Progress in Organic Coatings 77 (2014) 665–673

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Optimized silyl ester diblock methacrylic copolymers: A new class of binders for chemically active antifouling coatings

Christine Bressy[a,*], Claire Hellio[b], Minh Ngoc Nguyen[a,c], Brigitte Tanguy[a], Jean-Philippe Maréchal[b], André Margaillan[a]

[a] *Université de Toulon, Laboratoire Matériaux Polymères Interfaces Environnement Marin (MAPIEM EA 4323), 83957 La Garde, France*
[b] *School of Biological Sciences, University of Portsmouth, King Henry Building, Portsmouth PO1 2DY, UK*
[c] *Department of Physical Chemistry, VNU University of Science, 19 Le Thanh Tong, Hoan Kiem, Hanoi, Viet Nam*

ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form 3 December 2013
Accepted 7 December 2013
Available online 28 December 2013

Keywords:
Antifouling
Bioassays
Self-polishing coating
Trialkylsilyl methacrylate
Diblock copolymer
In situ raft immersion

ABSTRACT

This work focuses on the assessment of the erosion properties and antifouling (AF) performance of silyl ester copolymer-based coatings through laboratory and field tests. Silyl ester diblock copolymers were synthesized via the reversible addition-fragmentation chain transfer polymerization and were selected as binders for developing copper-free chemically active coatings. AF coatings were subsequently prepared using biocides (Sea-Nine™ 211, Preventol® A4S, and zinc pyrithione). Laboratory-based bioassays, targeting the growth of selected microorganisms (bacteria and microalgae) and barnacle settlement, highlighted that the silyl ester methacrylic-based binders did not inhibit the growth of microorganisms, are essentially non-toxic to *nauplii* and reduced the settlement of *Amphibalanus amphitrite* cyprids. The corresponding biocidal coatings are potent toward bacteria and diatoms but were demonstrated to be toxic against the barnacle larvae. Field test results showed variations with geographical locations: in sub-tropical area, the silyl ester methacrylic-based coatings failed to inhibit the settlement of barnacles; however, field tests performed in Mediterranean Sea for 18 months demonstrated that biocidal silyl ester methacrylic-based coatings were promising candidates.

1. Introduction

Surfaces that are immersed in seawater are subjected to biofouling i.e. the settlement of undesired marine micro- and macroorganisms. This leads to negative economic consequences on marine structures such as vessels, platforms, buoys and fishnets. Ocean-going vessels have been plagued by the deleterious effects of biofouling for centuries. In addition to marine 'bio' risks from non-invasive species transfers [1], biofouling reduces vessel speed due to a reduction in hydrodynamics and maneuverability, causing increased fuel, gas emissions and maintenance costs [2].

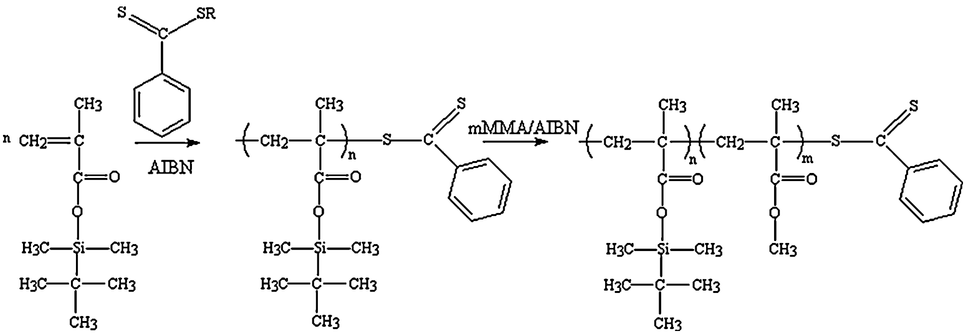
To prevent the settlement and growth of marine organisms, antifouling (AF) coatings are mainly used. These coatings are generally composed of film-forming binders, pigments, fillers, and active molecules called biocides. The most successful AF coatings were based on acrylic binders bearing tributyltin (TBT)-ester side groups, which could be hydrolyzed by seawater, generating self-polishing behavior of the coating and long term efficiency over time [3]. However, due to growing awareness of the impact of TBT-based compounds to the marine environment [4], the application of TBT-based AF paints was first banned in France for ships less than 25 m long in 1982 [5] and then globally in 2003. Since the early 1990s, random copolymers composed of zinc acrylate, copper acrylate or silyl acrylate monomer units were used as substitutes for TBT-acrylate based copolymers in AF paints. These binder technologies are based on acrylic copolymers bearing ester side groups which are easily hydrolyzed in seawater [3]. This degradation process is associated with a progressive thickness depletion confined at the extreme surface of the coating which leads a continuously renewed bioactive surface. Fouling prevention of these three tin-free technologies mainly relies on the release of other biocidal ingredients contained in the paint formulation since the dissolved zinc or copper ions coming from the binders do not provide sufficient biocidal efficiency. These copolymers blended with biocides confer an ability of controlling/regulating biocides leaching rate through controlling the binder erosion rate [3,5,6]. These early tin-free self-polishing coatings have been reported to be active for up to five years [7].

Recently, research efforts were concentrated toward the development of "non-stick" or fouling release (FR) coatings which are now available on the marine coating market. These coatings are known to release both hard and soft fouling when used under suitable hydrodynamic conditions [7]. Their poor activity under static and low flow conditions leads to the need for further investigations

---

[*] Corresponding author. Tel.: +33 4 94 14 25 80; fax: +33 4 94 14 24 48.
E-mail address: christine.bressy@univ-tln.fr (C. Bressy).

0300-9440/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2013.12.004



Scheme 1. Synthetic pathway of trialkylsilyl ester-based block copolymers via the RAFT process.

on alternative technologies: amphiphilic surfaces and hydrogels have been considered as fouling control surfaces [8]; a growing interest in enzyme-based coatings and engineered topographical surfaces as "promising" coatings has appeared in marine applications since the early 2000s [9]. The enzyme-based technology lacks long-term efficiency against biofouling. The 'superhydrophobic' coatings derived from hydrophobic and physically rough surfaces were proven to reduce macrofouling [10,11] after 18 months of exposure to seawater in comparison to the equivalent flat surfaces [12]. Nevertheless its up scale and use on ship hulls have not been reported yet. Therefore, self-polishing copolymers and mainly trialkylsilyl (meth)acrylate-based copolymers are still under investigation in our laboratory to mimic the well-known TBT-based self-polishing copolymers. Although a complete list of alkyl groups linked to the silicon atom could be found in the scientific literature [13,14], *tert*-butyldimethylsilyl ester side groups have been selected as seawater hydrolyzable groups for self-polishing binders (Scheme 1, [13]).

Optimized copolymers are currently studied using polymer chains with controlled architectures such as block copolymers in replacement of random copolymers to better control the erosion properties under static and dynamic conditions [13]. The reversible addition-fragmentation chain transfer (RAFT) polymerization was selected to synthesize diblock copolymers with controlled molecular weights and narrow molecular weight distribution as previously demonstrated [15]. Copper-free paints were prepared by blending silyl ester methacrylic copolymers with commercially available biocides including Sea-Nine^{TM} 211, Preventol$^{®}$ A4S and zinc pyrithione (ZnPT). The resulting coatings were characterized in terms of erosion and AF properties. AF coatings were previously assessed mostly for their efficiency toward the inhibition of settlement of macrofoulers such as algae, mussels, hydroids and barnacles [16,17]. Nowadays, increasing attention is being paid to microfoulers that develop on coatings and assessment is made through laboratory-based bioassays [18–21]. Because of the large diversity of marine biofoulers, a wide range of microfoulers, including bacteria, microalgae and larvae of barnacles, was investigated in this study in order to assess the AF efficiency of optimized silyl ester methacrylic copolymers-based coatings. As bioassays can never fully mimic the environmental conditions because of the absence of the film conditioning process, field experiments were performed to assess *in situ* AF coating performances [21,22]. AF performances of the copper-free coatings were evaluated in two immersion sites with variations of the fouling pressure, i.e. Mediterranean Sea and North Atlantic Ocean.

2. Experimental

2.1. Chemical compounds

Methyl methacrylate (MMA) and toluene were purchased from Acros, and distilled under reduced pressure prior to use. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from methanol. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) and *tert*-butyldimethylsilyl methacrylate (SiMA) were prepared according to the literature [23]. A tributyltin based copolymer containing around 30 mol% of tributyltin methacrylate monomer units (Cutinox 1120$^{®}$, 50 wt% in toluene, from ACIMA) was used as reference (TBT-REF). Xylene (from Aldrich) is used to dissolve TBT-REF. Rutile titanium dioxide (TiO_2) supplied by Kronos was used as hydrophobic pigments (purity $\geq$ 98%, average particle size around 0.5 μm). Zinc oxide (ZnO) was supplied by Silar & Silox. Zinc pyrithione ZnPT (Progiven), Sea-Nine^{TM} 211 SN (kindly furnished by Rohm and Haas) and Preventol$^{®}$ A4S (dichlofluanid, Bayer) were used as biocides. Hydrogenated castor oil (Cognis) was used as rheological thickener. Soy lecithin (Cargill) was used as a spreading and mixing aid. A commercially available tributyltin-based paint (M150) purchased from Kolorian (France) and a copper-free commercial paint (Paint A) were used as positive reference paints. This latter paint was composed of 2.5–10 wt% of Sea-Nine^{TM} 211 as reported in its materials safety data sheet.

2.2. Synthesis of tert-butyldimethylsilyl ester-based methacrylic binders by the RAFT process

Diblock copolymers poly(*tert*-butyldimethylsilyl methacrylate)-*block*-poly(methyl methacrylate), PSiMA-*block*-PMMA, were prepared by the RAFT process as previously reported by Nguyen et al. [15,23] (Scheme 2). Similar experimental conditions were used to synthesize random copolymers from a mixture of MMA and SiMA. BC*x* and RC*x* were used as abbreviations of block copolymer (PSiMA-*block*-PMMA) and random copolymer (P(SiMA-*stat*-MMA)) with *x* mol% of SiMA, respectively.

The average molecular weights (M_n and M_w) and the molecular weight distribution (M_w/M_n or $Đ$) of polymers were determined by size exclusion chromatography (SEC) with a universal calibration and their chemical structure was assessed by ^{1}H NMR spectrometry [15]. Features of polymers selected as binders for AF coatings are reported in Table 1. PMMA (M_n = 6300 g mol^{-1}; $Đ$ = 1.14) was used for preparing polymer blends.

Table 1
Features of polymers used as binders for silyl ester methacrylic-based paints. controls.

Name	M_n (g mol^{-1})	$Đ$	[MMA]/[SiMA] molar ratio
BC21	14,000	1.07	79/21
BC27	18,500	1.10	73/27
BC42	14,900	1.07	58/42
BC63	15,800	1.08	37/63
BC73	15,200	1.10	27/73
RC27	11,000	1.16	73/27

BC*x*: block copolymer PMMA-*block*-PSiMA with *x* mol% of SiMA; RC*x*: random copolymer P(MMA-*stat*-SiMA) with *x* mol% of SiMA.