as a colorless crystalline solid. ^{1}H-NMR(400 MHz, $CDCl_3$, δ, ppm): 1.88 (s, 24H, 8C**H**$_3$), 4.27 (s, 8H, 4C**H**$_2$). ^{13}C-NMR(100 MHz, $CDCl_3$, δ, ppm): 29.7 (8**C**H_3), 42.9 (**C**$(CH_2O)_4$), 54.3 (4**C**Br), 61.8 (4**C**H_2O), 169.8 (4**C**=O). (Scheme S2)

6-arm initiator The procedure was the same as discussed in the previous section except that dipentaerythritol (2.20g, 7.85mmol) was used instead of ethylene elycol. TEA (10.0mL, 71.5mmol), anhydrous THF (100 mL) and 2-bromo-2-methylpropanoyl bromide (8.8mL, 70.9mmol) dissolved in anhydrous THF (20 mL) was added sequentially in this reaction (Scheme 2). This procedure afforded 5.1g (yiled: 52%) of 6-arm initiator as a colourless crystalline solid. 1H-NMR(400 MHz, CDCl3, δ, ppm): 1.94 (s, 36H, 12CH3), 3.60 (s, 4H, CH2OCH2), 4.29 (s, 12H,

6CH2O). 13C-NMR(100MHz, CDCl3, δ, ppm): 30.6 (12CH3), 43.9 (2C(CH2)4), 55.2 (6CBr), 63.2 (6CH2O), 69.3 (CH2OCH2), 170.6 (6C=O). (Scheme S2)



Scheme S2. Synthesis of the multi-functional initiators

Table S1 Reaction conditions of the star PVBCz

Sample	VBCz (mmol)	Initiator (mmol)	CuBr (mmol)	PMDETA (mmol)	[M]/[I]	Cyclohexanone (mL)	Reaction Time（h）
1-arm PVBCz	8.00	0.80	0.80	1.60	10	10	1
4-arm PVBCz	8.00	0.27	0.27	0.54	30	10	2
6-arm PVBCz	8.00	0.16	0.16	0.32	50	10	2

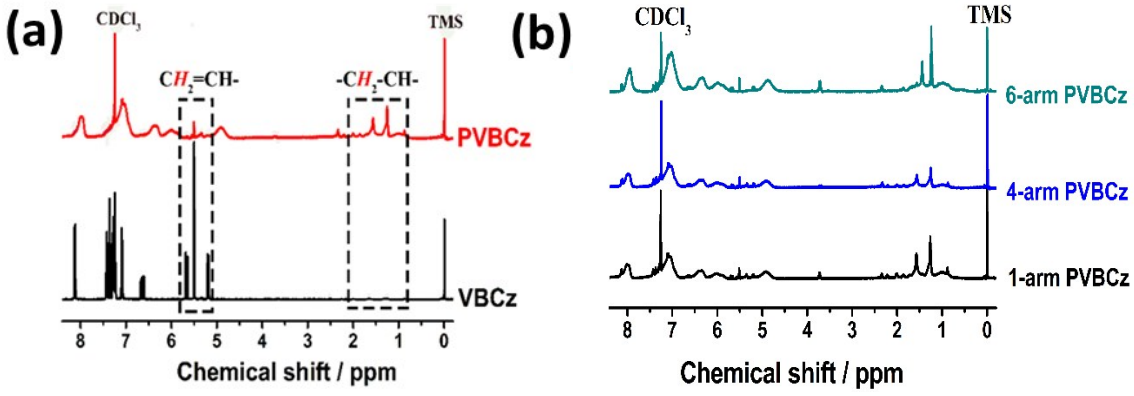


Fig. S1 [1]H-NMR spectra of (a) VBCz and 4-arm PVBCz. (b) the PVBCz linear and star polymers.

Table 2 Polymerization conditions and molecular weight parameters of the 6-arm PVBCz-*b*-PDMAEMA block copolymers.

Sample	feed ratio[a]	Reaction Time (h)	M_n[b] (×10⁴ g·mol⁻¹)	M_w[b] (×10⁴ g·mol⁻¹)	PDi[b]	DP_{arm}[c]	$Ratio_{arm,GPC}$[d]	$Ratio_{arm,NMR}$[d]
L6-1	100	2	4.17	5.80	1.39	8+30	1 : 3.8	1 : 4.4
L6-2	500	5	8.41	11.86	1.41	8+75	1 : 9.4	1 : 11.9
L6-3	800	7	13.33	15.86	1.19	8+106	1 : 13.3	1 : 12.4

[a] feed ratio is the ratio of VBCz to the initiator. [b] Determined by GPC. [c] DP, the number-average degree of polymerization of PVBCz ; [c] DP_{arm} , the number-average degree of polymerization of PVBCz on every arm.

[d] $Ratio_{arm,GPC}$, the block ratios of PVBCz to PDMAEMA calculated according to the GPC results; [d] $Ratio_{arm,NMR}$, the block ratios calculated according to the ^{1}H-NMR spectra.

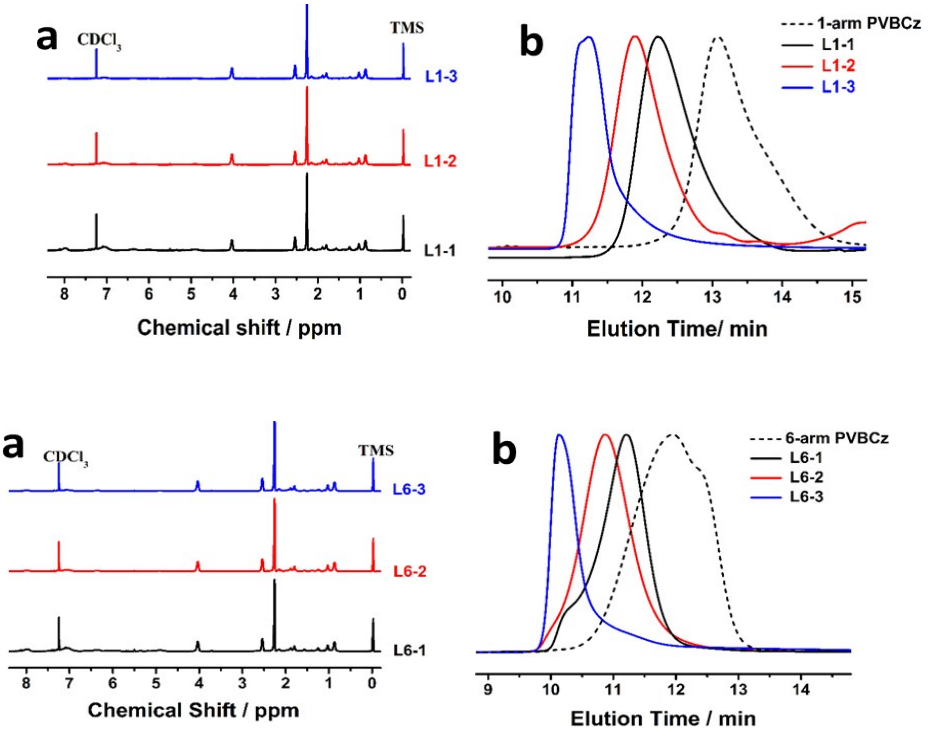


Fig. S2 ^{1}H-NMR spectra (a) and GPC traces (b) of the 1- and 6-arm PVBCz-*b*-PDMAEMA

Notes and references

1. J. L. Liu, W. W. He, L. F. Zhang, Z. B. Zhang, J. Zhu, L. Yuan, H. Chen, Z. P. Cheng and X. L. Zhu, *Langmuir* **2011**, 27, 12684-12692.

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3. Z. Zhang, T. Hughes, X. Hao and G. G. Qiao, *Polymer* **2013**, 54, 4446-4454.

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