Electronic Supplementary Material (ESI) for Polymer Chemistry

SUPPORTING INFORMATION

Optimizing The Generation Of Narrow Polydispersity 'Arm-First' Star Polymers Made Using RAFT Polymerization

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Additional Informtaion: Polymerization

Synthesis of arm poly(OEG-A) polymer.

Scheme S1. RAFT polymerization of OEG-A.

$OEG\text{-}A_{480}$, AIBN, RAFT agent, and acetonitrile were introduced in 50 mL round bottom flask (as indicated in the Table S1) equipped with a magnetic stirrer bar. The round bottom flask was cooled in an ice bath, and degassed with nitrogen for 20 minutes. The degassed solution was stirred at 70 °C for 6 hours. The reaction sampled for GPC and ^1H NMR analysis at this point. The remaining acetonitrile was removed by rotary evaporation. The polymer was purified by dialysis using membrane cut off 3500 Da.

Table S1. Summary of poly(OEG-A) prepared in this study.

Polymers	Reagents	M_w (g/mol)	mmol	Quantity (g)
P1	$OEG\text{-}A_{480}$	480	20.83	10.00
	RAFT-CTA	272	2	0.544
	AIBN	164.21	0.4	0.064
P2	$OEG\text{-}A_{480}$	480	10.4	5.00
	RAFT-CTA	272	0.416	0.113
	AIBN	164.21	0.09	0.015
P3	$OEG\text{-}A_{480}$	480	10.4	5.00
	RAFT-CTA	272	0.25	0.068
	AIBN	164.21	0.05	0.008

GPC Data used for Polymer P1-3

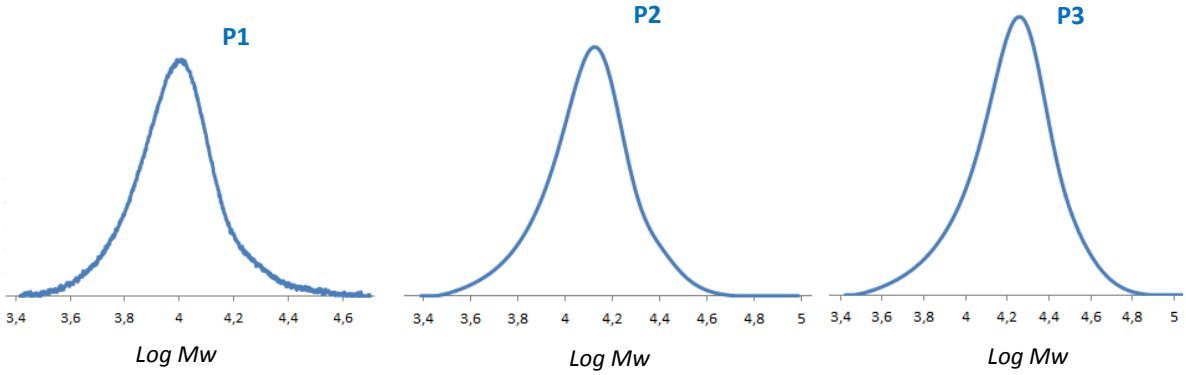

Figure S1. GPC traces of poly(OEG-A), P1-P3, obtained via RAFT polymerization.

POLYMERS	M_n GPC (g/mol)	PDI
O1	7 000	1.12
O2	11 500	1.18
O3	18 500	1.18

Synthesis of poly(*tert*-butyl acrylate) arm (P4-P6).

Scheme S2. RAFT polymerization of *tert*-butyl acrylate.

Tert-butyl acrylate (10 g, 0.08 mol), AIBN (0.05 g, 0.3 mmol), RAFT agent (0.4 g, 1.5 mmol), and acetonitrile (70 mL) were placed into a 100 mL round bottom flask, equipped with a magnetic stirrer bar. The reaction mixture was cooled on an ice bath, and degassed by

purging with nitrogen for 20 minutes. The degassed solution was stirred at 70°C for 6 hours. The reaction sampled for GPC and ^{1}H NMR analysis at this point. Acetonitrile was removed by rotary evaporation. The polymer was precipitated in water/methanol mixture (70/30 vol-%). A similar process was used for the synthesis of poly(*tert*-BuA) with M_n = 14 000 g/mol and 18 000 g/mol.

Synthesis of Arm poly(OEG-A-*co*-DEG-A) copolymers.

OEG-A_{480} (6.7 g, 14 mmol), DEG-A_{174} (14.00 g, 80 mmol), AIBN (0.04 g, 0.25 mmol), the RAFT agent (0.34 g, 1.25 mmol), and acetonitrile (20 mL) were placed into a 100 mL round bottom flask, equipped with a magnetic stirrer bar. The reaction mixture was cooled on an ice bath, and degassed by purging with nitrogen for 20 minutes. The degassed solution was stirred at 70°C for 6 hours. The reaction sampled for GPC and ^{1}H NMR analysis at this point. The remaining acetonitrile was removed by rotary evaporation. The polymer was purified by dialysis using membrane cut off 3500 Da.

Synthesis of arm first star

Star polymers were prepared according to the following procedure:

The synthesis of Star S1 from Table 1 is given as an example: Polymer (P1, poly(OEG-A), M_n = 7 000 g/mol, 200 mg), 10 μL of AIBN stock solution (50 mg/mL), monomer (OEG-A_{480}, 20 mg) and crosslinker (*C1*, 23 mg*)* and acetonitrile (1 mL) were added into 3 mL flask. The vial was sealed and purged under nitrogen for 20 minutes in an ice bath. The reaction solution was placed in an oil bath at 70°C for 24 hours. At the end of the polymerization, the polymer was sampled for ^{1}H NMR and GPC analysis. The arm incorporation was calculated by deconvulation of GPC trace using origin software, and the following equation: Arm incorporation (%) = $Area^{star}$ / ($Area^{Arm}$ + $Area^{Star}$) × 100. Star polymer was purified by dialysis against methanol using MWCO = 3 500 g/mol. Star polymer was analyzed by ^{1}H NMR.

Table S2 presents the synthesis of poly(OEG-A) star polymers using *N*,*N*′-bis(acryloyl)cistamine as crosslinker.

Table S2. Summary of poly(OEG-A) star polymers prepared in this study using C1 (*N*,*N*′-bis(acryloyl)cistamine) as crosslinker.

Stars	Reagents	M_n (g/mol)	(×10^{-5}) mol	[C]/[RAFT] Ratio[a]	Quantity (mg)
S1	P1	7 000	2.9	-	200
	C1	260	5.8/11.6/23.2/46.4	2/4/8/16	15/30/60/120
	AIBN	164	0.29	-	0.5
	Monomer	480	4.2	-	20
	Acetonitrile	-	-	-	1 mL
S2	P2	11 500	1.7	-	200
	C1	260	3.4/6.8/13.6/27.2	2/4/8/16	9/18/36/72
	AIBN	164	0.17	-	0.28
	Monomer	480	4.2	-	20
	Acetonitrile	-	-	-	1 mL
S3	P3	18 500	1.2	-	200
	C1	260	2.4/4.8/9.6/19.2	2/4/8/16	6/12/24/48
	AIBN	164	0.12	-	0.20
	Monomer	480	4.2	-	20
	Acetonitrile	-	-	-	1 mL

Note: C1 corresponds to *N*,*N*′-bis(acryloyl)cistamine.