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ANTIMICROBIAL COPOLYMERS FROM PARA-AMINOPYRIDINE METHACRYLATE AND METHYL METHACRYLATE: SYNTHESIS AND STRUCTURE–PROPERTY RELATIONSHIPS

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Abstract

Functional copolymers based on para-aminopyridine methacrylate (p-APM) and methyl methacrylate (MMA) were synthesized via radical polymerization in benzene at 60 °C using azobisisobutyronitrile as the initiator. The copolymerization parameters determined by the Fineman–Ross method (r_1 = 0.85 ± 0.04, r_2 = 0.45 ± 0.03) indicated a higher reactivity of *p*-APM, resulting in copolymers enriched in aminopyridine units. IR and ^{1}H NMR analyses confirmed that polymerization proceeds through the vinyl groups with complete retention of amino and pyridine functionalities in the side chains. Thermogravimetric analysis revealed high thermal stability up to 380 °C, exceeding that of polymethyl methacrylate. Mechanical tests showed enhanced strength (91–95 MPa) and Vicat softening temperatures of 148–152 °C, surpassing commercial Plexigum M-272. Antimicrobial activity, evaluated by the agar diffusion method, demonstrated pronounced inhibitory effects against both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) strains. Copolymers containing 89.2 mol% *p*-APM exhibited the highest antimicrobial efficiency, while moderate activity was observed at lower functional-monomer ratios. The biocidal efficiency correlated with both the content and distribution of *p*-APM units along the polymer chain. The combination of high thermal stability, mechanical strength, and antimicrobial activity suggests that *p*-APM–MMA copolymers are promising materials for biomedical coatings, membranes, and polymer systems with controlled antimicrobial properties.

Keywords: p-aminopyridinemethacrylate; methyl methacrylate; copolymers; biocidal activity.

АНТИМІКРОБНІ КОПОЛІМЕРИ З ПАРА-АМІНОПІРИДИНМЕТАКРИЛАТУ ТА МЕТИЛМЕТАКРИЛАТУ: СИНТЕЗ ТА ВЗАЄМОЗВ'ЯЗКИ МІЖ СТРУКТУРОЮ ТА ВЛАСТИВОСТЯМИ

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Анотація

Функціональні кополімери на основі пара-амінопіридину метакрилату (р-АРМ) та метилметакрилату (ММА) були синтезовані шляхом радикальної полімеризації в бензолі за 60 °С з використанням азобісізобутиронітрилу як ініціатора. Параметри кополімеризації, визначені за методом Файмана–Росса (r_1 = 0.85 ± 0.04, r_2 = 0.45 ± 0.03), вказали на вищу реакційну здатність *p*-АРМ, що привело до отримання кополімерів, збагачених амінопіридиновими ланками. Аналіз ІЧ та 1Н ЯМР підтвердив, що полімеризація проходить через вінілові групи з повним збереженням аміно- та піридинових функціональних груп у бічних ланцюгах. Термогравіметричний аналіз виявив високу термічну стабільність до 380 °С, що перевищує стабільність поліметилметакрилату. Механічні випробування показали підвищену міцність (91–95 МПа) і температуру розм'якшення за Вікатом 148–152 °С, що перевищує показники комерційного Plexigum M-272. Антимікробна активність, оцінена методом агарової дифузії, продемонструвала виражений інгібуючий ефект як проти грампозитивних (*Staphylococcus aureus*), так і грамнегативних (*Escherichia coli*) штамів. Кополімери, що містять 89.2 моль% *p*-АРМ, продемонстрували найвищу антимікробну ефективність, а помірна активність спостерігалася за нижчих співвідношень функціональних мономерів. Біоцидна ефективність корелювала як із вмістом, так і з розподілом одиниць *p*-АРМ уздовж полімерного ланцюга. Поєднання високої термічної стабільності, механічної міцності та антимікробної активності свідчить про те, що кополімери *p*-АРМ–ММА є перспективними матеріалами для біомедичних покриттів, мембран та полімерних систем з контрольованими антимікробними властивостями.

Ключові слова: р-амінопіридинметакрилат; метилметакрилат; кополімери; біоцидна активність.

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Journal of Chemistry and Technologies, 2026, *34*(1), 42-48

Introduction

Polymers containing functional groups exhibit a wide range of biomedical activities and are widely used as bactericides, fungicides, and pharmaceutical materials [1–6]. In recent years, vinyl monomers and new monomeric systems containing carbonyl and amino functional groups have attracted significant attention due to their potential biological activity [7–12]. It is well established that compounds containing amino groups often demonstrate enhanced antimicrobial properties and are relatively safe biocidal agents [13–17].

Methyl methacrylate (MMA) is a widely used monomer in the synthesis of polymeric materials due to its good optical transparency, mechanical strength, chemical resistance, and ease of processing [18–20]. Polymethyl methacrylate (PMMA) is extensively applied in biomedical fields, including dental materials, optical devices, and prosthetics, owing to its biocompatibility and stability [21–23]. However, PMMA exhibits limited antimicrobial properties and poor interaction with biological systems when used in environments prone to microbial contamination, which significantly restricts its application in biologically active and antimicrobial systems.

To overcome these limitations, copolymerization of MMA with functional monomers containing biologically active groups has become an effective approach. Among such monomers, para-aminopyridine methacrylate (p-APM) attracts increasing attention due to the presence of nitrogen-containing heterocyclic fragments, which are known to impart biological activity and antimicrobial properties to polymeric systems.

The introduction of p-APM units into the MMA chain is expected to enhance the antimicrobial properties of the resulting copolymers while preserving desirable mechanical and physicochemical characteristics of PMMA. In addition, the presence of pyridine moieties provides potential sites for further functionalization and interaction with biological targets.

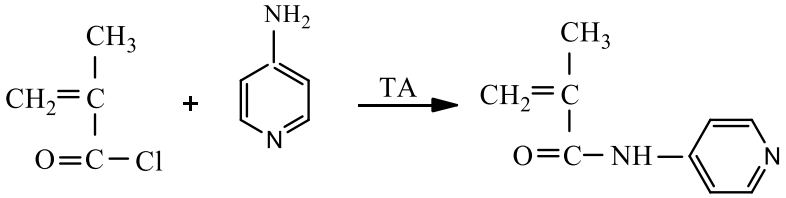
The aim of this work is to synthesize novel copolymers of para-aminopyridine methacrylate and methyl methacrylate, investigate their copolymerization behavior, determine their structural and physicochemical characteristics, and evaluate their antimicrobial activity.

Experimental part

Materials. Methyl methacrylate (MMA, Sigma-Aldrich, 99 %) was purified by vacuum distillation before use. Para-aminopyridine methacrylate (p-APM) was synthesized in our laboratory. Azobisisobutyronitrile (AIBN, Merck, 98 %) was recrystallized from ethanol (C_2H_5OH, Sigma-Aldrich, 99.8 %). Benzene (C_6H_6, Sigma-Aldrich, 99.5 %) was used as the solvent without further purification.

Synthesis of para-aminopyridine methacrylate (p-APM)

Para-aminopyridine methacrylate was synthesized by esterification of para-aminopyridine with methacryloyl chloride. The reaction was performed in dry tetrahydrofuran under a nitrogen atmosphere. Triethylamine was used as an acid scavenger. The reaction mixture was stirred at 0–5 °C for the first 1 h and then allowed to warm to room temperature and stirred for an additional 5 h. After completion, the reaction mixture was filtered to remove triethylamine hydrochloride, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization and dried in vacuum. The structure of the synthesized monomer was confirmed by IR and ^{1}H NMR spectroscopy.

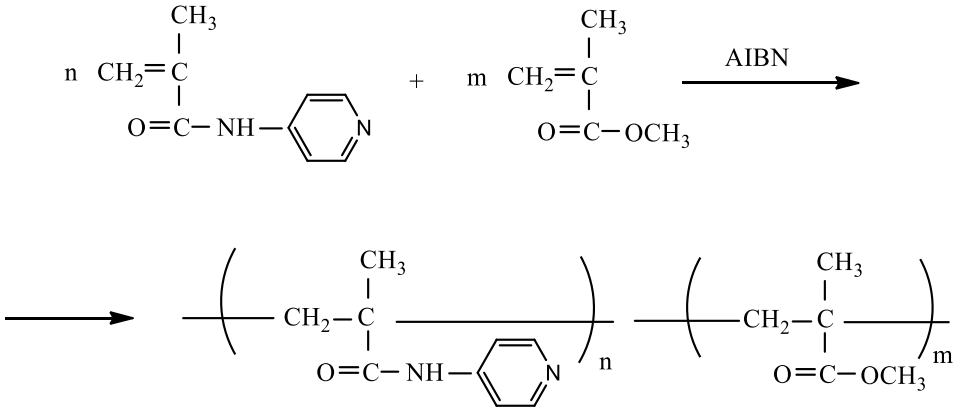


Schema 1. Synthesis of para-aminopyridine methacrylate (p-APM) from para-aminopyridine and methacryloyl chloride in the presence of triethylamine (TA).

Copolymerization procedure.

Radical copolymerization of MMA and p-APM was carried out in benzene at 60 ± 1 °C in sealed glass ampoules under a nitrogen atmosphere. AIBN was used as the initiator at a concentration of 0.2 mol% relative to the total monomer content. The total monomer concentration was maintained at 2 mol/L. The sealed ampoules were placed in a thermostated oil bath, and the polymerization was carried out for 6 hours.

Journal of Chemistry and Technologies, 2026, *34*(1), 42-48



Schema 2. Radical copolymerization of para-aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA) initiated by AIBN.

The reaction conditions were selected to ensure that the monomer conversion did not exceed 8–10 % in order to minimize compositional drift. The degree of monomer conversion was determined by a gravimetric method based on the mass of the dried copolymer after precipitation and purification relative to the initial monomer feed.

After polymerization, the reaction mixture was cooled and poured into an excess of methanol to precipitate the polymer. The precipitated copolymer was filtered and dried under vacuum to constant weight. For further purification, the polymer was redissolved in benzene and reprecipitated three times in methanol.

The copolymerization constants r_1 and r_2 were determined using the Fineman–Ross method based on the copolymer composition data [24]. The Alfrey–Price Q and e parameters were calculated to characterize the reactivity and polarity of the synthesized monomer [25].

The elemental composition (C, H, N) of the synthesized copolymers was determined using a PerkinElmer 2400 Series II CHN elemental analyzer (PerkinElmer, USA).

Results and discussion

Copolymerization results

The radical copolymerization of para-aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA) was studied over a wide range of initial monomer compositions. The dependence of the p-APM unit content in the synthesized copolymers on the feed composition is summarized in Table 1.

Table 1

Copolymerization of para-aminopyridine methacrylate (p-APM, M_1) with methyl methacrylate (MMA, M_2): composition of initial mixtures and resulting copolymers (mol%), copolymerization constants (r_1, r_2), activity parameter (Q), and polarity parameter (e).

Composition of the initial mixture, mol %		Composition of the copolymer, mol % *		r_1	r_2	Q_1	e_1	$r_1 \cdot r_2$
M_1	M_2	m_1	m_2					
90	10	89.2	10.8					
75	25	75.5	24.5					
50	50	56	44	0.85±0.04	0.45±0.03	1.1	-0.57	0.38
25	75	35.1	64.9					
10	90	17.4	82.6					

*The composition of the copolymer was determined at low conversion depths (6 – 12%).

As seen from the data, the condition $r_1 > r_2$ indicates that p-APM exhibits higher reactivity compared to MMA. This difference results in the formation of a predominantly statistical copolymer structure. However, noticeable enrichment of copolymers with p-APM units is mainly observed at the equimolar (1:1) monomer feed ratio, while at other compositions the copolymer composition more closely follows the initial monomer ratio.

The higher reactivity of p-APM can be attributed to the presence of electron-donating functional groups in its structure. The copolymerization constants r_1 and r_2, determined using the Fineman–Ross method, characterize the relative tendencies of both monomers to propagate. Additional insight is provided by the Alfrey–Price Q–e parameters, where the Q parameter reflects overall reactivity and the e parameter reflects the electronic nature and polarity of the monomer.

These parameters provide a quantitative and conceptual basis for interpreting the copolymerization behavior of the p-APM/MMA system and confirm that the electronic and structural features of p-APM play a key role in governing the copolymerization process.

Structural characterization

The structure of the synthesized copolymers was confirmed by IR and ^{1}H NMR spectroscopy.

In the IR spectra (Fig. 1), the absorption band at 1715 cm^{-1} corresponds to the stretching vibrations of the carbonyl (>C=O) group of the ester functionality. The band at 1725 cm^{-1}, characteristic of the ester carbonyl group of MMA, and the band at 1380 cm^{-1}, corresponding to deformation vibrations of the methyl group, are also observed.

The disappearance of the characteristic vinyl group absorption bands of the monomers at 950 cm^{-1} and 1640–1635 cm^{-1} confirms that copolymerization proceeds exclusively through the vinyl double bonds. The presence of absorption bands in the region 2800–2700 cm^{-1} and 3007–3436 cm^{-1}, related to pyridine and N–H vibrations, confirms the incorporation of p-APM fragments into the copolymer chain.

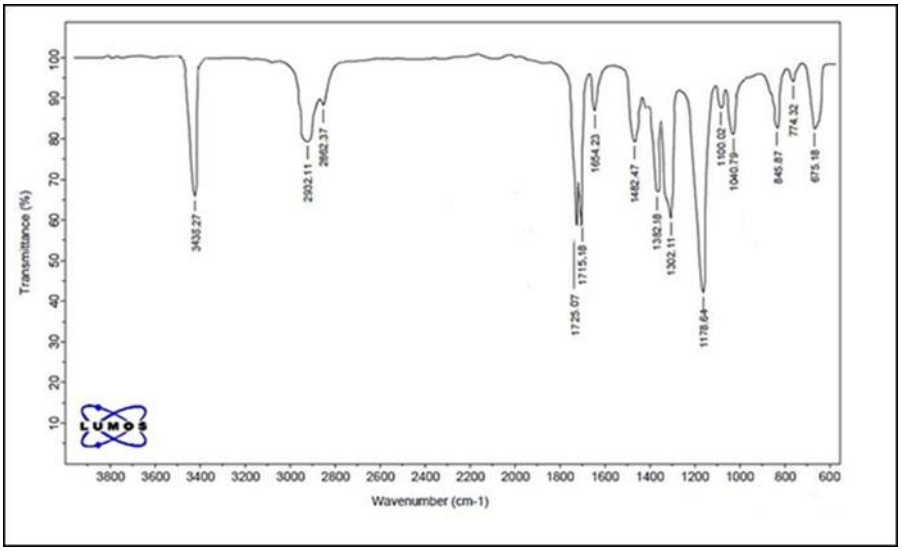


Fig.1. IR spectra of the copolymer of para-aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA)

The ^{1}H NMR spectra (Fig. 2) further support the copolymer structure. Signals at 6.5–7.2 ppm correspond to aromatic protons of the aminopyridine fragment, while signals at 1.8–2.1 ppm are assigned to the methyl protons of the MMA units.

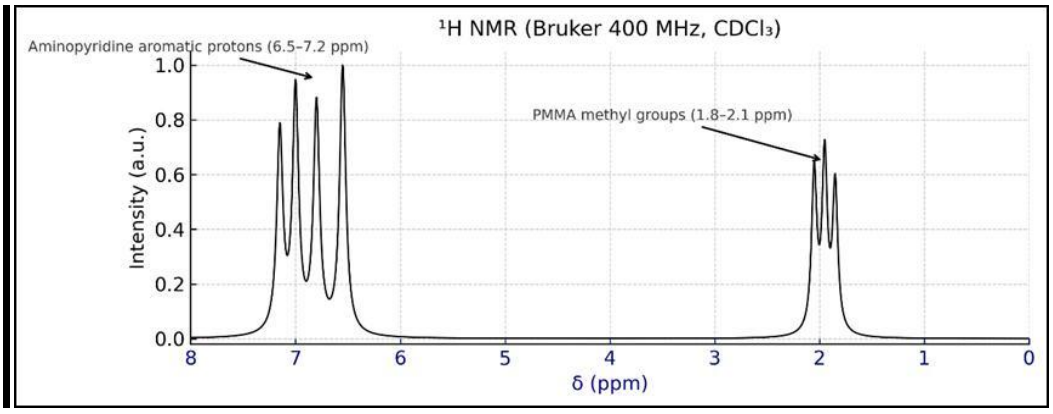


Fig. 2. ^{1}H NMR spectra of the copolymer of para - aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA)

Thus, spectral analysis confirms that copolymerization proceeds through vinyl groups with preservation of the functional fragments of both monomers.

Physical and mechanical properties

The physicochemical and mechanical properties of the synthesized copolymers are presented in Table 2. Compared to the commercial PMMA grade Plexigum M-272, the obtained copolymers demonstrate: higher tensile strength,

Journal of Chemistry and Technologies, 2026, *34*(1), 42-48

improved impact toughness, increased Vicat softening temperature.

Table 2

Physicochemical and mechanical properties of copolymers of para-aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA): tensile strength (MPa), impact toughness (kJ/m^2), and Vicat softening temperature (°C).

Polymers	Tensile strength, MPa		During compression testing	Specific impact toughness, kJ/m^2	Vicat softening temperature, °C
	During tensile testing	During flexural testing			
Copolymer 89.2:10.8	95	175	125	26–31	152
Copolymer 56:44	91	162	118	25–30	148
Plexigum M-272	70	120	105	18–25	90

These improvements indicate enhanced mechanical performance and thermal resistance of the modified materials, which is particularly important for their potential application in biomedical and engineering fields.

Thermogravimetric analysis (TGA) shows that the copolymer exhibits only about 22 % mass loss at 380 °C, indicating relatively high thermal stability. The initial mass loss is attributed mainly to the degradation of side-chain functional groups, while the polymer backbone remains stable up to higher temperatures compared to conventional PMMA.

Antimicrobial activity

The antimicrobial activity of the copolymers against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) was evaluated using the agar diffusion method. The results are presented in Table 3 and Fig. 3.

Table 3

Antimicrobial activity of copolymers of para-aminopyridine methacrylate (p-APM) with methyl methacrylate (MMA) against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria, evaluated by agar diffusion method; inhibition levels indicated as strong (+++), moderate (++), weak (+), or none (–).

Copolymer composition (p-APM : MMA, mol%)	E. coli (Gram–)	S. aureus (Gram+)	Activity level*
89.2 : 10.8	+++	+++	Strong
56 : 44	-++	-++	Moderate
35.1 : 64.9	-+	-+	Weak
p-MMA (control)	–	–	None

* Legend: +++ strong inhibition; ++ moderate inhibition; + weak inhibition; – none.

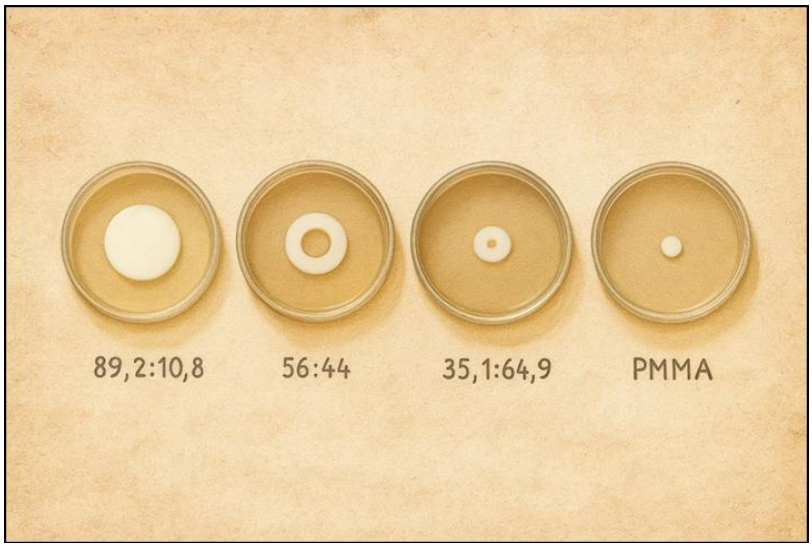


Fig. 3. Antimicrobial activity of p-APM–MMA copolymers against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) determined by the agar diffusion method. The diameter of inhibition zones increases with p-APM content (89.2:10.8 > 56:44 > 35.1:64.9 >> PMMA control)

The inhibition zone diameter increased with increasing p-APM content in the copolymer. The copolymer with a composition of 89.2:10.8 (p-APM:MMA) exhibited strong antibacterial activity against both bacterial strains.

However, the antimicrobial activity is not solely determined by the overall p-APM content. The spatial distribution of p-APM units along the polymer chain and their separation by MMA units also play an important role. This suggests that not only composition, but also microstructure and functional group distribution govern the biocidal behavior.

The observed complete lysis of bacterial cells indicates strong bactericidal action, while partial lysis after 48–72 h indicates a prolonged antimicrobial effect. These properties make the synthesized copolymers promising candidates for biomedical and sanitary applications.

Directions for future research

Future research should focus on: extending antimicrobial tests to a wider range of microorganisms, including fungi, incorporating other functional comonomers to enhance biological activity, studying practical applications such as coatings, membranes and biomedical implants. Unlike earlier studies, which mainly focused on structural or mechanical properties, the present work demonstrates both improved mechanical and biological performance of p-APM–based copolymers, significantly extending the scope of functionalized PMMA materials.

Conclusions

In this study, copolymers based on para-aminopyridine methacrylate (p-APM) and methyl methacrylate (MMA) were successfully synthesized via radical copolymerization. The composition, structural features, and reactivity of the obtained copolymers were systematically investigated using IR and ^{1}H NMR spectroscopy, together with the determination of copolymerization constants and Alfrey–Price Q–e parameters. The results demonstrated that the p-APM monomer exhibits higher reactivity compared to MMA, leading to a predominantly statistical copolymer structure with partial enrichment in p-APM units, especially at equimolar compositions.

Spectral analysis confirmed that copolymerization proceeds through the vinyl groups while preserving the functional amino and pyridine fragments within the polymer backbone. The synthesized copolymers also showed good solubility in common organic solvents and enhanced thermal stability, which makes them promising candidates for functional polymer materials and further chemical modification.

Importantly, the copolymers exhibited significant antimicrobial activity against both Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria. The strongest biocidal effect was observed for copolymers with higher p-APM content, particularly the 89.2:10.8 (p-APM:MMA) composition, which demonstrated pronounced inhibition zones in agar diffusion tests. The antimicrobial performance was shown to depend not only on the monomer composition but also on the distribution of p-APM units along the polymer chain.

Overall, the combination of improved mechanical, thermal, and antimicrobial properties highlights the potential of these copolymers for advanced applications in biomedical materials, antimicrobial coatings, membrane technologies, and protective polymer systems.

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