Antifouling Evaluation of Novel Zwitterionic Polymers in the Sea

Anbanandam PARTHIBAN,[1*] Vivek ARJUNAN VASANTHA,[1] Satyasankar JANA,[1] Julius G. VANCSO,[1,2] Serina Siew-Chen LEE,[3] Chin-Sing LIM,[3] Serena Lay-Ming TEO[3].

[1]Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research (A*STAR), 1, Pesek Road, Jurong Island, Singapore 627833
[2]MESA+ Research Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P. O. Box 217, 7500 AE Enschede, The Netherlands
[3]Tropical Marine Science Institute, National University of Singapore, 18 Kent Ridge Road, Singapore 119227
Corresponding author: Anbanandam Parthiban; e-mail: a_parthiban@ices.a-star.edu.sg; Tel.: 65 67963910 Fax: 65 63166188

Abstract

Ionic polymers of different types such as ion-pair polymers, zwitterionic polymers, dual hydrophilic block copolymers bearing zwitterionic moieties were synthesized and characterized. The zwitterionic polymers were designed in such a way to avoid hydrolysable linkages in the polymer chain. These polymers were evaluated for its antifouling characteristics in the sea. In order to make coated surfaces durable upon submerging in sea, the polymers were mixed with a primer used in marine coatings. Some of the polymers were also subjected to antifouling evaluation without mixing of primer to ensure any prevailing antifouling nature of ionic polymer is uninhibited by the primer. The coated surfaces showed strong hydrophilic characteristics as indicated by static water contact angle measurements. Moderate antifouling activity was noticed in dual hydrophilic block copolymers bearing zwitterionic blocks and polyethylene glycol segments.

Keywords: Zwitterionic polymers, fouling, field evaluation, ion-pair polymers, primer

1 Introduction

Efforts to find solutions for preventing fouling have emerged as one of the major areas of research ever since heavy metal derived carboxylates were banned due to its deleterious effects on the environment (Vold 2003). Increasing environmental concerns, regulations on consumption of fuels by marine bound vessels and the associated emission control on the release of greenhouse gas CO_2, invasion of marine species, etc. are some of the major driving forces in the efforts towards finding a suitable antifouling solution. It has been estimated that a very large crude carrier coated with a suitable antifouling paint can save US $28.5 million and reduce CO_2 gas emission by 125,000 metric tons over 15 years (Buskens et al. 2013). There are three major approaches, currently being pursued as a means of preventing fouling, viz metal based and metal free biocides, hydrophobic / non-stick foul release surfaces and hydrophilic surfaces, quite apart from a number of other approaches with limited success. Each of these approaches has its own advantages as well as disadvantages. Thus there is a continued effort to come up with a "universal" surface based approach which is considered to be the most favorable in terms of environmental friendliness to prevent fouling. Among the hydrophilic surface based approaches, the one involving zwitterionic polymers are worth mentioning. Because of its ionic nature, zwitterionic polymers display many interesting characteristics. Ability to form hydration layers similar to polyethylene glycol albeit through polar in addition to H-bonding interactions is one such interesting property of zwitterionic polymers and zwitterionic polymer brushes. Zwitterionic polymer brushes have been reported to prevent adsorption of proteins under controlled conditions in the lab. However, reports in the open literature on the ability of zwitterionic polymers to prevent fouling of surfaces immersed in sea are rare.

Recently, many ionic polymers of the type ion pair (Jana et al. 2013) and zwitterionic (Vasantha et al. 2013) have been reported. These polymers were designed in such a way that they are free from hydrolysable linkages unlike the commonly employed zwitterionic polymers. Large majority of commonly employed zwitterionic polymers possess hydrolysable linkages in the form of ester (–COO-) and amide (-CONH-) bonds. As a result the zwitterionic monomers undergo hydrolysis to a varying degree even during polymerization. Hydrolytic cleavage beyond a certain limit would adversely affect the ability of zwitterionic polymers to form hydration layers thereby affecting its antifouling performance. Thus avoiding hydrolysable linkages in zwitterionic polymers is a fundamental requirement to preserve long term antifouling performance. This article describes recent attempts made by us to study the effectiveness of zwitterionic and ion pair polymers as antifouling agents in the waters surrounding Singapore.

2 Results and Discussion

The polymers were prepared as reported before by Jana et al. (2013) and Vasantha et al. (2014 and 2015). Details on sample preparation and antifouling evaluation can be found in Vasantha et al. (2015). In order to form stable coated surfaces under water, the polymers were dispersed in epoxy primer used in marine coatings (Vasantha, et al. 2015). Figures 1 and 2 show the antifouling evaluation of zwitterionic polymers and ion pair polymers respectively in the field. Ion pair polymers did not show any effect on either soft fouling or hard fouling in the field evaluation. The polysulfobetaines exhibited swelling tendency in deionized water and in weak electrolyte solutions. The polysulfabetaines were soluble only in stronger electrolyte solutions, the concentration of which exceeded the salt concentration of sea water. Because of the ability of zwitterionic polymers to form well coated surfaces, glass slides coated with these polymers were evaluated without using any primer and also for comparison with primer. The glass slides coated with zwitterionic polymers were found to be highly hydrophilic to strongly hydrophilic. The hydrophilicity was substantially higher than that of uncoated glass slides ($\Delta\theta$ = 43-26^o). However, the antifouling behavior was absent in both sets of slides (Figure 3). The lack of antifouling characteristics could be the result of inability to prevent early stage of fouling caused by the extracellular matter and microorganisms as well as the inability to prevent the growth of tubeworms which are the dominant fouling organisms in the test site. Slime and tubeworms were the dominant foulants revealed by Photogrid analysis of submerged slides. Even though hydrophilic surfaces are proposed to prevent fouling, it is useful to note that there are quite a large number of fouling species which prefer hydrophilic surfaces to settle. E.g. barnacles (Rittschof and Costlow 1989), *Mytillus galloprovicialis* (Carl et al. 2012). In fact the composition of bacterial community has been found to be independent of initial surface wettability which in turn attracted settlement of H. elegans (Huggelt et al. 2009). This clearly indicates the significance of the role played by earliest form of "surface preparation" to recruit subsequent "settlers". These antifouling results obtained from the field are in contrast to the lab based assays formed by zwitterionic polymer brushes (Quintana et al. 2014) clearly indicating the challenges faced in the field. Although lab based assays offer controlled conditions and also the convenience of introducing variables in a predetermined manner, it is still far from predictability that is desired to speed up the antifouling evaluation reliably. However, recently a good correlation was reported on hydrophobic surfaces between lab based assays and field evaluation (Stafslein et al. 2016). Another challenge of strongly hydrophilic coatings is the durability of these coatings on submerged structures. A diblock copolymer architecture whereby a hydrophobic block anchored to the surface with a zwitterionic block constituting the outer layer of polymer brush showed superior stability as compared to the zwitterionic polymer alone (Quintana et al. 2013).

Zwitterionic block copolymers composed of polysulfabetaine blocks and polyethylene glycol (PEG) segments showed "Schizopherenic" micellization behavior. Accordingly, PEG segments constituted the corona in deionized water where it is the core of micelles formed in salt solution. Figure 4 shows the antifouling evaluation of zwitterionic block copolymers in the field. Surprisingly antifouling behavior was observed unlike the other zwitterionic polymers discussed in the foregoing sections (Vasantha et al. 2015). The antifouling behavior is more due to the block copolymer than due to the presence of PEG can be noticed by the absence of antifouling behavior in PEG based polymers as shown in Figure 5. As can be noticed in figure 5, PEG independent of its molecular weight as well as the nature of linkages prevailing in the backbone did not show any antifouling behavior in the field evaluation. Once again it is useful to note that PEG is a well-studied protein resisting polymer.

3 Figures and tables

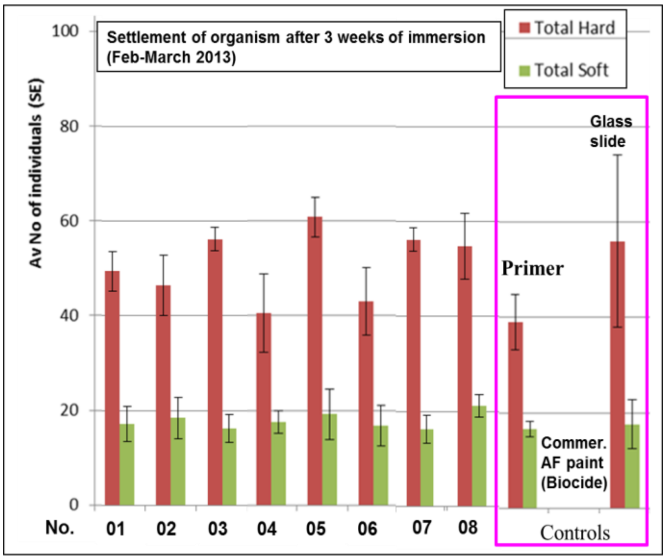


Figure 1. Antifouling evaluation of zwitterionic polymers (for notations please refer to Schemes 1 and 2. **07** is **01** at twice the concentration. **06** is **04** at twice the concentration).

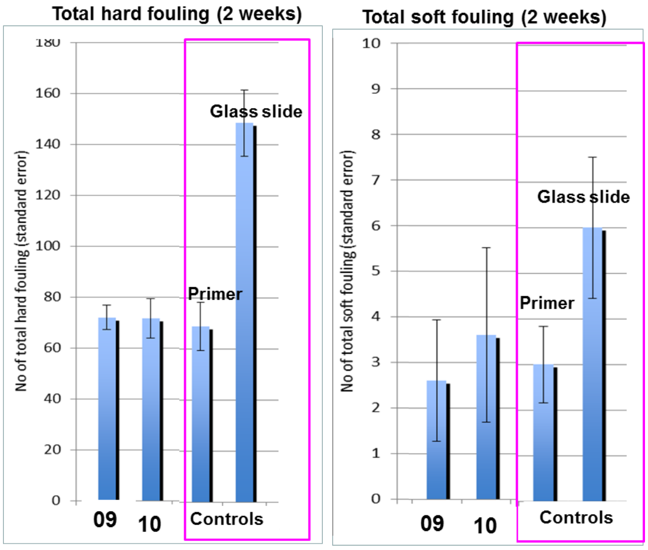


Figure 2. Field evaluation of ion pair polymers (for notations please refer to Scheme 3).

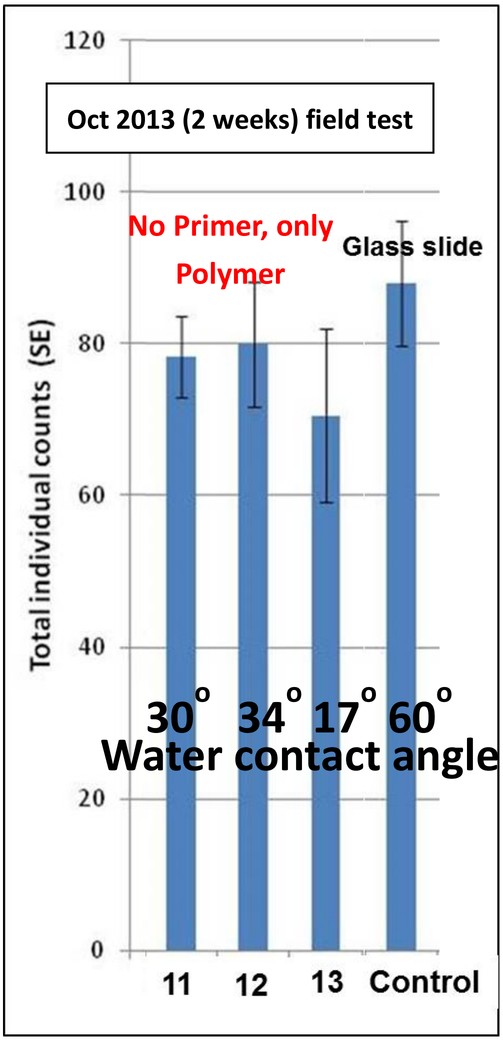


Figure 3. Field evaluation of zwitterionic polymers without mixing of primer (**11** is **01**, **12** is **07** and **13** is **08**).

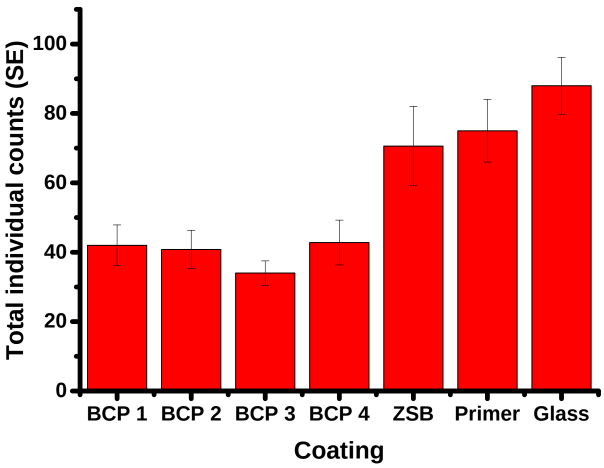


Figure 4. Antifouling evaluation of zwitterionic block copolymers (for notations please refer to Scheme 4) ©Royal Society of Chemistry 2015.

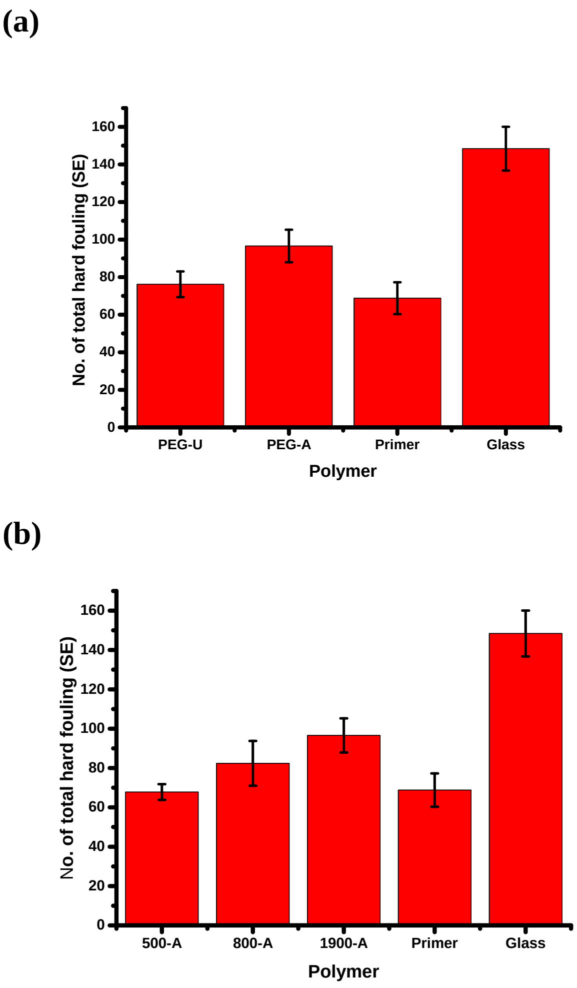
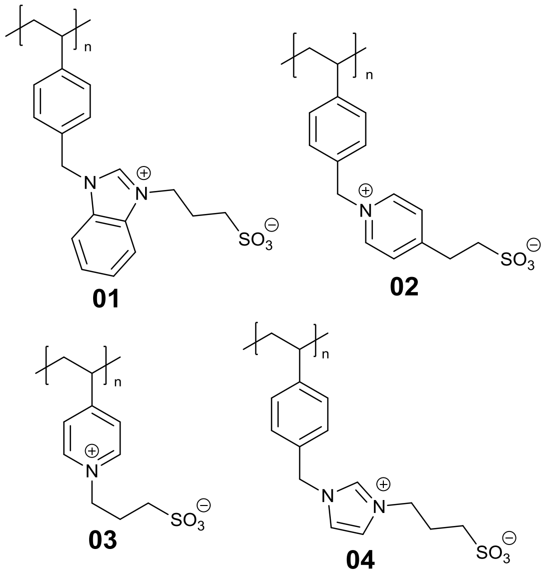


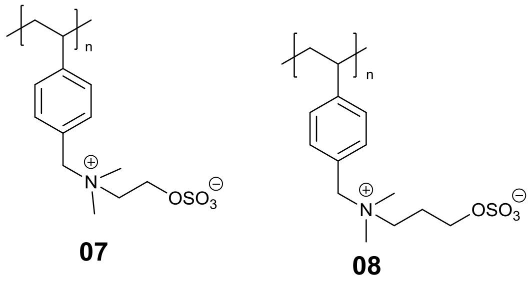
Figure 5. Field evaluation of PEG **(a).** PEG-urethane (PEG-U) and PEG-amide (PEG-A) of

MW 1900 **(b).** PEG amides 500-A, 800-A and 1900 A of MWs 500, 800 and 1900 respectively.

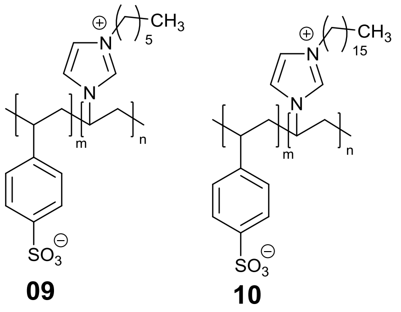
4 Chemical structure of polymers



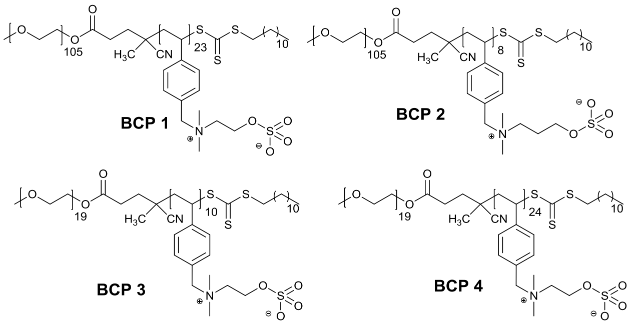
Scheme 1. Chemical structure of zwitterionic polysulfobetaines.



Scheme 2. Chemical structure of zwitterionic polysulfabetaines



Scheme 3. Chemical structure of ion-pair polymers



Scheme 4. Chemical structure of block copolymers (BCPs).

5 Conclusions

The zwitterionic polymers though exhibited hydration layer forming tendency, did not prevent fouling in the sea. Even though increasing the dosage further in order to potentially boost the activity is an option, it has limitations. Due to the insoluble nature of (zwitter)ionic polymers these were dispersed as solids in the paint samples. At high concentrations, due to their ionic nature, these solids aggregate thereby affecting the consistency, shelf life and flowability characteristics as well as appearance and durability of coated surfaces. These results are supported by the recent findings of Yandi et al (2016). It is useful to note here that fouling is a complex phenomenon involving hundreds if not thousands of species and organisms. Because of this complexity, simple mechanisms like ability to form hydration layers may not be an effective strategy to prevent fouling in its entirety since it does not address various processes involved during fouling. It is worth noting that approaches based on topography are not effective against fouling hydroid *Ectopleura larynx* (Bloecher et al. 2013). Various fouling organisms differ not only in size but also mode and number of attaching points to surfaces. The kind and nature of chemicals secreted for inducing attachment during primary and secondary stages of settlement differ as well. Thus an effective surface based approach to prevent fouling should also exhibit multiple functions.

Since fouling organisms constitute the lower end of food pyramid and in some cases these are consumed directly by the local population, killing of fouling organisms as an antifouling strategy may no longer be acceptable though this is the easiest and the most effective antifouling solution. It is quite likely that an effective surface based approach may demand the usage of more of the active ingredient, could be in the range 20 to 50 wt% of the formulation. Such situation is also likely to impose many restrictions on physical characteristics of the antifouling additive apart from cost considerations.

Acknowledgements

This work was funded by the Agency for Science, Technology and Research (A*STAR), Singapore under Innovative Marine Antifouling Solutions (IMAS) for high-value applications programme. The authors thank Ms. Chen Junhui and Ms. Foo Ming Choo for assisting in GPC and DLS studies.

References

Bloecher, N., de Nys, R., Poole, A. J. and Gunether, J. 2013 The Fouling Hydroid Ectopleura Larynx: a Lack of Effect of Next Generation Antifouling Technologies, Biofouling, 29, pp. 237-246.

Buskens, P., Wouters, M., Rentrop, C. and Vroon, Z. 2013 A Brief Review of Environmentally Benign Antifouling and Foul-release Coatings for Marine Applications. J Coating Technologies Research, 10, pp. 29-36.

Carl, C., Poole, A. J., Sexton, B. A., Glen, F. L., Vucko, M. J., Williams, M. R., Whalan, S. and de Nys, R. 2012 Enhancing the Settlement and Attachment Strength of Prediveligers of Mytillus Galloprovincialis by Changing Surface Wettability and Microtopography, Biofouling, 28, pp. 175-186.

Huggett, M. J., Nedved, B. T. and Hadfield, M. G. 2009 Effects of Initial Surface Wettability on Biofilm Formation and Subsequent Settlement of Hydroides Elegans, Biofouling, 25, pp. 387-399.

Jana, S., Vasantha, V. A., Stubbs, L. P., Parthiban, A. and Vancso, J. G. 2013 Vinyl-imidazole Based Asymmetric Ion Pair Comonomers: Synthesis, Polymerization Studies and Formation of Ionically Crosslinked PMMA, J Polymer Science Part A: Polymer Chemistry, 51, pp. 3260-3273.

Quintana, R., Janczewski, D., Vasantha, V. A., Jana, S., Lee, S. S. C., Parra-Velandia, F. J., Guo, S., Parthiban, A., Teo, S. L.-M. and Vancso, G. J. 2014 Sulfobetaine-based Polymer Brushes in Marine Environment: Is There an Effect of the Polymerizable Group on the Antifouling Performance?, Colloids and Surfaces B: Biointerfaces, 120, pp. 118-124.

Rittschof, D. and Costlow, J. D. 1989 Bryazoan and Barnacle Settlement in Relation to Initial Surface Wettability A Comparison of Laboratory and Field Studies, Scientia Marina, 53, pp. 411-416.

Stafslien, S. J., et al. 2016 Comparison of Laboratory and Field Testing Performance Evaluations of Siloxane-polyurethane Fouling-release Marine Coatings, Biofouling, 32, pp. 949-968.

Vasantha, V. A., Jana, S., Lee, S. S. C., Lim, C. S., Teo, S. L.-M., Parthiban, A. and Vancso, J. G. 2015 Dual Hydrophilic and Salt Responsive Schozophrenic Block Copolymers – Synthesis and Study of Self-assembly Behavior, Polymer Chemistry, 6, pp. 599-606.

Vasantha, V. A., Jana, S., Parthiban, A. and Vancso, J. G. 2014 Water Swelling, Brine Soluble Imidazole Based Zwitterionic Polymers – Synthesis and Study of Reversible UCST Behaviour and Gel-Sol Transitions, Chemical Communications, 50, pp. 46-48.

Vasantha, V. A., Jana, S., Parthiban, A. and Vancso, J. G. 2014 Halophilic Polysulfabetaines – Synthesis and Study of Gelation and Thermoresponsive Behavior, RSC Advances, 4, pp. 22596-22600.

Bloecher, N., de Nys, R.,

Vold, H. 2003 Prohibition of Organotin in Antifouling Systems: The Classification Societies' Perspective, J Protective Coatings and Linings, 20, pp. 30-32.

Yandi, W., Mieszkin, S., di Fino, A., Martin-Tanchereau, P., Callow, M. E., Callow, J. A., Tyson, L., Clare, A. S., Ederth, T. 2016 Charged Hydrophilic Polymer Brushes and Their Relevance for Understanding Marine Biofouling, Biofouling, 32, pp. 609-625.