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Designing and Characterization of Lithotomic Derived Poly (N-isopropyl acrylamide) copolymer

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Abstract

In this study synthesis and characterization of poly (N-isopropyl acrylamide-co-methyl 3α-methacryloyl-lithocholan 24-oate) [poly(NIPAM-co-MELCAME)] was carried out by esterification of lithocholic acid methyl ester and subsequently copolymerized with N-is opropylacrylamide (NIPAM) through free-radical polymerization using AIBN as an initiator. The chemical structures of the monomer and copolymers were confirmed using ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. Gel Permeation Chromatography (GPC) analysis revealed a linear correlation between the monomer feed ratio and the copolymer molecular weight and the number-average molecular weight (M_n) increased systematically from 3,564 kg/mol to 9,199 kg/mol, with polydispersity indices (PDI) ranging between 1.03 and 1.57. Thermogravimetric analysis (TGA) demonstrated that the copolymers possess high thermal stability. The integration of the rigid, hydrophobic lithocholic acid moiety provides a tunable platform for developing bio-inspired smart materials. These findings suggest that Poly (NIPAM-co-MELCAME) copolymers hold significant potential for applications in responsive coatings and advanced materials engineering.

Keywords: N-isopropylacrylamide, Lithocholic Acid, MELCAME, Free-radical polymerization, Thermal stability, GPC.

1. Introduction

In the field of advanced materials science, the development of "smart" or "stimuli-responsive" polymers has emerged as a cornerstone for next-generation technologies. These materials possess the unique ability to undergo rapid, reversible physical or chemical changes in response to small environmental variations. Among the various stimuli, temperature is the most widely used due to its ease of control and its relevance to biological systems [1-2]. Poly (N-isopropylacrylamide) (PNIPAM) is the prototypical thermoresponsive polymer, characterized by its sharp Lower Critical Solution Temperature (LCST) at approximately 32 °C in aqueous media. Below this temperature, PNIPAM chains adopt a hydrated, flexible-coil conformation [3-4]. Upon heating above the LCST, the polymer undergoes a phase transition to a dehydrated, collapsed globule state [5]. While PNIPAM is highly versatile, its inherent hydrophilicity and mechanical limitations often necessitate incorporating hydrophobic comonomers to fine-tune its transition temperature and structural integrity for specific applications [6]. In this context, copolymerization of NIPAM with functionalized monomers has emerged as to overcome these limitations, we propose enhancing thermal stability, mechanical robustness [7], and environmental responsiveness [8]. Such structural modification not only enables precise tuning of the phase transition behavior but also introduces additional functional groups, thereby expanding the applicability of PNIPAM-based systems. Consequently, NIPAM copolymers have found widespread use in biomedical fields, including drug delivery and bio interfaces, as well as in chemical sensing and nanoparticle stabilization [9, 10]. The synergistic combination of thermo-responsiveness and tailored amphiphilicity facilitates controlled self-assembly and efficient interaction with analytes or metal ions, making these copolymers promising candidates for multifunctional smart material platforms [11].

Therefore, functionalization of natural building blocks in polymer synthesis has gained momentum as researchers seek to combine synthetic functionality with the structural complexity of biomolecules. Bile acids, such as lithocholic Acid (LCA), are particularly attractive in this context [12, 13]. These tetracyclic steroid molecules are rigid, biocompatible, and possess a unique facially amphiphilic nature, having a hydrophobic steroid skeleton and hydrophilic hydroxyl/carboxyl groups [14]. Lithocholic acid (LCA) is a naturally occurring, highly hydrophobic secondary bile acid produced when gut bacteria metabolize the primary bile acid chenodeoxycholic acid (CDCA) in the colon [15]. It is considered the most hydrophobic and toxic bile acid in humans, characterized by a single hydroxyl group that limits its solubility. Structurally LCA is characterized by a rigid, hydrophobic tetracyclic steroid nucleus, specifically a C24 sterane skeleton. It is a C24 bile acid derived from the hydrogenation and oxidation of cholesterol [16]. Additionally, LCA contains a terminal carboxyl group (-COOH) at the C-24 position, which is the primary site for chemical conjugation, particularly for creating amide or ester linkages to other molecules. This carboxylic acid group is frequently used to create derivatives that enhance the pharmaceutical or biological properties of LCA, such as increased potency as an EphA2 antagonist or improved drug delivery when conjugated with amino acids or polymers [17].

Integrating bile acid moieties into a PNIPAM backbone offers a dual advantage: it introduces a rigid hydrophobic component that can significantly alter the polymer’s thermal stability and creates a "bio-hybrid" material with potential for enhanced molecular recognition [18-19]. Despite the potential, the synthesis of steroid-incorporated thermoresponsive copolymers requires precise control over the monomer ratio to maintain the desired responsive behavior. In this report synthesis of MELCAME and its subsequent free-radical copolymerization with NIPAM was demonstrated. Also demonstrated varying the molar feed ratio of MELCAME to NIPAM which influences the fundamental properties of the resulting Poly(NIPAM-co-MELCAME) chains The results presented herein provide a robust framework for designing tunable, steroid-based smart materials that satisfy the growing demand for functionalized polymers in materials engineering.

2. Experimental

2.1. Materials

Lithocholic acid (LCA, 98%), N-isopropylacrylamide (NIPAM), 2,2'-azobisisobutyronitrile (AIBN), triethylamine, and methacryloyl chloride were procured from Sigma-Aldrich (India). Analytical grade methanol (MeOH), hydrochloric acid (HCl), and sodium hydroxide (NaOH) pellets were sourced from LOBA Chemie (India). All reagents and solvents were utilized as received without further purification. All glassware was thoroughly cleaned with aqua regia (HCl: HNO_3 3:1, v/v) and then rinsed multiple times with double-distilled water.

2.2. Characterization Methods

The structural and macromolecular properties of the synthesized monomer and copolymers were rigorously evaluated using a suite of analytical techniques. ^{1}H NMR and ^{13}C NMR Nuclear Magnetic Resonance (NMR) spectra were acquired on a Bruker Avance 300 MHz spectrometer, utilizing either DMSO-d_6 or $CDCl_3$ as the solvent with tetramethylsilane (TMS) serving as the internal reference standard. Fourier Transform Infrared (FT-IR) measurements were performed using a PerkinElmer spectrophotometer; samples were prepared by grinding the polymer with potassium bromide (KBr) and compressing the mixture into translucent pellets. The macromolecular characteristics, including the number-average and weight-average molecular weights and the polydispersity index (PDI), were determined via Gel Permeation Chromatography (GPC). Furthermore, the thermal stability and degradation profiles of the copolymers were investigated through Thermogravimetric Analysis (TGA) under a controlled heating environment.

2.3 Synthesis of Methyl 3α-methacryloyl-lithocholan 24-oate (MELCAME)

The lithocholic acid-derived methacrylate monomer **(b)** was synthesised from lithocholic acid methyl ester (LCAME) as the precursor [20]. **(a)** LCAME (3.9 g, 10 mmol) and triethylamine (1.62 g, 16 mmol) were dissolved in dry tetrahydrofuran (THF, 30 mL). The resulting solution was cooled to 0 °C in an ice bath. After stirring for 30 minutes, methacryloyl chloride (1.57 g, 15 mmol) in dry THF (10 mL) was added dropwise with continuous stirring. The reaction mixture was maintained for 24 hours, and progress was monitored by thin-layer chromatography (TLC). After completion, the reaction was quenched with deionized water (50 mL), and the mixture was transferred to a separatory funnel. The organic layer was extracted with ethyl acetate (3 × 20 mL), washed with brine, and dried over anhydrous sodium sulfate (Na_2SO_4). The solvent was removed by rotary evaporation, and the crude product was purified by recrystallization from ethyl acetate to yield the methacrylate-functionalized lithocholic acid (MELCAME) monomer (b) as a solid with a melting point of 185-215 °C. White solid, yield 94%; FT-IR (ATR) νmax: 1734, 1643 and 1017cm^{-1}; H^1 NMR (300 MHz, $CDCl_3$) δH (ppm): 6.00, 5.46 (s, =CH2-), 3.90 (s, O-CH_3), 3.59 (s, 7β-H), 3.10-3.05 (d), 1.60-1.30 (m, steroidal H), 1.18 (d, J =12.6Hz, 21-Me), 0.80 (s, 19-Me), 0.61 (s, 18-Me); C^{13} NMR (300 MHz, $CDCl_3$) δC: 175.51, 171.19, 168.83, 139.33, 121.04, 61.75,61.55 53.04, 48.45, 46.37, 40.52, 40.28, 35.49, 35.29, 35.19, 33.15, 32.89, 18.73, 17.77, 17.64, 17.54, 17.44, 14.28.

2.3. Synthesis of Poly (N-isopropyl acrylamide-co-methyl 3α-methacryloyl-lithocholan 24-oate) [poly (NIPAM-co-MELCAME)]

A typical copolymerization was carried out as follows. MELCAME **(b)** was maintained at a constant amount (5 g, 10 mmol), while the NIPAM feed was varied (5, 10, 15, and 20 mmol) to obtain copolymers with different compositions. The monomers were dissolved in dry THF (10 mL), and azobisisobutyronitrile (AIBN, 0.1 mmol) was added as the radical initiator. The reaction mixture was transferred to a 20 mL sealed vial equipped with a magnetic stir bar, purged with dry nitrogen for 20 min, and placed in a preheated reaction block maintained at 70 °C. Polymerization was allowed to proceed under continuous stirring for 24 h. Upon completion, the reaction mixture was cooled to room temperature and precipitated into excess diethyl ether. The resulting copolymers Poly (NIPAM-co-MELCAME) **(c)** were collected by filtration, washed thoroughly with diethyl ether, and dried under vacuum at 40 °C for 24 h. All polymerizations were performed under anhydrous conditions, and both monomers and initiator were dried prior to use to avoid premature initiation. **(Scheme 1).** GPC was used to ascertain the molecular weight and molecular weight distribution of Poly (NIPAM-co-MELCAME) copolymers synthesized at different MELCAME/NIPAM feed ratios. Measurements were performed using THF as the eluent at a flow rate of 1.0 mL min^{-1}, and calibration was performed using narrow-dispersity polystyrene standards. The absence of low-molecular-weight impurities or residual monomers, indicated by unimodal elution profiles, confirms that all copolymer samples were formed homogeneously. White solid, yield 94%; FT-IR (ATR) νmax: 1655, 1552 1300-1150 cm^{-1}. H^1 NMR (300 MHz, DMSO-D6) δH: 7.27 (s, -NH, NIPAM), 3.83 (q, N-CH NIPAM), 3.57, 2.68-1.24 (m, steroidal H), 1.16 (d, CH_2-CH), 1.05 (d, 21-Me), 0.90 (s, 19-Me), 0.87 (s, 18-Me); C^{13} NMR (300 MHz, DMSO-D6) δC: 174.82, 172.29, 172.22, 77.34,

3. Result and Discussion

3.1 Synthesis of MELCAME and Poly (NIPAM-co-MELCAME)

The synthesis of the methacrylate-functionalized lithocholic acid monomer (MELCAME) was achieved through the esterification of lithocholic acid methyl ester (LCAME) with methacryloyl chloride. This reaction, conducted in the presence of triethylamine, facilitated the selective functionalization of the 3α-hydroxyl group, successfully incorporating a polymerizable methacrylate moiety while maintaining the integrity of the steroidal backbone. The successful synthesis was validated by FT-IR spectroscopy, which showed characteristic ester carbonyl and vinyl stretching bands associated with the methacrylate group. Subsequently, Poly (NIPAM-co-MELCAME) copolymers were synthesized via free-radical copolymerization in anhydrous THF, using AIBN as the initiator **(Scheme 1)**. The copolymer composition was systematically regulated by varying the NIPAM feed ratio while keeping the MELCAME concentration constant. The progress of polymer was confirmed by FT-IR analysis, which showed the complete disappearance of vinyl stretching bands and the emergence of characteristic amide and ester functional group signals. The isolation of the resulting copolymers as solid materials via precipitation and vacuum drying confirmed efficient chain propagation under inert conditions. Furthermore, Gel Permeation Chromatography (GPC) analysis verified that the molecular weight and polymer composition were precisely controlled by the monomer feed ratios. This underscores the effectiveness of the synthetic strategy for producing well-defined, steroid-based the more responsive copolymers.

3.2. FT-IR and NMR Spectroscopy

The formation of MELCAME monomer and copolymer of Poly (MELCAME-co-NIPAM) was characterized by FT-IR and NMR spectroscopy as shown in **(Figures 1, 2 and 3, a & b)**. The MELCAME monomer FTIR spectra exhibited characteristic absorption bands at 1734 cm^{-1} for ester C=O stretching, and C-O ester stretching 1178 cm^{-1}, 1643 cm^{-1} for acrylate C=C stretching, and 1017 cm^{-1} for the vinyl bending mode. Furthermore, the retention of MELCAME moieties was confirmed by the persistent ester C-O-C stretching observed in the 1300-1150 cm^{-1} region. In the copolymer spectra, the complete disappearance of the acrylate C=C and vinyl bands confirms that the double bonds were fully consumed during the polymerization process. The emergence of new vibrational bands at (amide I C=O) 1655 cm^{-1} and 1552 cm^{-1} (amide II N–H bending and C–N stretching) verifies the successful incorporation of hydrophilic NIPAM units into the polymer backbone. While ^{1}H and ^{13}C NMR spectrum was confirmed copolymer formation showing characteristic signals corresponding to NIPAM side chain protons at H 7.27 (-NH) and 3.83 (N-CH) and 1.16 ppm, disappearance of vinyl protons signals (6.00, 5.46 ppm), duration ester carbonyl carbons appear in ^{13}C NMR spectrum exhibiting characteristic resonances at 174.82, 172.29 and amide carbonyl carbons appeared 172.22 ppm. Peaks appeared at 56.50-51.49 ppm are attributed to NIPAM steroidal methane carbons. These results confirm the synthesis of hydrophilic NIPAM and hydrophobic steroid segments into the copolymer backbone.

3.3. GPC Analysis and Molecular Weight Distribution

The macromolecular properties of the Poly (MELCAME-co-NIPAM) copolymers were evaluated using Gel Permeation Chromatography (GPC). As illustrated in **Figure 4 (a),** the GPC traces exhibit a systematic shift toward lower elution volumes as the NIPAM feed concentration increased from 5 to 20 mmol while maintaining a constant MELCAME concentration. This trend indicates a progressive increase in the number-average molecular weight (M_n), which rose steadily from 3564 to 9200 g/mol. The data presented in **Tables 1 and 2** confirm that the polymer chain composition is effectively regulated by the initial monomer feed ratio. The nearly linear increase in M_n as a function of NIPAM concentration suggests that higher NIPAM levels enhance chain propagation, resulting in the formation of higher molecular weight chains. Minor deviations from ideal linearity, as observed in the comparison between experimental (M_n, GPC) and theoretical (Mn, Theo) values in **Figure 4 (b),** are attributed to steric hindrance from the bulky steroid moieties of MELCAME, differences in monomer reactivity ratios, and potential chain-transfer events. The **Figure 4 (c)** polydispersity index (PDI) exhibited an upward trend, generally increasing with higher NIPAM fractions (ranging from 1.03 to 1.57). This broadening of the molecular weight distribution at elevated monomer concentrations suggests that higher NIPAM levels may promote chain-transfer phenomena and foster more heterogeneous propagation kinetics. This GPC analysis verifies that the molecular weight and distribution of Poly (MELCAME-co-NIPAM) can be systematically controlled by adjusting the feed composition, demonstrating a predictable regulation of polymer growth.

3.4. The rmogravimetric Analysis (TGA)

The thermal stability of the Poly (MELCAME-co-NIPAM) copolymers was investigated across various molecular weights (Mn= 3564, 5483, 7094, and 9200 g/mol). All samples exhibited a minor initial weight loss below 150 °C, attributed to the evaporation of physio's orbed moisture and traces of volatile organic compounds **(Figure 5a, b, c and d).** A second degradation stage was observed between 200 °C and 350 °C, corresponding to the thermal cleavage of side chains and ester/amide linkages. The primary degradation of the polymer backbone occurred in the temperature range of 350-480 °C. Higher molecular weight copolymers demonstrated superior thermal stability, characterized by increased onset degradation temperatures and a delay in maximum decomposition. At temperatures exceeding 500 °C, a residual char of 5-10% was observed, could be due to the degradation from the rigid MELCAME segments. These findings indicate that the thermal robustness of the copolymer system is directly enhanced by the increase in overall molecular weight. The specific thermal parameters, including degradation temperatures and residual mass, are summarized in **Table 3**.

4. Conclusion

In this study, a novel series of steroid-based thermoresponsive copolymers, Poly (NIPAM-co-MELCAME), was successfully synthesized through the free-radical copolymerization of N-isopropylacrylamide and a methacrylate-functionalized lithocholic acid monomer. Structural characterization using ^{1}H and ^{13}C NMR and FT-IR spectroscopy confirmed the successful incorporation of the steroidal moiety into the polymer backbone and the complete consumption of the vinyl groups. GPC analysis demonstrated that the macromolecular properties of these copolymers are highly tunable, with the number-average molecular weight (M_n) increasing systematically from 3,564 to 9,200 g/mol in direct correlation with the NIPAM feed ratio. Furthermore, thermogravimetric analysis (TGA) revealed that the integration of rigid lithocholic acid segments significantly enhances the thermal robustness of the system, with the backbone remaining stable up to 350 °C, and that higher-molecular-weight variants exhibit greater stability. These results demonstrate that combining naturally derived bile acids with stimuli-responsive monomers provides a predictable and effective strategy for developing advanced bio-inspired materials. The tunable nature and thermal stability of Poly (NIPAM-co-MELCAME) make it a promising candidate for applications in responsive coatings and smart materials.

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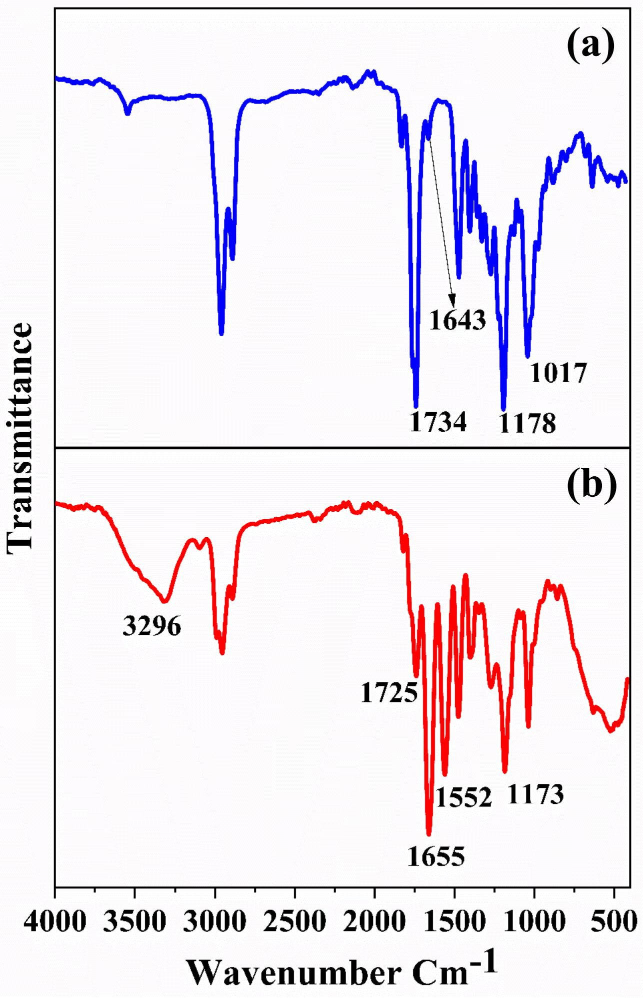


Figure 1 : IR spectra of the 3α-MELCAME (a) and (b) poly (NIPAM-co-MELCAME)

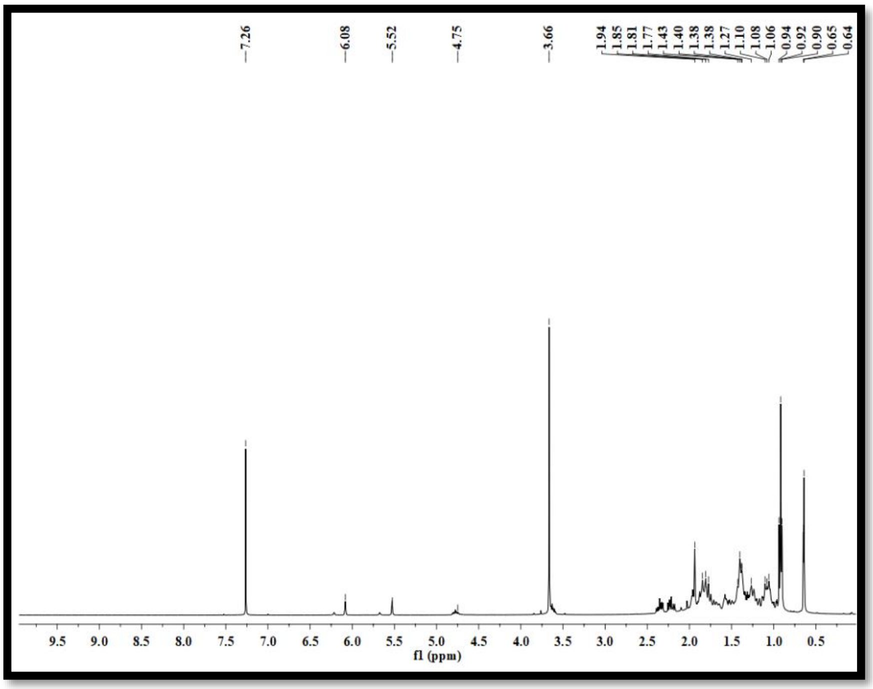


Figure 2a: H1 NMR spectra of the 3α-MELCAME

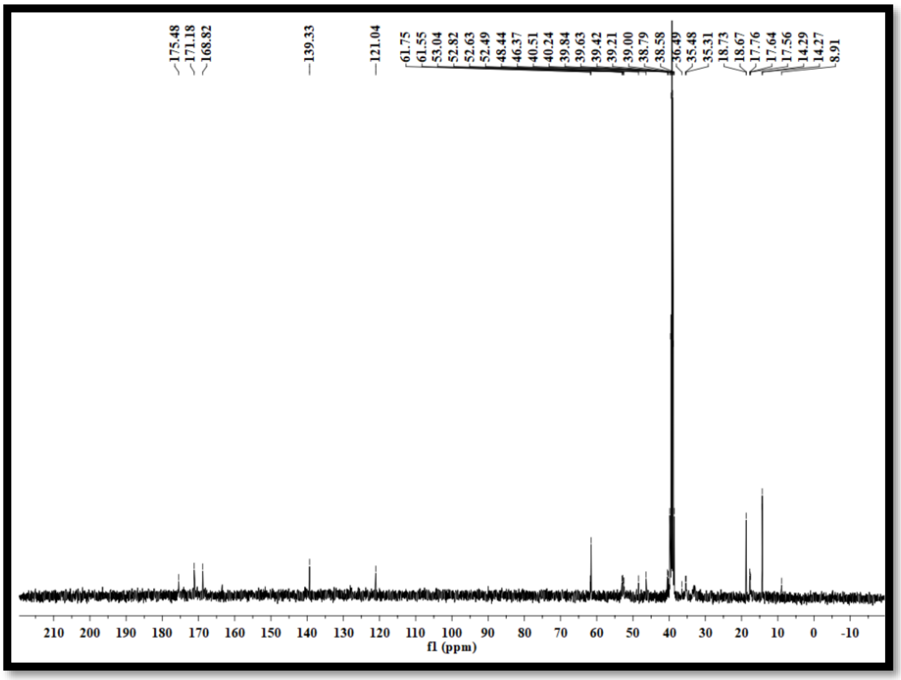


Figure 2b: C13 NMR spectra of the 3α-MELCAME

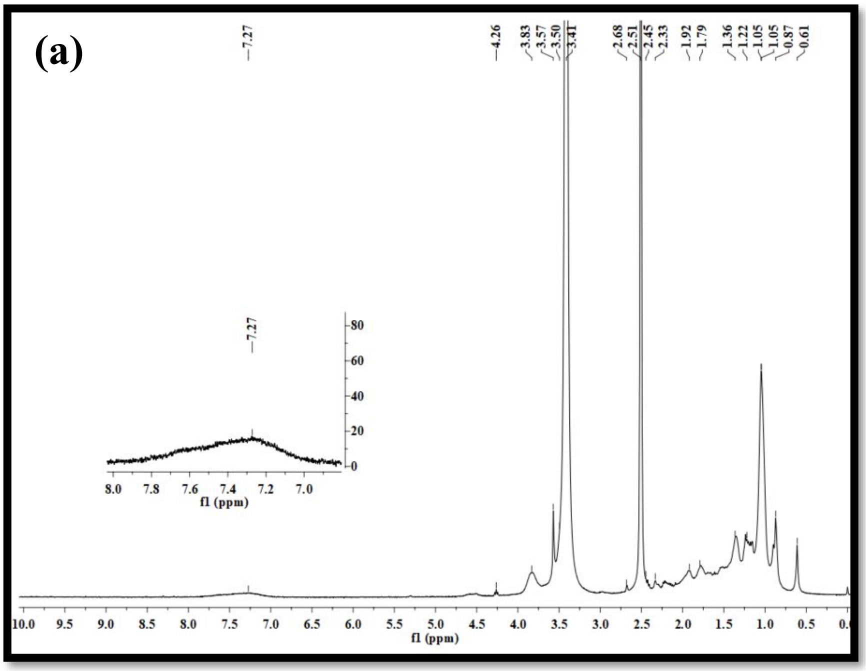


Figure 3a: H^1 NMR spectra of the 3α- poly (NIPAM-co- MELCAME)

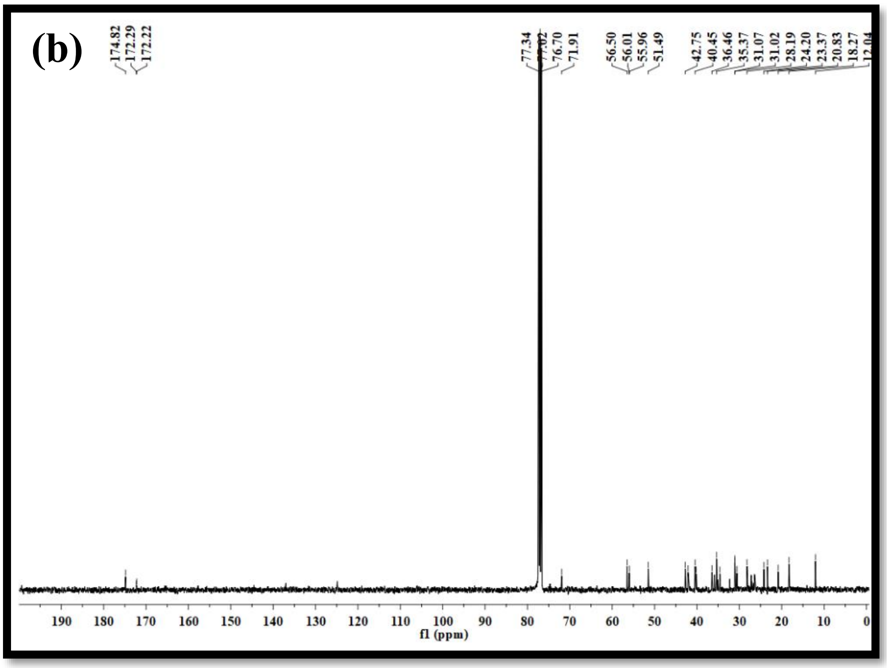


Figure 3b: C^{13} NMR spectra of the 3α- poly (NIPAM-co- MELCAME)

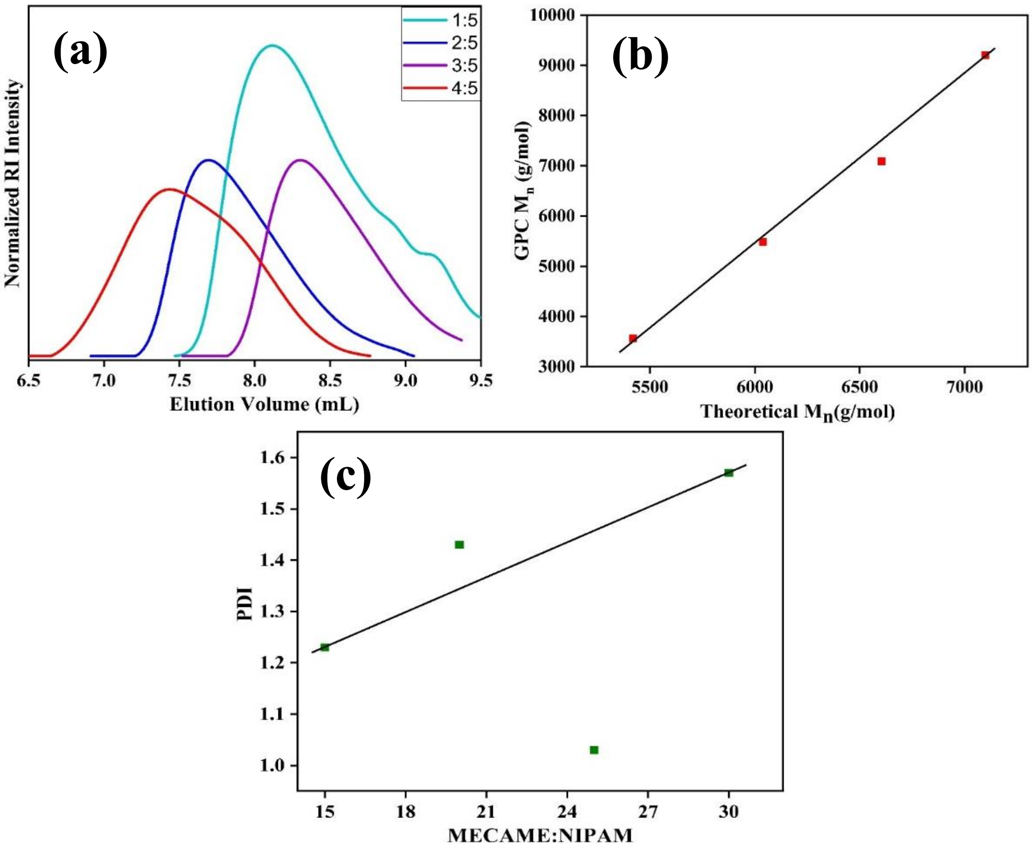


Figure 4 : (a) GPC traces of Poly (MELCAME-co-NIPAM) as a function of (MELCAME/NIPAM) different feed monomers ratios, and (b) Correlation between Theoretical and Experimental variation of number average molecular weight (Mn), and (c) Variation of PDI as a function of (MELCAME: NIPAM) mole feed ratio

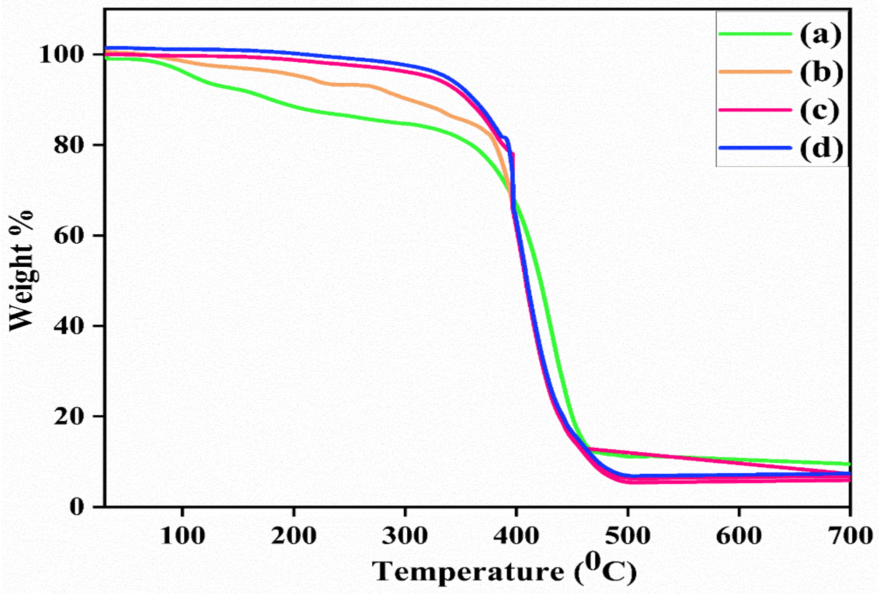


Figure 5: Thermogravimetric analysis (TGA) curves of Poly (NIPAM-co-MELCAME) copolymers with varying monomer compositions, showing (a, b, c and d) the effect of Copolymer content on thermal

stability and decomposition behaviour. (a) Poly (NIPAM-co-MELCAME) 1:0.5 (b) Poly (NIPAM-co-MELCAME) 1:1; (c) Poly (NIPAM-co-MELCAME) 1:1.5 (d) Poly (NIPAM-co-MELCAME) 1:2

Table 1: Effect of Monomers Feed Mole Ratio on Copolymer Composition and Number and Weight Average Molecular Weight. The data are illustrative and based on typical trends observed in Free-Radical Copolymerization.

Total Monomer Moles Ratio	**MELCAME (M_1) Mole fraction in Copolymer (F_1)**	**NIPAM (M_2) Mole fraction in Copolymer (F_2)**	**Conversion (%)**	**Mn,theo ($gmol^{-1}$)**	**Mn,GPC ($gmol^{-1}$)**
1:0.5	0.66	0.33	80%	5418	3564
1:1	0.5	0.5	75%	6038	5483
1:1.5	0.4	0.6	76%	6604	7094
1:2	0.33	0.66	86%	7098	9199

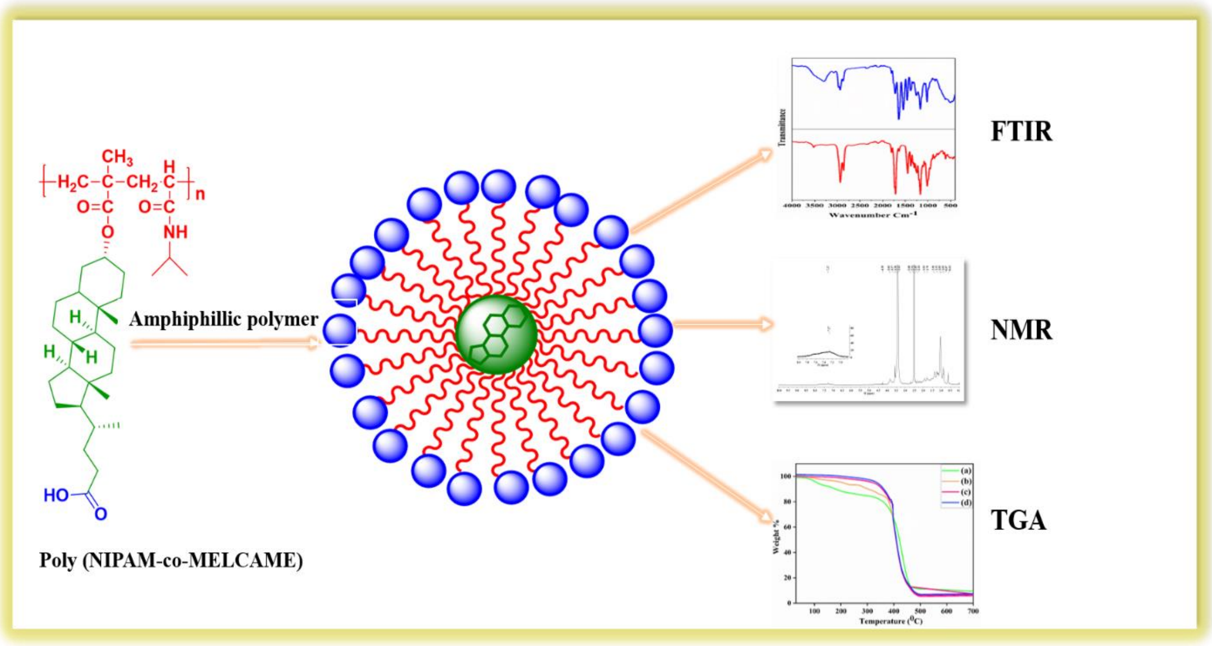
Table 2: Copolymer composition, conversion, theoretical Mn, and GPC Mn of MELCAME–NIPAM copolymers prepared at different NIPAM feed ratios with constant AIBN initiator concentration.

MELCAME (M_1) mM	**NIPAM (M_2) mM**	**Number Average Molecular Weight (Mn, kg/mol)**	**Weight Average Molecular Weight (Mw, kg/mol)**	**Polydispersity Index (PDI)**
10	5	3564	4387	1.23
10	10	5483	7789	1.43
10	15	7094	7304	1.03
10	20	9199	14450	1.57

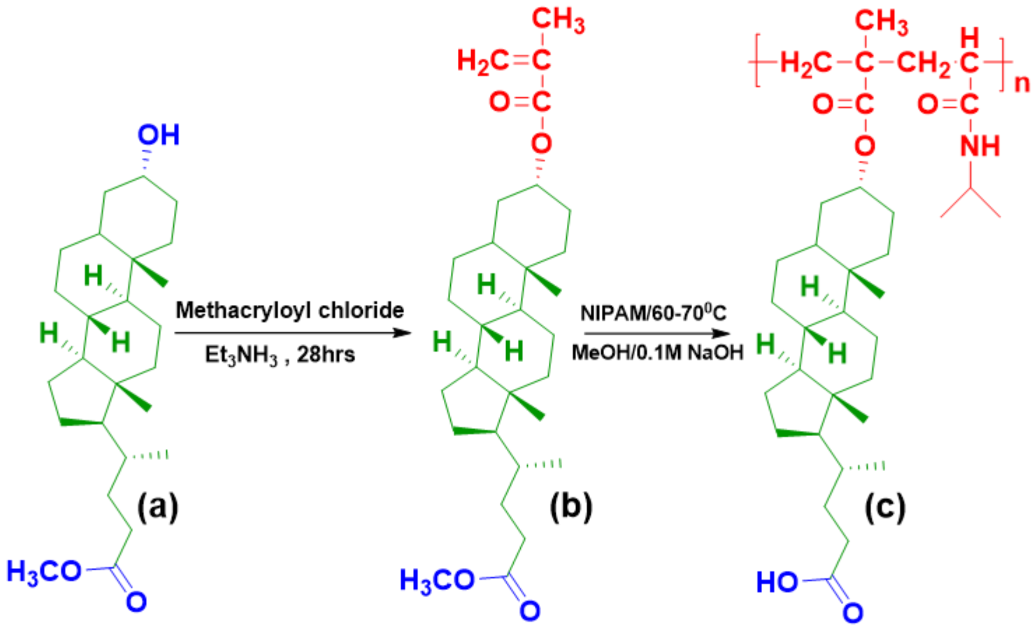
Table 3: Thermal parameters obtained from TGA graph curves. The temperature corresponding to T_5% and T_{10}% weight loss respectively (95% and 90% remaining mass). The maximum (T_{max} ^{0} C) degradation temperature was derived from weight loss region of (450 – 500 ^{0}C). The residual weight loss observed from the remaining weight percentage region at 700 ^{0}C

Samples	**T_5% (^{0}C)**	**T_{10}% (^{0}C)**	**T_{max} (^{0}C)**	**Residue at 700 ^{0}C (%)**
(a)	180	240	455	9.7
(b)	220	280	470	7.7
(c)	260	310	490	6
(d)	280	300	495	7

Graphical Abstract



Scheme-1



Scheme 1: Synthesis of poly (NIPAM-co-MELCAME) Copolymer