Supramolecular Four-Armed A₂B₂ Star Copolymer (Miktoarm Star) via Host-Guest Complexation and Nitroxide Mediated Radical Polymerization

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GENERAL

Reagents were purchased and used as received unless otherwise noted. Melting points were taken in capillary tubes with a Haake-Buchler apparatus and are corrected. ¹H NMR spectra were obtained on JEOL ECLIPSE-500, BRUKER 500 and AGILENT NMR vnmrs400 spectrometers. ¹³C NMR spectra were collected on these instruments at 125, 125 and 101 MHz, respectively. ¹H NMR splitting abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), h (heptet), b (broad), br u (broad, unresolved). High resolution mass spectrometry (HR MS) was carried out using an Agilent LC-ESI-TOF system. SEC analyses of the polymers were performed at 20 °C in THF using a Waters system with refractive index or uv detector calibrated with PS standards. DSC data were obtained on a TA Instrument Q2000 differential scanning calorimeter under N₂; heating and cooling were carried out at a rate of 5 °C/min; T_g values were recorded on second heating scans as the midpoint of the change in heat capacity.

SYNTHETIC PROCEDURES

N,N'-bis{ω-[(2-phenyl-2-(2',2',6',6'-tetramethylpiperidine-N-oxyl)carbethoxy]pentyl}-4,4'-bipyridinium bis(hexafluorophosphate) (2).



A mixture of N,N'-bis(ω -carboxypentyl)-4,4'-bipyridinium bis(hexafluorophosphate) ^[S1] (0.676 g, 1.0 mmol) and freshly distilled thionyl chloride (5 mL) was stirred at 50 °C for 3 days. After removing excess thionyl chloride by vacuum, the residue was dissolved in dry MeCN (5 mL). Into the solution cooled in an ice bath, 2-(2',2',6',6'-tetramethylpiperidine-Noxyl-2-phenylethanol^[S2] (0.676 g, 2.4 mmol) was added and then dry pyridine (0.166 g, 21 mmol) was slowly added. The mixture was stirred for 3 days at rt. A precipitated salt was removed by filtration. After concentration of the filtrate, deionized water (25 mL) was added to precipitate the product. The filtered precipitate was washed with 1M HCl solution once and water 5 times. The solid product was also washed with boiling ethyl ether to remove any unreacted alcohol. Drying in a vacuum oven gave an off-white solid (0.80 g, 69%), mp 150.8-155.4 °C (dec.). ¹H NMR (400 MHz, acetone- d_6 , 22 °C): δ 1.10~1.97 (m, 44H), 2.17~2.34 (m, 8H), 4.48 (m, 2H), 4.66 (m, 2H), 4.98 (s, 4H), 6.10 (m(br), 2H), 7.39 (m, 8H), 7.53 (m, 2H), 8.89 (d, J=2, 4H), 9.50 (d, J=2, 4H). ¹³C NMR (100 MHz, acetone- d_6 , 22 °C): δ 13.37, 13.43, 21.9, 22.0, 25.1, 25.2, 29.0, 29.3, 30.4, 30.5, 49.0, 50.0, 121.0, 122.0, 122.5, 123.8, 124.0, 136 (18 signals observed; theory: 20 signals). HRMS (ESI): m/z 904.6094 $([M-2PF_6]^+$, calcd. for C₅₆H₈₀N₄O₆ 904.6078, error 1.8 ppm).

Star polystyrene-poly(*n*-butyl methacrylate) copolymeric [2]rotaxane 4.



A solution of the crown centered polystyrene $\mathbf{1}^{[S3]}$ (0.2700 g, $M_n = 13.5$ kDa, 2.00 x 10⁻⁵ mol, PDI = 1.25) and viologen 2 (0.0239 g, 2.00 x 10^{-5} mol) in *n*-butyl methacrylate (0.5688 g, 4 mmol) was degassed by $N_{\rm 2}$ bubbling for 30 min at room temp. The yellow solution was immersed in an oil bath (135 °C) and stirred under N2 for 3 days. After cooling, the polymer solution was diluted with chloroform (5 mL) and added slowly to MeOH (150 mL) with vigorous stirring. The precipitated solid was filtered and dissolved in THF (5 mL). The solution was added to MeOH (150 mL) with vigorous stirring. The precipitated solid was dissolved in chloroform (5 mL) and precipitated into MeOH (450 mL). Filtration and drying in a vacuum oven gave a fine colorless powder (0.302 g). In the SEC trace (Figure 2), a small broad peak in the high molecular weight region was present, attributed to poly(BMA) most likely arising from initiation by free uncomplexed 2. Therefore, a fractionation was performed using a solution of the product in 1:1 dioxane/THF. With vigorous stirring, MeOH was dropped into the solution until a small amount of precipitate appeared. After removing the precipitate by filtration, the solvent was removed from the filtrate solution to give copolymer 4. GPC (Figure 2): $M_n = 22.5$ kDa, PDI = 1.30 (THF, refractive index detector, PS standards calibration).

N,N'-Bis(bromoisobutyryloxyethyl)-4,4'-bipyridinium bis(hexafluorophosphate) (5).



To an ice cold solution of 2.14 g (4.0 mmol) of N,N'-bis(β -hydroxyethyl)-4,4'-bipyridinium bis(hexafluorophosphate) (**S1**)^[S4] and 0.760 g (9.6 mmol) of dry pyridine in 20 mL of dry acetonitrile was added 2.21 g (9.6 mmol) of α -bromoisobutyryl bromide via syringe. After it had stirred for 1.5 h at RT, the solution was evaporated to dryness and the residue was dispersed in 30 mL of 1 M HCl and stirred for 1 h. The filtered solid was dispersed in a saturated solution of NH₄PF₆ and stirred 18 h. Filtration and drying yielded 2.52 g (76%) of colorless solid, mp 192.2-195.1 °C. ¹H NMR (400 MHz, DMSO-*d*₆, 22 °C): δ 1.79 (s, 12H), 4.66 (t, *J* = 5, 4H), 5.02 (t, *J* = 5, 4H), 8.78 (d, *J* = 7, 4H), 9.36 (d, *J* = 7, 4H). ¹³C NMR (100 MHz, DMSO-*d*₆, 22 °C): δ 30.41, 57.21, 59.82, 64.40, 126.88, 146.92, 149.38, 170.68 (8 signals; theory: 8 signals). HR MS (FAB): m/z 687.0058 ([M-PF₆]⁺, calcd. for [C₂₂H₂₈Br₂F₁₂N₂O₄P₂ – PF₆] 687.0052, error 0.8 ppm).

Viologen Centered Polystyrene (6).



A mixture of viologen bis(bromoisobutyryate) **5** (0.4171 g, 0.5 mmol), 0.1438 g (1 mmol) of CuBr, 0.4685 g (3 mmol) of 2,2'-bipyridine and 5.208 g (50 mmol) of styrene in 5 g of N,N-dimethylformamide was heated under nitrogen at 130 °C for 3 days. After it had cooled, the mixture was diluted with 20 mL of chloroform and passed through a basic alumina column twice to remove the catalyst. The solvent was removed and the residue was dispersed in methanol with stirring. The solid was filtered and dried in a vacuum oven at 40 °C: 3.62 g (64%). GPC results (THF, polystyrene equivalents): M_n 35.5 kDa, M_w 55.7 kDa, PDI 1.57.



Figure S1. 400 MHz ¹H NMR spectra of viologen initiator **2**: top) in CDCl₃, 22 °C; middle) in acetone- d_6 , 22 °C. 100 MHz ¹³C NMR spectrum (bottom) of viologen initiator **2** (acetone- d_6 , 22 °C). Note: the OCH₂ protons are diastereotopic.



Figure S2. 400 MHz ¹H-NMR spectrum (CDCl₃, 22 °C) of BMP32C10 centered polystyrene 1.^[S3]



Figure S3. 400 MHz ¹H NMR spectrum (upper) and 100 MHz ¹³C NMR spectrum (lower) of viologen ATRP initiator **5** (acetone- d_6 , 22 °C).



Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of star copolymer **4** with integration numbers. The integration reference peak at δ 3.63 was set at 16.00 for the 16 δ - and γ -protons of the crown ether moiety.

 $DP_{PS} \sim 699/5 \sim 140$. $M_{nPS} \sim (140)(104) + 748$ ($C_{34}H_{46}Cl_2O_{14}$ for the crown moiety and end groups) ~ 14.5 kDa + 748 Da ~ 15.2 kDa. $DP_{PBMA} \sim 108/2 \sim 54$. $M_{nPBMA} \sim (54)(130) \sim 7.0$ kDa.

The signal at 0.65 ppm was assigned to the methyl groups of TEMPO end groups on the poly(*n*-butyl methacylate) chains. There are 12 of these protons: 2.53/12 = 0.21 TEMPO units; this indicates that ~10 % of the chains are terminated by TEMPO units.



Table S1. Polymerization of Neat Dimethylaminoethyl Methacrylate ($[M]_0 = 5.94 \text{ M}$) at 125								
°C with TEMPO-based Polystyryl Initiators Without Added TEMPO.								
Entry	Init.	[M] ₀ / [I] ₀	Time	Conv.	DP _n ^b	PDI		
			(h)	(%) ^a		(SEC) ^c		
1a	$PS-T(8)^{d}$	$11 \ge 10^5$	2	5.3	345	1.25		
1b	$PS-T(8)^{d}$	$11 \ge 10^5$	4	5.7		1.26		
1c	PS-T (8) ^d	$11 \ge 10^5$	6	5.3	357	1.26		
1d	$PS-T(8)^{d}$	$11 \ge 10^5$	8	6.0	329	1.26		
2a	PS-T (8) ^e	5.4×10^5	2	2.6	94.9	1.28		
2b	PS-T (8) ^e	5.4×10^5	4	2	110	1.30		
2c	PS-T (8) ^e	5.4×10^5	6	2	89.8	1.26		
2d	PS-T (8) ^e	5.4×10^5	8	2.6		1.25		

Summary of the Results of Lokaj et al. ⁸⁵

By gravimetry from yield.

Methacrylate block; calc. from SEC result and NMR analysis of the ratio of monomers in the b copolymer.

^c By SEC based on PMMA standards.

 d M_n 53.4 kDa, PDI 1.13 by SEC based on PMMA standards. e M_n 28.1 kDa, PDI 1.10 by SEC based on PMMA standards.

Monomer: MW 157, density 0.933 g/mL

Purity of monomer not mentioned. Assumed to be as received, i. e., containing stabilizer.



These results demonstrate three important points:

- 1. The reaction is finished in less than 2 hours.
- 2. The conversion depends on the initial concentration of the polystyryl initiator.
- 3. In spite of the low conversions, the PDI values are low.



Dynamic light scattering results for a dilute (1 mg/mL) solution of a viologen-terminated polystyrene ($M_n 20.3 \text{ kDa}$) in CH₂Cl₂.^{S3}



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