Monomer Sequence Determination in the Living Anionic Copolymerization of Styrene

and Asymmetric Bi-Functionalized 1,1-Diphenylethylene Derivatives

Wei Sang,[‡] Hongwei Ma,[‡] Qiuyun Wang, Xinyu Hao, Yubin Zheng, Yurong Wang, Yang Li*

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

Liaoning Key Laboratory of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

[‡]These authors contributed equally as co-first.

* E-mail: mahw@dlut.edu.cn (H. Ma), liyang@dlut.edu.cn (Y. Li)

Synthesis of (4-bromophenyl)(4'-dimethylamino)methanone (BP-Br/NMe₂)

BP-Br/NMe₂ was prepared as in the literature¹. Specifically, a grain of iodine and 30 g of magnesium shavings (1.25 mol) were placed in a 2,000-mL three-necked Schlenk flask. Then, 50 g of 4-bromo-N,N-dimethylaniline (0.25 mol) was dissolved in 600 mL of dry THF, and 50 mL of the solution was added dropwise into the flask under vigorous stirring and heated until bubbles appeared on the surfaces of the magnesium shavings. Then, the remainder of the solution was added dropwise into the flask. Subsequently, the flask was heated to THF reflux and kept at the temperature for 2 h. After the reaction was completed, the orange color solution was transferred into the other 2,000-mL three-necked round-bottom flask. Then, 50 g of 4-bromobenzonitrile (0.275 mol) was dissolved in 200 mL of THF and added dropwise into the flask. After refluxing the THF for 2 h, 200 mL of deionized water was added dropwise into the reaction solution. The solution was stirred and kept at room temperature overnight for hydrolysis. Then, the mixture was diluted with brine and extracted with diethyl ether (3×200 mL). The aqueous layer was further extracted with diethyl ether and the organic layer was collected and dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate 4:1 v/v (R_f =0.35) followed by recrystallization twice to yield pure BP-Br/NMe₂ as a yellow powder in 75% yield (57.0 g, 0.187 mol). ¹H NMR (CDCl₃): δ 3.09 (s, 3H, N-CH₃), 6.69, 7.60, 7.76 ppm (m, 8H, aromatic C-H).

Synthesis of 1-(4-bromophenyl)-1'-(4-dimethylamino)ethylene (DPE-Br/NMe₂)

A cooled (ice bath, 0 °C), 1,000-mL three-necked round-bottom flask was equipped with a magnetic stirring bar, and methyltriphenylphosphonium bromide (62.0 g, 0.174 mol) and dry THF (100 mL) were added successively with stirring. Potassium tert-butoxide (18.0 g, 0.16 mol) was dissolved in 100 mL of THF and added dropwise into the flask at 0 °C under an argon atmosphere. After stirring for 30 min, BP-Br/NMe₂ (30.4 g, 0.1 mol) was dissolved in 300 mL of THF and added dropwise into the flask. The reaction was stirred under an argon atmosphere for 12 h, and 10 mL of deionized water was added to the flask to terminate the reaction. The mixture was diluted with brine and extracted with diethyl ether 3 times (3×200 mL). Then, the aqueous layer was further extracted with diethyl ether and the organic layer was collected and dried with anhydrous MgSO₄ overnight. The solution was filtered and concentrated under reduced pressure, and then, flash column chromatography was performed twice using hexane (R_f =0.4). A 92% yield of DPE-Br/NMe₂ (27.8 g, 0.092 mol) was reserved, and it was characterized by ¹H NMR (CDCl₃): ¹H NMR (CDCl₃): δ 2.97(d, 6H, N(CH₃)₂), δ 5.23, 5.37(d, 2H, =CH₂), 6.67, 7.19, 7.24, 7.44 ppm (m, 8H, aromatic C-H).

Synthesis of 1-(4-dimethylamino)-1'-(4-dimethylsilanephenyl)ethylene (DPE-SiH/NMe₂)

A grain of iodine and 12 g of magnesium shavings (0.5 mol) were added to a 1,000-mL three-necked round-bottom flask. DPE-Br/NMe₂ (30.2 g, 0.1 mol) was dissolved in 600 mL of dried THF, and added dropwise into the flask. Then, the flask was heated to THF reflux and kept under an argon atmosphere for 4 h. Until the Grignard reaction was completed, the solution was transferred to another three-necked flask. Then, chlorodimethylsilane (18.8 mL, 0.15 mol) was added

dropwise into the same flask, and the solution was stirred at room temperature overnight. Then, the reaction was terminated by adding deionized water. The mixture was diluted with brine and extracted with diethyl ether 3 times (3×200 mL). The aqueous layer was further extracted with diethyl ether and the organic layer was collected and dried over anhydrous MgSO₄ overnight. The solution was filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/dichloromethane 9:1 v/v ($R_f = 0.7$) followed by silica gel column chromatography using hexane/dichloromethane 9:1 v/v ($R_f = 0.7$) followed by silica gel column chromatography using hexane/ethyl acetate 19:1 v/v ($R_f = 0.6$) to give pure DPE-SiH/NMe₂ at a 75% yield (21.0 g, 0.075 mol). ¹H NMR (CDCl₃, Fig. 1Sb in ESI⁺): δ 0.36, 0.38 (d, 6H, Si(CH₃)₂), 2.98 (m, 6H, N(CH₃)₂), 4.45 (m, 1H, Si-H), 5.28, 5.39(d, 2H, =CH₂), 6.68, 6.70, 7.23, 7.25, 7.36, 7.38, 7.50, 7.52 ppm (m, 8H, aromatic C-H). ¹³C NMR (CDCl₃, Fig. 2Sb in ESI⁺): δ -3.40 (Si-(CH₃)₂), 40.69 (N(CH₃)₂), 112.23 (C=C^{*}H₂), 136.61 (aromatic C^{*}-Si(CH₃)₂H), and 149.99 ppm (>C^{*}=CH₂). ²⁹Si NMR (CDCl₃): δ -4.424 (aromatic C-Si^{*}(CH₃)₂H). The mass spectrum is shown in Fig. 3Sb.

Synthesis of (4-bromophenyl)(4'-methoxyphenyl)methanone (BP-Br/OMe)

The synthesis methods have been reported in the literature². 4-Bromobenzoyl chloride (22.0 g, 0.1 mol) and AlCl₃ (21.3 g, 0.16 mol) were dissolved in nitrobenzene (200 mL), and the mixture was added dropwise into a 500-mL threenecked round-bottom flask. While stirring in an ice bath under an argon atmosphere, anisole (10.8 mL, 0.1 mol) dissolved in nitrobenzene (90 mL) was added to the flask. The temperature was kept below 15 °C, and the solution was stirred for 3 h. Aqueous HCl (38%, 25 mL) and 200 g of crushed ice were placed in a 1,000-mL beaker, and the reaction solution was poured slowly into the ice-water mixture with strong stirring. Then, the solution was hydrolyzed overnight, and the layers were delaminated. The aqueous layer was further extracted with CH_2Cl_2 (3×200 mL). The organic layer was collected and washed with brine, dried over anhydrous MgSO₄ overnight, filtered, and concentrated under reduced pressure. The red-brown solid was added to activated carbon and dissolved in alcohol, refluxed for more than 48 h, filtered, and recrystallized twice in alcohol to afford 24.8 g (0.085 mol, 85% yield) of pure BP-Br/OMe as a white solid. ¹H NMR (CDCl₃): δ 3.90 (s, 3H, O-CH₃), 6.97, 7.63, 7.79ppm (m, 8H, aromatic C-H).

Synthesis of 1-(4-bromophenyl)-1'-(4-methoxyphenyl)ethylene (DPE-Br/OMe)

DPE-Br/OMe was prepared in a similar manner as DPE-Br/NMe₂, and the experimental operations have been reported in the literature³. A cooled (ice bath, 0 °C), 1000 mL three-necked round-bottomed flask was equipped with a magnetic stirring bar, methyltriphenylphosphonium bromide (62.01 g, 0.174 mol) and dry THF (100 mL) was added successively and stirring. Potassium tert-butoxide (17.95 g, 0.16 mol) was dissolved in 100 mL THF, and added dropwise into the flask at 0 °C under nitrogen atmosphere. After stirred half an hour, BP-Br/OMe (29.1 g, 0.1 mol) was dissolved in 300 mL THF, and drop-wise added into the flask. The reaction was stirred under a nitrogen atmosphere for 12 h, and 10 mL H₂O was added into the flask to terminate the reaction. The mixture was diluted with brine and exacted with diethyl ether for 3 times (3×200 mL), then the aqueous layer was further extracted with diethyl ether and the organic layer was collected and dried with anhydrous MgSO₄ overnight. The solution was filtrated and concentrated under reduced pressure, and then the flash column chromatography was taken as twice using hexane (R_f =0.46). The 91% yield of DPE-Br/OMe (26.3 g, 0.091 mol) was reserved, and it was characterized by ¹H NMR (CDCl₃): δ 5.33, 5.39 (d, 2H, =CH₂), 3.80 (s, 3H, O-CH₃), 6.86, 7.23, 7.45 ppm (m, 8H, aromatic C-H).

Synthesis of 1-(4-methyloxyphenyl)-1'-(4-dimethylsilanephenyl)ethylene (DPE-SiH/OMe)

DPE-SiH/OMe was prepared in a similar manner as DPE-SiH/NMe₂, and the experimental operations have been reported in the literature³. A grain of iodine crystal and 12 g magnesium shavings (0.5 mol) were added into a three-necked, round-bottom flask. DPE-Br/OMe (28.9 g, 0.1 mol) was dissolved in 600 mL dried THF, and drop-wise added into the flask. Then the flask was heated to THF reflux and kept for four hours under a nitrogen atmosphere. Until the Grignard reaction was completed, the solution was transferred to another three-necked flask. Then chlorodimethylsilane (16.7 mL, 0.15 mol) was drop-wise added into the same flask, and the solution was stirred at room temperature overnight. Then the reaction was terminated by adding deionized water, the mixture was diluted with brine and exacted with diethyl ether for 3 times (3×200 mL), the aqueous layer was further extracted with diethyl ether and the organic layer was collected and dried over anhydrous MgSO₄ overnight. The solution was filtrated and

concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate 29:1 v/v (R_f =0.6) followed by re-crystallization twice to give pure DPE-SiH/OMe in 78% yield (20.9 g, 0.078 mol). ¹H NMR (CDCl₃, Fig. 1Sa in ESI⁺): δ 0.35, 0.37 (d, 6H, Si(CH₃)₂), 3.83 (s, 3H, O-CH₃), 4.44 (m, 1H, Si-H), 5.37, 5.41(d, 2H, =CH₂), 6.86, 6.88, 7.27, 7.29, 7.33, 7.35, 7.50, 7.52 ppm (m, 8H, aromatic C-H). ¹³C NMR (CDCl₃, Fig. 2Sa in ESI⁺): δ -3.56 (Si-(CH₃)₂), 55.32 (O-CH₃), 113.70 (C=C^{*}H₂), 136.86 (aromatic C^{*}-Si(CH₃)₂H), and 149.60 ppm (>C^{*}=CH₂). ²⁹Si NMR (CDCl₃): δ -17.446 ppm (aromatic C-Si^{*}(CH₃)₂H). The mass spectrum is shown as Fig. 3Sa.



Fig. 1S ¹H NMR spectra (in CDCl₃, 400 MH_z) of DPE derivative monomer: a) DPE-SiH/OMe b) DPE-SiH/NMe₂



Fig. 2S ^{13}C NMR spectra (in CDCl_3, 400 MH_z) of DPE derivative monomer: a) DPE-SiH/OMe b) DPE-SiH/NMe_2



Chemical Formula: C₁₇H₂₀OSi Exact Mass: 268.13 Molecular Weight: 268.43 m/z: 268.13 (100.0%), 269.13 (23.7%), 270.13 (4.5%), 270.14 (1.6%) Elemental Analysis: C, 76.07; H, 7.51; O, 5.96; Si, 10.46



Fig. 3S Mass spectra of DPE derivative monomer: a) DPE-SiH/OMe b) DPE-SiH/NMe₂.

Table 1S.	Equations	referred t	to in th	is paper.	

No.	Equation Expression	Note
		ref. ^{4,5} , "Area[-OCH ₃]" is δ 3.6-3.8 ppm, "Area[-
1	$\frac{SN_{\rm D}}{8N_{\rm D}+5N_{\rm c}} = \frac{Area[-0CH_3]}{Area[aromatic region]}$	$N(CH_3)_2]$ " is δ 2.7-3.0 ppm, "Area[aromatic
		region]" is δ 5.0-7.5 but subtracted the area of
2	$6N_{D}$ _ Area[-N(CH ₃) ₂]	CDCl_3 region (δ 7.25-7.30 $$ ppm), N_S and N_D are
2	$\frac{1}{8N_{p}+5N_{s}}$ Area[aromatic region]	the average numbers of styrene and DPE
_		derivative units in the polymer chains,
3	$N_{D} \times M_{D} + N_{S} \times M_{S} = M_{n}$	respectively; M_S and M_D are the molecular
		weights of styrene and DPE derivative,
4	$Conv_{DPE} = \frac{N_D}{[M_1]} \times 100\% = (\frac{[M_S]_0}{[M_1]} / \frac{N_S}{N}) \times 100\%$	respectively; and $[M_S]_0$ and $[M_D]_0$ are the initial
4	$N_{s} \times \frac{[M_{D}]_{0}}{[M_{s}]_{0}} \qquad [M_{D}]_{0} \qquad N_{D}$	monomer concentrations of styrene and DPE
	- 340	derivative, respectively.
5	F= <u>Area[e]</u> ×100%	"e" is the proton in the end of polymer chain, δ
5	$^{-\text{DPE}}$ Area[-OCH ₃]/3/N _D	2.8-2.9 ppm.
		$[M_S]$ and $[M_D]$ are the final monomer
6	$[M_{D}]_{p} = [M_{D}]_{0} - [M_{D}]$	concentrations of styrene and DPE derivative,
		respectively; $[M_S]_p$ and $[M_D]_p$ are the content of
		styrene and DPE derivative in the polymer
		chains, respectively, and $[M_S]_p/[M_D]_p=N_S/N_D$ due
7	$[M_{s}]_{0} = [M_{s}]_{0} - [M_{s}]$	to the solution volume remains unchanged
		during polymerization process. If styrene
		monomer was consumed completely, then have
		$[M_{S}]=0$ and $[M_{S}]_{0}=[M_{S}]_{P}$.
8	$\ln \frac{[M_{D}]}{1} + \frac{1}{1} \ln \{\frac{[M_{S}]_{0}}{1} + (r_{S} - 1) + 1\} = 0$	ref. ⁶ , the graphical method for simplified
-	$[M_D]_0$ r _s -1 $[M_D]_0$	calculation of r _s was shown in ESI ⁺ .
0	$a_{s}^{0} - \alpha_{s}$	ref.5, ρ is the reactivity constant, and σ is the
9	r _s	substituent constant.
10	$T = (^{\circ}C) - 100 - (8.4 \times 10^4 / M)$	raf ⁵
10	$r_{g,PS}$ (C)=100 (0.4×10 / W_n)	
11	$B = -\frac{dM_s}{dM_s} = (k [S^{-1/2} + k [D^{-1/2})]M] = k [M]$	
11	$dt = \frac{1}{2} \left(\frac{1}{2} \frac{1}$	raf ⁷
10	$dM_{p} = dM_{p}$	
12	$\kappa_{\rm D} = -\frac{1}{dt} = (\kappa_{\rm SD}[S_{\rm D}]^{*} + \kappa_{\rm DD}[D_{\rm D}]^{*})[[m_{\rm D}] = \kappa_{\rm D}[m_{\rm D}]$	
13	[S [*]]+[D [*]]=[I]	[I] is the concentration of the initiator.
14	$\ln \frac{[M_s]_0}{2} - k + 1$	
14	$[M_s]^{-\kappa_s c}$	rof 7
	[M_]	101.7.
15	$\ln \frac{1}{[M_{\rm D}]} = k_{\rm D} t$	
	- 6-	ref. ⁵ , w _s and w _D are the fractions of styrene and
16	$1/T_{e} = W_{c}/T_{ec} + W_{D}/T_{eD}$	DPE derivative in the copolymer, respectively.
	ט,איט געס ג א	and $T_{e,S}$, $T_{e,D}$, and T_{e} are the glass transition

temperatures of the homopolystyrene, the homopolymer of DPE derivative, and the copolymer of styrene with the corresponding DPE derivative, respectively.

Sample ^a	Time	M _n ^b	PDI ^b	N _S /N _D ^c	N _S ^d	Conv. _{St} ^e	Conv. _{st} ^e N _D ^h	Conv. _{DPE} ⁱ	$E_{DPE}{}^{j}$
	(min)	(kg/mol)				(%)		(%)	(%)
	0	N/A	N/A	N/A	N/A	N/A	1.0	N/A	N/A
	30	2.9	1.10	4.5	17.4	48.5	3.9	43.3	96.1
	60	4.4	1.13	4.4	26.3	73.3	6.0	66.7	92.3
	90	5.0	1.15	4.4	29.9	83.3	6.8	75.6	96.8
I	120	5.3	1.15	4.3	31.6	88.0	7.3	81.1	94.1
	150	5.5	1.16	4.3	32.7	91.1	7.6	84.4	99.6
	180	5.7	1.16	4.2	33.6	93.6	8.0	88.9	>99.9
	210	5.8	1.17	4.2	34.3	95.5	8.1	90.0	>99.9
	240	5.9	1.19	4.2	34.8	96.9	8.3	92.2	99.5
	270	5.9	1.18	4.2	34.8	96.9	8.3	92.2	98.2
	300	6.0	1.18	4.2	35.5	98.9	8.4	93.3	99.3
	360	6.1	1.18	4.2	35.9	100.0	8.6	95.6	>99.9
	420	6.1	1.18	4.2	35.9	100.0	8.6	95.6	>99.9
	0	N/A	N/A	N/A	N/A	N/A	1.0	N/A	N/A
II	30	2.1	1.19	4.9	12.7	36.2	2.6	29.5	N/A
	60	2.8	1.23	4.6	16.6	47.3	3.6	40.9	N/A
	90	3.5	1.24	4.5	20.7	59.0	4.6	52.3	N/A
	120	4.2	1.24	4.4	24.7	70.4	5.6	63.6	N/A
	150	4.6	1.23	4.4	27.0	76.9	6.2	70.5	N/A
	180	4.9	1.25	4.4	28.8	82.1	6.6	75.0	N/A
	210	5.2	1.24	4.4	30.5	86.9	7.0	79.5	N/A
	240	5.5	1.24	4.3	32.0	91.2	7.5	85.2	N/A
	270	5.8	1.25	4.3	33.8	96.3	7.9	89.8	N/A
	300	5.9	1.25	4.3	34.5	98.3	8.0	90.9	N/A
	360	6.0	1.25	4.3	35.1	100.0	8.2	93.2	N/A
	420	6.0	1.25	4.3	35.1	100.0	8.2	93.2	N/A

Table 2S The time sampling results for the copolymerization of styrene (M_s) and DPE-SiH/R (M_D).

^{*a*} P(St-co-DPE-SiH/OMe) (I), P(St-co-DPE-SiH/NMe₂) (II) are copolymerized at 25 °C, the monomer molar feed ratio [M_s]₀/[M_p]₀=4, and [M_s]₀/[I] is set to 30. ^{*b*} Determined by SEC. ^{*c*} The ratio of the two monomer units in the final copolymer, calculated from the ¹H NMR spectra of the copolymers using Equations 1 and 2. ^{*d*} The average number of styrene units in each chain is calculated from the ¹H NMR spectra. ^{*e*} The relative conversion of styrene. ^{*f*} The average number of DPE in each chain is calculated from the ¹H NMR spectra using Equation 3. ^{*g*} The relative conversion of DPE. ^{*h*} The end-capped ratio of DPE-SiH/OMe, is calculated using Equation 5. The end-capped ratio of DPE-SiH/NMe₂, could not be calculated from the corresponding ¹H NMR spectra.



Fig. 4S DSC curves of polymers: a) O1-O7 in Table 2, AO1-AO3 and PS in Table 6; b) N1-N7 in Table 3, AN1-AN3 and PS in Table 6.







Fig. 5S MALDI-TOF mass spectra of I in Table 4.



Fig. 6S MALDI-TOF spectrum for the copolymer of AN3.



Fig. 7S 1 H NMR spectra (in CDCl₃, 400 MH_z) of AO3 and AN3.



Fig. 8S HSQC NMR spectra (in $CDCI_3$, 400 MH_z) of AO3 and AN3.

A Graphical Method of Simplified Calculation for r_s:

To simplify Equation 8 in Table 1S, the first step is transposition:

$$\left(\frac{[M_{\rm D}]}{[M_{\rm D}]_{\rm 0}}\right)^{1-r_{\rm S}} = \frac{[M_{\rm S}]_{\rm 0}}{[M_{\rm D}]_{\rm 0}}(r_{\rm S}-1)+1$$
(S1)

Set

$$\frac{[M_{s}]_{0}}{[M_{D}]_{0}} = m, \qquad \frac{[M_{s}]_{p}}{[M_{D}]_{p}} = n.$$

Then

$$\left[\mathsf{M}_{\mathsf{D}}\right]_{\mathsf{0}} = \frac{\left[\mathsf{M}_{\mathsf{S}}\right]_{\mathsf{0}}}{\mathsf{m}} \tag{S2}$$

$$\left[\mathsf{M}_{\mathsf{D}}\right]_{\mathsf{p}} = \frac{\left[\mathsf{M}_{\mathsf{S}}\right]_{\mathsf{p}}}{\mathsf{n}} \tag{S3}$$

Equations S2 and S3 were substituted into Equation 6 in Table 1S, then

$$\frac{[\mathsf{M}_{s}]_{0}}{m} - \frac{[\mathsf{M}_{s}]_{p}}{n} = [\mathsf{M}_{D}]$$

Transpose

$$[\mathsf{M}_{\mathsf{D}}] = \frac{\mathsf{n} \times [\mathsf{M}_{\mathsf{S}}]_{\mathsf{0}} \cdot \mathsf{m} \times [\mathsf{M}_{\mathsf{S}}]_{\mathsf{p}}}{\mathsf{m} \times \mathsf{n}}$$
(S4)

Because styrene monomers were consumed completely, Equation 7 in Table 1S can be regarded as

$$[M_s]_0 - [M_s]_p = [M_s] = 0$$

That is

$$\left[\mathsf{M}_{\mathsf{S}}\right]_{\mathsf{O}} = \left[\mathsf{M}_{\mathsf{S}}\right]_{\mathsf{P}} \tag{S5}$$

Equation S5 was substituted into Equation S4, then

$$[\mathsf{M}_{\mathsf{D}}] = [\mathsf{M}_{\mathsf{S}}]_{\mathsf{O}} \times \frac{(\mathsf{n} - \mathsf{m})}{\mathsf{m} \times \mathsf{n}}$$
(S6)

S6 was divided by S2, then

$$\frac{[M_{\rm D}]}{[M_{\rm D}]_0} = [M_{\rm S}]_0 \times \frac{(n-m)}{m \times n} \times \frac{m}{[M_{\rm S}]_0} = \frac{n-m}{n} = 1 - \frac{m}{n}$$
(S7)

Equation S7 and $m=[M_S]_0/[M_D]_0$ were substituted into Equation S1, then

$$(1-\frac{m}{n})^{1-r_s} = m \times (r_s - 1) + 1$$
 (S8)

Set x=r_s, and implicit Equation S8 was expressed in the form of the function group:

$$\begin{cases} y = (1 - \frac{m}{n})^{1 - x} \tag{S9} \\ (x - x) = 1 \end{cases}$$

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O1 in Table 2 was taken as sample, m=10.0 and n=10.6, the graphics from Equations S9 and S10 were drawn using the function plotter software -- Desmos (https://www.desmos.com/), the horizontal coordinates for the intersection of the two function graphics (except (1,1)) represented the reactivity ratio (r_s) of copolymerization O1. (Fig. 9S):



Fig. 9S A graphical method of simplified calculation for r_s.

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