

Well-Defined Poly(sulfobetaine) Brushes Prepared by Surface-Initiated ATRP Using a Fluoroalcohol and Ionic Liquids as the Solvents

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1. Preparation of sulfobetaine monomers

3-(*N*-2-Methacryloyloxyethyl-*N,N*-dimethyl) ammonatopropanesulfonate)

To a solution of 2-(dimethylamino)ethyl methacrylate (DMAEMA, 29 g, 0.19 mol) diluted with acetone (100 mL), 1,3-propane sultone (23 g, 0.17 mmol) was added dropwise at room temperature and stirred for 12 h under a nitrogen atmosphere. The heterogeneous reaction mixture was filtered off to collect the white solid and was washed with cool acetone and then vacuum dried at 40 °C for 24 h. Subsequently the solid was dissolved in methanol and poured into diethyl ether to twice precipitate the product to remove the unreacted DMAEMA and some impurities. The obtained white powder was dried under vacuum at 40 °C for 12 h. Yield 80 %. ¹H-NMR (300 MHz, CD₃OD), δ 1.90 (s, 3H, -CH₃), δ 2.18 (m, 2H, NCH₂CH₂CH₂), δ 2.81 (m, 2H, CH₂SO₃), δ 3.14 (s, 6H, N(CH₃)₂), δ 3.59 (m, 2H, NCH₂CH₂CH₂), δ 3.72 (m, 2H, OCH₂CH₂N), δ 4.56 (t, 2H, OCH₂CH₂N)), δ 6.10, 5.66 (d, 2H, CH₂=C).

Chloroethanesulfonyl Chloride

A mixture of sodium isethionate (10 g, 0.068 mmol) and thionyl chloride (SOCl₂, 85 mL) was refluxed. A portion of dimethyl formamide (2 mL) was slowly added to the reaction mixture during reflux for 24 h. After reaction, excess SOCl₂ was removed under vacuum and distilled under reduced pressure (70 °C, 0.6 kPa) to give chloroethanesulfonyl chloride as a yellow liquid. Yield: 67 %. ¹H NMR (300 MHz, CDCl₃), δ 3.96–4.11 (m, 4H, -CH₂CH₂-).

Ethylenesulfonyl Chloride

A solution of chloroethanesulfonyl chloride (6.4g, 0.039 mol) in 40 mL of dry diethyl ether was cooled with stirring to -55 °C (chloroform with dry ice bath). A solution of

2,6-dimethylpyridine (4.6 g, 0.042 mol) diluted with 16 mL of dry diethyl ether was added dropwise over 20 min so that the bath temperature did not exceed $-50\text{ }^{\circ}\text{C}$. After titration, the reaction mixture was allowed to warm to room temperature for 1 h. The reaction was then cooled to $0\text{ }^{\circ}\text{C}$, and 100 mL of ice-cold 1 wt% aqueous H_2SO_4 solution was added. The reaction mixture was extracted with diethyl ether and dried over MgSO_4 . Yellow viscous liquid was obtained by distillation under reduced pressure ($55\text{ }^{\circ}\text{C}$ and 0.7 kPa). Yield: 58 %. ^1H NMR (300 MHz, CDCl_3), δ 6.25, 6.55 (dd, 2H, $\text{CH}_2=\text{CHSO}_2\text{Cl}$), δ 7.02 (m, 1H, $\text{CH}_2=\text{CHSO}_2\text{Cl}$).

2-(*N*-2-Methacryloyloxyethyl-*N,N*-dimethyl) ammonatoethanesulfonate)

To a solution of DMAEMA (2.8 g, 0.018 mol) in 20 mL of acetic acid, ethylenesulfonyl chloride (1.1 g, 0.0090 mol) was added dropwise at $0\text{ }^{\circ}\text{C}$ and stirred for 12 h at room temperature. The reaction mixture was solved in THF and precipitated in diethyl ether. The obtained product was dried under vacuum, solved in 2,2,2-trifluoroethanol, and precipitated in diethyl ether. The obtained white powder was dried under vacuum at $40\text{ }^{\circ}\text{C}$ for 24 h. Yield: 24 %. ^1H NMR (300 MHz, CD_3OD) δ 1.75 (s, 3H, $-\text{CH}_3$), δ 3.07 (s, 6H, $\text{N}(\text{CH}_3)_2$), δ 3.29 (m, 2H, CH_2SO_3), δ 3.65 (m, 4H, CH_2NCH_2), δ 4.47 (m, 2H, OCH_2), δ 5.59, 5.98 (m 2H, $\text{CH}_2=\text{C}$).

4-(*N*-2-Methacryloyloxyethyl-*N,N*-dimethyl) ammonatobutanesulfonate) (MABS)

A solution of DMAEMA (29 g, 0.19 mol), 1,3-dinitrobenzene (0.10 g, 0.60 mmol), and 1,4-butanedisulfone (23 g, 0.17 mol) in 300 mL of acetonitrile was refluxed for 12 h. The reaction mixture was washed with acetonitrile and then dried under vacuum at $40\text{ }^{\circ}\text{C}$ for 24 h. Subsequently, the dried white powder was solved in methanol and twice precipitation in diethyl ether to remove the unreacted DMAEMA and some impurities. The obtained white powder was dried under vacuum at $40\text{ }^{\circ}\text{C}$ for 12 h. Yield: 63 %. ^1H NMR (300 MHz, CD_3OD): δ 1.67 (2H, $\text{CH}_2\text{CH}_2\text{SO}_3$), δ 1.90 (5H, CH_3 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3$), δ 2.82 (2H, CH_2SO_3), δ 3.05 (6H, $\text{N}(\text{CH}_3)_2$), δ 3.32 (2H, CH_2NCH_2), δ 3.66 (2H, $\text{OCH}_2\text{CH}_2\text{N}$), δ 4.49 (2H, OCH_2), δ 5.64, 6.02 (2H, $\text{CH}_2=\text{C}$).