

## Variable surface coatings composed of organic-inorganic hybrid polymers

Daniel Kessler<sup>1</sup>, Stefan Bahnmüller<sup>2</sup>, Patrick Theato<sup>\*1</sup>

<sup>1</sup>Institute of Organic Chemistry, University of Mainz, 55099 Mainz, Germany, theato@uni-mainz.de

<sup>2</sup>Bayer MaterialScience AG, New Business – New Technologies, 51368 Leverkusen, Germany

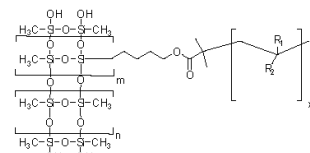


Figure 1. General formula of hybrid polymers.

Table 1. Properties of the block copolymer.

polymer	Mw	Block ratio org. : inorg.	T <sub>K,cond</sub> [°C]	T <sub>Decomp</sub> [°C]	T <sub>g</sub> [°C]
PMSSQ- <i>b</i> -PMA	73900	4.47 : 1	252.3	431.1	4.1
PMSSQ- <i>b</i> -PMMA	72700	1.44 : 1	186.1	417.7	131.6
PMSSQ- <i>b</i> -PEMA	14600	2.14 : 1	300.6	397.7	106.2
PMSSQ- <i>b</i> -PEHA	94600	0.81 : 1	280.2	415.9	-63.2
PMSSQ- <i>b</i> -PDMA	14600	1.51 : 1	293.9	403.2	-93.8

To investigate the behavior of the hybrid polymers in thin films, a 10 wt% solution in THF was spin coated and dip coated on silicon wafers and the surface contact angle of water was measured (table 2).

Table 2. Contact angles on silicon wafers.

Si-Wafer Film	Spin coating Θ <sub>a</sub> H <sub>2</sub> O [°]		Dip coating Θ <sub>a</sub> H <sub>2</sub> O [°]	
	uncured	cured	uncured	cured
PMSSQ	91,75	102,65	--	--
PMMA	84,2	91,6	--	--
PMMA- <i>b</i> -PMSSQ	99,6	102,5	105,8	104,6
PMA- <i>b</i> -PMSSQ	120,8	105,9	106,2	110,6
PEMA- <i>b</i> -PMSSQ	98,4	104,8	98,5	105,9
PEHA- <i>b</i> -PMSSQ	125,4	145,1	122,3	122,9
PDMA- <i>b</i> -PMSSQ	126,6	145,4	124,3	120,9

After curing PMMA-*b*-PMSSQ, PMA-*b*-PMSSQ, and PEMA-*b*-PMSSQ surfaces showed a contact angle similar to contact angle of a PMSSQ surface. Surprisingly, the systems containing an organic block, which had a T<sub>g</sub> below room temperature, showed a very high contact angle (Θ<sub>a</sub> > 145°). Experiments to understand this behavior are in progress.

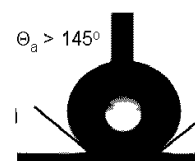


Figure 2. Contact angle of water on a PMSSQ-*b*-PDMA film.

The adhesion on different substrates was tested by Tape-test, all block copolymers show very high adhesion on glass, plastics as well as metals.

### Conclusions

Inorganic-organic block copolymers could be obtained via controlled radical polymerization from a PMSSQ macroinitiator. Used as a coating material on silicon wafers, the polymers with high T<sub>g</sub> organic block showed the hydrophobic behavior similar to a PMSSQ surface. Polymers with a low T<sub>g</sub> organic block showed an extreme hydrophobic behavior when coated on silicon wafer.

### References

- [1] R.D. Miller, *Science*, **1999**, 286, 421; P. Singer, *Semicond. Int.*, **1998**, June, 90.
- [2] H.W. Ro, K.J. Kim, P. Theato, D.W. Gidley, D.Y. Yoon, *Macromolecules* **2005**, 38 (3), 1031-1034.
- [3] J.F. Brown, L. Vogt, A. Katchman, K. Euslance, K. Kriser, *J. Am. Chem. Soc.* **1960**, 6294.
- [4] P. Theato, K.J. Kim, D.Y. Yoon, *Phys. Chem. Chem. Phys.* **2004**, 6, 1458

### Introduction

Surfaces attain more and more in the focus of industrial applications. So the challenge for material science and engineering rises to develop new surface coatings adapted to variable industrial problems.

Surface properties like hydrophobicity, hardness, scratch resistance, color and stimuli responsibility should be easy to modify. Covalent stability, adhesion on the substrate and processability must be given. But the basis for a broad applicability of a surface coating is a flexible tuning on different substrates, e.g. glasses, plastics, metals.

Our approach of a variable surface coating with the potential to fulfill the requirements of industry is an inorganic-organic block copolymer with an adjustable architecture.

As an inorganic block functionalized Polymethylsilsesquioxanes (PMSSQs) were synthesized. In a second step an organic block is grafted from incorporated functions in the inorganic block via controlled radical polymerization methods.<sup>1,2,3</sup> Via modification in the inorganic block as well as in the organic block and later curing promising surface coatings on different substrates could be achieved<sup>4</sup>.

### Experimental

**2-Bromoisobutyroic acid pent-4-enylate.** 160 mmol (13.9 g) pentenol and 50 mL chloroform were placed in a flask and cooled to 0 °C. Slowly 160 mmol (36.8 g) 2-bromoisobutyroic acid bromide in 20 mL chloroform were added and stirred for 4 h at room temperature. The reaction solution was washed three times with water, dried over MgSO<sub>4</sub> and the solvent was evaporated. The crude product was distilled in high vacuum. Bp. 50 °C at 3.3\*10<sup>-2</sup> mbar. Yield: 34,79 g (148 mmol, 92.5%) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) = 5.74 (m, 1H), 4.96 (m, 2H), 4.12 (t, <sup>3</sup>J = 6,6 Hz, 2H), 2.10 (m, 2H), 1.87 (s, 6H), 1.72 (quin., <sup>3</sup>J = 6,3 Hz, 2H)

**2-Bromoisobutyroic acid 5-(trichlorosilyl)pentyl ester (D).** 50 mg platinum on charcoal and 100 mL toluene were placed in a flask, 75 mmol (10.8 g) trichlorosilane and 50 mmol (11.75 g) 2-bromoisobutyroic acid pent-4-enylate were added. The solution was stirred at 80 °C for 24 h. After filtration and evaporation of the solvent the crude product was distilled in high vacuum. Bp. 104 °C at 7\*10<sup>-3</sup> mbar. Yield: 16.12 g (44 mmol, 88.0%) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) = 4.11 (t, <sup>3</sup>J = 6,6 Hz, 2H), 1.86 (s, 6H), 1.66 (m, 2H), 1.57 (d, <sup>3</sup>J = 6,9 Hz, 2H), 1.47 (d, <sup>3</sup>J = 6,6 Hz, 2H), 1.38 (m, 2H)

**Co-condensation to the PMSSQ-macroinitiator (MI).** Methyltrimethoxysilane (MTMS) and 2-bromoisobutyroic acid 5-(trichlorosilyl)pentyl ester were added in different ratios in a flask. Then 20 mL THF, 1000 mol% Water and 3 mol% HCl were injected. The solution was stirred at 0 °C for 3 h, dissolved in diethyl ether, washed with water and dried over MgSO<sub>4</sub>. The solvent was evaporated and the product was dried at high vacuum.

**ATRP.** CuBr, 2,2'-bipyridine, PMSSQ-macroinitiator, monomer and dioxane were placed in a Schlenk-flask and degassed. The solution was stirred at 90 °C and precipitated in heptane. The polymer was reprecipitated and dried at high vacuum.

### Results and discussion

Via co-condensation of MTMS and the functionalized trichlorosilane PMSSQ-macroinitiators for the ATRP could be obtained. The polymerization via ATRP from the PMSSQ-macroinitiator was carried out successfully with a wide range of different monomers: methylacrylate (MA), methylmethacrylate (MMA), ethylmethacrylate (EMA), ethylhexylacrylate (EHA) and decylmethacrylate (DMA). The resulting block copolymers were characterized with <sup>1</sup>H-NMR, GPC and TGA (Table 1).