Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI) :

Sythesis of the macroinitiator MPEG2000-Br :

In a typical reaction, MPEG2000 (5.5 g, 5 mmol) and triethylamine(1.21 g, 12 mmol) were mixed in anhydrous CH_2Cl_2 (100 mL) in an ice bath. A solution of 2.37 g (11 mmol) of 2-bromopropionyl bromide in anhydrous CH_2Cl_2 (20 mL) was added dropwise over 2 h under dry argon. The solution was then allowed to warm to room temperature and was stirred for 48 h. The precipitate was removed by filtration. The filtrate was poured into water and the water phase was extracted with CH_2Cl_2 three times. The combined organic phase was further washed with 1.0 M HCl and 1.0 M NaOH aqueous solutions successively and dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified twice by dissolving in 10 mL of CH_2Cl_2 and precipitation with 300 mL of diethyl ether.

Synthesis of the block copolymers PEG-*b*-PA444 and PEG-*b*-PMAazo444:

A general ATRP procedure for the synthesis of PEG-*b*-PA444 is as follows. A Schlenk flask with a magnetic stir bar was charged with $Cu^{I}Br$ (14.42 mg, 0.1 mmol), MPEG-Br macroinitiator (0.213g, 0.1 mmol), 4,4'-di(*n*-nonyl)-2,2'-bipyridine (bpy9) (from Aldrich) (81.6 mg, 0.2 mmol) and monomer A444 (0.632 g, 1 mmol). The flask was degassed by four vacuum-argon cycles. Toluene (1 mL), degassed by argon bubbling for 30 min, was then introduced into the flask using a syringe purge with argon. The flask was further degaseed by three freeze-pump-thaw cycles, and then immersed in an oil bath thermostated at 80 ^{o}C. After 24 h of reaction, the mixture was cooled to room temperature. The resulting polymer solution was poured into a large volume of diethyl ether. The precipitated diblock copolymer was purified 3 times by dissolution in a small amount of acetone and precipitation into a large volume of diethyl ether, and once by dissolution in acetone and precipitation into methanol. The purified polymer was dried under vacuum at room temperature for 2 days. Yield: 0.4g (47%).

In the synthesis of PEG-*b*-PMAazo444, $Cu^{II}Br_2$ (1.11 mg, 0.005 mmol, 5 mol% relative to $Cu^{I}Br$) and additional bpy9 (4.08 mg, 0.01 mmol) were introduced into the polymerization system. The reaction solution was stirred at 40^{o}C for 2.5 h. All other reaction conditions and purification procedures for this copolymer were the same as described above. Yield: 0.32g (37%).

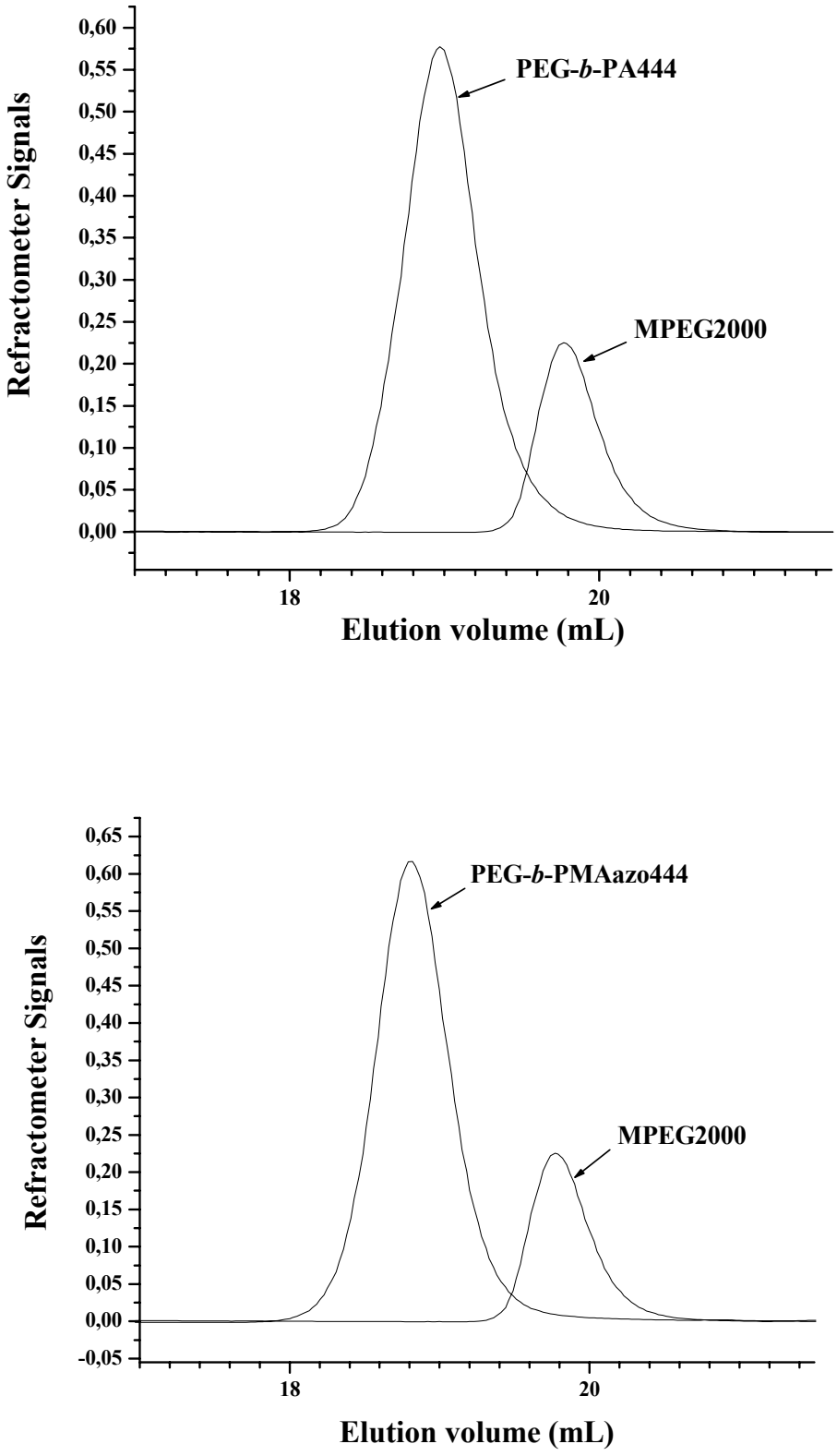

Figure 1. SEC chromatograms of MPEG2000 and the two block copolymers PEG-*b*-PA444 and PEG-*b*-PMAazo444.

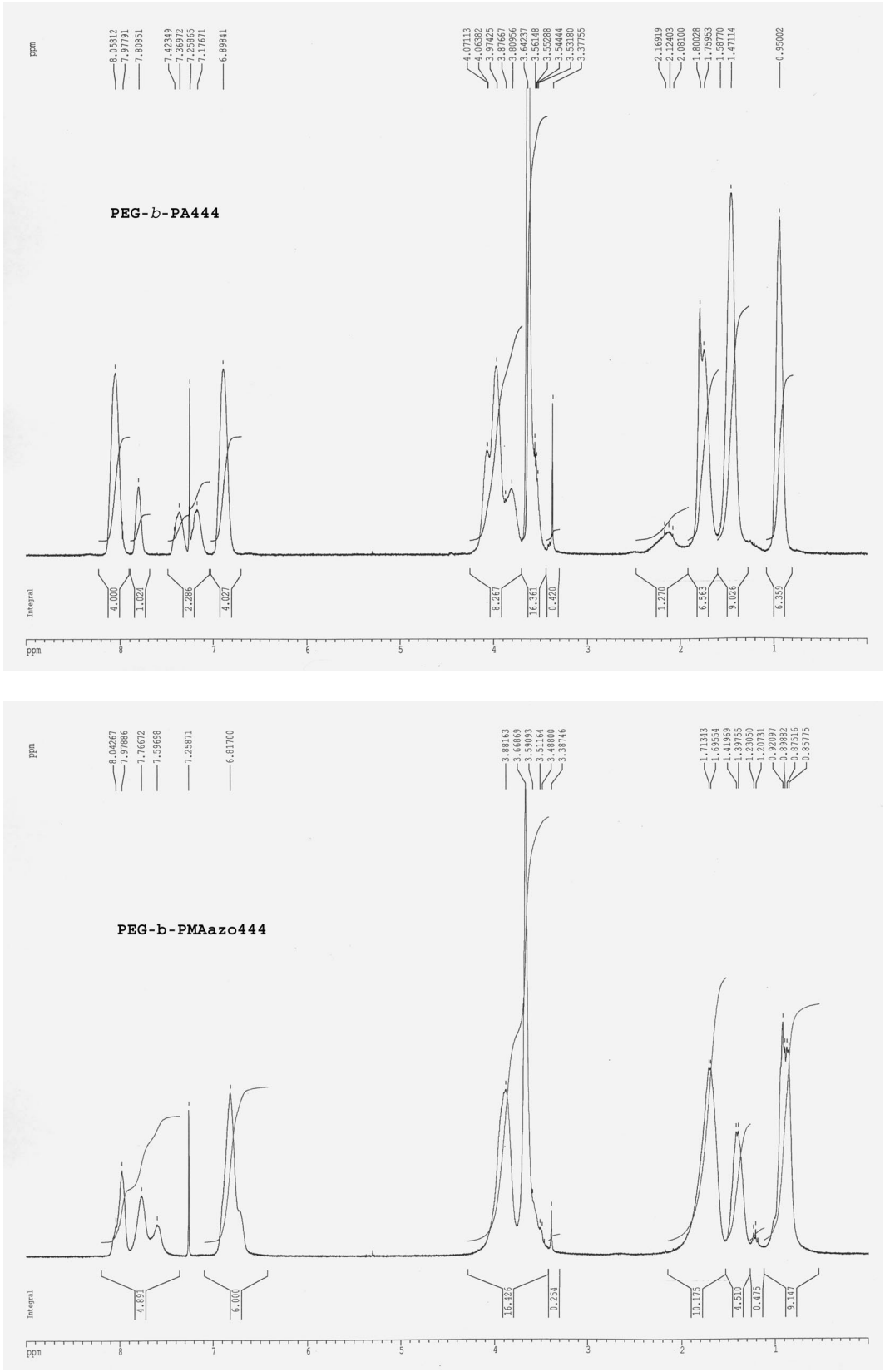

Figure 2. [1]H NMR spectra of PEG-*b*-PA444 and PEG-*b*-PMAazo444