

Electronic Supporting Information

AN EASY WAY TO THE PREPARATION OF MULTI-MIKTOARM STAR BLOCK COPOLYMERS VIA SEQUENTIAL DOUBLE CLICK REACTIONS

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EXPERIMENTAL

Materials

Styrene (St, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99%, Aldrich) were passed twice through basic alumina column to remove inhibitor and then distilled over CaH₂ in vacuum prior to use. Divinylbenzene (DVB, 80%, Aldrich) was purified twice by passing through a column of basic alumina to remove the inhibitor. *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99 % Aldrich) was distilled over NaOH prior to use. Tetrabutylammonium fluoride (TBAF, 1 M in THF, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), and CuBr (99.9%, Aldrich) were used as received. Dichloromethane (CH₂Cl₂, 99.9 %, J. T. Baker) was used after distillation over P₂O₅. Tetrahydrofuran (THF, 99.8%, J. T. Baker) was dried and distilled over benzophenone-Na. Solvents unless specified here were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received without further purification.

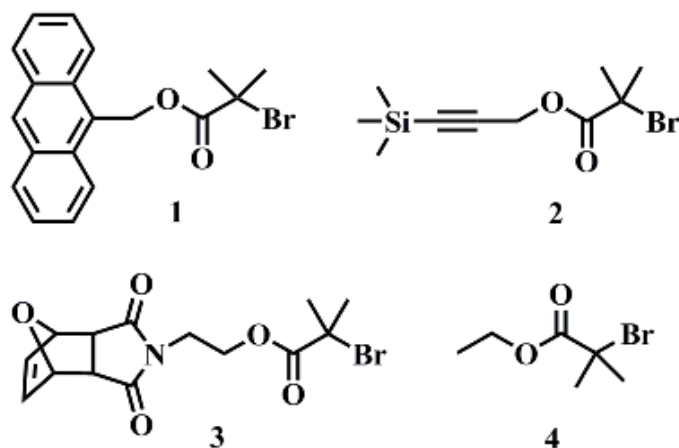
Instrumentation

The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective

molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500-20,000, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights ($M_{n,GPC}$ and $M_{w,GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS or linear PMMA standards using PL Caliber Software from Polymer Laboratories. The second GPC set-up (TD-GPC) with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering (DLS) ($\lambda = 670$ nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{w,TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard having narrow molecular weight distribution ($M_n = 115,000$ g/mol, $M_w/M_n = 1.02$, $[\eta] = 0.519$ dL/g at 35°C in THF, $dn/dc = 0.185$ mL/g) provided by Viscotek company. Data was collected by using Omni-Sec version 4.5 software from Viscotek Company. DVB conversion was determined by using an Agilent 6890N gas chromatography, equipped with an FID detector using a wide-bore capillary column (HP5, 30 m X 0.32 mm X 0.25 μ m, J and W Scientific). Injector and detector are kept constant at 280 and 285 °C, respectively. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2 .

Synthesis of initiators

9-Anthryl methyl 2-bromo-2-methyl propanoate **1**,¹ 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate **2**,² 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)-ethyl ester **3**³ were prepared according to published procedures.



ESI Scheme 1 chemical structure of initiators used for the preparation of linear precursors

One-pot synthesis of α -silyl protected alkyne- and α -anthracene-end-functionalized PS mixture (PS- α -silyl alkyne + PS-anthracene)

St (20.0 mL, 175 mmol), PMDETA (0.182 mL, 0.872 mmol), CuBr (0.125 g, 0.871 mmol), **1** (0.312 g, 0.873 mmol) and **2** (0.242 g, 0.873 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum. After the tube was placed in a thermostated oil bath at 110 °C for 40 min, the dark green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, precipitated in methanol and dried for 24 h in a vacuum oven at 40 °C. ($[M]_0/[I]_0 = 200$; $[I]_0:[CuBr]_0:[PMDETA]_0 = 1:1:1$, conversion (%) = 23, $M_{n,theo} = 5100$, $M_{n,NMR} = 6030$ (47 mol % α -anthracene- and 53 mol % α -silyl protected alkyne-end-functionalized PS), $M_{n,GPC} = 5400$, $M_w/M_n = 1.10$, relative to linear PS standards). 1H NMR ($CDCl_3$, δ) 8.4 (bs, 1H, ArH of anthracene), 8.2 (bs, 2H, ArH of anthracene), 7.9 (bs, 2H, ArH of anthracene), 7.5 (bs, 4H, ArH of anthracene), 7.2–6.5 (ArH of PS), 5.8 (CH_2 -anthracene), 4.4 (bs, $CH(Ph)$ -Br), 4.1 (m, $C\equiv CCH_2O$), 2.3-0.8 (CH_2 and CH), 0.16 ($(CH_3)_3Si$).

Synthesis of furan protected maleimide end-functionalized PMMA (PMMA-MI)

PMMA-MI was prepared according to a previously reported procedure⁴ ($[M]_0/[I]_0 = 50$, $[I]_0:[CuCl]_0:[PMDETA]_0=1:1:1$, conversion (%) = 56, $M_{n,theo} = 2800$, $M_{n,NMR} = 3000$, $M_{n,GPC}$

= 3900, $M_w/M_n = 1.17$, relative to linear PMMA standards). ^1H NMR (CDCl_3 , δ) 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, $\text{CHCH}=\text{CHCH}$, bridge-head protons), 4.1 (m, 2H, $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$), 4.0-3.2 (m, OCH_3 of PMMA and $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$), 2.9 (s, 2H, $\text{CH}_2\text{NC}=\text{OCH}-\text{CH}$, bridge protons), 2.5-0.5 (m, CH_2 and CH_3 of PMMA).

Synthesis of azide end-functionalized PtBA (PtBA- N_3)

PtBA- N_3 was prepared in two steps according to a previously reported procedure.⁵ First, bromo end-functionalized PtBA (PtBA-Br) was prepared by ATRP of *t*BA using ethyl 2-bromoisobutyrate (EiBr) as an initiator and CuBr/ PMDETA as catalyst in ethylene carbonate for 30 min at 80 °C. ($[\text{M}]_0/[\text{I}]_0 = 100$, $[\text{I}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0 = 1:1:1$, conversion = 25%, $M_{n,\text{theo}} = 3400$, $M_{n,\text{NMR}} = 5100$, $M_{n,\text{GPC}} = 3500$, $M_w/M_n = 1.16$, relative to PS standards). ^1H NMR (CDCl_3 , δ), 4.07 (d, $\text{CH}_3\text{CH}_2\text{OC}=\text{O}$ and CHBr end group of PtBA), 2.2 (bs, CH of PtBA), 2.0–1.0 (m, CH_2 and CH_3 of PtBA). Second, PtBA-Br was converted into azido group using NaN_3 in DMF at 50 °C. (Yield = 0.9 g, 95%, $M_{n,\text{theo}} = 3350$, $M_{n,\text{NMR}} = 5100$, $M_{n,\text{GPC}} = 3800$, $M_w/M_n = 1.10$, relative to linear PS standards). ^1H NMR (CDCl_3 , δ), 4.05 (d, $\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 3.65 (d, CHN_3 end group of PtBA), 2.2 (bs, CH of PtBA), 2.0-1.0 (m, CH_2 and CH_3 of PtBA).

Synthesis of (alkyne-PS)_m-polyDVB-(PS-anthracene)_m multiarm star polymer bearing alkyne and anthracene functionalities at the periphery

PS- α -silyl alkyne + PS-anthracene (2.1 g, 0.38 mmol, based on $M_{n,\text{GPC}}$), anisole (13.0 mL), PMDETA (0.080 mL, 0.38 mmol), DVB (0.815 mL, 5.72 mmol), and CuBr (0.055 g, 0.38 mmol) were charged to a Schlenk tube equipped with a magnetic stirrer bar under argon. The first sample was quickly taken from the reaction mixture for GC measurement, before it was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in a 110 °C oil bath. At specified intervals, samples were taken from the reaction mixture with argon purged-syringe under positive argon atmosphere. The samples were

diluted with THF and purified by passing through short neutral alumina column to remove the copper salt and then filtered through poly(tetrafluoro ethylene) (PTFE) filter (0.2 μm pore size) prior to GC and GPC analyses. The reaction was stopped after 12 h at 94 % conversion via exposure to air. The reaction mixture was diluted with THF, then filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was easily purified via dissolution in THF and then precipitation in methanol/ether (1/2; v/v) mixture to remove the linear chains. Finally, the polymer was dried under vacuum at 40 $^{\circ}\text{C}$ for 24 h.

Subsequently, silyl groups at the periphery of the multiarm star homopolymer (1.2 g, 4.8 μmol) was deprotected by using tetrabutyl ammonium fluoride (TBAF) (0.2 mL, 0.2 mmol) in THF (20 mL). The reaction mixture was stirred for 2 h at room temperature and precipitated in methanol. The recovered polymer was dried under vacuum at 40 $^{\circ}\text{C}$ for 24 h.

Synthesis of (PtBA)_n-(PS)_m-polyDVB-(PS-anthracene)_m multi-miktoarm star block copolymer via click reaction

The (alkyne-PS)_m-polyDVB-(PS-anthracene)_m multiarm star polymer (0.3 g, 1.20 μmol , based on $M_{w,\text{TDGPC}}$) and PtBA-N₃ (0.122 g, 0.024 mmol, based on $M_{n,\text{NMR}}$) were dissolved in nitrogen purged DMF (8 mL) in a Schlenk tube. CuBr (8.5 mg, 0.06 mmol) and PMDETA (12 μL , 0.06 mmol) were added in that order, and the reaction mixture was degassed by three FPT cycles, and stirred at room temperature for 24 h. The solution was passed through a column of neutral alumina to remove the copper salt and precipitated into methanol. The crude product was purified by dissolution in THF and then precipitation in methanol/diethyl ether mixture (1/1; v/v). Finally, polymer was dried in a vacuum oven at 40 $^{\circ}\text{C}$ for 24 h.

Synthesis of (PtBA)_n-(PS)_m-polyDVB-(PS)_m-(PMMA)_k multi-miktoarm star block copolymer via Diels Alder click reaction

A solution of PMMA-MI (0.025 g, 8.33 mmol, based on $M_{n,NMR}$) in 10 mL of toluene was added to a 10 mL solution of (PtBA)_n-(PS)_m-polyDVB-(PS-anthracene)_m (0.15 g, 0.422 μmol, based on $M_{w,TDGPC}$). The reaction mixture was bubbled with nitrogen for 30 min and refluxed for 48 h under nitrogen in the dark. After a specified time toluene was evaporated under vacuum and the residual polymer was dissolved in THF, subsequently precipitated in methanol. The dissolution-precipitation was repeated two times and finally polymer was dried in a vacuum oven at 40 °C for 24 h.

TD-GPC measurements for all star polymers

Refractive index (RI), light scattering (LS) and differential viscometer detectors in Viscotek TD-GPC instrument provides more advanced and accurate technique to measure the absolute molecular weight ($M_{w,TDGPC}$) of star polymer, if refractive index increment (dn/dc) of the analyzed polymer is known. After introducing this dn/dc to the instrument, $M_{w,TDGPC}$, $[\eta]$ and R_h of the analyzed polymer is obtained using the OmniSEC software.

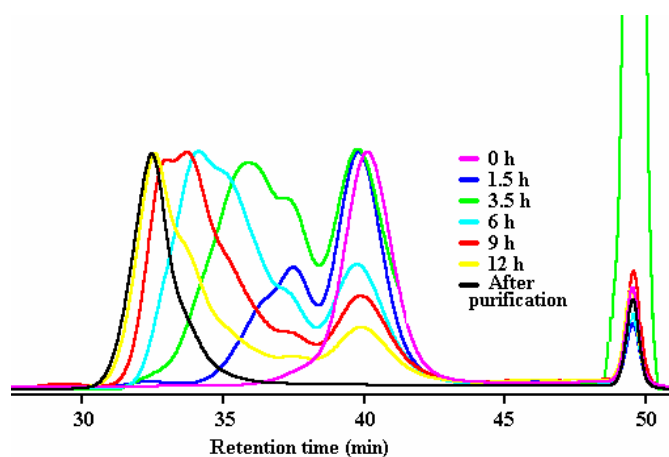
Although, dn/dc of linear PS is available, an attempt has been made to clarify the effect of cross-linked DVB core on dn/dc value of PS multiarm star polymer. Therefore, the dn/dc of (alkyne-PS)_m-polyDVB-(PS-anthracene)_m star polymer was measured by TD-GPC instrument and found to be 0.185 mL/g in THF at 35 °C, which is equal to that of linear PS. Here, the dn/dc value was calculated from a slope of RI Area-concentration (g/mL) linear plot containing at least four different polymer concentrations. The calculation is based on an assumption that truly size-exclusion mechanism is operative in the columns of GPC. This experimental dn/dc value is subsequently introduced to the TD-GPC to give $M_{w,TDGPC}$, $[\eta]$ and R_h of the analyzed (alkyne-PS)_m-polyDVB-(PS-anthracene)_m star polymer.

Moreover, dn/dc values of star block copolymers are obtained by using two methodologies. The first methodology depends on assumption that dn/dc value correlates linearly with composition of block copolymer in the following equation:

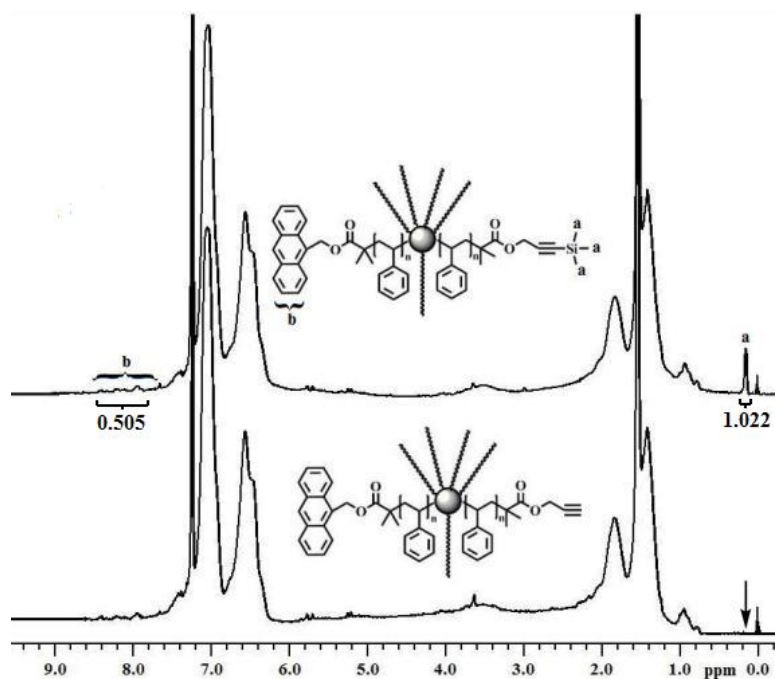
$$(dn/dc)_{\text{block copolymer}} = x (dn/dc)_A + y (dn/dc)_B$$

Where x and y are weight fractions of A and B blocks of star block copolymer from $^1\text{H NMR}$. This calculated dn/dc value is then introduced to the TD-GPC in order to achieve $M_{w,\text{TDGPC}}$, $[\eta]$ and R_h of the analyzed star block copolymer.

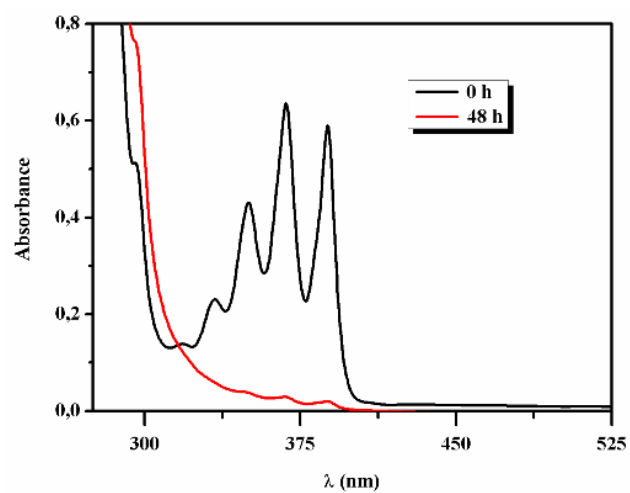
In a second methodology, the dn/dc value of the star block copolymer was calculated from a slope of RI Area-concentration (g/mL) linear plot containing at least four different star block copolymer concentrations. The calculation is based on the assumption that truly size-exclusion mechanism is operative in the columns of GPC. The experimental dn/dc value is then introduced to the TD-GPC to give $M_{w,\text{TDGPC}}$, $[\eta]$ and R_h of the analyzed star block copolymer.



ESI Figure 1 Evolution of GPC traces during the preparation of (alkyne-PS)_m-polyDVB-(PS-anthracene)_m multiarm star polymer ($[DVB]_0/15 = [PS-Br]_0 = [CuBr]_0 = [PMDETA]_0 = 0.023$ M in anisole at 110 °C).



ESI Figure 2 ¹H NMR spectra of α -silyl alkyne-PS)_m-polyDVB-(PS-anthracene)_m and (alkyne-PS)_m-polyDVB-(PS-anthracene)_m multiarm star polymers in CDCl₃.



ESI Figure 3 UV spectra of $(PtBA)_n$ - $(PS)_m$ -polyDVB- $(PS$ -anthracene) $_m$ (at 0 h) and $(PtBA)_n$ - $(PS)_m$ -polyDVB- $(PS)_m$ - $(PMMA)_k$ (after 48 h) multi-miktoarm star block copolymer ($C_0 = 2.27 \times 10^{-6}$ mol anthracene /L in CH_2Cl_2 at 366 nm, $\epsilon_{max} = 9451$).

ESI Table 1 TD-GPC characterization of multiarm star and multi-miktoarm star block copolymers

Polymers	TD-GPC ^a							
	M_w/M_n	M_w	$M_{w,theo}$	$[\eta]$ (dL/g)	R_h (nm)	dn/dc (mL/g)	f	
(alkyne-PS) _m -polyDVB-(PS-anthracene) _m	(1.26)	(250000)	250000	(0.155)	(8.28)	(0.185)	31 ^e	27 ^f
(PtBA) _n -(PS) _m -polyDVB-(PS-anthracene) _m	1.25 (1.26)	355000 (350000)	321000 ^b	0.142 (0.150)	9.03 (9.13)	0.146 ^d (0.151)	-	-
(PtBA) _n -(PS) _m -polyDVB-(PS) _m - (PMMA) _k	1.30 (1.31)	407000 (414000)	385000 ^c	0.177 (0.171)	10.1 (10.0)	0.137 ^d (0.133)	-	-

^a data in parentheses are obtained from TD-GPC by using experimental dn/dc values.

^b $M_{w,theo} = M_{w,TDGPC}$ of (alkyne-PS)_m-polyDVB-(PS-anthracene)_m + 17 X $M_{w,GPC}$ of linear PtBA-N₃;

^c $M_{w,theo} = M_{w,theo}$ of (PtBA)_n-(PS)_m-polyDVB-(PS-anthracene)_m + 14 X $M_{w,GPC}$ of linear PMMA-MI;

^d calculated according to: $(dn/dc)_{block\ copolymer} = x (dn/dc)_{PS} + y (dn/dc)_{PtBA\ or\ PMMA}$

where x and y are weight fractions of PS and PMMA/or PtBA blocks calculated from ¹H NMR.

After dn/dc value is introduced to the OmniSec software, corresponding M_w , $[\eta]$ and R_h data are obtained.

^e number of arms in multiarm star polymer was calculated according to:

$$f = M_{w,star} / (M_{w,arm} + MW\ of\ DVB\ X\ conv.\ of\ DVB\ X\ ([DVB]_0/[PS-Br]_0))$$

where $M_{w,star}$ and $M_{w,arm}$ are the absolute molecular weights of the (alkyne-PS)_m-polyDVB-(PS-anthracene)_m star polymer and linear PS-Br (a mixture of PS- α -silyl alkyne and PS-anthracene), respectively obtained from TD-GPC instrument introducing the predetermined dn/dc = 0.185 value of the PS to the OmniSEC software.

^f number of arms in multiarm star polymer was calculated according to: $g' = [\eta]_{star} / [\eta]_{linear}$ ($M = constant$) and

$\log g' = 0.36 - 0.8 \log f$ where $[\eta]_{star}$ and $[\eta]_{linear}$ are the intrinsic viscosities of star polymer and the linear polymer with the same molecular weight and the composition, respectively.

REFERENCES

1. M. Erdogan, D. Hayrabetyan, G. Hizal, U. Tunca, O. Pekcan, *Polymer* 2002, **43**, 1925-1931.
2. J. A. Opsteen, J. C. M. Van Hest, *Chem. Commun.*, 2005, **1**, 57-59.
3. G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornellisen, K. Velonia, *J. Am. Chem. Soc.*, 2005, **127**, 2966-2973.
4. A. Dag, H. Durmaz, G. Hizal, U. Tunca, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 302-313.
5. H. Durmaz, A. Dag, E. Erdogan, A. L. Demirel, G. Hizal, U. Tunca, *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48**, 99-108.