

Functionalization of titanium oxide surfaces by means of poly(alkyl – phosphonates)

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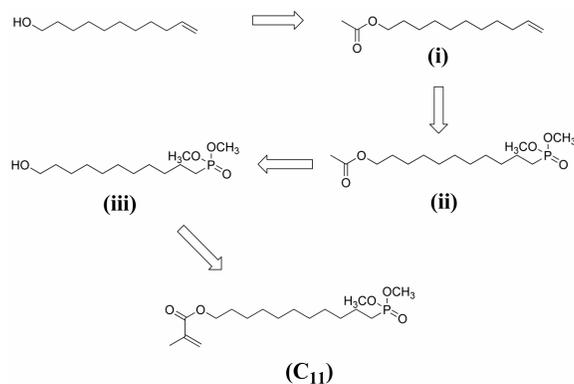
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Supporting Information

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1. Improvements of the synthesis of the Dimethyl(11-methacryloyloxy undecyl)phosphonate monomer (C₁₁)



Dimethyl(11-methacryloyloxy undecyl)phosphonate monomer (C₁₁) was synthesized based onto the protocols presented in Ref. ¹. However few purification stages were improved and are reported thereafter.

Synthesis of undec-10-enyl acetate (i):

50.0 g (0.294 mol) of 10-undecenol and 35.6 g (0.352 mol) of triethylamine were dissolved in dichloromethane (250 ml). The reaction mixture was degassed, saturated under a nitrogen atmosphere and cooled to 0 °C in an ice bath. While maintaining the temperature around 0 °C, 27.7 g (0.353 mol) of acetyl chloride (freshly distilled) previously dissolved in dichloromethane (20 ml) were added dropwise. Subsequently, the reaction mixture was stirred under reflux at 40 °C for 16 hours. The resulting white precipitate (triethylammonium hydrochloride) was removed by filtration, the solvent was evaporated using a rotary evaporator and replaced by diethyl ether. This mixture was cooled down to 6 °C for 20 minutes in order to improve the precipitation of the ammonium salt. After a new filtration stage, the organic phase was washed with basic water (5%, w/w, NaHCO₃), then with pure water and finally dried with MgSO₄. Solvent was distilled with a rotary evaporator and the product was dried under high-vacuum (10⁻² mbar). Yield of undec-10-enyl acetate: 61 g (98%). Purity was checked by ¹H-NMR.

Synthesis of dimethyl(11-acetyloxyundecyl)phosphonate (ii):

95.1 g (0.864 mol) of dimethyl hydrogenphosphonate were introduced in a round bottom flask equipped with a condenser and a pressure-equalizing dropping funnel containing the undec-10-enyl acetate (0.29 mol) and subsequently degassed and saturated with nitrogen. The temperature was raised to 135 °C and di-*tert*-butyl peroxide (2.1 g, 14 mmol) was injected in the funnel. The reactants were added dropwise during 20 hours. After addition completion, the dimethylhydrogenphosphonate excess was distilled partially under high vacuum (10⁻² mbar at 110 °C). Finally dimethyl(11-acetyloxyundecyl)phosphonate was extracted with n-pentan, dissolved into diethyl ether and washed twice with a water solution saturated with sodium chloride. Product yield: 82 g (88%). Purity was checked by both ¹H-NMR and ³¹P-NMR.

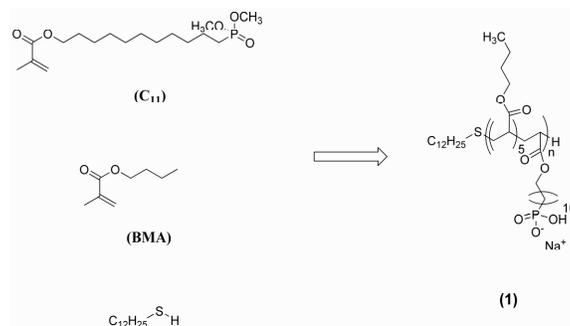
Synthesis of dimethyl(11-hydroxy- undecyl)phosphonates (iii):

Dimethyl(11-acetyloxyundecyl)phosphonates (0.25 mol) was dissolved with 2.14 g (0.038 mol) of potassium hydroxide into methanol (250 ml). The mixture was degassed, saturated with nitrogen, heated up to 60 °C and stirred under reflux until the disappearance of the triplet signal at 4 ppm in ¹H-NMR characteristic of the CH₃-CO-O-CH₂- protons. After the cleavage of the acetyl protection, KOH was precipitated into acetone previously dried on molecular sieves. Then dimethyl(11-hydroxy- undecyl)phosphonate was diluted into diethyl ether and washed with a water solution saturated with sodium chloride. The disappearance of the single peak at 1.95 ppm detected by ¹H-NMR was carefully checked. Yield: 60 g (84%). Purity was additionally verified by ³¹P-NMR.

Synthesis of dimethyl(11-methacryloyloxy undecyl)phosphonate monomer (C₁₁):

Dimethyl(11-hydroxyundecyl)phosphonate (0.21 mol) and 25.9 g (0.256 mol) of triethylamine was dissolved into dichloromethane (250 ml). The reaction mixture was degassed, saturated with nitrogen and cooled down to 0 °C in an ice bath. Then 26.8 g (0.256 mol) of methacryloyl chloride (freshly distilled) previously dissolved into dichloromethane (20 ml) were added dropwise While maintaing the same cooling conditions. At the end of the addition, the reaction mixture was stirred under reflux at 40 °C for 16 hours. Subsequently triethylammonium hydrochlorides were filtered off and the mixture was dissolved into diethyl ether. Finally the remaining methacryloyl derivatives were removedby washings, first with a saturated NaHCO₃ aqueous solution followed with a water solution saturated with sodium chloride until the disappearance of the ¹H-NMR signals at around 5.5 ppm and 6 ppm from ethylenic proton of methacryloyl side product derivatives. Final yield: 39 g (52%) of dimethyl(11-methacryloyloxy undecyl)phosphonate monomer were obtained. Purity was checked by both ¹H-NMR and ³¹P-NMR and corresponds to the previously published values¹.

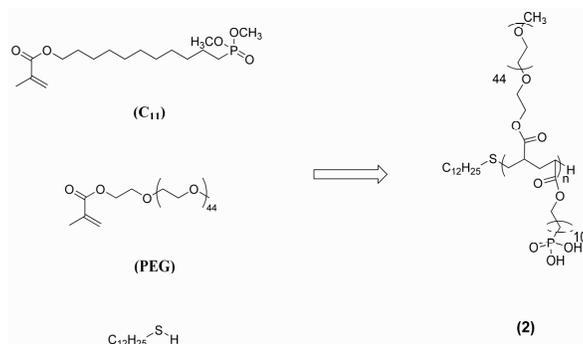
2. Synthesis of Polymer (1)



1.225 g of Dimethyl(11-methacryloyloxy undecyl)phosphonate monomer (C₁₁) (3.520 mmol) (see previous chapter), 4 g (28 mmol) of freshly distilled n-Butyl methacrylate monomer (BMA) (Aldrich, cat 23, 586-5) and 0.267 g (1.319 mmol) of 1-dodecanthiol (Aldrich, cat D22, 140-6) were dissolved into acetonitrile (SdS - 60521) (310 ml). The mixture was carefully degassed and saturated with nitrogen at room temperature. Prior addition of benzoyl peroxide (Fluka - 33581) (0.077 g, 0.318 mmol) dissolved into 10 ml acetonitrile) the reaction temperature was raised up to 85 °C. At this point the polymerization occurred during 16 hours under reflux and strong stirring conditions. Subsequently the solvent was evaporated and the polymer precipitated into n-pentan (SdS - 640521). Purification was repeated until obtaining a ¹H-NMR spectrum without any peaks at 5.5 and 6 ppm coming from any residual monomer. After filtration, the polymer was dissolved again into acetonitrile to be able to get collected and finally dried at first with a rotary evaporator and then under high vacuum (10⁻² mbar at 85 °C). The chemical structure as well as purity was checked with both ¹H- (ratio calculation between C₁₁ and BMA monomers) and ³¹P- (purity of the product means no side-polymerization signals involving phosphonate functions noticed) NMR. Yield: 3.4 g (61.6 %).

The purified diester polymer was thus dissolved into dichloromethane (Carlo Erba - Code n°: 463003) (50 ml) and the reaction mixture was carefully degassed and saturated under an atmosphere of argon. After having protected the solution from light by means of an aluminum foil, 2 ml (1.5 · 10⁻² mol) of bromotrimethylsilane (Aldrich, cat 19, 440-9) were added². The progress of the reaction was followed by ³¹P-NMR by observing a strong down field shift of the single peak at about 6 ppm from the initial position (≈ 36 ppm). When no more signal from the reactant was detected, the solvent was evaporated (rotary evaporator followed by high vacuum pumping at 10⁻² mbar) and the remaining silanized intermediate was immediately dissolved in a methanol solution of NaOH (Carlo Erba - PF369777000) (0.13 g dissolved into 50 ml methanol) and the mixture was stirred for additional 16 hours. After evaporation of the solvent, the polymer obtained as white powder (1) was pilled in a mortar and then dried under high vacuum (10⁻² mbar at 85 °C) and then. Yield after methyl cleavage: 1.04 g, (30.84 %).

3. Synthesis of Polymer (2)



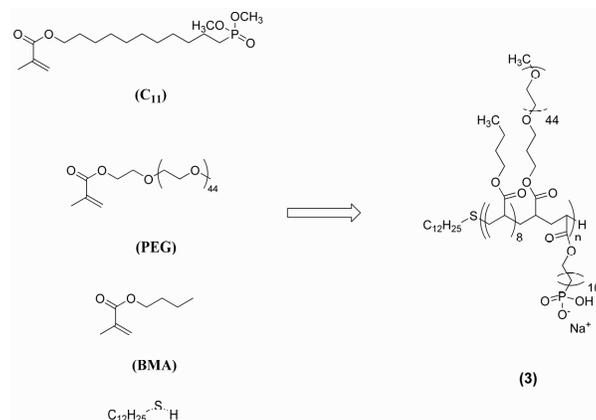
Same chemical reaction conditions as for polymer **1** were adopted. Changes are described below.

BMA was replaced by carefully dried poly(ethylene glycol) methyl ether methacrylate (mPEG-methacrylate) (Aldrich – cat 447951). The reactant amounts dissolved into acetonitrile (115 ml in total) were: 2.0 g (5.7 mmol) of C₁₁, 12.0 g (5.7 mmol) of mPEG-methacrylate, 0.097 g (0.479 mmol) of 1-dodecanthiol, 0.0200 g (0.0825 mmol) of benzoyl peroxide.

After polymerization, the polymer was purified by precipitation into diethyl ether (Acros – 60005) instead of n-pentan (yield: 7.6 g, 53.8 %).

For the cleavage step, 2 ml (15 mmol) bromotrimethylsilan was required and afterwards the silanezed intermediate was dissolved into pure methanol without addition of NaOH. The final polymer was purified twice. Firstly, by filtration over silica (SdS – 2100017) eluting with dichloromethane and then with methanol. In between the polymer was dried under high vacuum (10⁻² mbar) at room temperature, frozen (liquid nitrogen) and pilled. Secondly by dialysis against ultra pure water (MilliQ system) for one week (Spectra/Por® 3, Dialysis Membrane – MWCO: 3,500). Finally, the polymer (**2**) was lyophilized by freeze-drying (for 48 hours at -48°C and 0.2 mbar). Yield after methyl cleavage: 0.47 g, (6.20 %).

4. Synthesis of Polymer (3)

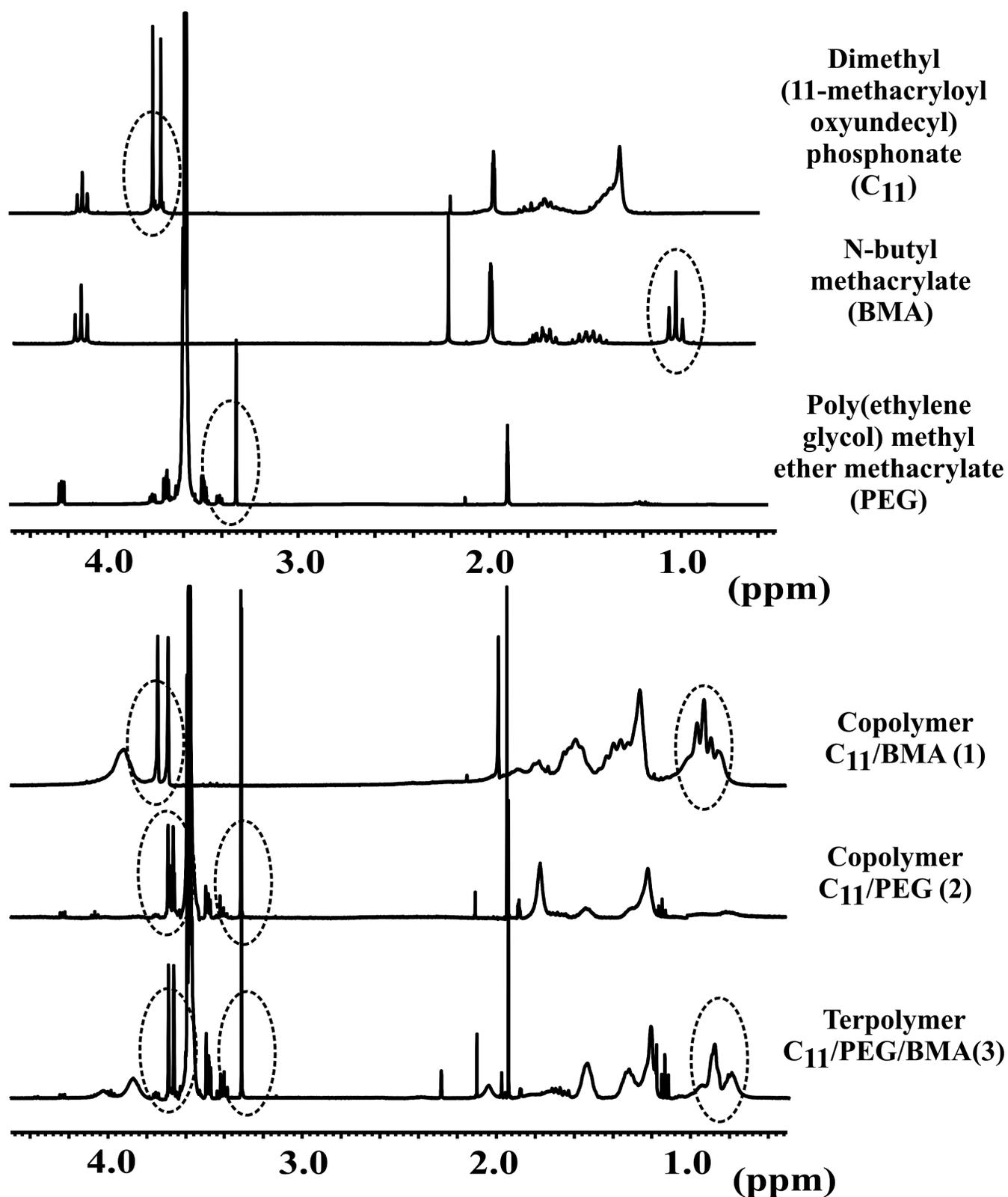


Same chemical reaction and purification conditions as for polymer **2** were adopted. Changes are described below.

All three monomers (C₁₁, BMA and mPEG-methacrylate) were dissolved into acetonitrile (360 ml in total) using the following amounts: 1.392 g (4.000 mmol) of C₁₁, 4 g (28 mmol) of BMA, 8.24 g (3.96 mmol) of PEG, 0.303 g (1.497 mmol) of 1-dodecanthiol, 0.087 g (0.359 mmol) of benzoyl peroxide. After polymerization and purification, 2.0 g were obtained (yield: 14.3%).

For the cleavage step, 0.5 ml (3.8 mmol) of bromotrimethylsilane were required and 25.70 mg (0.64 mmol) of NaOH were dissolved into methanol to cleave the silanezed intermediate. Yield after purifications (precipitation and dialysis): 0.68g of terpolymer (33.11 %).

5. $^1\text{H-NMR}$ spectra



NMR spectra were recorded on a Bruker 250 MHz spectrometer using CDCl_3 as solvent and tetramethylsilane as reference. The main differences between the polymer structures are noticed at $\delta \approx 0.9$ ppm (BMA multiplet signal: $-\text{CH}_2-\text{CH}_3$, methacrylic multiplet signal: $-\text{CH}_2-\text{C}(\text{CH}_3)-$) and at $\delta \approx 3.3$ and $\delta \approx 3.6$ ppm (PEG multiplet signal: $-\text{CH}_2-\text{CH}_2-\text{O}-$ and singlet: $-\text{CH}_2-\text{O}-\text{CH}_3$, respectively). Doublet coming from dimethyl-phosphonate is located at $\delta \approx 3.7$ ppm ($-\text{PO}-(\text{OCH}_3)_2$).

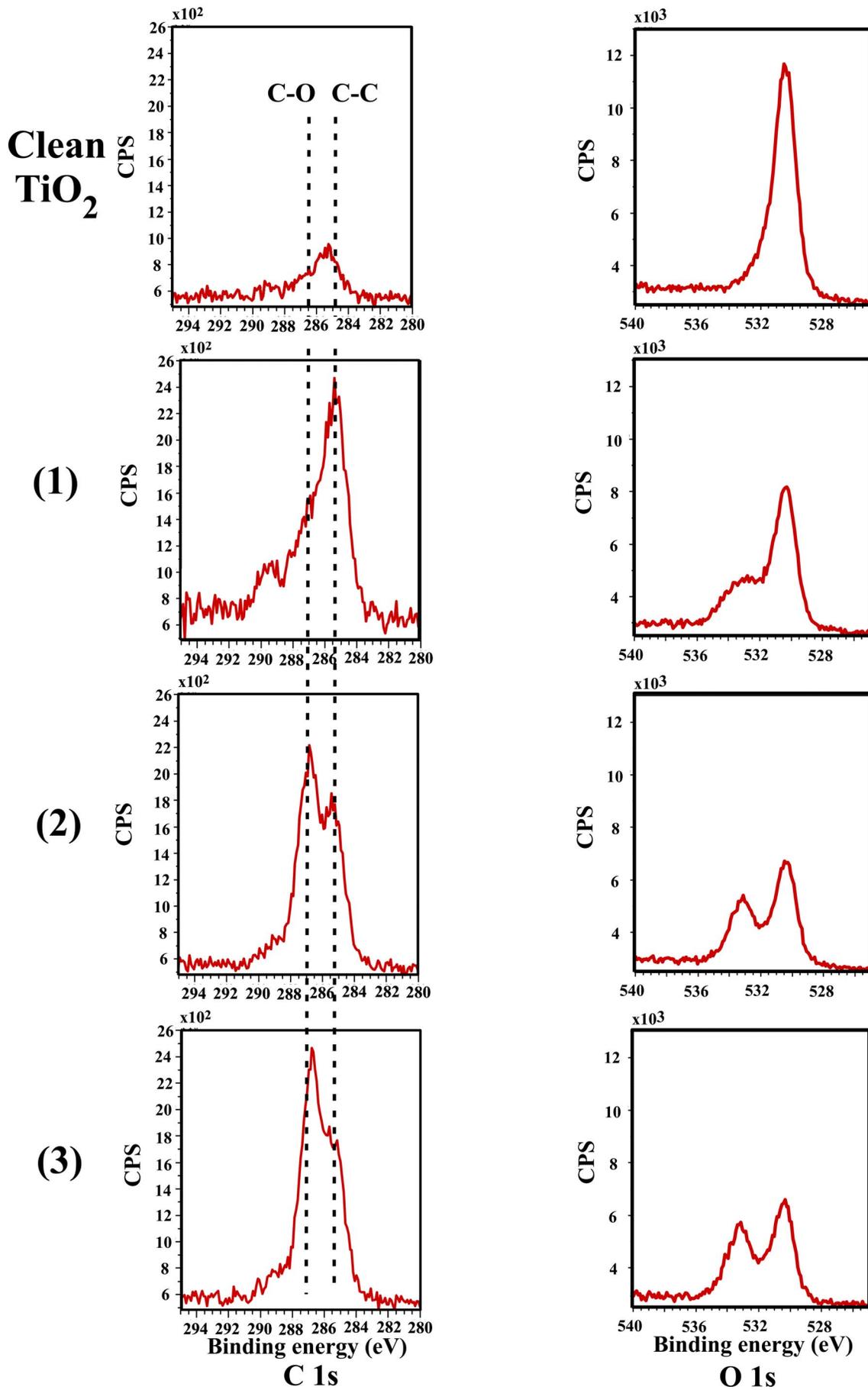
6. X-ray photoelectron spectroscopy

XPS spectra were recorded at a 90° emission angle with a SAGE 100 instrument (Specs, Berlin, Germany) using non-monochromatized Al K α radiation at 320 W (13 kV) and an electron-energy analyzer pass energy of 50 eV for low resolution survey and of 14 eV for high-resolution element detail scans. The analyzed area was 6 mm² giving therefore a lateral averaged chemical composition. To determine the quantitative surface composition from XPS measurements, Scofield's sensitivity factors³ were used. The data processing was performed with CASA XPS software (Ver. 2.2.24) and the energy given as the electron binding energy. The spectra were calibrated to aliphatic carbon 1s signal at 285.0 eV.

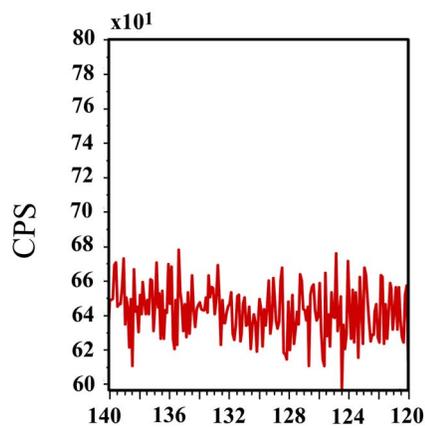
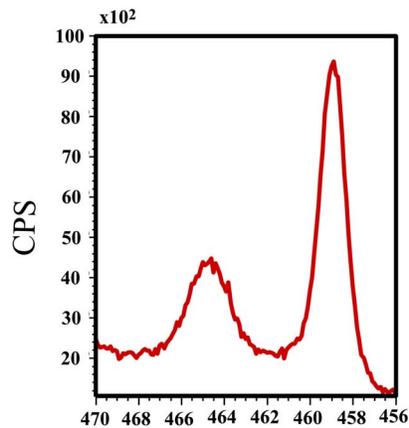
The three different polymers (**1**, **2** and **3**) were adsorbed on smooth silicon wafers coated with 2.3 nm natural SiO₂ and 20 nm sputter coated TiO₂. In order to reduce the number of species and components detected the TiO₂ thickness was chosen in order to be bigger than the XPS information depth (ca. 6-8 nm).

Normalized atomic concentrations measured on three independent samples are given thereafter.

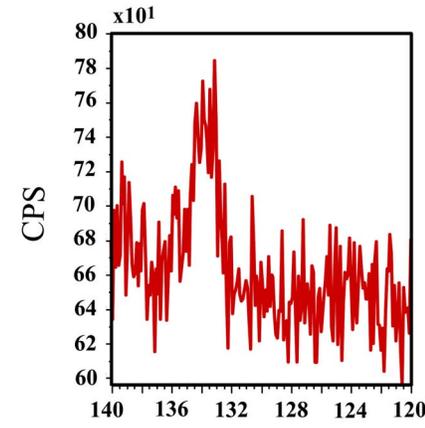
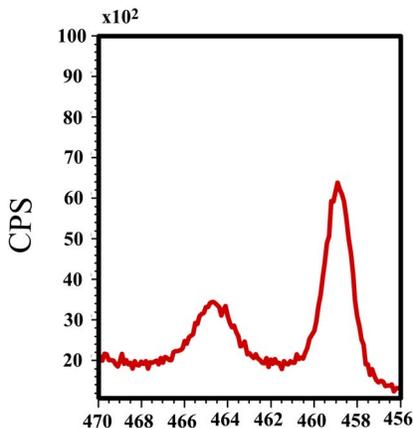
Sample	%C	%O	%Ti	%P
TiO ₂	10.8 ± 0.5	62.0 ± 0.2	26.7 ± 0.3	0.1 ± 0.1
TiO ₂ +(1)	45.0 ± 0.8	41.6 ± 1.1	12.5 ± 0.8	1.0 ± 0.2
TiO ₂ +(2)	46.4 ± 0.7	41.5 ± 0.3	11.7 ± 0.4	0.4 ± 0.3
TiO ₂ +(3)	47.3 ± 0.8	41.5 ± 0.9	10.5 ± 0.4	0.5 ± 0.4



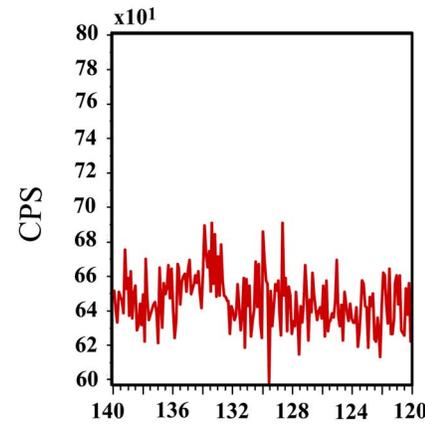
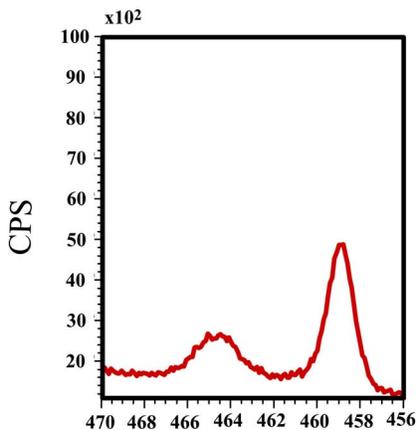
**Clean
TiO₂**



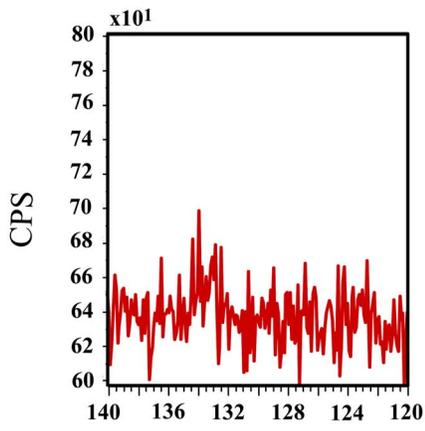
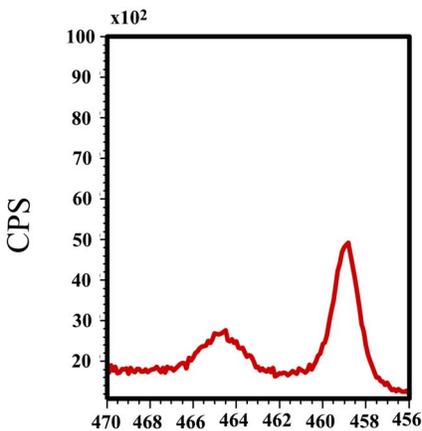
(1)



(2)



(3)



Binding energy (eV)

Ti 2p

Binding energy (eV)

P 2p

7. References

- (1) Senhaji, O.; Robin, J. J.; Achchoubi, M.; Boutevin, B. *Macromol. Chem. Phys.* **2004**, *205*, 1039-1050.
- (2) McKenna, Charles E.; Higa, M. T.; Cheung, N. H.; McKenna, M.-C. *Tetrahedron Letters* **1977**, *18*, 155-158.
- (3) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129-137.