METHACRYLATE COPOLYMERS FOR ANTI-BIOFOULING COATINGS: A CHEMICAL APPROACH

D. Pospiech1, S. Starke1,2, T. Bünker1, F. Müller1,2, R. Frenzel1, F. Simon1, K. Grundke1, U. Oertel1, M. Opitz3, R. Kruspe3 and B. Voit1,2

1 Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany (pospiech@ipfdd.de)
2 Technische Universität Dresden, Organic Chemistry of Polymers, Mommensenstraße 9, 01069 Dresden, Germany
3 IDUS Biologisch Analytisches Umweltlabor GmbH, Radeberger Straße 1, 01458 Ottendorf-Okrilla, Germany

ABSTRACT

The project discussed here aims at the development of materials for anti-biofouling coatings in freshwater applications, in particular for aluminum and glass surfaces. To create such coatings by a chemical approach new copolymers containing three or more comonomers were prepared. Each of the comonomers adds a specific function to the final material. Incorporation of metal ion complexing monomer units allows the formation of complexes with ions working as biocide and should result in a drastic reduction of the necessary biocide concentration in coatings because complexation of ions takes place only at the outer surface of the material and thus, the total concentration tends to be negligible. Moreover, generation of strong complexes should prevent leaching of the metal ions and improve the durability of the biocide effect. Here, results concerning synthesis, physical characterization, preparation of coatings on glass and the effect of these coatings on biofouling as probed with bacteria and algae in freshwater is presented. A considerable reduction of biofouling by bacteria (Staphylococcus aureus) and algae (type Achnanthidium spec.) could be detected.

INTRODUCTION

Biofouling is a serious problem which disturbs almost everywhere it appears. The term summarizes all biological processes and phenomena occurring on the surface of materials in contact with different environments. Examples of these different types of fouling are marine biofouling in aquatic environment, freshwater fouling in sweet water environment, membrane fouling in water treatment processes, biofouling of (bio)materials in body fluids or during medical treatments (e.g. at dialysis membranes), to name just a few. The complex processes of biofouling involve colonization of structures that are either living or artificial (Briand, 2009). Depending on the environment, different foulers play a role which significantly influences the resulting biofouling film. Each of the various kinds of fouling needs to be solved by a special strategy and general solutions are almost impossible.

The present work is directed at developing coatings able to prevent freshwater biofouling, in order to limit the variety of parameters and to understand basic relations between chemistry of the surfaces and biofouling. These polymer materials are intended to be used as coatings for constructions in contact with freshwater, e.g. on boats, as protecting layer in aquaria, shower cubicles and bathrooms, but also in heat exchangers. Biofouling in heat exchangers yields the formation of biofilms which reduce the heat transfer coefficient, heat transfer rates and thus, efficiency of the heat exchanger drastically (Müller-Steinhagen, 2010). Glass surfaces require coatings which are transparent with good adhesion; heat exchanger surfaces require adhesion to the substrate, high performance against biofouling and high durability. Strategies to reduce heat exchanger fouling include biocide treatment of the water used, impregnation of the parts of the heat exchanger system, cleaning of the exchanger parts, and others (IKSR, 2002). Currently, there is no main pathway known to prevent biofouling completely, and therefore further studies, in particular with respect to structure-action relationships, are required.

The work presented here is focused on the creation of materials applicable as impregnation coatings. The chemical approach includes synthesis of new copolymers consisting of different comonomers which are randomly distributed along the polymer chains and insert different functions into the material. The concept follows work about fouling release surfaces by the group of C. K. Ober et al. performed within the EU Ambio project (Krishnan, 2008, Marabotti, 2009). Here, fouling is in a first step prevented by anti-adhesive surfaces with fluorinated parts. If fouling however occurs, foulers were destroyed by biocides and removed/released by soft parts of the coatings. Combination can be achieved either by incorporation into copolymers, block copolymers or by physical mixing in blends.

The polymeric system examined here is based on methacrylate chemistry, allowing versatile replacement of monomers by others. Several attempts have been reported to prevent biofouling by means of methacrylic or acrylic polymers with quaternary units, respectively (Lu, 2007, Charnley, 2011).
The project covers a broad experimental field from synthesis and characterization of the new copolymers to determination of physical properties, preparation of coatings and their wetting behavior, finally performing biofouling investigations. Thus, systematic variations of the chemical structure are possible and the direct influence of the chemistry on biofouling processes can be elucidated.

CHEMICAL CONCEPT

The important basic structure of the system under study is poly(methylmethacrylate) (PMMA), providing mechanical stability, durability, hardness to the material. PMMA coatings alone, however, could be removed by shear stresses in water from the substrate. Thus, they need to be stabilized, which we do here by introduction of cross-linking. Cross-linking allows only to swell the coating and not to be detached.

The ability to cross-link is added by 4-benzoylphenyl methacrylate (BPMA) monomer which can connect polymer chains (cross-link) by reactions initiated by irradiation with UV-light. The comonomer is inserted in a concentration of 10 mol% in maximum.

Besides these two comonomers, more functions are needed to design an optimal anti-biofouling polymer material. Copolymerization with a metal ion-complexing monomer should allow chemical incorporation of biocide-acting metal ions not as free ions, but as a complex. Thereby, the required concentration of metal-based biocide (we used as model copper acetate) could be significantly lowered compared to standard formulations. The metal is not incorporated by mixing with the coating base as in standard coatings, but fixed in a stable complex. Thus, the stability against leaching should be enhanced. In this work, 2-acetoacetoxy ethyl methacrylate (AAMA) was employed as complexing unit. The ability to form complexes was examined using UV-VIS spectroscopy on the monomer because complexation of the polymers would generate insoluble precipitates due to physical cross-linking and do not allow to prepare films.

Incorporation of semifluorinated methacrylates, such as 1H,1H,2H,2H-perfluorodecyl methacrylate (sfMA-H2F8) adds very hydrophobic properties to the material. In addition, the semifluorinated polymethacrylate is soft (reflected by the low glass transition temperature, Tg). Both properties should cause fouling release, i.e. rejection of death bacteria after action of the biocide, in combination with a certain suppression of fouler attachment by hydrophobicity.

The chemical structure of a typical copolymer example is shown in Fig. 1.

**METHODOLOGY**

After synthesis and characterization of the polymers, thin films on test surfaces (glass slides or aluminum specimens) were prepared by spin-coating. The films were dried and cross-linked by UV-irradiation. The wetting behavior was investigated on these films. Complexation with copper ions directly on the surface of the film was performed by the so-called solvent annealing procedure (Li et al., 2007) with copper(II)acetate dissolved in tetrahydrofurane. After thorough washing and drying the copolymer films were tested for their anti-biofouling properties with different classes of foulers representative for freshwater fouling: *Staphylococcus (S.) aureus* as representative for bacteria, and *Achnanthidium spec.* (diatom algae) as representative for algae were employed.

**EXPERIMENTAL**

**Materials**

1H,1H,2H,2H-perfluorodecyl methacrylate, methyl methacrylate (both ABDR) and 2-acetoacetoxy ethyl methacrylate (Sigma Aldrich) were used after purification over alumina. 4-hydroxybenzophenone and methacryloyl chloride (Sigma Aldrich) were used as received. 2,2’-Azobisisobutyronitrile (AIBN) (Sigma Aldrich) was recrystallized twice from diethyl ether and stored at 4 °C. Chloroform, ethanol, acetone, tetrahydrofurane, diethyl ether, n-hexane, 1,3-bis(trifluoromethyl) benzene (BFMB) and methyl ethyl ketone (Sigma Aldrich) were used without further purifications. Copper(II)acetate was received from ABDR.

**Synthesis of copolymers**

All polymers were synthesized by free radical polymerization. A typical synthesis included AAMA, MMA, sfMA-H2F8, BPMA (for compositions see Table 1) and AIBN (3 mol% with respect to the total concentration of monomers) in solution of BFMB. All constituents of the

[Fig. 1 Chemical structure of the copolymers developed to prevent freshwater biofouling.]
mixture were introduced in a Schlenk tube, sealed under
nitrogen and degassed by several freeze-thaw pump cycles.
The polymerization reaction was carried out under nitrogen
and mechanical stirring for 6 hours at 70 °C. After that time,
the polymer was precipitated from chloroform or BFMB
solution into the tenfold amount of methanol, filtered off
and dried under vacuum at 50 °C (yield > 85%). The molar
masses achieved were high enough to ensure appropriate
polymer coating properties.

The detailed analytical results are reported elsewhere
(Starke, 2013). Table 1 summarizes the composition of
copolymer samples selected for the present study. The
samples are chosen to outline basic trends.

### Table 1 Chemical composition of the copolymers studied.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>MMA (mol%)</th>
<th>AA (mol%)</th>
<th>stMA (mol%)</th>
<th>BP (mol%)</th>
<th>Tg (°C)</th>
<th>Adv. CA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>116.0</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>80</td>
<td>10</td>
<td>0</td>
<td>67.8</td>
<td>126</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>80</td>
<td>10</td>
<td>0</td>
<td>67.4</td>
<td>126</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>104.2</td>
<td>84</td>
</tr>
</tbody>
</table>

Tg: Glass transition temperature.
CA: Advancing contact angle measured with water as probe.

### Preparation of coatings

Glass slides (76 mm x 26 mm x 1 mm) were cleaned
subsequently with acetone, Caro’s acid, and bi-distilled
water, then dried under reduced pressure in a vacuum oven
at 50 °C. Aluminum specimens were cleaned by subsequent
washing with acetone, ethanol and water. The films were
prepared by spin coating using a POLOS wafer spinner BL-
type spin-coater (APT GmbH, Germany) with spinning
speed of 2000 rpm for 30 s from a 2 wt.-% polymer solution
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(type spin-coater (APT GmbH, Germany) with spinning
speed of 2000 rpm for 30 s from a 2 wt.-% polymer solution
in chloroform or BFMB, respectively. The coated substrates
were dried in vacuum at 80 °C for 1 h. After drying, the
polymer films were cross-linked by UV-irradiation with an
UV-lamp at 365 nm at room temperature for 45 min.

For the solvent annealing step performed to initiate
copper complexation, the coated slides were treated with
Copper(II)acetate solution in THF according to Li et al.
(2007) after treatment thoroughly rinsed with bi-distilled
water and dried at 80 °C for 1 h in vacuum.

### UV/VIS spectroscopy

Titration experiments of the copper salts with AAMA
monomer with a starting volume of 1 mL for 0.4 cm
standard quartz cuvettes were carried out at room
temperature (22 ± 2 °C) in a sealed quartz cuvette (quartz
glass Suprasil, HELMA, Germany) by stepwise addition
of appropriate amounts of concentrated AAMA solution in
ethanol into the solution of the appropriate copper(II) salt
through the serum cap by using a gas-tight micro liter
syringe.

### Differential scanning calorimetry

The polymer samples were dried in a vacuum oven
under reduced pressure at 60 °C for several hours to remove
water prior to investigation in order to avoid failures in the
glass transition temperature determination. Modulated
differential scanning calorimetry was performed with a
DSC Q 100 (TA Instruments) under nitrogen. The samples
were measured in the temperature range from -80 °C –
150 °C with 2 K/min heating/cooling rate. The modulation
of the heating rate was ± 0.31 K/40 s. The glass transition
temperature Tg was determined using the half-step method.

### Contact angle measurements

Dynamic contact angle measurements were performed
using an OCA 30 contact angle goniometer (DATA
Physics) with bi-distilled water as probe liquid using the
sessile drop method. Advancing contact angles θ were
determined using tangents on the drop. The dynamic
advancing contact angle was measured on polymer coated
glass slides on at least three positions.

### Biological assay

The coated test specimens were incubated for 24 h at
36 °C in a suspension of *Staphylococcus aureus* within a
growth chamber covered by a membrane. After rinsing the
membrane and the sample substrates with isotonic saline
solution, the diluted solutions were applied on nutrient agar
plates and further incubated for 24 h at 36 °C. The grown
colonies were counted under a microscope.

To assess the growth of diatom algae (*Achnanthidium
species*) on the coated surfaces, the slides were incubated
for 1 week at 20 °C in an aquarium with strong diatom
concentration. After that time, the slides were rinsed and the
attached cells were counted under a microscope.

### RESULTS AND DISCUSSION

#### Complexation experiments of AAMA monomer with
copper(II)acetate studied by UV/VIS spectroscopy

UV/VIS experiments were carried out to get
information about the formation of complexes between
AAMA monomer and copper(II) ions. As shown in Figure
2, complexation of both copper(II)sulfate and chloride with
the monomer AAMA worked successfully, as expected
from literature (Ummathur, 2009).

The difference in the increase of the absorbance at
283 nm between the two copper salts (copper(II) sulfate and
chloride) indicates that CuSO4 forms the more stable
complex with AAMA. The observed slope of the curve is
higher than that for the copper(II) chloride.

If the complex would not have been formed a curve as
in the absence of copper(II) (i.e., a line with the slope of the
blue curve) would be observed.
Wetting behavior of the copolymer films with water

The results of dynamic contact angle measurements with water are summarized in Table 1. Generally, the coatings result in surfaces more hydrophobic than glass and metals. The high advancing contact angles \( \theta_{a} \) of 126° of the copolymers with the semifluorinated monomer sFMA-H2F8 reflect the strong hydrophobicity effect of these units, as already recognized for other semifluorinated polymers (Pospiech, 2003). Polymer 1 (PMMA) resembles the well-known value for PMMA, polymer 4 reflects a comparable wetting behavior. These two polymers are more hydrophilic and polar in nature.

Biofouling results

Effect of the polymer chemistry on attachment and growth of \( S. \) aureus

The biocide and fouling release activity towards \( S. \) aureus were investigated using spin-coated copolymer films on glass slides. It has to be pointed out that reproducibility of different experiments is complicated by the fact that each bacteria culture contains different total amounts of \( S. \) aureus. This explains deviating results in two experiments.

The results obtained are shown in Figure 3. Even on a pure PMMA surface, attachment and growth of \( S. \) aureus is reduced compared to the glass control. Incorporation of the semifluorinated comonomer sFMA-H2F8 in polymer 2 reduces the fouling further. Additional incorporation of the complexing comonomer AAMA in polymer 3 and polymer 4 together with complexation with copper results in the largest suppression of \( S. \) aureus growth by almost one order of magnitude.

Attachment and growth of brown algae and diatom algae on copolymer films on glass

Figure 4 illustrates what happens when the test glass slides without coating are exposed to the experiment. Significant encrustation is observed in both cases.

Fig. 2 Absorbance at 283 nm during titration of copper(II) salt solutions with AAMA in ethanol.

Fig. 3 Effect of coating chemistry on the adsorption and growth of \( S. \) aureus.

Fig. 4 Microscopic images of biofouling films on glass specimens (left: layer of brown algae; right: settlement of \( Achnanthidium \ spec. \)).

To determine the effect of the copolymer films on diatom algae (\( Achnanthidium \ spec. \)) growth the coated glass slides were incubated for a defined time in an aquarium with strong diatom presence. The results are given in Figure 5.

The populations of \( Achnanthidium \ spec. \) growth well on glass, PMMA-covered glass and the glasses coated with PMMA-rich copolymers with a molar concentration of 80 mol% MMA. In contrast, copolymers 2 and 3 with low molar concentration of MMA, but 80 mol% semifluorinated comonomer appear to be more efficient in their biocide and fouling release function, independent of the presence of copper complexes. This can only be understood as action of the soft, hydrophobic, semifluorinated copolymer segments.
Fig. 5 Biofouling results: effect of coating chemistry on the growth of Achnanthidium spec.

CONCLUSIONS

Tailored PMMA-based copolymers were designed, synthesized and characterized in order to provide new materials with biocide and fouling release properties.

The settlement and growth bacteria and algae on polymer-covered glass specimens was examined. Complexation of the AAMA monomer with Cu²⁺ was successfully proven by UV/VIS measurements. Mechanically stable films could be prepared employing the cross-linking by UV irradiation. A clear reduction of the growth of S. aureus and Achnanthidium spec. (diatom algae) in freshwater aquaria could be observed.

In a next step, the copper complexes used so far will be replaced by zirconium complexes.

Future work will chemically focus on the exchange of AAMA by phosphonic acid-containing and imidazolium-containing monomers as biocides. Furthermore, biofouling examination of polymer-coated stainless steel surfaces will provide information if the polymer materials may be of use for coatings of heat exchanger parts.

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NOMENCLATURE

AAMA  2-acetoacetoxyethyl methacrylate
BFMB  1,3-bis(trifluoromethyl) benzene
BPMA  4-benzoylphenyl methacrylate
CA  contact angle
DSC  differential scanning calorimetry
MMA  methyl methacrylate
PMMA  poly(methyl methacrylate)
S. aureus  Staphylococcus aureus
sfMA-H2F8  1H,1H,2H,2H-perfluorodecyl methacrylate

Subscript

A  advancing contact angle
\( \beta \)  glass transition temperature (onset of macro-Brownian segmental motions in the amorphous phase of polymers)

REFERENCES


