

Research Article

Design of Novel Poly(Propranolol) Acrylate and Methacrylate Polymers through Radical Polymerization for Antibacterial Activity and Metal Ion Absorption

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The monomer 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanoacrylate (IANOPA) and monomer 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanomethacrylate (IANOPMA) were synthesized by treating 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanol with acryloylchloride/methacryloyl chloride. The above esterification reactions were carried out in the presence of triethylamine. By employing the free radical polymerization method, the synthesized monomers were converted into polymers by using an initiator 2, 2'-azobisisobutyronitrile in the presence of nitrogen environment at $70 \pm 2^{\circ}$ C. The monomers and polymers were characterized by various techniques such as FT-IR, UV, ¹H NMR, and ¹³C NMR spectroscopic analyses. Further, differential scanning calorimetry (DSC) was used to estimate the glass transition temperature (T_g). Gel permeation chromatography (GPC) was used to estimate the molecular weight of the polymers. In addition, monomer and polymer surfaces' morphology was analyzed using SEM analysis. As a primary application, the effectiveness of synthesized monomers and polymers was explored as antibacterial agents against gram-positive bacteria (Staphylococcus aureus) and gram-negative bacteria (Pseudomonas aeruginosa) which were measured from their inhibitory zone diameters. Further, the synthesized polymers, poly-IANOPA and poly-IANOPMA, were utilized for the uptake ability study of heavy metal ions such as Zn^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} present in water sources by equilibrium method.

1. Introduction

Acrylate functionalized polymers are commercially important homopolymers and copolymers. Having higher thermal stability nature, they getting much interest in industrial applications. The first discovered acrylic/acrylate polymers are used for storage applications of automobiles due to their high-temperature stability behavior [1, 2], based on the pendant functional groups present in the acrylate polymers varying their physical and chemical properties and used in various applications including adhesives and coating materials in the industries. In 1949, British ophthalmologist, Sir Nicholas Harold prepared an intraocular lens using poly(methyl methacrylate) as a medical beneficial material [3, 4]. Then, newly developed polymers are rapidly utilized for medical applications based on their monomer's functional group properties. Having aromatic rings, phenyl methacrylate is considered a reactive monomer, and it is suitable to tune their biological behavior by substituting various functional groups in different ring positions [5, 6]. Aliphatic substituted methacrylate copolymers are showing high efficiency against human pathogenic organisms [7]. Generally, synthetic polymers have various interesting characteristics and are easily available to be fine-tuned for their suitability for biomedical applications.

In recent decades, functionalized acrylate polymers have been used as drug-delivery materials. Mansoor et al. and Xie et al.'s research group reported poly acrylic-derived polymers having controlled porous are used for insulin delivery systems [8, 9]. Polyethylene acrylate copolymer blends with sulfonates are attested to improve blood compatibility with the addition of platelets and with bacterial repellence [10]. It is interesting that acrylic composite with metal oxides are reported to their an effective mucoadhesive carrier for buccal drug delivery [11]. Also, they study their antimicrobial properties with pathogenic microorganisms namely Staphylococcus aureus, Bucillus subtilis, and Escherichia coli. Moreover, polymeric antimicrobial candidates are suitable polymers for biomedical applications due to having their own advantage for nonvolatile, chemically stable, and significantly nil photolytic decomposition nature [12].

Sensing metal concentrations in living organisms and our ecosystems is significantly exigent work. The presence of high metal ion concentrations in water resources seriously affects plant and animal life. Indeed, there are many industries including wood processing, petroleum refineries, and electrochemical industries, where wastes contain toxic heavy metals and contaminate the groundwater. Among the available methods for purifying contaminated water, controlling the contamination of toxic metals in the groundwater is a highly suitable one. Many of these metals take part in a variety of physiological and pathological responses and are also physiologically active, and some metals can impair endocrine and endothelial vascular functioning [13–15]. Epidemiologic and experimental data evidence that ambient metals might obstruct the enzymes responsible for one-carbon and citric acid metabolism as well as the histone modification pathways. As a result, the genome's DNA methylation state is abnormal, and gene expression is altered [16].

Considering the simple and regular application materials in human life, nickel is utilized extensively in the production of coins, jewellery, watches, and buttons, as well as stents, braces, and other orthopaedic applications. People are exposed to nickel through diet (cacao and nuts), tobacco use, and contamination of the air, land, and water from burning fossil fuels. Occupational exposure to nickel is known to cause respiratory malignancies, especially when it takes the form of nickel sulphide and nickel oxide. Other long-term negative health consequences of nickel include rhinitis, sinusitis, perforations of the nasal septum, asthma, skin allergies, and reproductive issues. Nickel has been tested in whole blood, serum, plasma, and urine, despite the fact that biomarkers of nickel exposure are not well confirmed [17]. With a half-life of 20 to 27 hours, nickel is known to be rapidly excreted through urine, with additional excretion occurring through saliva and perspiration [18]. Therefore, it is important to monitor and remove heavy metals in order to protect public health from adverse effects. However, the commercially available polymers generally lack selectivity in the metal ion adsorption process [19, 20].

As we aimed to synthesize the acrylate polymer for metal ion sensors as well as biological applications; the synthesizing polymer must have easily undergone docking with biomacromolecules of living things. So, our polymer pendant unit with a heteroatom, such as a "nitrogen atom" which is highly involved in the biological process, is suitable for our scope of the research. In this current article, the synthesis will be enhanced by one of the prominent methods which is by acrylating/methacrylating the propranolol by esterification technique. Further, the double bonds of the acrylic/methacrylic group will be suitable candidates for the free-radical polymerization technique in order to develop propranolol pendant polymers. Also, we expect that the presence of a secondary amine group in the propranolol-substituted acrylic/methacrylic polymers will be suitable candidates for developing bacterial resistance response.

2. Materials and Methods

2.1. Materials. Propranolol [1-(isopropylamino)-3-(1-naphthyloxy)-2-propanol] (TCI, Tokyo, Japan) and acrylic and methacrylic acid (Merck, Mumbai, India) were used. From ethanol, AIBN (Aldrich, Bengaluru, India) was recrystallized. Prior to use, distillation was used to purify all the solvents.

2.2. Synthetic Methodology. Individual monomer IANOPA/ IANOPMA and an initiator AIBN (0.5% wt of monomer) were made into solution in 10 mL of tetrahydrofuran solvent and purged with N_2 gas for 20 minutes in polymerization tubes. The solution was then heated to 70°C and allowed for 8 hours to polymerize. Then, for precipitation, this mixture was added to methanol. By periodically reprecipitating the obtained polymers from chloroform with methanol, the polymers were purified and dried at ambient temperature.

2.3. Characterization Techniques. The Fourier transformation infrared (FT-IR) spectra of monomers and polymers were recorded on the Perkin-Elmer FT-IR spectrometer RXI. Using KBr, the specimen was converted into a pellet. A UV-vis spectrophotometer (double beam UV-vis spectrophotometer, MODEL UVD-3500, Labomed, Inc.) was employed to record UV-vis diffuse reflectance spectra analysis, and analytically pure DMSO solvent was used to record the spectra. On a Bruker 300 MHz FT NMR spectrometer, the ¹H NMR spectra of each monomer and polymer sample were recorded using tetramethylsilane (TMS) as an internal reference at ambient temperature. The chemical shifts were acquired under comparable circumstances, and the protondecoupled ¹³C NMR spectra were carried out on the same instrument operating at 22.63 MHz at ambient temperature. Surface morphology was studied using a scanning electron microscope (FEI Nova NanoSEM 450, USA) of the surface gold-coated sample that was taken under liquid nitrogen. Using Waters 501 gel permeation chromatography (GPC) with an ultrastar gel column and a differential refractometer index detector, the number (M_n) , weight (M_w) average molecular weight, and polydispersity index (PDI) value of polymers were calculated. Tetrahydrofuran was utilized as an eluent, and polystyrene standards given by Millipore were used to calibrate the GPC. NETZSCH STA 409C=CD thermal analyzer was used to perform the thermogravimetric analysis in the air at a rate of 10°C/min. Using a differential scanning calorimeter (DSC) NETZSCH DSC 204 thermal analyzer, the glass transition temperature of the polymer was ascertained in nitrogen.

2.4. Antibacterial Property Measure of Monomers IANOPA and IANOPMA and Polymers IANOPA and IANOPMA. The biodegradability of synthesized monomers and polymers was measured using a variety of microorganisms that are routinely used in biodegradability experiments. In a well diffusion assay medium, bacterial strains (Staphylococcus aureus and Pseudomonas aeruginosa) were cultivated. On sterile Petri plates, prepared nutrient agar was poured where it solidified. It was swabbed with developing bacterial cultures (S. aureus and P. aeruginosa). Then, using a sterile cork borer, five wells (8 mm diameter) were created. The wells were filled with four different samples. Analytical grade with purity >99.9% Sigma-Aldrich DMSO was used as a negative control. The plates were kept for incubation at 37°C for 24 hours. After incubation, the inhibition diameter was measured [21-23].

2.5. Metal Ion Absorption Ability of Synthesized Polymers: Poly-IANOPA and Poly-IANOPMA. The metal ion absorption ability of synthesized polymers IANOPA and IANOPMA was studied with 0.1 M concentration of Zn²⁺, Cu^{2+} , Ni^{2+} , and Pb^{2+} metal ion studies by equilibrium techniques. The inductively coupled plasma optical emission spectroscopy (ICP-OES) method was adopted for studies using the Perkin Elmer Optima 5300 DV ICP-OES instrument. In the study procedure briefly, an individual aqueous solution of 0.1 M solution of Zn²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ using deionized water is prepared using corresponding nitrate salts. Further, 5 mL of the metal nitrate solution and 20 mg of synthesized polymer are taken in a 10 mL Erlenmeyer flask and stirred. The polymers were soaked in constant immersion time and swollen by absorbing metal ion solution. After 24 hours of stirring, the mixture was filtered and the collected filtrates were used for analysis. The unabsorbed metal ions in the filtrate are used to evaluate to quantify the metal ions adsorbed by the polymers.

Percentage of metal ions absorbed (%)

= Total amount of metal ion in solution

(1)

3. Experimental

3.1. Synthesis of 1-(Isopropylamino)-3-(1-Naphthyloxy)-2-Propanoacrylate (IANOPA) and 1-(Isopropylamino)-3-(1-Naphthyloxy)-2-Propanomethacrylate (IANOPMA). Acryloyl/methacryloyl chloride was synthesized from their respective acrylic/methacrylic acids using Stempel et al.'s method in the presence of benzoyl chloride [24, 25]. For the production of 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanoacrylate/methacrylate, a three-necked roundbottomed flask (500 mL) containing 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanol (10g), hydroquinone (0.5g), dichloromethane (DCM) (200 mL), and triethylamine (13.6 mL) were cooled at 0-5°C. Simultaneously, the dissolved acryloyl/methacryloyl chloride in DCM (20 mL) taken in a dropping funnel was gently added to the aforementioned mixture at 0 to 5°C (Scheme 1). It continued to stir for an hour. After the removal of the cooling bath, the reaction mixture was stirred at room temperature for a further two hours. Triethylammonium chloride that had accumulated was filtered out. With 0.1% NaOH solution, the residue was washed and then with distilled water. By using a rotary evaporator, the solvent DCM was removed and followed by drying with dehydrated sodium sulfate. As we aimed to synthesize ester polymer, we recovered the minor product, which was obtained by the nucleophilic attack of secondary alcohol with acryloyl/methacryloyl chloride. The yield of the product obtained is found to be around 20%. The reaction mechanism of monomer formation is presented in Scheme 2.

3.1.1. Mechanism of Monomer Formation

3.2. Polymerization. Individual monomer IANOPA/ IANOPMA and an initiator AIBN (0.5% wt of monomer) were made into solution in 10 mL of tetrahydrofuran solvent and purged with N_2 gas for 20 minutes in polymerization tubes [26]. The solution was then stirred constantly at 70°C for 8 h to polymerize. Then, for precipitation, this mixture was added to methanol (Scheme 1). By periodically reprecipitating the obtained polymers from chloroform with methanol, the polymers were purified and dried at ambient temperature. The polymerization pathway is explained in Scheme 3, and the reaction condition and the catalyst concentration with reaction time are presented in Table 1.

Polymerization occurs in a three-step process which is radical initiation, propagation of free radicals, and termination of free radical species. In the first step, the initiator AIBN underwent breaking the bonds under thermal conditions and generated two isobutyronitrile radicals with the elimination of neutral molecule nitrogen. In step 2, the generated isobutyronitrile radical initiates the monomer unit and generates a monomeric radical. This newly generated monomer radical is readily available to propagate the polymeric chain until it consumes all monomers. As we utilize less amount of initiator, the longer chain polymerization will occur during the propagation step. In step 3, the termination may happen by consuming all the radical species or the rad-

⁻ Total amount of metal ions remaining in the filtrate.



SCHEME 1: Synthesis of monomers (IANOPA and IANOPMA) and polymers (poly-IANOPA and poly-IANOPMA).



SCHEME 2: The proposed reaction mechanism of the obtained monomer.

icals can couple with currently existing polymeric chains. These three stages of reaction progress are presented in the title of the mechanism of polymer formation.

3.2.1. Mechanism of Polymer Formation

3.3. Characterization of Monomers

3.3.1. Solubility. The monomers (IANOPA) and (IANOPMA) are both soluble in dimethylsulphoxide, dimethylformamide, and tetrahydrofuran; whereas in water, n-hexane, and solvents that contain hydroxyl groups, the synthesized monomers are insoluble.

3.3.2. UV Spectroscopy Studies. The IANOPA and IANOP-MA's UV absorbance values have been measured between 200 and 400nm, as shown in Figure 1. The monomer IANOPA shows λ_{max} at 278 nm and 248 nm and monomer IANOPMA shows λ_{max} at 284 nm and 246 nm. This observed absorption around 240 nm corresponds to the resonance of aromatic naphthol π electron delocalization and the maxima around 290 nm due to the hyperconjugation between the unsaturation unit and the carbonyl group of the acryloyl group present in the molecule. Also, monomer absorption values 278 nm and 284 nm may correspond to the presence of different R substitutions that is H and Me groups. Methacrylate substitution shows around ~6 nm bathochromic shift due to the higher hyperconjugation effect of three hydrogen in the methyl group.

3.3.3. Infrared Spectroscopy Data of Monomers

(1) Monomer IANOPA. 3435 cm⁻¹: -NH (secondary amine) stretch; 2928 cm⁻¹: -CH stretch (alkyl group); 1726 cm⁻¹: -

C=O (ester carbonyl) stretch; 1584 cm^{-1} : -C-C stretch in aromatic ring; 1599 cm^{-1} : -C=C stretch in olefins; 1291 cm^{-1} : -C-N (secondary amine) stretch shown in Figure 2.

(2) Monomer IANOPMA. 3433 cm⁻¹: -NH stretch (secondary amine); 2930 cm⁻¹: -CH stretch (alkyl group); 1724 cm⁻¹: -C=O (ester carbonyl) stretch; 1598 cm⁻¹: -C=C (olefins) stretch; 1285 cm⁻¹: -C-N (secondary amines) stretch shown in Figure 2.

3.3.4. ¹H NMR Spectroscopic Analysis of Synthesized Monomers. The structure of synthesized monomers and polymers is thoroughly analyzed, the spectroscopic data are presented, and the corresponding NMR spectrum is presented, as shown in S1(a-d) and S2(a-d) in the Supporting Information file[#] (SIF[#]).

(1) Monomer (IANOPA)—¹H NMR Spectrum (CDCl₃, δ_{ppm}). The monomer (IANOPA) proton NMR spectrum is displayed in Figure S1(a). Signals corresponding to the isopropyl methyl group are at 1.0–1.1 ppm. The methine – NH proton shows a signal at 1.95 ppm. The signals at 2.8 and 2.95 correspond to isopropyl methine proton and doublet of methylene proton (–CH₂–N), respectively. The methylene proton (–O–CH₂–) shows a signal at 4.1 ppm. Vinyl protons are responsible for the emergence of distinctive peaks at 5.8–6.2 ppm, whereas aromatic protons are responsible for the appearance of multiplets at 7.3– 8.1 ppm.

(2) Monomer (IANOPMA)—¹H NMR Spectrum (CDCl₃, $^{\delta}ppm$). The monomer (IANOPMA) proton NMR spectrum is depicted in Figure S1(b). Signals corresponding to isopropyl methyl group are at 1.1–1.2 ppm. The methine –



SCHEME 3: The polymerization pathways by the reaction of monomer initiated by AIBN.

TABLE 1: Reaction condition for synthesis of poly-IANOPA and poly-IANOPMA.

Monomer	Weight of monomer (g)	Weight of AIBN (g)	Reaction time (h)	THF (mL)	Temperature (°C)	Conversion (%)
IANOPA	1	0.05	0.5	10	70	3.8
IANOPMA	1	0.05	0.5	10	70	5.5

NH proton shows a signal at 1.8 ppm. The signals at 2.6 and 2.8 correspond to isopropyl methine proton and doublet of methylene proton $(-CH_2-N)$, respectively. The methylene proton $(-O-CH_2-)$ shows a signal at 4.2 ppm. The appearance of characteristic peaks at 5.6–6.2 ppm is due to vinyl protons, and 7.4–8.1 ppm shows multiplet of aromatic protons. The signal at 1.9 corresponds to acrylic (-CH) methyl proton.

3.3.5. ¹³C NMR Spectroscopic Analysis of Synthesized Monomers

(1) ¹³C NMR Spectrum of Monomer (IANOPA) (CDCl₃, ^{δ}ppm). Figure S2(a) shows a decoupled ¹³C NMR spectrum of monomer (IANOPA). Resonance signals at 23 ppm correspond to isopropyl carbons (-CH₃). The (-H₂C-NH) and (-HC-NH) show resonance signals at 45 and 48 ppm, respectively. Similarly (-H₂C-O) and (-HC-O) shows



FIGURE 1: UV spectra of IANOPA and IANOPMA monomers and polymers.



FIGURE 2: FT-IR spectra of IANOPA and IANOPMA monomers and polymers.

resonance signals at 68 and 73 ppm, respectively. The aromatic carbons show a resonance signal at 132 ppm, whereas the vinyl carbons show a signal at 125 as well as 138 ppm. The ester carbonyl carbon (-C=O) is represented by the resonance signals at 168 ppm.

(2) ¹³C NMR Spectrum of Monomer (IANOPMA) (CDCl₃, $^{\delta}ppm$). Figure S2(b) shows a decoupled ¹³C NMR spectrum of monomer (IANOMPA). The methacrylate (– CH₃) carbon and isopropyl carbons (–CH₃) show resonance signals at 19 and 23 ppm, respectively. The (– H₂C–NH) and (–HC–NH) show resonance signals at 45

TABLE 2: Molecular weight M_n , M_w , and D of the synthesized acrylate polymers.

	Molecu	lar weight distrib	ution
Polymer	M_w	$(D = M_w/M_n)$ M_n	Đ
Poly-IANOPA	22135	13439	1.6
Poly-IANOPMA	65682	32347	2.0

and 49 ppm, respectively. Similarly $(-H_2C-O)$ and (-HC-O) shows resonance signals at 67 and 72 ppm, respectively. The aromatic carbon resonance signal appears at 130 ppm, whereas the vinyl carbons show a signal at 128 as well as 135 ppm. The ester carbonyl carbon (-C=O) is represented by the resonance signals at 169 ppm.

3.4. Characterization of Polymers

3.4.1. Solubility. The polymers (poly-IANOPA and poly-IANOPMA) are soluble in acetone, dimethylsulphoxide, and dimethylformamide. In water, the polymers are insoluble, but they can be soakable, whereas hydrocarbons like n-hexane and solvents containing hydroxy-groups having less polar the synthesized polymers are insoluble.

3.4.2. UV Spectroscopy Studies. Figure 1 shows the UV spectra of polymer (IANOPA)/(IANOPMA). The poly-IANOPA has maximum absorbance at λ_{max} 290 and 244 nm, whereas the poly-IANOPMA also shows maximum absorbance at λ_{max} 290 and 244 nm. It is clearly shown that the presence of hyperconjugation effect of electron delocalization of 3 C-H bonds in the CH3 group for poly-IANOPMA and one C-H bond in the poly-IANOPA is nullified in the polymers due to the large amount of electron cloud in the polymer. Instead, unlike polymer, the absorption difference due to the hyperconjugation effect between methacryloyl and acryloyl functionalities is clear in the monomers due to the absence of electron cloud overlap.

3.4.3. Infrared Spectroscopy of Polymers

(1) Poly-IANOPA. The NH stretch in secondary amine is shown by the absorption band at 3400 cm^{-1} whereas at 2928 cm⁻¹ corresponds to aromatic C-H stretching (naphthyl ring) of poly-IANOPA. The -CH stretching in the alkyl group causes a band around 2670 cm⁻¹. The C=O stretch in ester carbonyl makes a strong absorption band at 1725 cm⁻¹, while aromatic (-C-C) stretching absorption is seen at 1585 cm⁻¹. The -C-N stretching in secondary amines results in the absorption bands at 1282 cm⁻¹ that can be observed in Figure 2.

(2) Poly-IANOPMA. The NH stretch in secondary amine is shown by the absorption band at 3414 cm^{-1} whereas at 2958 cm⁻¹ corresponds to aromatic C-H stretching (naphthyl ring) of poly-IANOPMA. The -CH stretching in the alkyl group makes an absorption band at 2671 cm⁻¹. The C=O stretching in ester carbonyl makes a strong absorption band at 1725 cm⁻¹, while the absorption of the -C-C aromatic stretching is observed at 1598 cm⁻¹. The band



FIGURE 3: Thermogravimetric analysis curves of poly-IANOPA and poly-IANOPMA.



FIGURE 4: DSC curves of synthesized poly-IANOPA and poly-IANOPMA.

TABLE 3: Response of synthesized polymers (poly-IANOPA and poly-IANOPMA) under thermal conditions.

Polymers	T_a (°C)	<i>T_i</i> (°C)	Temperature (°C) with respect to weight loss (%)				
	9		10	25	50	75	90
Poly-IANOPA	94	110	175	228	275	315	400
Poly-IANOPMA	90	109	169	226	275	315	400

 T_i : initial decomposition temperature; T_a : glass transition temperature.

observed at 1278 cm^{-1} may be due to secondary amines (-C-N stretching), which is shown in Figure 2.

3.4.4. ¹H NMR Spectroscopic Analysis of Synthesized Polymers

(1) Poly-IANOPA—¹H NMR Spectrum (CDCl₃, δ ppm). Figure S1(c) shows proton NMR spectrum poly-IANOPA. The signals at 1.1 ppm correspond to the isopropyl methyl group, whereas at 1.95 ppm correspond to the methine (-NH) proton. The signal at 2.5 ppm corresponds to acrylic (-CH) methyl proton. The signals at 2.8 and 2.95 ppm correspond to isopropyl methine proton and doublet of methylene proton (-CH₂-N), respectively. The methylene proton (-O-CH₂-) shows a signal at 4.2 ppm. The multiples of aromatic protons show signals at 7.3–8.0 ppm. The disappearance of characteristic peaks in region δ 5.8–6.2 confirms the polymerization of the monomer.

(2) Poly-IANOPMA—1H NMR Spectrum (CDCl₃, $^{\delta}$ ppm). Figure S1(d) shows the proton NMR spectrum of poly-IANOPMA. The signals at 1.0 ppm correspond to the isopropyl methyl group whereas at 1.6 ppm correspond to the methine (-NH) proton. The signals at 2.5 and 2.9 ppm correspond to isopropyl methine proton and doublet of methylene proton (-CH₂-N), respectively. The methylene proton (-CH₂-) shows a signal at 4.1 ppm. The multiples of aromatic protons show signals at 7.4–8.3 ppm. The signal at 2.1 ppm corresponds to acrylic (-CH) methyl proton. The disappearance of characteristic peaks in regions 5.6–6.2 confirms the polymerization of the monomer.

3.4.5. ¹³C NMR Spectroscopic Analysis of Synthesized Polymers



FIGURE 5: SEM images of monomers (a) IANOPA and (b) IANOPMA and polymers (c) poly-IANOPA and (d) poly-IANOPMA.

(1) ¹³C NMR Spectrum of Poly-IANOPA (CDCl₃, ^{δ}ppm). Figure S2(c) shows a decoupled ¹³C NMR spectrum of poly-IANOPA. The resonance signals at 24 ppm may be due to isopropyl carbons (-CH₃). The (-H₂C-NH) and (-HC-NH) show resonance signals at 45 and 49 ppm, respectively. Similarly, (-H₂C-O) and (-HC-O) show resonance signals at 68 and 73 ppm, respectively. The aromatic carbons show a resonance signal at 132 ppm. Ester carbonyl carbon (-C=O) provides resonance signals at 168 ppm. The disappearance of the signal at 138 ppm confirms the polymerization of the monomer.

(2) ¹³C NMR Spectrum of Poly-IANOPMA (CDCl₃, $^{\delta}ppm$). Figure S2(d) shows the decoupled ¹³C NMR spectrum of poly-IANOPMA. Signals for isopropyl carbons (-CH₃) and methacrylate carbons (-CH₃) are 24 and 28 ppm, respectively. The (-H₂C-NH) and (-HC-NH) show resonance signals at 44 and 47 ppm, respectively. Similarly, (-H₂C-O) and (-HC-O) show resonance signals at 67 and 73 ppm, respectively. The aromatic carbons show a resonance signal at 132 ppm. At 168 ppm, the resonance signals correspond to the ester carbonyl carbon (-C=O).

The disappearance of the signal at 138 ppm confirms the polymerization of the monomer.

3.5. Molecular Weights of Poly-IANOPA and Poly-IANOPMA. The average molecular weight (M_m) and number (M_n) of the polymers were determined by using gel permeation chromatography (GPC). The average molecular weight (M_m) of polymers, poly-IANOPA and poly-IANOPMA, is found to be 22135 and 65682, respectively. Whereas number average molecular weight (M_n) of poly-IANOPA and poly-IANOPMA was found to be 13492 and 32347, respectively. The polydispersity index (D) of poly-IANOPA was found to be 1.6, whereas in the case of poly-IANOPMA, it was found to be 2.0. Theoretically, the polymer made by radical recombination has a D value of 1.5, whereas the polymer made by the disproportionation process has a D value of 2.0 [27, 28]. The obtained data is summarised in Table 2. The synthesized acrylate polymer (poly-IANOPA) undergoes termination via radical recombination, and the methacrylate polymer (poly-IANOPMA) undergoes



FIGURE 6: Effect of monomers and polymers on (a) gram-positive S. aureus and (b) gram-negative P. aeruginosa bacteria at various concentrations.



FIGURE 7: The schematic plausible antibacterial mechanism of synthesized monomers and polymers against *S. aureus* and *P. aeruginosa.*

termination by disproportionation, as shown in Figure S3(a) and Figure S3(b) in SIF[#].

3.6. Thermogravimetric Studies of Poly-IANOPA and Poly-IANOPMA. The weight loss of the polymer was determined using TGA and DSC in order to evaluate its thermal stability, as illustrated in Figures 3 and 4, and its resulting data are presented in Table 3. It is found that the poly-IANOPA has an initial decomposition temperature (T_i) of 110°C. Poly-IANOPA decomposes in two stages, with the first stage occurring between 175°C and 275°C and losing 50% of its weight. In this first stage decomposition mainly corresponded to the elimination of internal water, residual monomers, oligomers, and some cross-linker contents. In the second stage, decomposition occurred between 275 and 400°C and lost 90% of its weight. In this stage, the backbone chains of the polymers might get decomposed. Similarly, the initial decomposition temperature (T_i) of poly-IANOPMA is found to be 109°C. Poly-IANOPMA decomposes in two stages, with the first stage taking place between 169 and 275°C and losing 50% of its weight due to internal water and other monomer compounds. In the second stage, losing 90% of it between 275 and 400°C denotes the decomposition of the entire chain of synthesized polymers. Both of these polymers have a maximum and excellent thermal stability of around 400°C.

3.7. Differential Scanning Calorimetry Analysis of Poly-IANOPA and Poly-IANOPMA. The glass transition temperatures of the polymers, poly-IANOPA and poly-IANOPMA, were assessed by DSC analysis, and both polymers showed glass transition temperatures between 60 and 76°C, as shown in Figure 4.

3.8. Morphology Analysis of Monomers and Polymers. SEM images of the monomers IANOPA and IANOPMA are shown in Figures 5(a) and 5(b), respectively, while images of poly-IANOPA and poly-IANOPMA are shown in Figures 5(c) and 5(d). The SEM image of Figures 5(c) and 5(d) shows SEM images of polymers between the magnification of 250 kX to 1.63 kX in high voltage (10 kV) current. As observed from SEM analysis, the synthesized polymers have



FIGURE 8: Absorption capacity of synthesized polymers, poly-IANOPA and poly-IANOPMA, for selected heavy metal ions.

TABLE 4: The metal ion absorption percentage under 24 h stirring of synthesized polymer and the corresponding 0.1 mM metal sulfate solutions.

Motal	Poly-IANOPA		Poly-IANOPMA		
ion	Remain in filtrate (%)	Uptaken (%)	Remain in filtrate (%)	Uptaken (%)	
Ni ²⁺	08.2	91.8	10.1	89.9	
Cu^{2+}	16.8	83.2	17.0	83.0	
Zn ²⁺	14.0	86.0	14.2	85.8	
Pb ²⁺	22.2	77.8	24.8	75.2	

a smooth surface without any pores. Comparing the monomers and polymers SEM images, the polymer became denser and got smooth surface on their morphology. However, the appearance of disordered surface morphology is probably due to their powder nature [29].

4. Applications

4.1. Antibacterial Evaluation of Monomers and Polymers. The antibacterial ability of monomers IANOPA and IANOPMA, as well as poly-IANOPA and poly-IANOPMA, against *Staphylococcus aureus* and *Pseudomonas aeruginosa*, was studied. A well diffusion method was used to carry out the controlled experiment using a DMSO solution. In the SIF[#] Figures S4(a), S4(b), S4(c), and S4(d), photographic images of polymers are presented. Table S1 shows the antibacterial capacity of synthesized polymers to inhibit the development of the tested microorganisms on a solid medium, and Figures 6(a) and 6(b) demonstrate graphically. Polymers seem to have more antibacterial action than their corresponding monomers against *S. aureus* and *P. aeruginosa*. The bactericidal potential of synthesized monomers and polymers is also highly commendable with the commercially available poly(methyl methacrylate) (PMMA). Interestingly, the antibacterial efficacy is almost equal to the commercially available PMMA polymers, proving that the synthesized polymers are valuable materials like PMMA polymers [30].

The biocidal response of microorganisms depends on several factors including cell wall strength, physical form, morphology, structural properties, and biocompatibility [31]. However, the antibacterial activity of synthesized polymers may be attributed to different mechanisms. As per the literature [32, 33], here, we propose the plausible mechanism of observed antibacterial activity of IANOPA and IANOPMA, as well as poly-IANOPA and poly-IANOPMA. In the initial stage, the polymer is absorbed onto the target bacteria cell wall by the electrostatic attractions between the positively charged polymer chains and negatively charged bacterial cell walls, and further, this electrostatic attraction may lead to cell wall disruption. Further, the reaction oxygen species will generate and bind/chelate with cytoplasmic components such as DNA and protein molecules. As a result, the bacteria cytoplasmic components collapse and also damage the cell wall leading to cell death. The plausible mechanism of antibacterial activity is represented in Figure 7. The obtained results encourage us to do further research to improve mechanical performance and other material properties for biomedical applications of our synthesized 1-(isopropylamino)-3-(1-naphthyloxy)-2-propanomethacrylate polymers. The activity difference in this study could be due to more reactive sites in the polymer chains, such as secondary amine (-NH), oxygen atoms, and aromatic rings, which interact with the cytoplasmic membrane and cell wall of microbes and effectively kill them, whereas easier diffusion occurs with shorter chain lengths [34-37].

4.2. Metal Ion Uptake Ability of Synthesized Polymers. Figure 8 shows the concentration of various metal ions absorbed by synthesized polymers poly-IANOPA and poly-IANOPMA. The figure plotted based on the percentage of uptaken metal ions determined by ICP spectroscopic analysis [38]. The observed and calculated values are presented in Table 4. The absorption of Ni²⁺ ions by poly-IANOPA and poly-IANOPMA are higher in terms of percentage concentration than three d-block metal ions and one p-block metal ion. That is, the absorption of other d-block metal ions, Cu²⁺ (83.2%, 83.0%) and Zn²⁺ (86.0%, 85.8%) uptake, is also at higher levels than Pb²⁺ (77.8%, 75.2%). It is interesting to note that the selectivity of metal ion uptakes of the synthesized polymers is reduced based on the atom size that is in the following order:

$$Ni^{2+} > Zn^{2+} > Cu^{2+} > Pb^{2+}$$
 (2)

This may be the presence of R substitution of IANOPA and IANOPMA polymers. The presence of methyl substitution in methacrylate polymers shows less selectivity than the acrylate polymer. Also, the larger atom ion Pb²⁺ showing

less selectivity in both polymers further concludes that the structure of the polymer groups is playing the role.

5. Conclusions

The secondary amine functionalized polymers (poly-IANOPA and poly-IANOPMA) were synthesized by the free radical polymerization method. The structural and physical properties of the synthesized monomers and polymers were studied using UV, FT-IR, ¹H NMR, and ¹³C NMR spectroscopic methods. TGA was found that the polymers can withstand thermal stability up to 400°C. The GPC analysis confirms that the polydispersity index (D) of synthesized poly-IANOPA and poly-IANOPMA was found to be D =1.6 and D = 2.0, respectively. Propranolol's promising qualities combined with acrylic and methacrylic groups demonstrated a number of novel features, including thermal conductivity, antibacterial activity, and metal ion uptake ability. The synthesized polymers were successfully studied as absorbent polymers for the removal of heavy metal ions such as Ni²⁺, Cu²⁺, Zn²⁺, and Pb²⁺. It was observed that the d-block metal ions are effectivity removed than the pblock metal ion Pb²⁺ and it may be based on the atom size and substitution of the acryloyl group. The antibacterial study was carried out from polymers and monomers, in which polymers show better activity on S. aureus than P. aeruginosa. As these polymers possess good thermal property, antibacterial property, and metal ion adsorption ability, they can be exploited as potential materials in biomedical and environmental applications.

Data Availability

All materials for this study are presented in this article, and further clarification will be available on request.

Disclosure

The earlier version of this manuscript was presented as a preprint in the research square platform in the weblink https://www.researchsquare.com/article/rs-2466734/v1 [39].

Conflicts of Interest

The authors declare no competing interests.

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Supplementary Materials

The corresponding authors will provide any necessary information and clarifications on request to support. Also, some of the related images and data were presented in the Supporting Information file. The data in the supporting information file includes all spectra and images, such as the experimental procedure for the synthesis of monomer and polymers, ¹H NMR and ¹³C NMR spectra of monomers and polymers (Figures S1 and S2), images of GPC analysis of synthesized polymers (Figures S3a and S3b), Petri dish images of antibacterial inhibition area (Figure S4), and antibacterial zone of inhibition values (Table S1). (*Supplementary Materials*)

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