

## Supplementary Information

### **Synthesis of AB Block and A<sub>2</sub>B<sub>2</sub> and A<sub>3</sub>B<sub>3</sub> Miktoarm Star-shaped Copolymers Using $\omega$ -End-functionalized Poly(methyl methacrylate) with A Hydroxyl Group Prepared by Organocatalyzed Group Transfer Polymerization**

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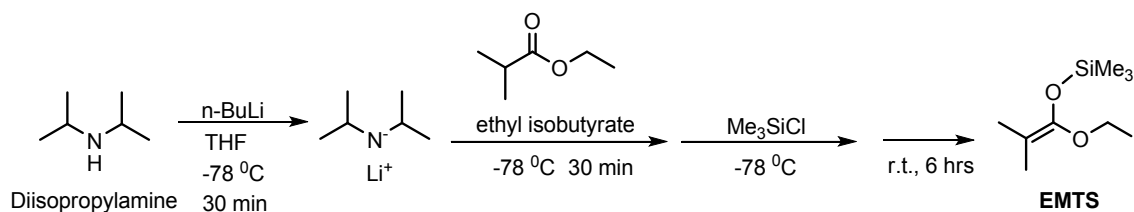
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## Experimental Section

### Scheme S1. Synthesis of 1-ethoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA<sub>Et</sub>)



### Synthesis of 1-ethoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA<sub>Et</sub>)<sup>1-2</sup>.

Diisopropylamine (11.5 ml, 94.7 mmol) and THF (ca. 50 mL) were added into a 100-mL cock-attached schlenk flask under an argon atmosphere. The mixture was cooled to  $-78\text{ }^\circ\text{C}$  and *n*-butyllithium (59.5 ml, 94.7 mmol, 1.6 M in *n*-hexane) was added. The mixture was then allowed to react for 30 min, after which ethyl isobutyrate (11.5 ml, 86.07 mmol) was added and the reaction was allowed to proceed further for 30 min at  $-78\text{ }^\circ\text{C}$ . Trimethylsilyl chloride (13.1 ml, 0.103 mol) was finally added and the reaction was allowed to proceed at  $-78\text{ }^\circ\text{C}$  for 30 min. It was then allowed to react further for 6 hours at room temperature. At the end of the reaction, solvent was removed at reduced pressure and product purified by vacuum distillation ( $58\text{-}59\text{ }^\circ\text{C}$ , ca. 2.0 kPa) to give SKA<sub>Et</sub> as a colorless liquid. Yield, 4.1g (25.3%).

### NMR Data

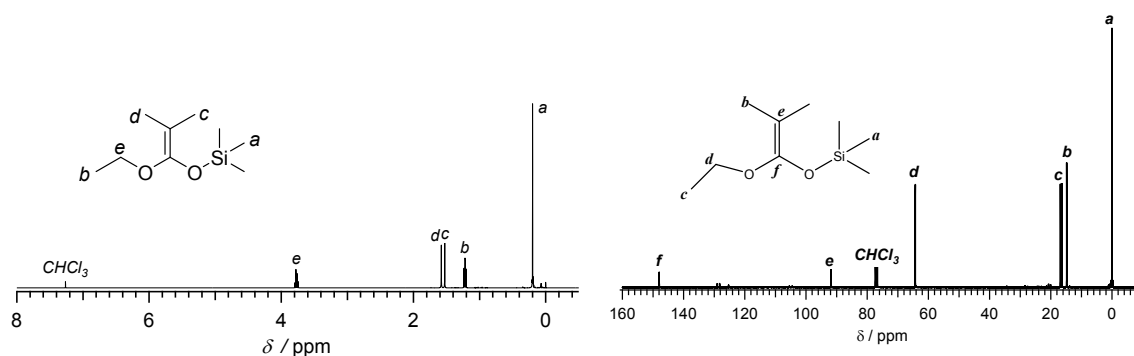
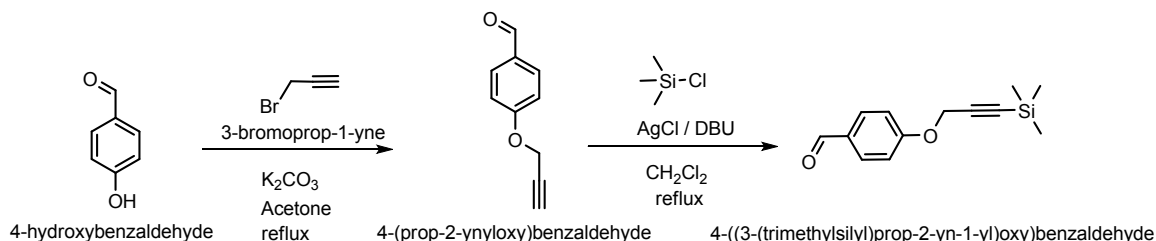


Figure S1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of SKA<sub>Et</sub> in CDCl<sub>3</sub>.

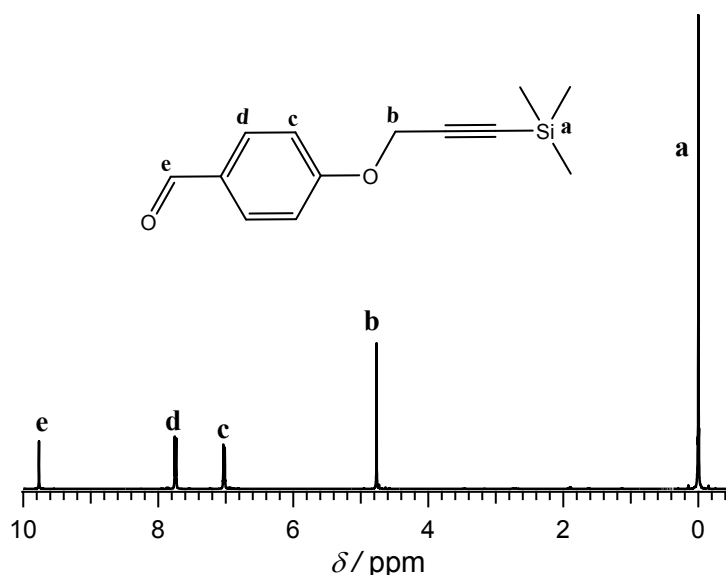
**Scheme S2.** Synthesis of 4-(3-(trimethylsilyl)prop-2-ynoxy)benzaldehyde



**Synthesis of 4-(3-(Trimethylsilyl)prop-2-ynoxy)benzaldehyde**<sup>3-6</sup>. A 300 mL round bottom flask equipped with a magnetic stir bar was charged with 4-hydroxybenzaldehyde (5.00 g, 40.9 mmol), potassium carbonate (22.63 g, 0.164 mol), propargyl bromide (19.48 g, 0.164 mol), and acetone (250 mL). The heterogeneous mixture was heated to reflux for 4h and cooled to room temperature. After addition of water, the mixture was extracted twice with dichloromethane and the combined organic layers were dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to afford the crude product as pale yellow solid. The crude was then purified twice by column chromatography using a mobile phase mixture of hexane: ethyl acetate; 2:1 to afford 2.55 g (39 % yield) of pure product. To a two-neck 100mL round-bottom flask that contained the aldehyde (2.55 g, 15.9 mmol) and silver chloride (0.46 g, 3.18 mmol) was first added 50 mL of dry dichloromethane followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU 4.75 mL, 4.85 g, 31.8 mmol). The reaction mixture was then heated under reflux at 40 °C and chlorotrimethylsilane (6.1 mL, 5.2 g, 47.7 mmol) added dropwise, and the contents were stirred for 2 days. The mixture was allowed to cool to ambient temperature and diluted with 150 mL of n-hexane. The organic phase was subsequently washed successively with aqueous NaHCO<sub>3</sub>, 2M HCl, and water before being dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under

high vacuum. Beige solids were recovered (2.37 g, 24.9 % yield from the original aldehyde) and the product was used in the next step without further purification.

### NMR Data



**Figure S2.** <sup>1</sup>H NMR spectrum of 4-(3-(Trimethylsilyl)prop-2-ynoxy)benzaldehyde

### Reference

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**Table S1.** Synthesis of hydroxyl  $\omega$ -end-functionalized PMMAs by *t*-Bu-P<sub>4</sub>-catalyzed GTP using benzaldehyde (PhCHO) as terminator <sup>a</sup>

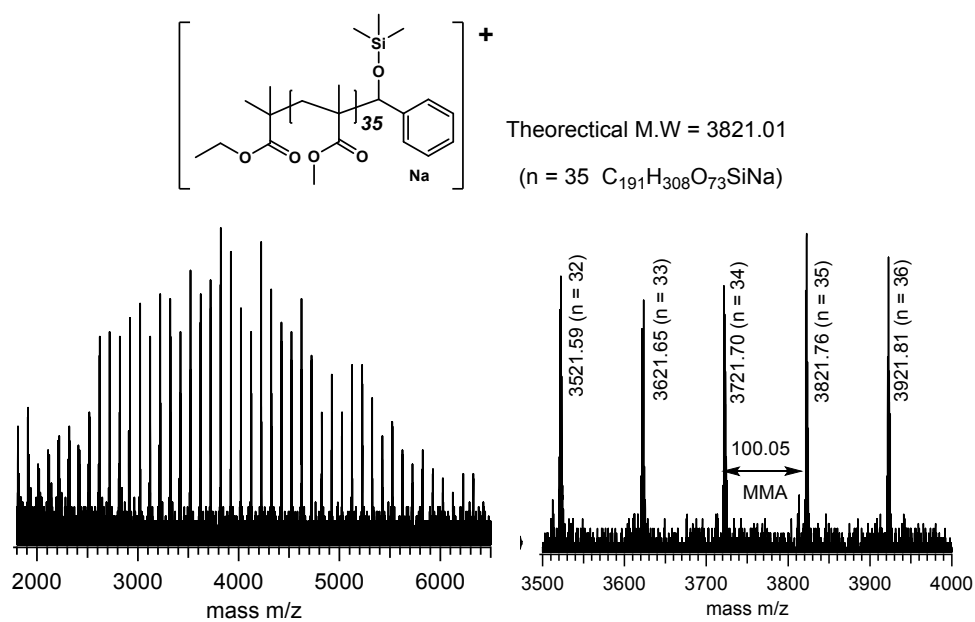
run	Catalyst	[PhCHO] <sub>0</sub> /[SKA <sub>Et</sub> ] <sub>0</sub>	$M_{n,calcd}$ <sup>b</sup> (kg mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>c</sup> (kg mol <sup>-1</sup> )	$M_{n,NMR}$ <sup>d</sup> (kg mol <sup>-1</sup> )	$M_w/M_n$ <sup>c</sup>	%F <sup>d</sup>
S1	<i>t</i> -Bu-P <sub>4</sub>	1	2.7	3.6	3.2	1.20	12.6
S2	<i>t</i> -Bu-P <sub>4</sub>	2	2.7	3.5	3.3	1.19	30.2
S3	<i>t</i> -Bu-P <sub>4</sub>	5	2.7	4.0	3.6	1.20	82.4
1	<i>t</i> -Bu-P <sub>4</sub>	10	2.7	4.1	3.5	1.23	>99

<sup>a</sup> Ar atmosphere; room temperature; Solvent, toluene; [MMA]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 25; [*t*-Bu-P<sub>4</sub>]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 0.01; Polymerization time, 3 min; [PhCHO]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 10; Termination time, 12 h; MMA conversion > 99%. <sup>b</sup> Calculated from ([MMA]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>) × (MMA conversion) × (M.W. of MMA) + (M.W. of initiator residue) + (M.W. of terminator residue) × %F. <sup>c</sup> Determined by SEC in THF using PMMA standards. <sup>d</sup> Estimated by <sup>1</sup>H NMR measurements in acetone-*d*<sub>6</sub>.

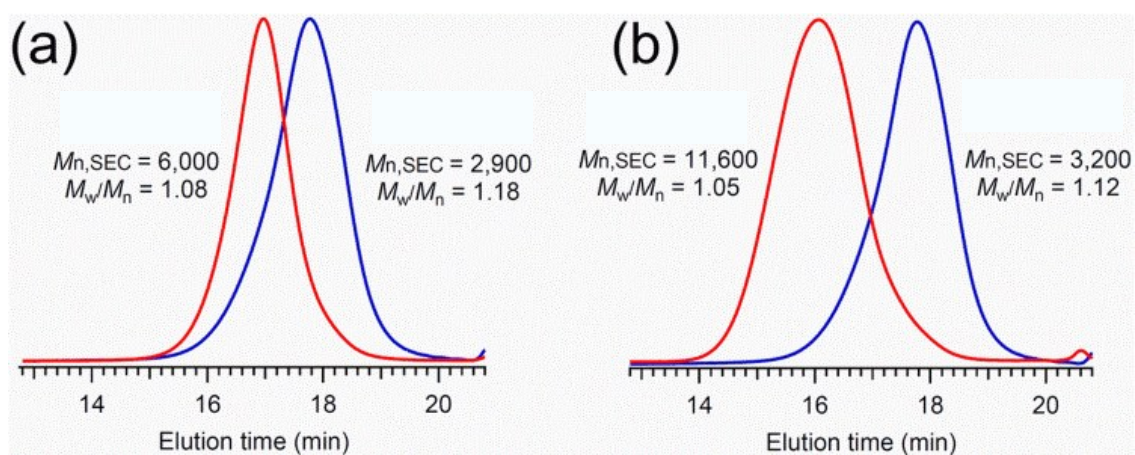
**Table S2.** Synthesis of  $\omega$ -end-functionalized PMMAs by *t*-Bu-P<sub>4</sub>-catalyzed GTP using functional benzaldehyde as terminator <sup>a</sup>

run	Terminator (T)	$M_{n,calcd}$ <sup>b</sup> (kg mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>c</sup> (kg mol <sup>-1</sup> )	$M_{n,NMR}$ <sup>d</sup> (kg mol <sup>-1</sup> )	$M_w/M_n$ <sup>c</sup>	%F <sup>d</sup>
S4	<i>p</i> -MeO-PhCHO	2.8	3.0	3.0	1.14	>99
S5	<i>p</i> -Ph-PhCHO	2.8	2.8	2.8	1.17	>99
S6	<i>p</i> -F-PhCHO	2.8	2.8	2.7	1.17	>99
S7	<i>p</i> -CF <sub>3</sub> -PhCHO	2.8	3.0	3.8	1.14	>99
S8	<i>p</i> -H <sub>2</sub> C=CHCH <sub>2</sub> O-PhCHO	2.8	3.3	3.2	1.21	>99
S9	<i>p</i> -Me <sub>3</sub> SiC≡CCH <sub>2</sub> O-PhCHO	2.8	3.5	3.3	1.17	>99
S10	<i>p</i> -Et <sub>2</sub> N-PhCHO	2.8	3.5	3.4	1.12	>99
S11	<i>p</i> - <i>t</i> BuO-PhCHO	2.8	3.6	3.8	1.20	>99

<sup>a</sup> Ar atmosphere; room temperature; Solvent, THF; [MMA]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 25; [*t*-Bu-P<sub>4</sub>]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 0.01; Polymerization time, 3 min; [T]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>, 10; Termination time, 12 h; MMA conversion > 99%. <sup>b</sup> Calculated from ([MMA]<sub>0</sub>/[SKA<sub>Et</sub>]<sub>0</sub>) × (MMA conversion) × (M.W. of MMA) + (M.W. of initiator residue) + (M.W. of terminator residue) × %F. <sup>c</sup> Determined by SEC in THF using PMMA standards. <sup>d</sup> Estimated by <sup>1</sup>H NMR measurements in acetone-*d*<sub>6</sub>.



**Figure S3.** MALDI-TOF MS spectra of trimethylsilyloxy  $\omega$ -end-functionalized PMMA (precursor of run 6).



**Figure S4.** SEC traces of (a) hydroxyl-functionalized two-arm PMMA (red) and its precursor (blue) and (b) hydroxyl-functionalized three-arm PMMA (red) and its precursor (blue).