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

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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 hulls. In recent years, AF polymers are predominantly used in the shipping industries. The AF polymers have many advantages over conventional AF formulations. The controlled releasing 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. Ambitual polymer 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 microorganisms.

Experimental
Materials. 4-hydroxyacetoacetophenone (HAP) (99%), Acryloyl chloride (Ac) (99%), Tributylphosphate (TBP) (99.5%) were procured from Acros Chemical Ltd. MMA (99%), MEK (99%), toluene and methanol were procured from StanChem Chemicals, South Korea.

Synthesis of AcAP. The AcAP was prepared by Ac with HAP as shown in the Figure 1. The HAP and TBP were taken in 4-neck round bottom flask containing MEK equipped with stirrer and thermometer. The slow addition of Ac to the round bottom flask was done by keeping funnel at 0 °C. The reaction was monitored by TLC and the product was characterized by GC-MS, IR and HPLC. 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 TBP were mixed in a glass tube equipped with magnetic stirrer and a reflux condenser. The solution was degassed by purging with purified Ar gas. The tube was sealed and placed in a regulated thermostat bath at 70 °C for fixed period of time. The polymer solution obtained was precipitated in excess methanol.

Figure 1. Synthesis of AcAP, p (AcAP), and d (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, Brooker (Scanning), TPRS / TPD, FTIR (TGA), Spectrum GX (on solid samples in KBr pellets) and NMR (1H/13C, 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 copolymer 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, 1H-NMR and GC-MS spectra. The IR spectrum shows characteristic absorption bands at 1598, 3000 cm⁻¹ (νC=O), and 1669 cm⁻¹ (νC=O). The 1H-NMR spectrum of AcAP (solvent, CDCl₃) exhibited several peaks at 2.2-2.6 (6H), 3.80-4.17 (2H), 6.60-6.68 (2H), 7.17-8.00 (6H). From the UV spectrum, the wavelength at maximum absorption was 242nm. The mass spectrum exhibited the mass (m/e) 190 (M+).

Identification of homo polymers. The poly (AcAP) was identified from its IR spectrum indicating absorptions at 2960 cm⁻¹, characteristic of the vinyl polymer backbones, with disappearance of vinyl absorptions of monomers of AcAP at 1598, 880 cm⁻¹. The number and weight average molecular weights of poly (AcAP-co-MMA) were 29,566 and 152,274 respectively. The poly (MMA) was identified by IR and 1H-NMR spectra. The number and weight average molecular weights of poly (MMA) were 77,250 and 173,290 respectively.

Identification of copolymers. The IR spectrum of poly (AcAP-co-MMA) indicated the absorptions at 2900, 1745 cm⁻¹ (C=O, CO₂Ac), 1729 cm⁻¹ (C=O, MMA) with the disappearance of vinyl absorptions at 1598, 880 cm⁻¹. The number and weight average molecular weights of poly (AcAP-co-MMA) were in the range 35,195 to 45,802 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 diatom assays conducted, the polymers treated poly AcAP and poly MMA, the highest inhibitory effects (8.6-10.5% of inhibitory zone) were observed against diatoms. Similarly it has significantly prevented the ship fouling diatom attachment at 4 mg cm⁻² level with a minimum of 9 cm²).

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

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Man. bacteria</th>
<th>Man. diatoms</th>
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<tbody>
<tr>
<td>PBP</td>
<td>p</td>
<td>d</td>
</tr>
<tr>
<td>control</td>
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<td>8.00</td>
<td>3.17</td>
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</table>

[a] Inhibition zone (mm). [b] Diatom attachment % (cm²). 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 microfouling. As it has controlled releasing properties this can be useful for preparing long lasting AF coatings.

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References