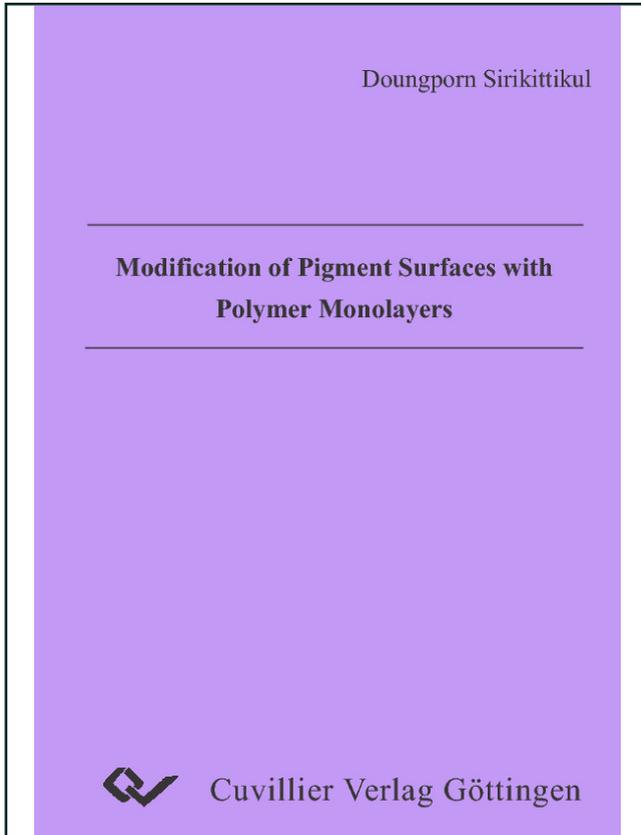




Doungporn Sirikittikul (Autor)
**Modification of Pigment Surfaces with Polymer
Monolayers**



<https://cuvillier.de/de/shop/publications/2852>

Copyright:
Cuvillier Verlag, Inhaberin Annette Jentsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen,
Germany
Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

Content

List of the abbreviation.....	i
1 Introduction	1
1.1 Historical perspective	1
1.2 Dyes and pigments	8
1.3 Pigments for special effects.....	9
1.4 Properties of pigments.....	10
1.4.1 Chemical properties of organic pigments.....	10
1.4.2 Chemical properties of inorganic pigments.....	12
1.4.3 Physical properties.....	14
1.5 Surface treatments of pigments	17
1.5.1 Physisorption	17
1.5.2 Chemisorption	18
1.5.2.1 Attachment of the polymer chains containing terminal functional groups	19
1.5.2.2 Grafting polymerization using surface-attached initiating groups	20
1.5.2.3 Grafting polymerization using surface-attached monomer units	25
1.5.3 Encapsulation of particles.....	25
2 Strategy of the described work.....	26
2.1 Concept of the surface modification.....	26
2.2 Pigments used in this work.....	28
2.2.1 Isoindoline pigments	28
2.2.2 Titanium dioxide	29
2.2.3 Pigment for special effects	29
2.3 Modification of pigment surfaces with polymer monolayers through hydrogen bonding	30
2.4 Modification of pigment surfaces through covalent bonds	31
2.4.1 Modification of organic pigment particles	32
2.4.2 Modification of inorganic pigment particles	33
2.5 Investigation of the fastness property of unmodified and modified pigments ...	33

3	Self-Organization of Melamine-Cyanuric Acid Analogues	34
3.1	Synthesis of an active ester of the initiator	37
3.2	Synthesis of a melamine coupling agent	40
3.2.1	Synthesis of melamine containing trialkoxy silane group.....	40
3.2.2	Synthesis of <i>N</i> -(6-amino-hexyl)-[1,3,5]triazine-2,4,6-triamine	42
3.2.3	Reaction of <i>N</i> -(6-amino-hexyl)-[1,3,5]triazine-2,4,6-triamine with an active ester or acid chloride.....	45
3.3	Model reactions on planar substrate: polymer monolayers through surface initiated polymerization	47
3.3.1	Immobilization of a melamine moiety onto a planar substrate	49
3.3.2	Preparation of a Melamine:PGL1840-PFB layer	51
3.3.3	Preparation of a Melamine:PGL1840:Mel-PFB layer.....	52
3.3.4	Preparation of a Melamine:PGL1840:Mel-ABCC:PMMA layer.....	55
3.3.5	Preparation of a Melamine:PGL1840:LPEI-ABCC:PMMA layer.....	58
3.3.6	Discussion.....	61
4	Surface Modification of Organic Pigments	62
4.1	XPS studies on the modification of various pigments with fluorinated probe molecules	63
4.2	Synthesis and immobilization of the initiator	67
4.3	“Grafting-from” polymerization via self-assembled azo-initiator monolayers..	73
4.3.1	Layer thickness as a function of monomer concentration	73
4.3.2	Graft density as a function of polymerization time	80
4.3.3	Polymerization with different monomers	85
4.3.4	Discussion and comparison with the pigment PGL1840.....	94
4.4	Grafting of polymers via copolymerization of surface-attached monomer.....	95
4.4.1	Immobilization of 2-methyl-acryloyl chloride (MA-Cl) on pigment surfaces... 95	
4.4.2	Layer thickness as a function of monomer concentration	96
4.4.3	Influence of the polymerization time.....	98
4.4.4	Influence of the initiator concentration	99
4.4.5	Polymerization with perfluorinated monomer (HDFDA)	100
4.4.6	Discussion and comparison with the pigment PGL1840.....	103

5	Surface Modification of Inorganic Pigments	104
5.1	Immobilization of initiators on pigment surfaces.....	104
5.1.1	Initiator monolayers from silanes	104
5.1.2	Initiator monolayers from phosphates	105
5.1.2.1	Immobilization of 2-aminoethyldihydrogenphosphate (AEP) on TiO ₂	106
5.1.2.2	Immobilization of 2-aminoethyldihydrogenphosphate (AEP) on PCG2020 ...	108
5.1.2.3	Immobilization of ABCC to the surface-attached amino monolayers	109
5.1.3	Qualitative characterization of initiator monolayers on inorganic pigments ...	110
5.1.3.1	TiO ₂ -ADS	110
5.1.3.2	TiO ₂ -ABCC	111
5.1.3.3	PCG2020-ABCC	113
5.1.4	Determination of the initiator graft density on the inorganic pigments	115
5.2	“Grafting-from” polymerization via self-assembled azo-initiator monolayers	117
5.2.1	Qualitative characterization of the polymer monolayer attached to pigment surfaces	117
5.2.1.1	FTIR spectroscopy.....	117
5.2.1.2	X-ray photoelectron spectroscopy (XPS).....	118
5.2.2	Quantitative characterization of polymer-attached surfaces with various polymerization parameters	121
5.2.2.1	Graft density as a function of monomer concentration	121
5.2.2.2	Graft density as a function of polymerization time	123
5.2.3	Discussion.....	125
5.3	Immobilization of 3-methacryloylpropyl trimethoxysilane on TiO ₂ particles.	126
5.3.1	Qualitative characterization of the methacrylate monolayer on TiO ₂ surfaces	126
5.3.2	Determination of the graft density of the methacrylate monolayer on TiO ₂ surfaces	129
5.4	Grafting of polymers via copolymerization of surface-attached monomers ...	131
5.4.1	Qualitative characterizations of the polymer-attached pigment surfaces.....	131
5.4.2	Quantitative characterization of polymer-attached surfaces with various polymerization parameters	132
5.4.2.1	Graft density as a function of monomer concentration	132
5.4.2.2	Graft density as a function of polymerization time	134
5.4.2.3	Layer thickness as a function of initiator concentration.....	135
5.4.3	Conclusions	136

6	Stability of Unmodified and Polymer-Modified Pigments against Alkaline Solutions	137
6.1	Investigation of the stability against various buffer solutions.....	137
6.2	Investigation of the stability of pigment with variation of the PMMA graft density.....	140
6.3	Investigation of the stability of pigment with different surface- attached monolayers.....	141
6.4	Discussion.....	142
7	Experimental Section	143
7.1	Chemicals and solvents	143
7.2	Method and characterizations	147
7.2.1	Differential scanning calorimeter (DSC).....	147
7.2.2	Elemental analysis	147
7.2.3	FTIR spectroscopy.....	147
7.2.4	Freeze-drying procedures	147
7.2.5	Gel permeation chromatography (GPC).....	147
7.2.6	Melting point determination	148
7.2.7	Nuclear magnetic resonance (NMR) spectroscopy	148
7.2.8	Titration experiment	148
7.2.9	UV-VIS spectroscopy.....	148
7.2.10	X-ray photoelectron spectroscopy (XPS).....	148
7.2.11	X-ray reflectivity (XRR)	149
7.3	Synthesis of 4-cyano-4-[1-cyano-3-(2,5-dioxo-pyrrolidin-1-yloxy carbonyl)-1-methyl-propylazo]-4-methyl-butyric acid 2,5-dioxo-pyrrolidin-1-yl ester (ABCC-AE).....	150
7.4	Synthesis of linear polyethylene imine containing initiator units	150
7.4.1	Preparation of linear polyethylene imine (LPEI) by hydrolysis of poly(2-ethyl-2-oxazoline).....	150
7.4.2	Preparation of linear polyethylene imine containing initiator units (LPEI-ABCC).....	151
7.5	Synthesis of the melamine derivatives	151
7.5.1	Synthesis of 1-(4,6-diamino-[1,3,5]triazin-2-yl)-3-{3'-[tris-(2-hydroxy-ethyl)-silanyl]-propyl}-urea (Mel-Silane).....	151
7.5.2	Synthesis of <i>N</i> -(6-amino-hexyl)-[1,3,5]triazine-2,4,6-triamine (Mel-C ₆ H ₁₂ -NH ₂).....	152

7.5.3	Synthesis of 4-cyano-4-{1-cyano-3-[6-(4,6-diamino-[1,3,5]triazin-2-ylamino)-hexylcarbamoyl]-1-methyl-propylazo}-N-[6-(4,6-diamino [1,3,5]triazin-2-ylamino)-hexyl]-4-methyl-butylamide (Mel-ABCC).....	153
7.5.4	Synthesis of <i>N</i> -[6-(4,6-diamino-[1,3,5]triazin-2-ylamino)-hexyl]-2,3,4, 5,6-pentafluoro-benzamide (Mel-PFB).....	153
7.6	Synthesis of the initiator for surface attachment	154
7.6.1	Synthesis of 4,4'-azobis-(4-cyanopentanoyl chloride) (ABCC)	154
7.6.2	Synthesis of symmetric dichlorosilane initiator ⁸⁶	154
7.6.2.1	4-(3-Allyloxycarbonyl-1-cyano-1-methyl-propylazo)-4-cyano-4-methyl-butyl acid allyl ester	154
7.6.2.2	4-{3-[4-(Chloro-dimethyl-silanyl)-butoxycarbonyl]-1-cyano-1-methyl-propylazo}-4-cyano-4-methyl-butyl acid 3-(chloro-dimethyl-silanyl)-propyl ester (ADS)	155
7.7	Preparation of layer-by-layer on planar substrate through H-bonding.....	156
7.7.1	Immobilization of Mel-Silane auf planar substrate	156
7.7.2	Complexation of complementary molecule on the Mel-Silane monolayer.....	156
7.7.3	Generation of polymer monolayers using initiator layers bound on the surfaces via H-bonding.....	157
7.8	Surface modification of organic pigment particles.....	157
7.8.1	Immobilization of fluorinated molecules	157
7.8.2	Immobilization of initiator molecules	157
7.8.3	Immobilization of monomer molecules.....	157
7.9	Surface modification of inorganic pigment particles	158
7.9.1	Immobilization of initiator based on chlorosilane onto pigments	158
7.9.2	Immobilization of initiator based on phosphoric acids onto pigments.....	158
7.9.2.1	Amino monolayers on the pigment surfaces	158
7.9.2.2	Immobilization of ABCC initiator onto the amino monolayers.....	158
7.9.3	Immobilization of monomer onto pigments	159
7.10	Polymerization of vinyl monomers with initiator-modified pigments	159
7.11	Polymerization of vinyl monomer with monomer-modified pigment.....	159
7.12	Stability of unmodified and polymer-modified pigments against alkaline solutions.....	160
8	Conclusion	161
9	Zusammenfassung	164

10	Appendix.....	167
10.1	XP spectra of unmodified PGL1840 and PFB-modified PGL1840	167
10.2	DSC measurements of the Pigment-Azo before and after polymerization at room temperature.....	168
10.3	Calibration curve via integration of the UV absorption band of various unmodified PGL1840 concentrations.....	169
10.4	“Grafting-from” polymerization on PGL1840 surfaces using self-assembled azo-initiator monolayers (PGL1840-Azo).....	170
10.4.1	Layer thickness as a function of monomer concentration	170
10.4.2	Graft density as a function of polymerization time	172
10.4.3	Polymerization with different monomers using PGL1840-Azo.....	174
10.5	Fitted curves of C(1s) detail spectra of various polymer-attached PGL1840 ..	176
10.6	Fitted curves of C(1s) detail spectra of various polymer-attached PGL1155 ..	177
10.7	Grafting of polymer on PGL1840 surfaces through copolymerization of surface-attached monomer.....	180
10.7.1	Layer thickness as a function of monomer concentration	180
10.7.2	Influence of the polymerization time.....	180
10.7.3	Influence of the initiator concentration	181
10.7.4	Polymerization with perfluorinated monomer (HDFDA)	182
10.8	“Grafting-from” polymerization on inorganic pigment surfaces via self-assembled azo-initiator monolayers (SAIMs).....	184
10.8.1	Graft density as a function of monomer concentration	184
10.8.1.1	PCG2020-ABCC as surface-initiated polymerization.....	184
10.8.1.2	TiO ₂ -ABCC as surface-initiated polymerization.....	184
10.8.1.3	TiO ₂ -ADS as surface-initiated polymerization.....	185
10.8.2	Graft density as a function of polymerization time	185
10.8.2.1	TiO ₂ -ABCC as surface-initiated polymerization.....	185
10.8.2.2	TiO ₂ -ADS as surface-initiated polymerization.....	186
10.9	Grafting of polymers via copolymerization of surface-attached monomer monolayers on inorganic pigment surfaces	186
10.9.1	Graft density as a function of monomer concentration	186
10.9.2	Graft density as a function of polymerization time	187
10.9.3	Layer thickness as a function of initiator concentration.....	187

10.10	Stability of unmodified and polymer-modified PGL1840 pigments against alkaline solutions	188
10.10.1	Investigation of the stability against various buffer solutions.....	188
10.10.2	Investigation of the stability with variation of the PMMA graft density and with different surface-attached polymer monolayers	189
11	Literature	190
	Danksagung	196