

## Copolymers of p-acryloyloxyacetophenone (AcAP) with MMA: Synthesis, Characterization and their Antifouling (AF) Efficiency

S. Elango, M. Sidharthan, G. S. Viswanadh, Ji-Young Cho, N. S. Park, H. W. Shin\*

Department of Marine Biotechnology, Soonchunhyang University, Asan City, South Korea 336 745. [hwshin@sch.ac.kr](mailto:hwshin@sch.ac.kr)

### Introduction

Biofouling on ship hulls cause severe damage to the shipping industry. Antifouling (AF) coatings are being used, in order to avoid the attachment of fouling organisms on ship hull. In recent years, AF polymers are prominently used in the shipping industries. The AF polymers have many advantages over conventional AF formulations. The controlled leaching rate of the AF polymers may decrease the risk of environmental pollution. Whereas the conventional soluble or insoluble matrix types of AF coatings are largely responsible for the environmental pollution. Antimicrobial polymers are widely used in various industrial applications. It is also employed in AF coatings to prepare effective AF paint formulations. In the present investigation, AcAP was synthesized and characterized as biocidal monomer. The homo- and copolymers of AcAP were synthesized and their antifouling activity was checked against microfoulers.

### Experimental

**Materials.** 4-hydroxyacetophenone (HAP) (99%), Acryloylchloride (Ac) (96%), Triethylamine (TEA) (99.5%) were procured from Acros Chemical Ltd. MMA (99%), MEK (98%), toluene and methanol were procured from Samchun Chemicals, South Korea.

**Synthesis of AcAP.** The AcAP was prepared by Ac with HAP as shown in the Figure 1. The HAP and TEA were taken in 4neck round bottom flask containing MEK equipped with stirrer and thermometer. The slow addition of Ac to the round bottom flask was done by dropping funnel at 0 °C. The reaction was monitored by TLC and the product was characterized by GC-MS, IR and NMR. The purity of AcAP was 96.5% determined by HPLC.

**Polymerizations.** The homo- and copolymers of AcAP were prepared by the solution polymerization with MMA as shown in Figure 1. The required quantities of AcAP, MMA, toluene and BPO were mixed in polymer tube equipped with magnetic stirrer and a septa cap. The solution was deoxygenated by purging with purified N<sub>2</sub> gas. The tube was sealed and placed in a regulated thermostat bath at 70 °C for fixed periods of time. The polymer solution obtained was precipitated in excess methanol.

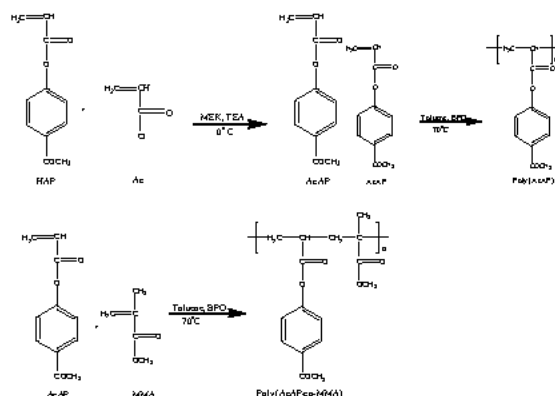


Figure 1. Synthesis of AcAP, p(AcAP) and p(AcAP-co-MMA)

The average molecular weight of the prepared polymers was determined by GPC (Waters-2690, 410, Waters Corporation, MA, USA) by using THF as a solvent. The polymers were characterized by IR (Bruker (Germany), IFS88 / Perkin Elmer (USA), Spectrum GX on solid samples in KBr pellets) and NMR (<sup>1</sup>H-NMR spectra were

recorded on Bruker-200). The copolymer poly(AcAP-co-MMA) was prepared by above mentioned procedure by using monomers, AcAP and MMA in different feed ratio by free radical polymerization at 70 °C. The homopolymers, poly(AcAP) and poly(MMA) were prepared as mentioned above by using the prepared monomer AcAP and MMA by solution polymerization at 70 °C respectively. The prepared homo- and copolymers were subjected to antibacterial activity, diatom attachment and biofilm formation assays to evaluate their efficiency against microfouling organisms (marine bacteria and diatoms).

### Results and discussion

**Identification of AcAP.** The synthesized AcAP was identified from its IR, <sup>1</sup>H-NMR and GC-MS spectra. The IR spectrum shows characteristic absorption bands at 1598, 980 cm<sup>-1</sup>(vinyl) and 1760 and 1696 cm<sup>-1</sup>(C=O). The <sup>1</sup>H-NMR spectrum of AcAP (solvent, CDCl<sub>3</sub>) exhibited several peaks at 2.5~2.6 (-CH<sub>3</sub>), 5.80~6.17 (-CH), 6.00~6.68 (-CH<sub>2</sub>), 7.17~8.00 (-Ar) ppm. From the UV spectrum, the wavelength at maximum absorption was 243nm. The mass spectrum exhibited the mass (m/e) was 190 (M<sup>+</sup>).

**Identification of homo polymers.** The poly(AcAP) was identified from its IR spectrum indicating absorptions at 2900 cm<sup>-1</sup>, characteristics of the vinyl polymer backbone, with disappearance of vinyl absorptions of monomeric AcAP at 1598, 980cm<sup>-1</sup>. The number and weight average molecular weights of poly(AcAP) were 29,366 and 152,274 respectively. The poly(MMA) was identified by IR and <sup>1</sup>H-NMR spectra. The number and weight average molecular weights of poly(MMA) were 77,500 and 173,590 respectively.

**Identification of copolymers.** The IR spectrum of poly(AcAP-co-MMA) indicated the absorptions at 2900, 1745 cm<sup>-1</sup> (C=O, AcAP), 1729 cm<sup>-1</sup> (C=O, MMA) with the disappearance of vinyl absorptions at 1598, 980 cm<sup>-1</sup>. The number and weight average molecular weights of poly(AcAP-co-MMA) were in the range 38,199 to 45,862 and 97,360 to 108,500 respectively. The polydispersity of the polymers varied in the range 2.3 to 2.7.

**Antifouling properties.** Prepared polymers exhibited efficient AF properties against marine bacteria and diatoms (Table 1). In disk assays conducted, among the polymers tested poly AcAP and 4:6 ratio of poly(AcAP:MMA), the highest inhibitory effects (8.6-10.6 mm of inhibitory zone) were observed against bacteria. Similarly it has significantly prevented the ship fouling diatom attachment at 4 mg cm<sup>-2</sup> levels with a minimum of 9 cm<sup>-2</sup>.

Table 1. AF efficiency of p(AcAP) [a] & p(AcAP-co-MMA) [b]

Conc.	*Marine bacteria		**Marine diatoms			
	<i>Pseudomonas</i> sp	<i>Bacillus</i> sp	<i>Amphora</i> sp	<i>Navicula</i> sp		
control	a	b	a	b	a	b
0.5	0.66	1.00	4.00	4.30	112	112
1.0	3.34	1.67	5.00	6.16	92	55
2.0	6.00	2.00	8.60	8.00	57	29
4.0	8.60	3.17	10.6	10.0	36	17

\*Inhibition zone (mm), \*\*diatom attachment % (cm<sup>-2</sup>). Results are mean of 3 individual replicates.

### Conclusions

Biocidal monomer AcAP and its polymers were synthesized and characterized. AF activity of the prepared copolymers was comparable to commercial AF coatings. Especially, these polymers showed significant effects against microfoulers. As it has controlled leaching properties this can be useful for preparing long lasting AF coatings.

**Acknowledgement:** We thank the Ministry of Maritime Affairs and Fisheries, South Korea for research grant.

### References

- [1] Pleurdean, A.; Bruneau, C.M.; Potin, C. In Proceedings of the 11<sup>th</sup> Int Conf Org Coat Sci Technol, 1985, p 293. (C.A. 1986, 105, 210460n).
- [2] J. R. Geigy A. G.; British Patent 1,024,022 (March 30, 1966).
- [3] Oh S. T.; Ha C. S.; Cho W. J.; *J Appl Polym Sci* 1994, 54, 859-866.
- [4] Tholmann, D., Kossman, B. and Sosna, F. *European Coatings Journal*, 2003, 1-2, 16-33.