Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for RSC Advances (Article)

Synthesis of Poly(*N*-(2-hydroxypropyl) Methacrylamide) Brushes by Interface-Mediated RAFT Polymerization

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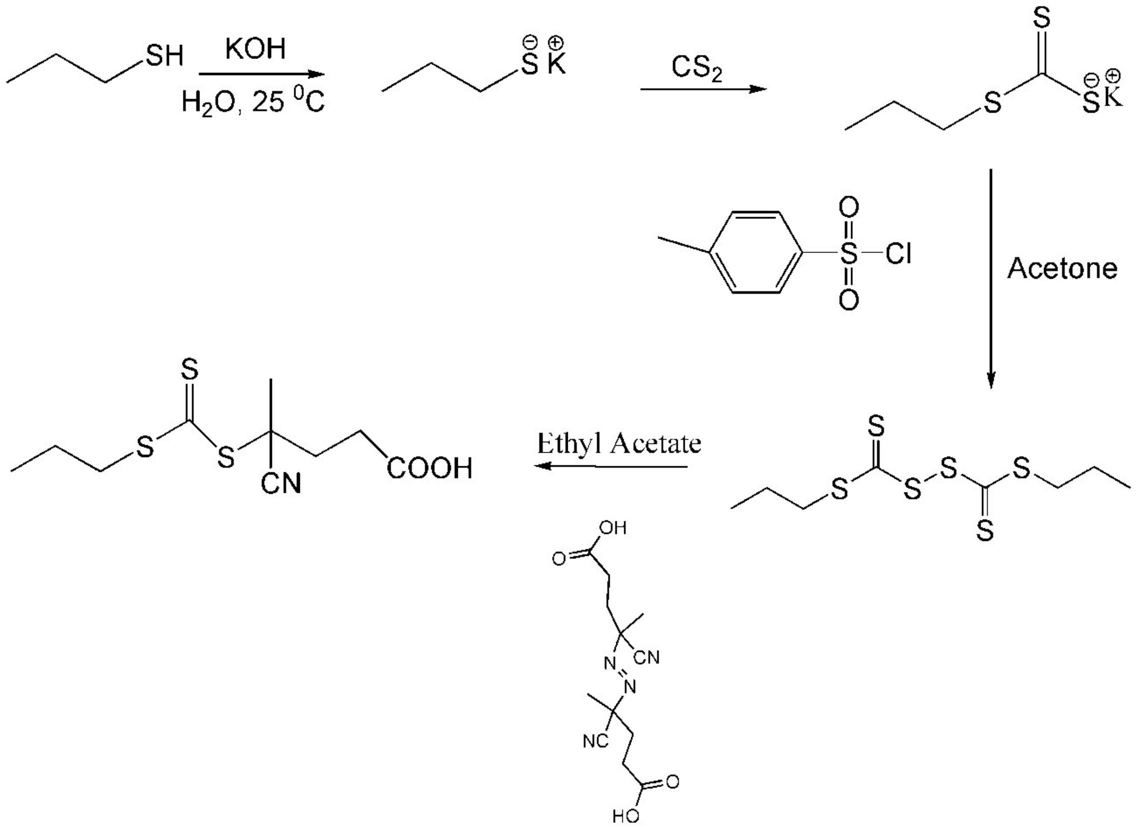
CONTENTS

Synthesis of RAFT Agent

RAFT agent 4-cyano-4-(propylsulfanylthiocarbonyl)sulfanylpentanoic acid (CPP) was synthesized according to literature procedure.[27] Briefly, 1-propanethiol (15 g, 0.2 mol) was added dropwise to a solution (70 mL) of KOH (14 g, 0.25 mol), followed by CS_2 (15 g, 0.2 mol) in one portion. This solution was vigorously stirred at 25 ^oC for 30 min and cooled to -5 ^oC. A solution of p-tosyl chloride (19 g, 0.1 mol) in acetone (100 mL) was added in portions over 10 min, and stirring was continued for 2 h. The acetone was then evaporated in an open vessel under stirring. Then, the red oil was extracted with dichloromethane; the organic layer was washed with water and dried over anhydrous $MgSO_4$ overnight. The $MgSO_4$ was filtered off, and dichloromethane was removed by rotary evaporation to yield solid bis(propylsulfanylthiocarbonyl) disulfide (25 g: %94) as a red solid. A solution of 4,4`-azobis(4-cyanopentanoic acid) (6.2 g, 0.02 mol) and bis(propylsulfanylthiocarbonyl) disulfide (6 g, 0.02 mol) in ethyl acetate (100 mL) was heated under reflux for 20 h. After removal of the volatiles in vacuo, the crude product was purified by column chromatography on silica gel with a mobile phase of diethyl ether/hexane (1:2, v:v), (9 g, yield; 84%)

Synthetic routes of CPP



SCHEME S1 Synthetic routes of CPP

^{1}H-NMR spectrum of CPP

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) ~1 (d, 3H, $-CH_3$); ~1.7 (m, 2H, $-CH_2-CH_3$); ~2.0 (s, 3H, CH_3-C-); ~2.5 (m, 4H, $-CH_2-CH_2$); ~3.3 (s, 2H, $-CH_2-S$).

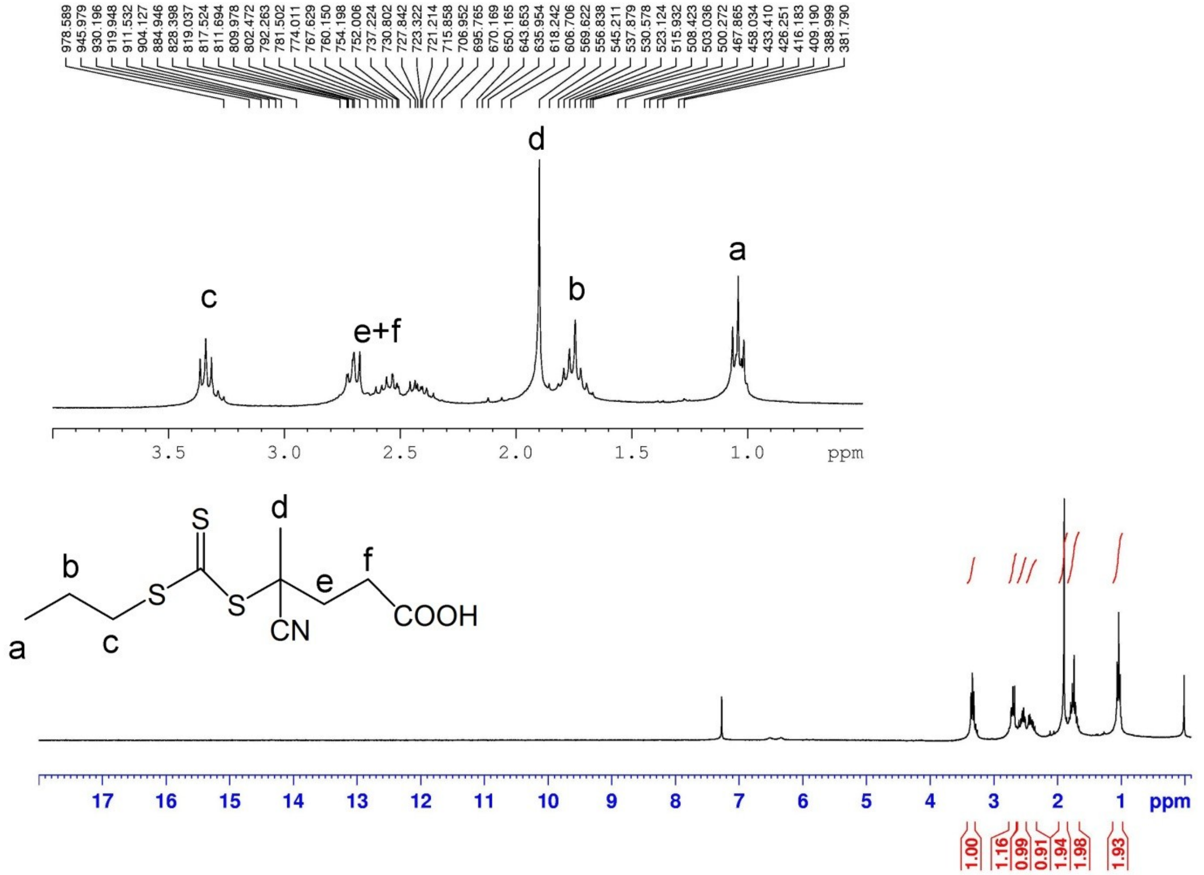


FIGURE S1 ^{1}H NMR spectrum of CPP (in $CDCl_3$)

^{13}C-NMR spectrum of CPP

^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 13.5 (-CH_3); 21,3 (-CH_3); 22,5 (-CH_2); 24,8 (-CH_2); 29,3 (-CH_2); 29,6 (-CH_2); 39,1 (-CH_2); 46.3 (-C-); 118.9 (-CN); 178.4 (-COOH); 220,0 (-C=S).

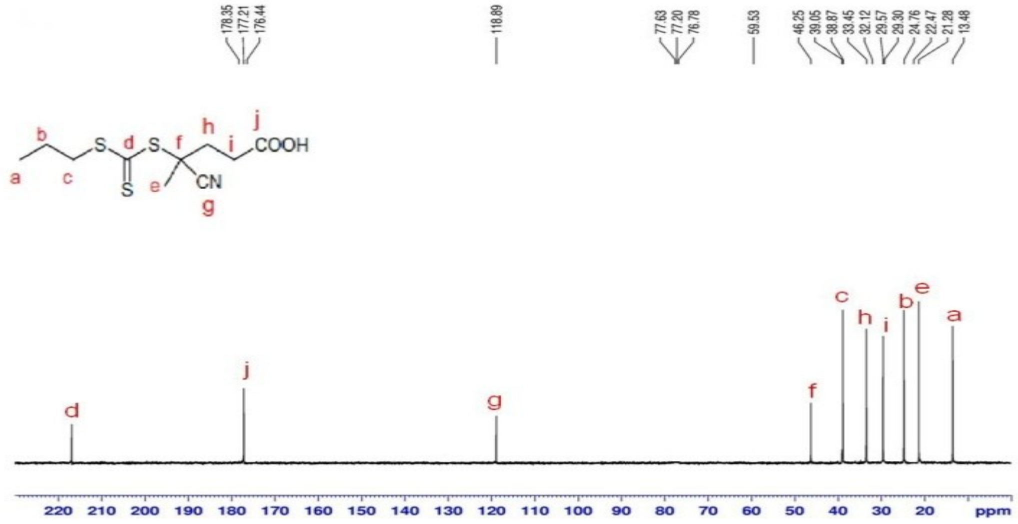


FIGURE S2 ^{13}C NMR spectrum of CPP (in $CDCl_3$)

FTIR spectrum of CPP

FTIR υ (cm^{-1}): ~3384-3000 (s, -O-H), ~2790-3000 (s, aliphatic -C-H), ~2245 (s, -CN), 1689 (s, -C=O), 1197 (s, -C=S).

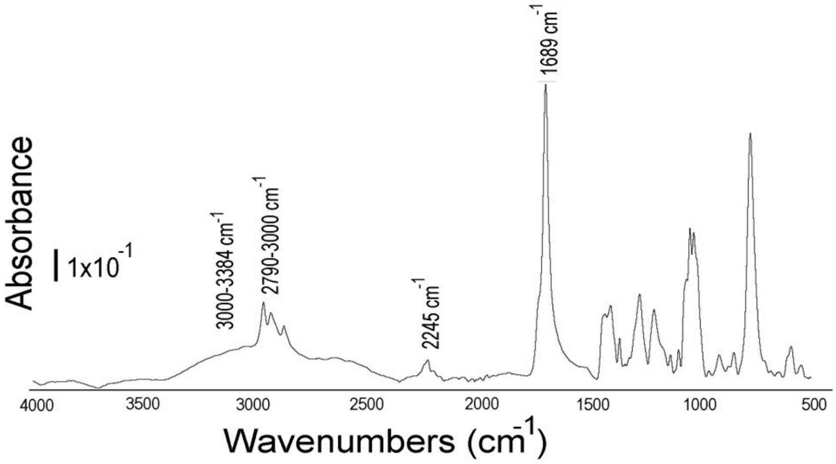
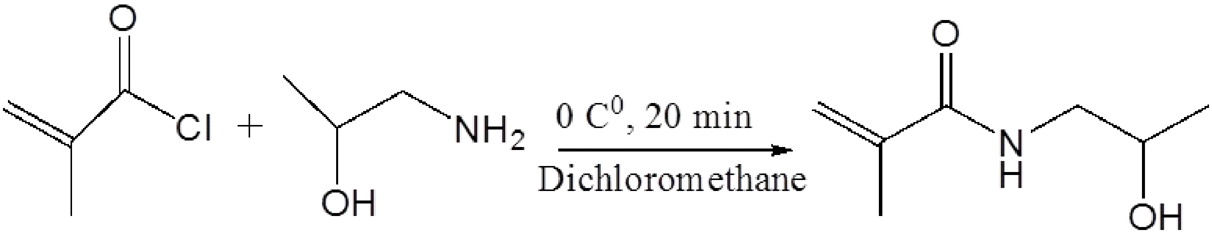


FIGURE S3 FTIR spectrum of CPP

Synthesis of HPMA

N-(2-hydroxypropyl) methacrylamide (HPMA) was synthesized according to a previously published protocol.[28,29] Briefly, distilled methacryloyl chloride (0.29 mol) was diluted in acetonitrile and added dropwise to a solution of 1-amino-2-propanol (0.30 mol) in acetonitrile at 0 °C. Precipitated 2-hydroxypropylammonium chloride was removed by filtration, and HPMA was isolated by precipitation from acetonitrile, recrystallization from a methanol-ether mixture (3:1), and a subsequent recrystallization from acetone. The crystalline monomer (mp = 68 °C) dried in vacuo and stored at –15 °C.

Synthetic route of HPMA



SCHEME S2 Synthetic route of HPMA

^{1}H-NMR spectrum of HPMA

^{1}H-NMR (300MHz, D_2O) δ (ppm): ~1.15 (d, 3H,$CH-CH_3$), ~1.78 (s, 3H, CH_3-C), ~3.10 (m, 1H,CH_2-NH), ~3.85 (m, 2H,$CH-CH_3$), ~5.30 (s, 1H, CH_2=C), ~5.60 (s, 1H, CH_2=C).

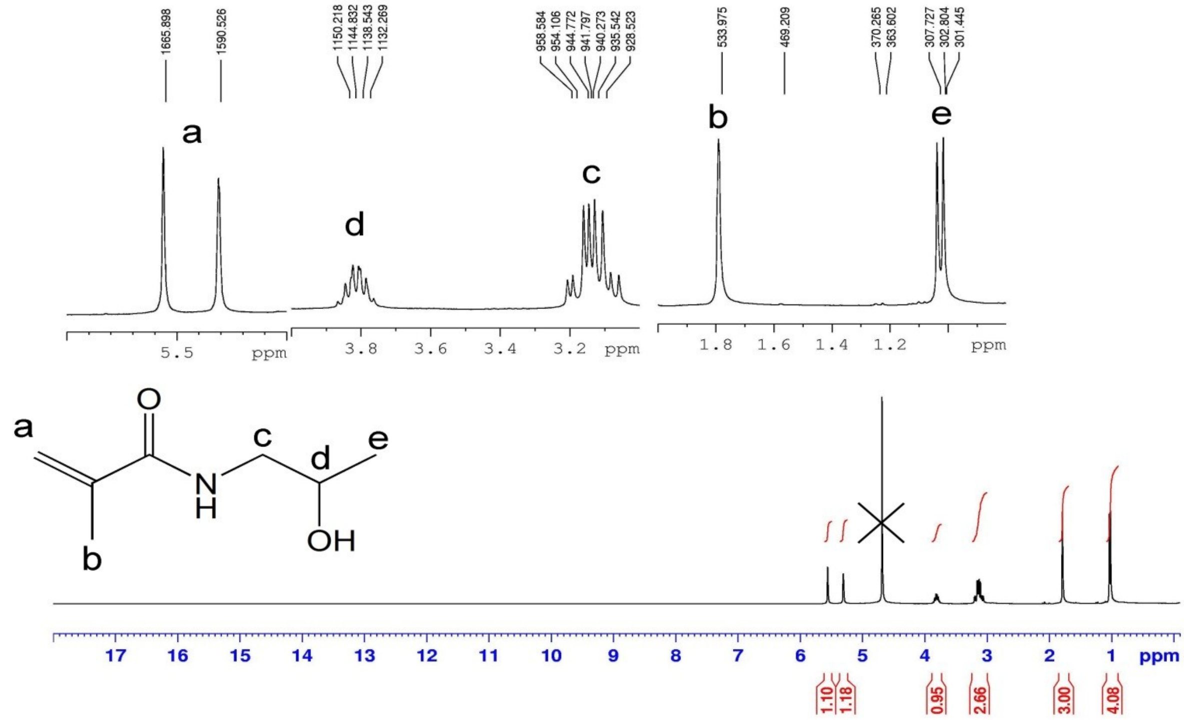


FIGURE S4 ^{1}H NMR spectrum of HPMA (in D_2O)

^{13}C NMR spectrum of HPMA

^{13}C NMR (300 MHz, d6-aseton): δ (ppm) ~17.6 ($-CH_3$), ~19.3 ($-CH_3$), ~46.2 ($-CH_2$), ~66.2 ($-CH$), ~120.9 ($-C=CH_2$), ~139.0 ($H_2C=C-$), ~172.1 ($-C=O$).

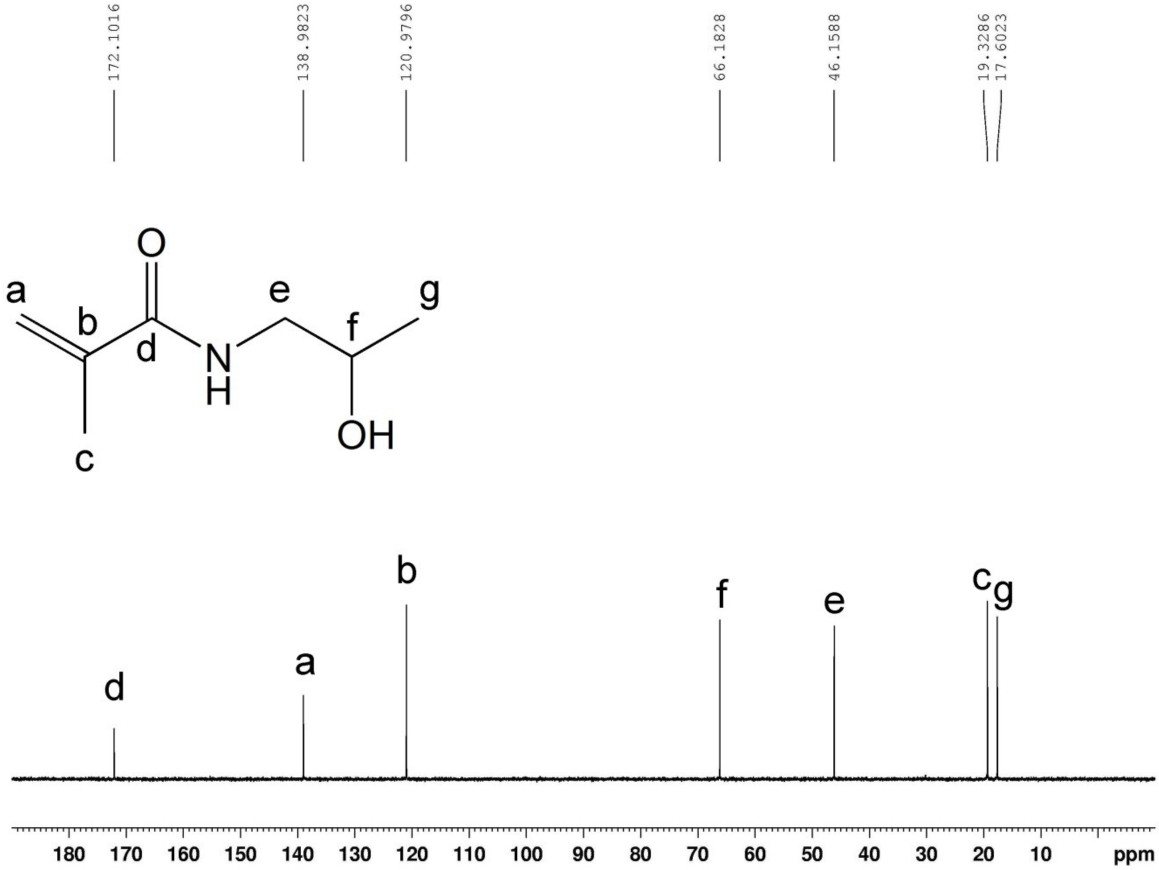


FIGURE S5 ^{13}C NMR spectrum of HPMA (in D_2O)

FTIR spectrum of HPMA

FTIR υ (cm^{-1}): ~3500-3000 (m,O-H) ~3273 (m, N-H), 3040 (s, =C-H), ~3000-2790 (s, aliphatic C-H), ~1652 (s, -C=O), 1615 (s, amide I, NH-C=O).

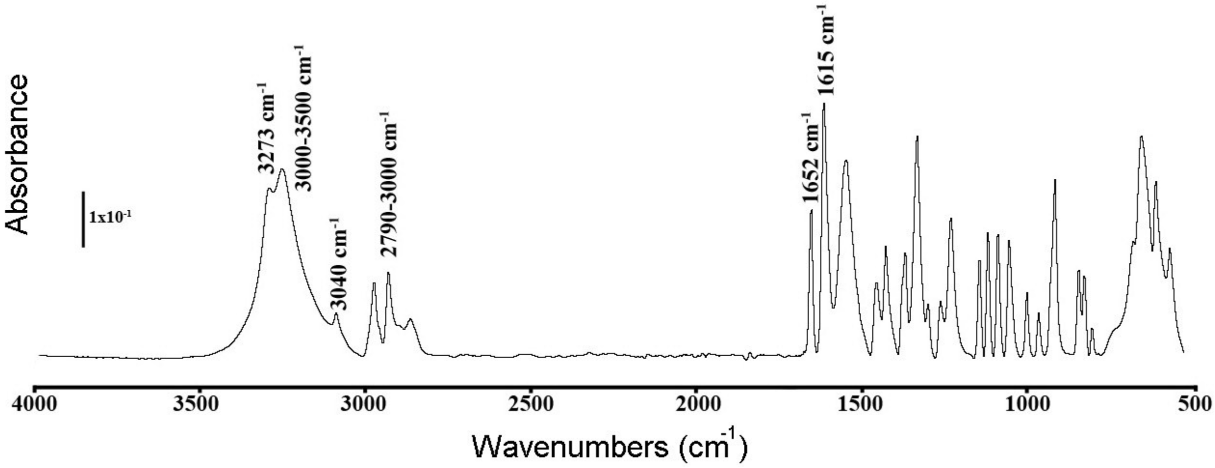


FIGURE S6 FTIR spectrum of HPMA

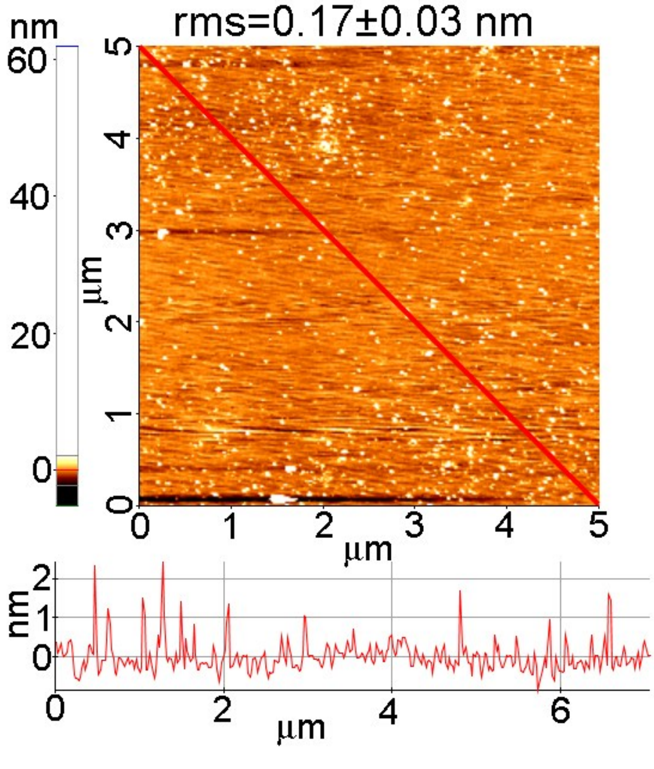


FIGURE S7 2D AFM image (5 x 5 $μm^2$) of the pure silicon wafer cleaned in a UV/O_3 cleaner