Synthesis, Characterization and Antimicrobial studies of N-tert-amyl acrylamide (NTA) and 7-methacryloyloxy-4-methylcoumarin (MACU) Copolymers

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Abstract

Copolymers of N-tert-amylacrylamide (NTA) and 7-methacryloyloxy-4-methylcoumarin (MACU) were prepared by free radical polymerization in DMF at 60^0C using AIBN as an initiator. The copolymer compositions were determined by 1H-NMR analysis. The reactivity ratios of monomers were determined by Fineman-Ross (FR) ($r1 = 1.33$ and $r_2 = 0.60$), Kelen-Tudos (KT) ($r1 = 1.33$and $r_2 = 0.59$). The $r_1.r_2 = 0.798$ indicated the formation of random copolymers.T_g found to increasing feed content of MACU. The antimicrobial studies showed that the copolymers are active against both Bacteria and Fungi.

***Keywords**: N-tert-amyl acrylamide, 7-methacryloyloxy-4-methylcoumarin, reactivity ratios, copolymer composition.*

Introduction

The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific application of copolymer [1]. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their [2-4]. ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [5, 6]. Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and monomer distribution in the copolymer are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer reactivity ratios are the parameters to be determined [7].

The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor-made copolymers with required physical and chemical properties and in evaluating the specific and application of the copolymers. The present article reports the synthesis and characterization of copolymers of N-tert-amylacrylamide with 7-

methacryloyloxy-4-methylcoumarin. The synthesis of antimicrobial polymers is one of the leading frontiers of research in polymer science. With this view our work N-tert-amyl acrylamide was copolymerized with 7-methacryloyloxy-4-methylcoumarin with different feed ratio were prepared and characterized by ^{1}H-NMR spectroscopy. The reactivity ratios of monomers were determined by Fineman-Ross (FR), Kelen-Tudos (KT) methods. The r_1 and r_2 value indicates the formation of random copolymers.

Experimental

Preparation of N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of tert-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene. The white crystals have amp.91° C (Lit.91-92° C) and the yield was -87%. The monomer was confirmed by both ^{1}H- NMR and ^{13}C-NMR.

Copolymerization of NTA and MACU

Copolymers of N-tert-amylacrylamide (NTA) and 7-methacryloyloxy-4-methylcoumarin (MACU) were prepared by free radical polymerization in DMF at 60^0C using AIBN as an initiator. (Scheme 1).

Characterization of copolymer spectra of Poly (NTA-co- MACU)

The ^{1}H-NMR spectra of copolymer, poly (NTA-co-MACU) is shown in Figure:1 and the following peaks appear in the copolymer spectrum : at 1.14 -2.96 ppm for CH_2 group and CH_3 of MACU at 3.08ppm for backbone CH_2 , at 7.07-8.01 ppm due to MACU aromatic protons.

Determination of copolymer composition of Poly (NTA-co- MACU)

The copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymer. The coumarin acrylate area is used to determine the copolymer composition. Resonance signal at 6.8-7.7ppm corresponds to aromatic proton, and their integrated intensity of this peak is compared to the total intensities of all the peaks in the copolymer spectrum, which is a measure of their relative areas. The copolymer compositions can be obtained using

$$X_{MACU} = \frac{15A\ (aryl)}{3A_{total} + 3A(aryl)} \qquad \text{------ (1)}$$

Where X= mole fraction and A= peak area.

Determination of Reactivity ratios

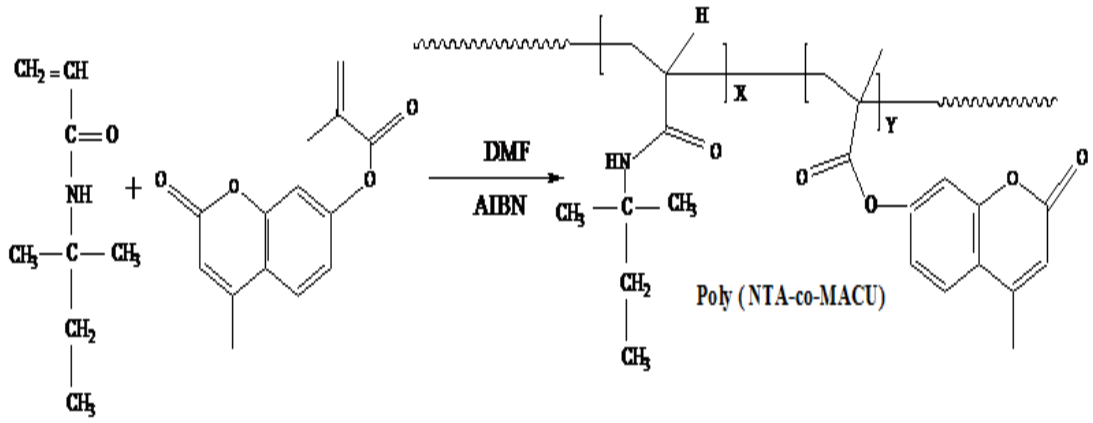
The reactivity ratios for NTA (r_1) and MACU (r_2) value from the F-R plot (Figure 2) K-T plot (Figure 3) are given in Table 3. The value(s) of r_1 is greater than 1 and r_2 is less than1.The r_1 shows that NTA favors homo-propagation as opposed to cross propagation and r_2 shows that MACU favors cross propagation over homo-propagation. The r_1 and r_2 together shows that NTA is generally more reactive than MACU, hence the copolymer contains a higher proportion of NTA units. The product of $r_1.r_2$ = 0.79 value indicates that the copolymers are weakly ordered and predominantly a random distribution of monomeric unit in the polymer chain.

Thermal studies of poly (NTA-co- MACU)

The thermal behaviors of poly (NTA-co-MACU) values are given in Table-4. Thermal behaviors of polymers were studied using TG and DSC traces. The thermo grams of poly (NTA-co-MACU) show three stage decomposition. The initial weight loss observed is due to moisture content. Weight loss at stage-1 is associated with scission of amide groups; Weight loss at stage-2 can be related to possible decarboxylation and/or other reactions of side-chain units. The stage-3 weight loss indicates the main-chain degradation reactions and breakdown of the polymer backbone.

Antimicrobial Activity of poly (NTA-co- MACU)

Antimicrobial analysis was carried out by well diffusion method [**8-10]** against various bacteria and fungi. Antimicrobial activity was evaluated by measuring the diameter of the zone of inhibition in against the test microorganisms. DMSO was used as solvent control. Chloramphenicol is used as reference antibacterial agent. Amphotericin B is used as reference antifungal agent. It is observed from the results that both antibacterial and antifungal activity is maximum. The inhibiting activity is found to be more than that of the standard. The antimicrobial activities are shown in Figure 4 and 5 and the zone of inhibition values are given in Table-5 and 6. It also showed good antimicrobial activities against selected microorganism. The antibacterial and antifungal activities are found to be more than the Chloramphenicol Amphotericin Drugs



Scheme 1: Copolymerization of NTA and MACU

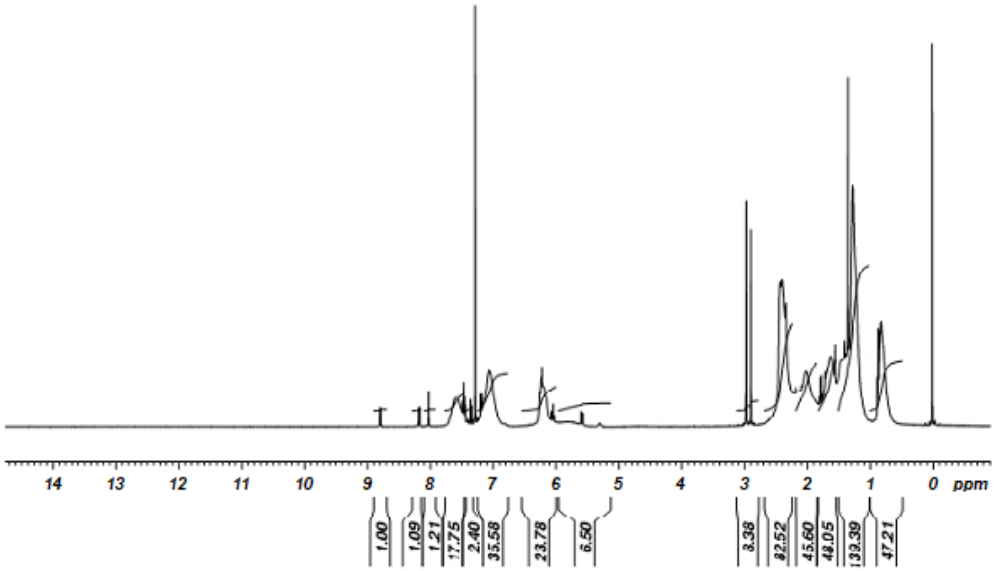


Figure 1:^{1}H-NMR spectrum of poly (NTA-co- MACU) (a) 0.5:0.5

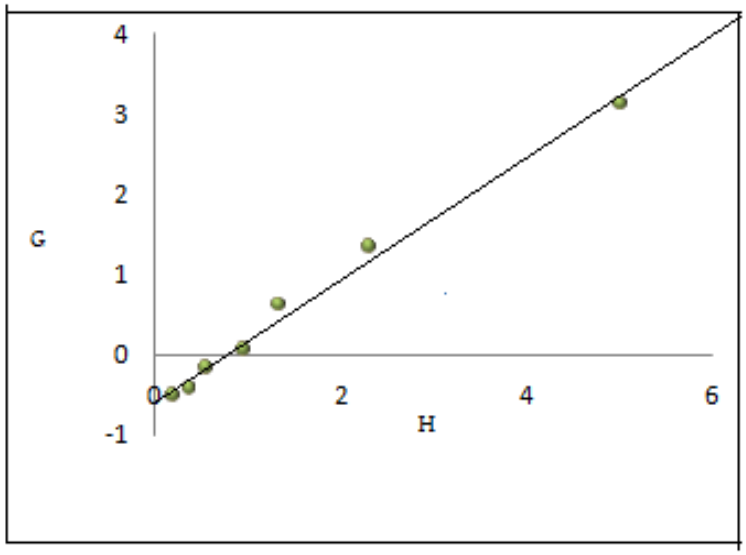


Figure 2: Fineman-Ross plot for Poly (NTA-co- MACU)

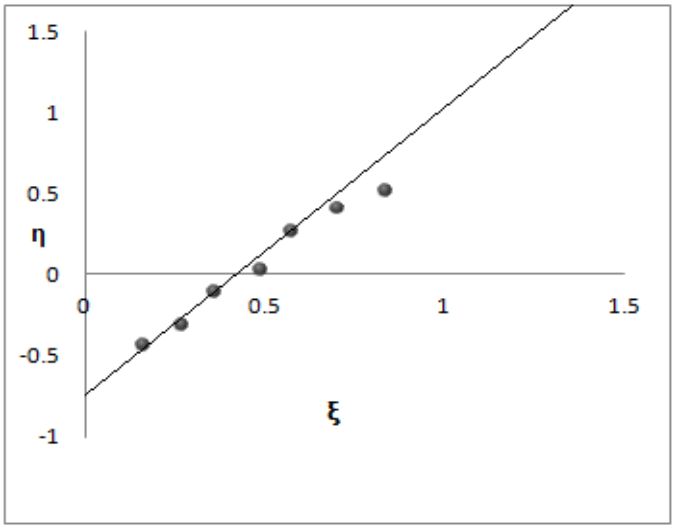


Figure 3: Kelen-Tudos plot for Poly (NTA-co- MACU)

Table 1: Mole fractions of the copolymers of N-tert-amylylacrylamide (NTA) and (MACU)

Mole fraction of NTA in feed, M1	Mole fraction of MACU in feed, M2	Mole fraction of NTA in copolymer,m1	Mole fraction of MACU in copolymer, M2	F= M1/M2	F=m1/ m2
0.2	0.8	0.2467	0.7533	0.2500	0.3275
0.3	0.7	0.3343	0.6657	0.4286	0.5022
0.4	0.6	0.4452	0.5548	0.6667	0.8025
0.5	0.5	0.5134	0.4866	1.0000	1.0551
0.6	0.4	0.6276	0.3724	1.5000	1.6853
0.7	0.3	0.7023	0.2977	2.3333	2.3591
0.8	0.2	0.7615	0.2385	4.0000	3.1929

Table 2: Fineman-Ross and Kelen – Tudos parameters for the Copolymers of NTA and MACU

G = F(f-1)/f	$H=F^2/f$	η=G/(α+H)	ξ=H/(α+H)
-0.5134	0.1908	-0.4357	0.1620
-0.4252	0.3665	-0.3141	0.2707
-0.1642	0.5544	-0.1065	0.3595
0.0522	0.9478	0.0270	0.4897
0.6100	1.3351	0.2626	0.5748
1.3441	2.3072	0.4079	0.7003
3.1200	5.0111	0.5201	0.8354

α=0.98

Table 3: Reactivity ratios of NTA (r_1) and MACU (r_2)

Methods	r_1	r_2	$r_1.r_2$
Fineman-Ross (FR)	1.33	0.600	0.798
Kelen-Tudos (KT)	1.33	0.596	0.793

Table 4: TGA data for Poly (NTA-co- MACU)

Copolymers	Mole fraction of NTA, in feed	Mole fraction of 8-MACU, in feed	Mole fraction of MACU ,in copolymer	IDT (°C)	T_{50} (°C)	T_f (°C)	T_g (°C)
NTA-MACU	0.70	0.30	0.2977	128	316	610	129
NTA-MACU	0.50	0.50	0.4866	135	350	622	135
NTA-MACU	0.30	0.70	0..6657	138	355	677	144
Poly-NTA		-	-	-	-		86.2

IDT: Initial Decomposition Temperature
T_{50}: decomposition temperature at 50% weight loss
T_f : final decomposition temperature
T_g : glass transition temperature

Table 5: Anti-bacterial activity of poly (NTA-co- MACU)

S.No	Copolymers	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas aeruginosa*
1	0.3 NTA:0.7 MACU	30	10	No zone
2	0.5 NTA:0.5MACU	26	6	No zone
3	0.7 NTA:0.3 MACU	14	6	No zone
4	Chloramphenicol	26	28	10

Table 6: Anti-fungal activity of poly (NTA-co- MACU)

S.No	Compounds	*Aspergillus niger*	*Candida albicans*	*Candida tropicalis*
1	0.3 NTA:0.7 MACU	40	27	31
2	0.5 NTA:0.5MACU	40	22	23
3	0.7 NTA:0.3 MACU	13	8	12
4	Amphotericin B	16	14	19

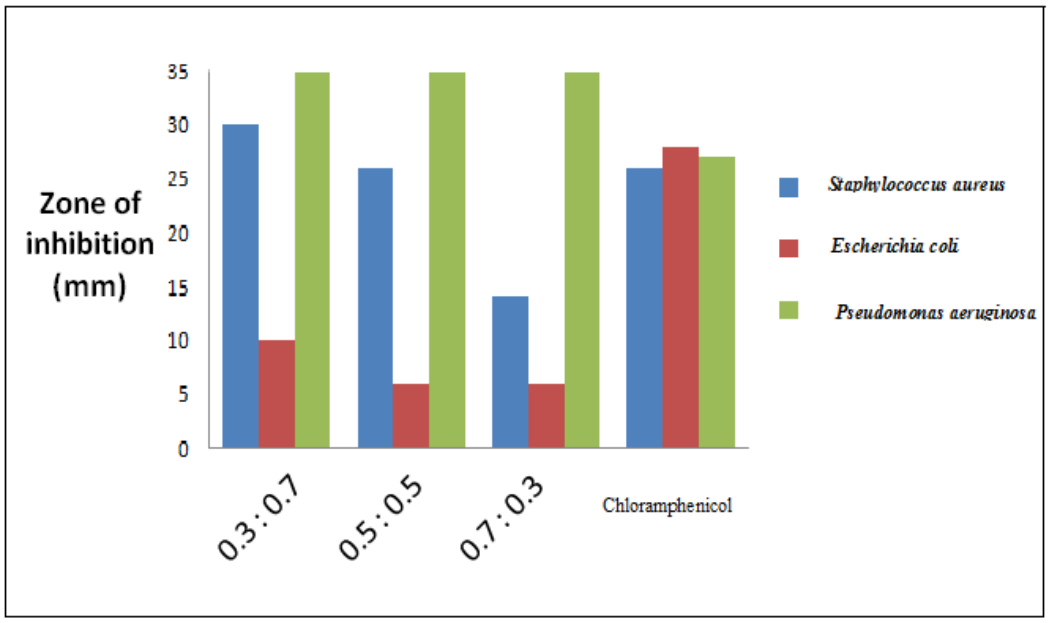
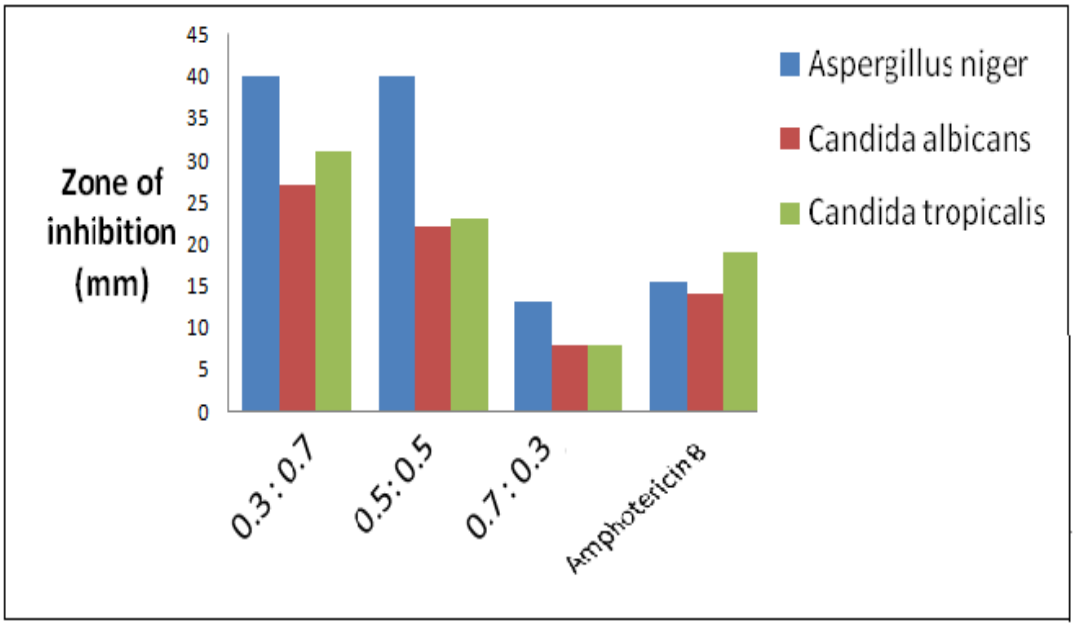


Figure 4: Comparison of Zone of inhibition of Poly (NTA-co- MACU) with bacteria



a

Figure 5 : Comparison of Zone of inhibition of Poly (NTA-co- MACU)with fungi

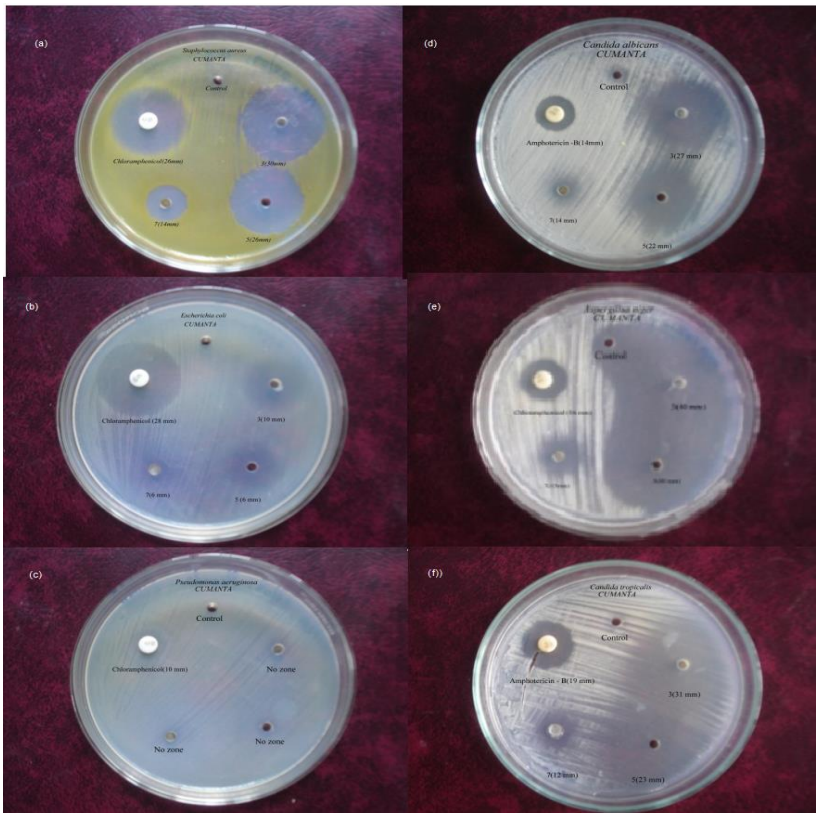


Figure 6: Antimicrobial studies of Poly (NTA-co- MACU)

Conclusions

Copolymers of N-tert-amylacrylamide (NTA) and 7-methacryloyloxy-4-methylcoumarin (MACU) were prepared by free radical polymerization. The copolymer compositions were determined by ^{1}H-NMR analysis. The reactivity ratios of monomers) ($r1 = 1.33$ and $r_2 = 0.60$),) ($r1 = 1.33$and $r_2 = 0.59$). Were determined by Fineman-Ross (FR) Kelen-Tudos (KT) respectively, The $r_1.r_2 = 0.798$ indicated the formation of random copolymers. T_g found to increasing feed content of MACU. The antimicrobial studies showed that the copolymers are active against both Bacteria and Fungi.

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