SYNTHESIS OF P-AMINOPYRIDINE METHACRYLATE–METHYL METHACRYLATE (P-APM–MMA) COPOLYMERS, EVALUATION OF COPOLYMERIZATION PARAMETERS, AND INVESTIGATION OF THEIR ANTIMICROBIAL ACTIVITY

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The synthesis of functional polymers is highly relevant for biomedical materials, antimicrobial coatings, and membrane technologies. While PMMA-based materials are widely used for their good mechanical properties, their biocidal activity is limited. Thus, copolymerizing MMA with nitrogen-containing functional monomers is a promising route to obtain materials that retain mechanical/thermal stability while gaining antimicrobial activity.

The aim of this study is to synthesize p-APM/MMA copolymers, determine key copolymerization parameters (r_1, r_2 and Q–e), confirm their structure by IR and ^{1}H NMR, and assess their mechanical, thermal, and antimicrobial properties.

The radical copolymerization of p-APM and MMA was performed in benzene at 60 ± 1 °C under nitrogen in sealed glass ampoules. AIBN (0.2 mol% vs. total monomers) was used at an overall monomer concentration of 2 mol L^{-1} for 6 h. To limit compositional drift, conversion was kept below 8–10 % and measured gravimetrically. The polymers were precipitated in methanol, vacuum-dried, and purified by dissolution in benzene followed by triple reprecipitation in methanol. Reactivity ratios were determined by the Fineman–Ross method, and Q–e values were estimated using the Alfrey–Price approach.

The p-APM/MMA copolymerization was examined across a broad range of feed compositions, and the resulting copolymer compositions are summarized in Table 1. Fineman–Ross analysis gave $r_1 = 0.85 \pm 0.04$ and $r_2 = 0.45 \pm 0.03$, indicating higher reactivity of p-APM than MMA and a predominantly statistical (largely random) copolymer microstructure.

In the IR spectra, disappearance of the monomer vinyl bands (~950 and 1640–1635 cm^{-1}) confirms consumption of C=C bonds during copolymerization. Bands at 2800–2700 and 3007–3436 cm^{-1}, assigned to pyridine and N–H vibrations, further indicate incorporation of p-APM fragments into the polymer backbone. ^{1}H NMR showed aromatic signals at 6.5–7.2 ppm from the aminopyridine fragment and methyl resonances at 1.8–2.1 ppm from MMA units, confirming the copolymer structure and retention of the functional groups.

Incorporating p-APM improved properties vs. PMMA (Plexigum M-272), increasing tensile strength to 91–95 MPa (70 MPa) and Vicat softening temperature to 148–152 °C (90 °C). The copolymer showed ~22 % mass loss at 380 °C; the initial loss is mainly due to decomposition of side-chain functional groups, while the backbone remains relatively stable at higher temperatures.

Antimicrobial activity against E. coli (Gram−) and S. aureus (Gram+) was evaluated by agar diffusion. Increasing the p-APM content enlarged inhibition zones: the 89.2:10.8 (p-APM:MMA) copolymer showed strong activity (+++) against both strains, the 56:44 sample was moderate, and the 35.1:64.9 sample was weak, while the PMMA control showed no activity. The antimicrobial activity depends not only on overall composition but also on copolymer microstructure, i.e., the sequence distribution of p-APM units and their separation by MMA segments. p-APM–MMA copolymers were successfully synthesized with retention of aminopyridine functionality, and copolymerization parameters confirmed higher reactivity of p-APM than MMA. Compared with PMMA, they show improved mechanical and thermal properties and composition/microstructure-dependent antimicrobial activity, supporting their potential for antimicrobial coatings, biomedical polymers, and membrane applications.