Supplementary Material for

Photo-crosslinking and surface-attachment of polyvinyl alcohol nanocoatings by C,H insertion to customize their swelling behavior and stability in polar media

Andre Michele,[a] Daniel Luft,[a] Günter E. M. Tovar,[a,b] Alexander Southan[a]

[a]Institute of Interfacial Process Engineering and Plasma Technology IGVP, University of Stuttgart, Nobelstr. 12, 70569 Stuttgart, Germany. Tel: +49 711 68568162; E-mail: alexander.southan@igvp.uni-stuttgart.de.

[b]Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Nobelstr. 12, 70569 Stuttgart, Germany.

Table of contents

1 List of reaction conditions during synthesis of benzophenone-modified PVA

Table S1: Reaction conditions of PVA-BP synthesis and yielded χ_{BP}.

χ_{BP} [%]	Equivalents 4-fluorobenzophenone	Reaction after adding 4-fluorobenzophenone	Used base and equivalents
25	0.3 eq	22 h at 25 °C	0.9 eq of NaH
20	0.4 eq	6 h at 25 °C	0.9 eq of NaH
15	0.2 eq	19 h at 25 °C	0.9 eq of NaH
10	0.3 eq	5 h at 25 °C	0.9 eq of NaH
5	0.1 eq	5 h at 25 °C	0.9 eq of NaH
5	0.07 eq	19 h at 25 °C	0.9 eq of NaH
2	0.3 eq	12 h at 100°C, 11 h at 25 °C	1 eq of Na_2CO_3
2	0.07 eq	60 h at 25 °C	1 eq of KOH
1	0.04 eq	16 h at 25 °C	0.9 eq NaH

2 [1]H NMR spectra of PVA-BP and 4-fluorobenzophenone

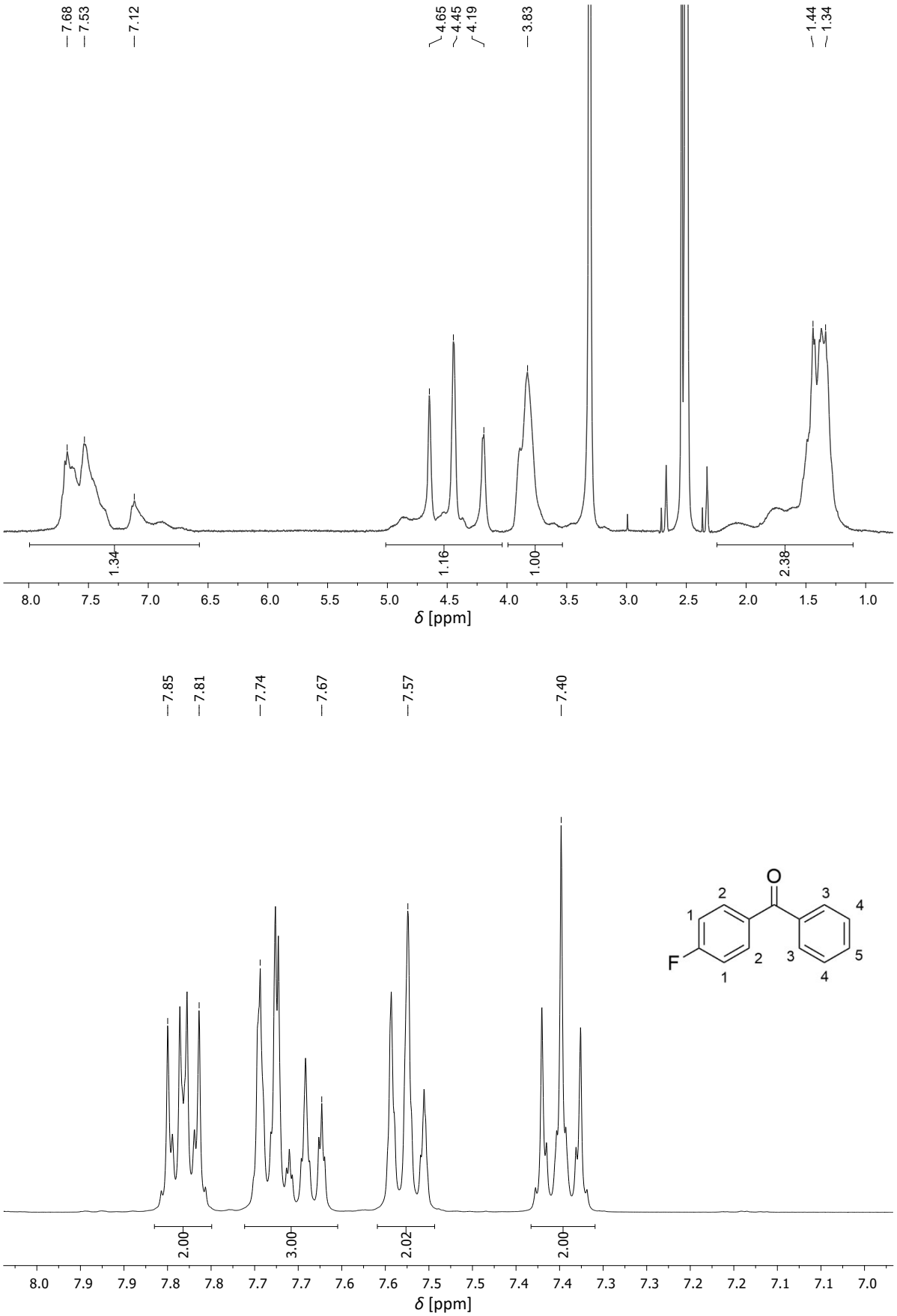


Figure S1: a) [1]H-NMR-spectrum of PVA-BP15. Assignment of the signals was described in the methods part of the main publication. b) [1]H-NMR-spectrum of 4-fluorobenzophenone. [1]H-NMR (500 MHz, DMSO-d6): δ [ppm] = 7.85-7.81 (m, 2H, H-2), 7.74-7.67 (m, 3H, H-3, H-5), 7.57 (t, 2H, H-4), 7.40 (t, 2H, H-1).

3 Photos of coated silicon wafers

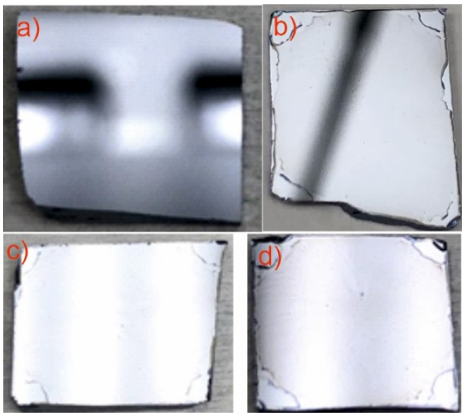


Figure S2: Photos of silanized and coated wafers according to the procedure described in the methods in the main text. A wafer only silanized without coating as reference was shown in (a). Wafers coated with PVA-BP5 (b), PVA-BP10 (c) and PVA-BP25 (d), respectively, had homogeneous yellowish layers on top without visible defects.

4 Correlation between gel yield and equilibrium degree of swelling

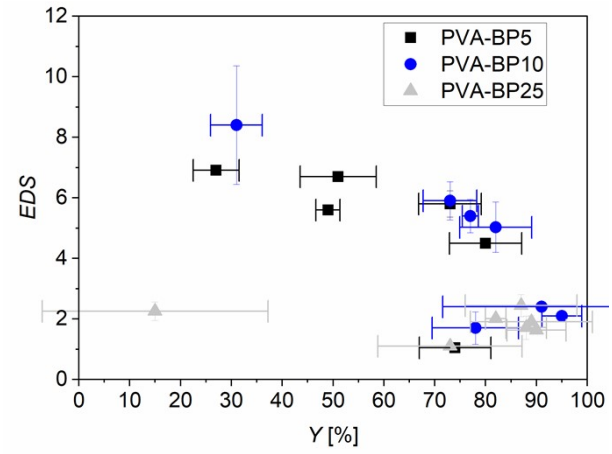


Figure S3: Equilibrium degree of swelling *EDS* of irradiated polymer films of PVA-BP5, PVA-BP10 and PVA-BP25 as a function of gel yield *Y*.

5 UV/VIS spectra of PVA-BP after irradiation

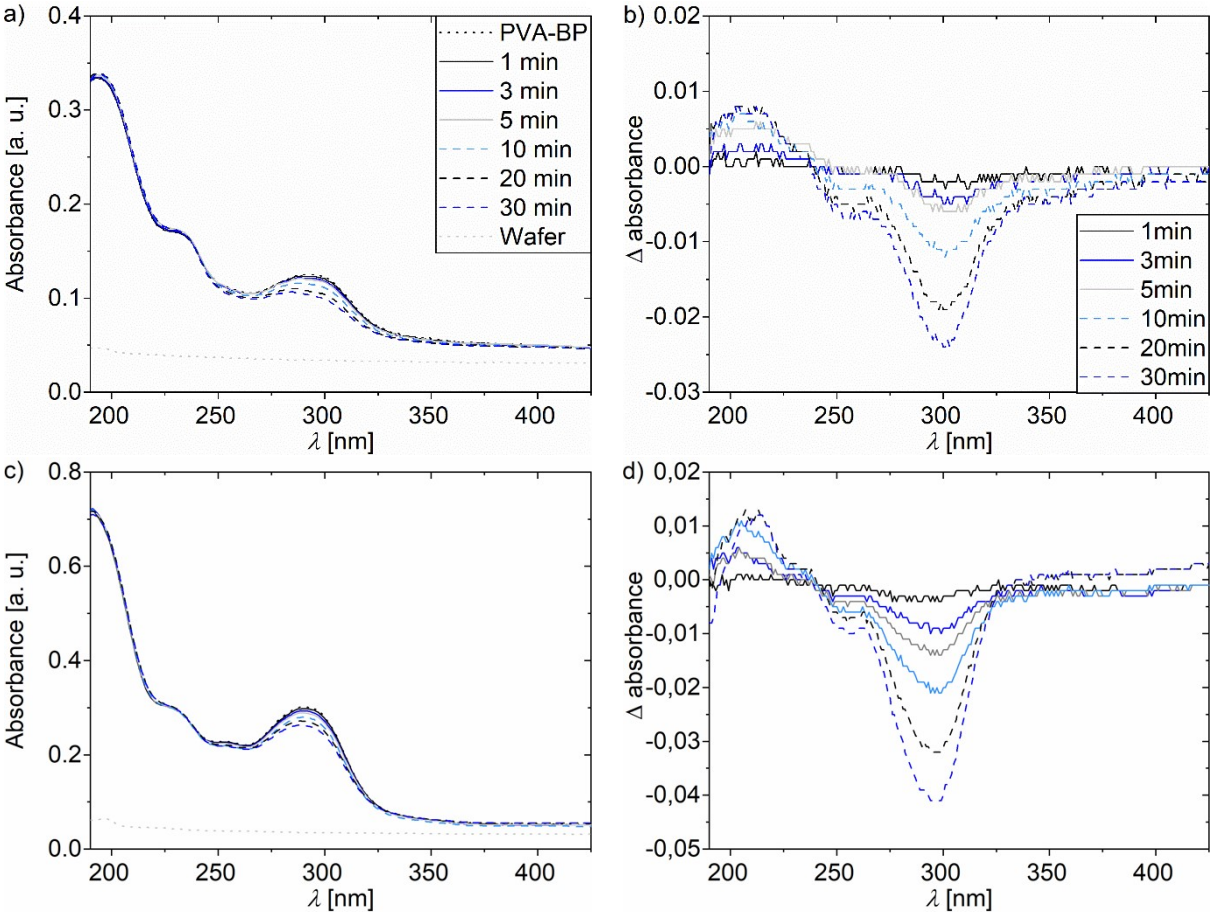
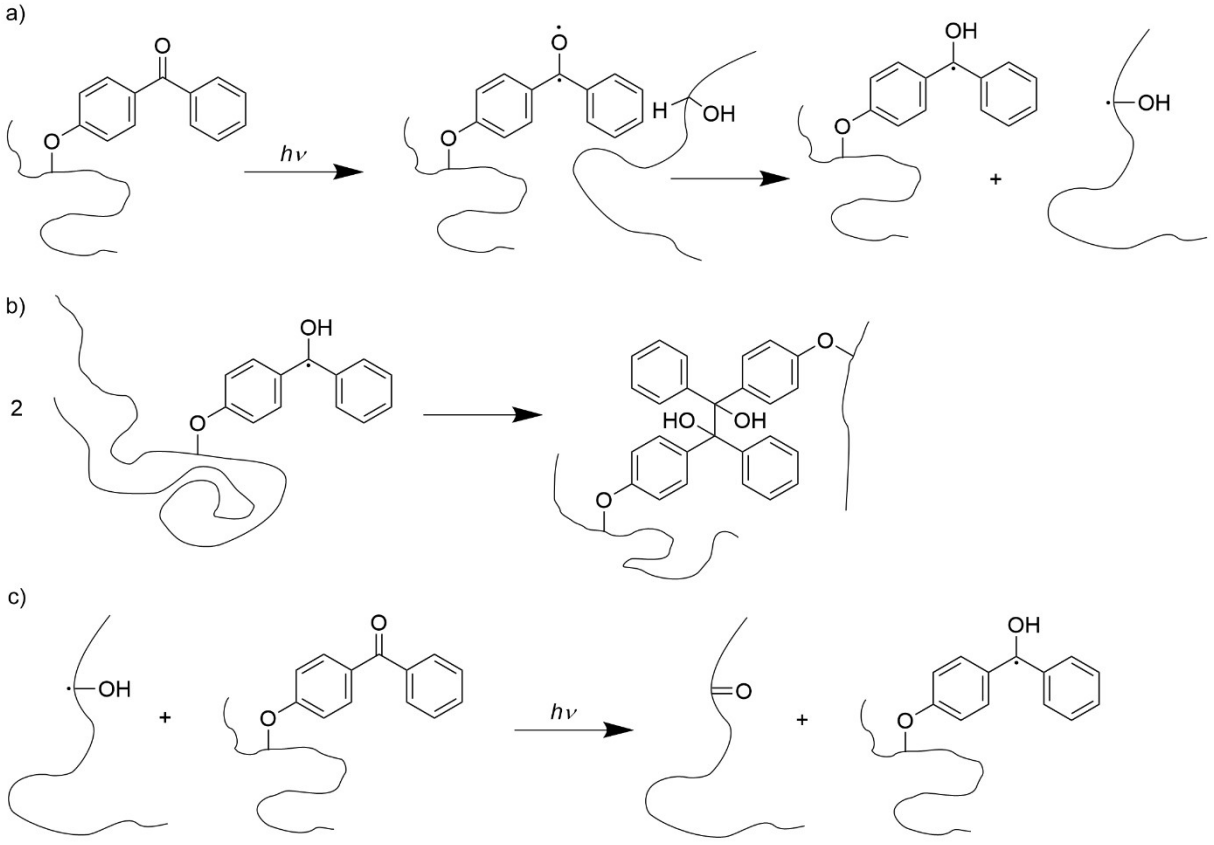


Figure S4: UV/VIS-spectra of PVA-BP10 (a, b) and PVA-BP25 (c, d) after irradiation for different times. Spectra (a, c) and difference spectra (b, d) share the legends.



Scheme S1: Possible photo reactions of PVA-BP. The BP moieties were activated by UV-light and formed biradicaloide triplet state carbonyl radicals. These radicals were prone to abstract hydrogens adjacent to the secondary hydroxyl groups (a). Subsequent recombination of two ketyl radicals would lead to a benzopinacol related structure (b). The aliphatic radicals could be oxidized to a carbonyl compound (c).