

REACTIVITY RATIOS AND ANTIMICROBIAL STUDIES OF N-TERT-AMYLACRYLAMIDE AND 8-QUINOLINYL ACRYLATE COPOLYMERS

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Article Received on
24 Oct. 2021,

Revised on 14 Nov. 2021,
Accepted on 05 Dec. 2021

DOI: 10.20959/wjpr20221-22521

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ABSTRACT

Copolymers of N-tert-amyl acrylamide (NTA) and 8-quinolinyl acrylate (8-QA) were prepared by free radical polymerization in Methanol Water (3:1) at 60°C using AIBN as an initiator. (Scheme 1) The copolymer compositions were determined by ¹H-NMR analysis. The reactivity ratios of monomers were determined by Fineman-Ross (FR) ($r_1 = 0.83$ and $r_2 = 2.0$), Kelen-Tudos (KT) ($r_1 = 0.83$ and $r_2 = 2.0$). The $r_1.r_2 = 1.66$ indicated the formation of random copolymers. T_g found to increasing feed content of QA. The antimicrobial studies showed that the copolymers are active against both Bacteria and Fungi.

KEYWORDS: N-tert-amylacrylamide; 8-quinolinylacrylate; reactivity ratios; copolymer composition.

1. 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] ¹H-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 8-quinolinyl acrylate. The synthesis of antimicrobial polymers is one of the leading frontiers of research in polymer science. With this view our work N-tert-amylacrylamide was copolymerized with 8-quinolinyl acrylate with different feed ratio were prepared and characterized by ¹H-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.

2. Experimental

2.1. Preparation of N-tert-amyl acrylamide (NTA)

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

2.2. Copolymerization of NTA and QA

Copolymers of N-tert-amylacrylamide (NTA) and 8-quinolinyl acrylate were prepared by free radical polymerization in Methanol/Water medium at 60 °C using AIBN as initiator (scheme-1).

3. RESULTS AND DISCUSSION

3.1. Characterization of copolymer spectra of Poly (NTA-co- QA)

The ¹H-NMR spectrum of copolymer, poly (NTA-co- 8-QA) (0.5: 0.5) is shown in Figure 1. The following peaks appear in the copolymer spectrum: at 1.03 -1.89 ppm for CH₂ group, at 3.57 ppm for backbone CH₂, at 7.1-8.2 ppm due to quinolinyl aromatic protons and 8.7ppm due to NH Proton.

3.2. Determination of copolymer composition of Poly (NTA-co- QA)

The copolymer composition was determined by ¹H-NMR spectral analysis of the copolymer. The assignment of the resonance peaks in the ¹H-NMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain.

The quinolinyl peak area^[8] is used to determine the copolymer composition. Resonance signal at 7.1-8.2 ppm 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

$$X_{8QA} = \frac{15 A (\text{aryl})}{5A_{\text{total}} + 7A (\text{aryl})} \quad \text{----- (1)}$$

Where X= mole fraction and A= peak area.

3.3. Determination of Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions (Table-1 & Table-2) the reactivity ratios of monomer 1 (NTA) and monomer 2 (8QA) were evaluated by the methods of Fineman-Ross (FR)^[9], Kelen- Tudos (KT)^[10,11] and are presented in Table-3.

The value(s) of r_1 is less than 1 and r_2 is greater than 1. The r_1 and r_2 together show that the QA is generally more reactive than NTA, hence the copolymer contains a higher proportion of NTA units in the polymeric chain. The product value of $r_1.r_2 = 1.64$ indicates the formation of random copolymers. As $r_1.r_2$ is greater than one, the sequence of monomeric units in the copolymer chains is random in nature.

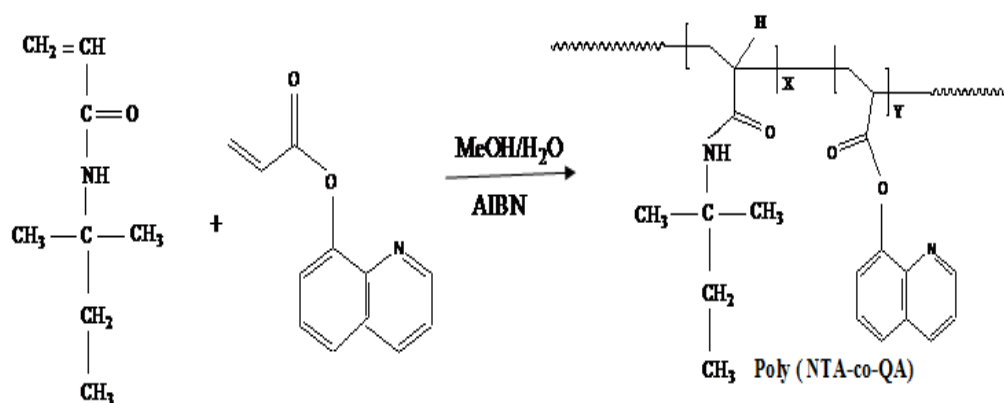
3.4. Thermal studies of Poly (NTA-co- QA)

The glass transition temperature (T_g) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The T_g depends on the morphology of the polymer. The T_g of poly (N-tert-amyl acrylamide) homopolymer is 86.2°C. The T_g of corresponding copolymers increases with increasing feed content of 8-QA. The increase in T_g may be due to a reduction in segmental mobility. The TGA data for the copolymers of NTA with 8-QA are given in Table-4. From the table, it was observed that all the copolymers undergo two stage decomposition. The initial weight loss is due to moisture content. The weight loss at stage 1 is associated with the scission of amide linkage and decarboxylation of side chain units. The weight loss at stage 2 due to breakdown of polymer main chain. The T_f value indicates that the thermal stability of copolymers increases with increasing amount of 8 QA.

3.5. Antimicrobial Activity of Poly (NTA-co- QA)

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. The tests were carried out in triplicates. It is observed from the results that both antibacterial and antifungal activity is maximum Table 5, 6. The inhibiting activity is found to be more than that of the standard. Therefore these kind of copolymers may be used as a potential drugs for bacterial infection particularly. *E. coli* and *staphylococcus aureus*. Comparative studies of both bacteria and fungi are given in Figure-6. The zone of inhibitions are more than the standard drugs for both bacterial and fungi.



Scheme 1: Copolymerization of NTA and QA.

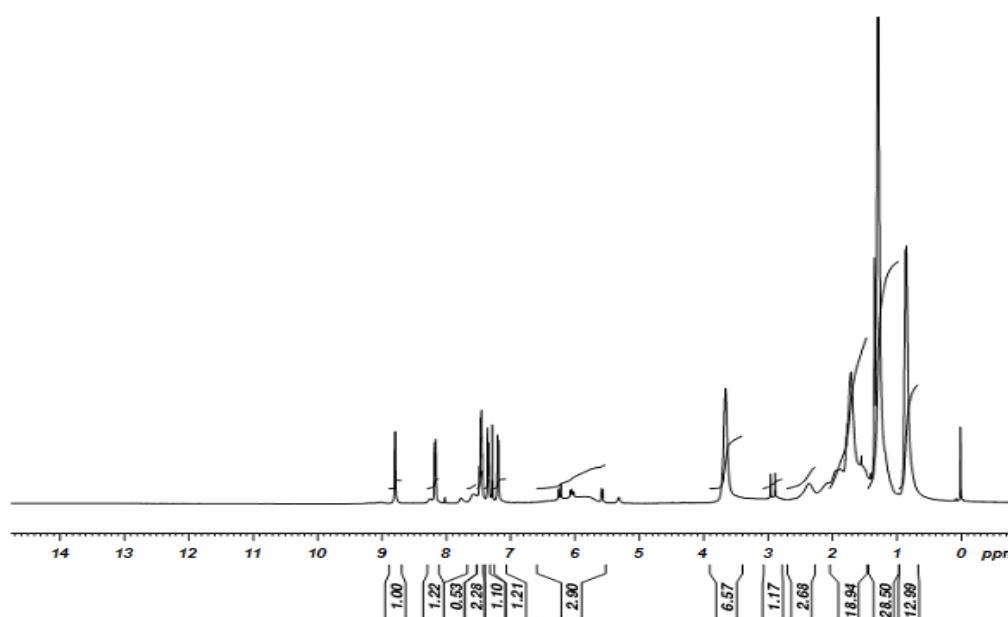


Fig. 1: ¹H-NMR spectrum of poly (NTA-co- QA) (a) 0.5:0.5.

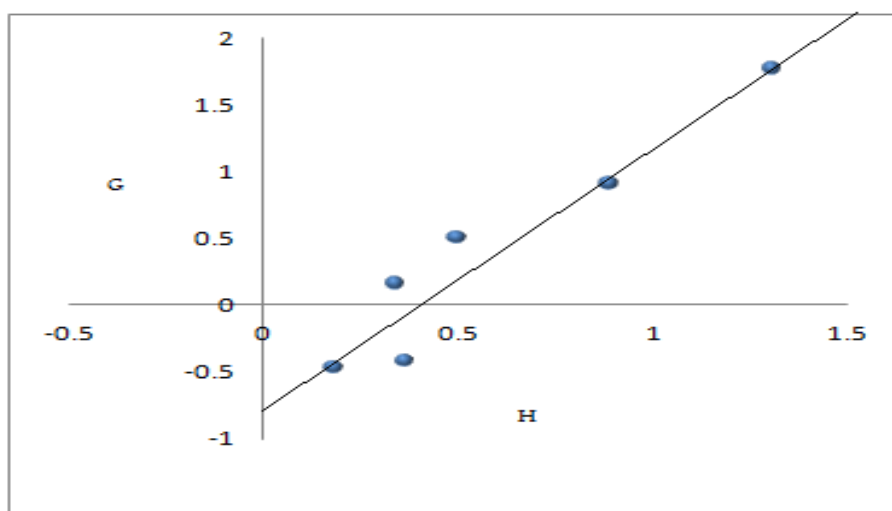


Fig. 2: Fineman-Ross plot for Poly (NTA-co- QA).

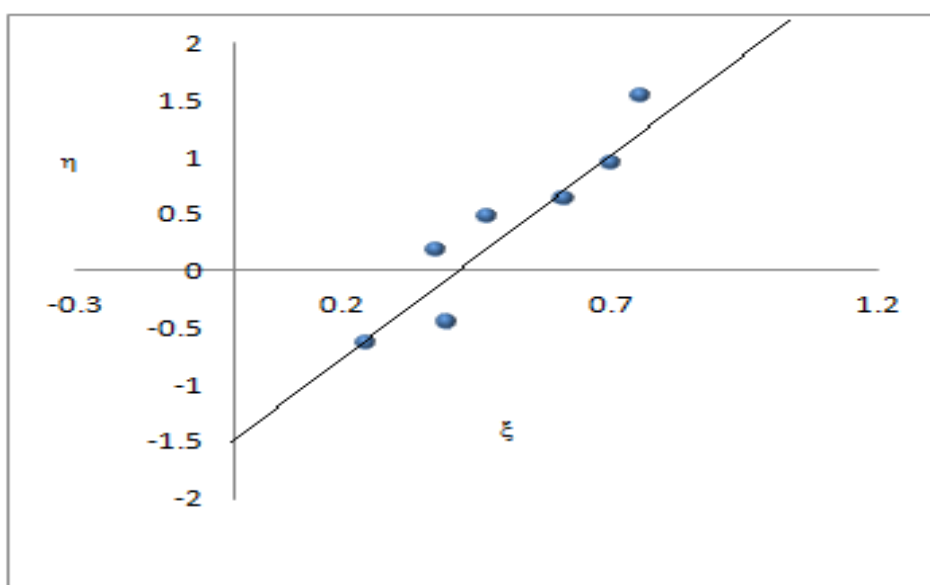


Fig. 3: Kelen-Tudos plot for Poly (NTA-co- QA).

Table 1: Mole fractions of the copolymers of N-tert-amylacrylamide (NTA) and 8-quinolinyl acrylate (QA).

Mole fraction of NTA in feed, M_1	Mole fraction of 8-QA in feed, M_2	Mole fraction of NTA in copolymer, m_1	Mole fraction of 8-QA in copolymer, m_2	$F = M_1/M_2$	$f = m_1/m_2$
0.2	0.8	0.2583	0.7417	0.2500	0.3483
0.3	0.7	0.3362	0.6638	0.4286	0.5065
0.4	0.6	0.5686	0.4314	0.6667	1.3180
0.5	0.5	0.6680	0.3320	1.0000	2.0120
0.6	0.4	0.7173	0.2827	1.5000	2.5373
0.7	0.3	0.8067	0.1933	2.3333	4.1733
0.8	0.2	0.9014	0.0986	4.0000	9.1420

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

$G = F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
-0.4680	0.1795	-0.6328	0.2427
-0.4180	0.3634	-0.4527	0.3935
0.1609	0.3375	0.1793	0.3761
0.5030	0.4970	0.4759	0.4702
0.9088	0.8868	0.6282	0.6129
1.7740	1.3042	0.9516	0.6996
3.5625	1.7502	1.5419	0.7575

 $\alpha = 0.56$ **Table 3: Reactivity ratios of NTA (r_1) and QA (r_2)**

Methods	r_1	r_2	r_1, r_2
Fineman-Ross (FR)	0.83	2.0	1.66
Kelen-Tudos (KT)	0.83	2.0	1.66

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

Copolymers	Mole fraction of NTA, in feed	Mole fraction of 8-QA, in feed	Mole fraction of 8-QA, in copolymer	IDT (°C)	T ₅₀ (°C)	T _f (°C)	T _g (°C)
NTA-8QA	0.70	0.30	0.1933	120	164	625	110
NTA-8QA	0.50	0.50	0.3320	140	169	650	120
NTA-8QA	0.30	0.70	0.6638	150	176	675	130
Poly-NTA		-	-	-	-	-	86.2

IDT : Initial Decomposition Temperature

T₅₀ : decomposition temperature at 50% weight lossT_f : final decomposition temperatureT_g : glass transition temperature**Table 5: Anti-bacterial activity of Poly (NTA-co- QA).**

S. No	Copolymers	Escherichia coli	Staphylococcus aureus	Pseudomonas aeruginosa
1	0.3 NTA : 0.7 QA	33	44	08
2	0.5 NTA : 0.5 QA	38	44	No zone
3	0.7 NT A : 0.3 QA	26	44	12
4	Chloramphenicol	26	26	10

Table 6: Anti-fungal activity of Poly (NTA-co- QA).

S.No	Copolymers	<i>Aspergillus niger</i>	<i>Candida albicans</i>	<i>Candida tropicalis</i>
1	0.3 NTA : 0.7 QA	No growth	No growth	No growth
2	0.5 NTA : 0.5 QA	No growth	No growth	No growth
3	0.7 NTA : 0.3 QA	No growth	No growth	No growth
4	Amphotericin B	No growth	No growth	No growth

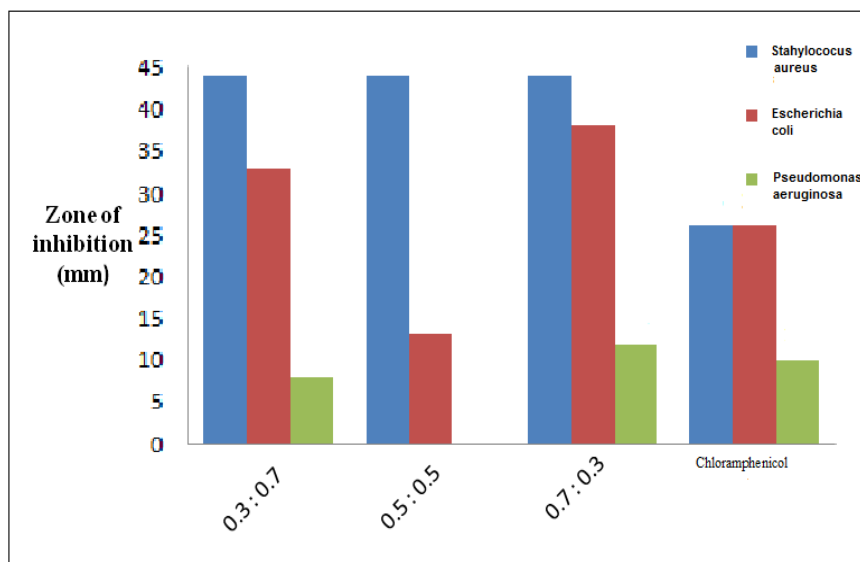
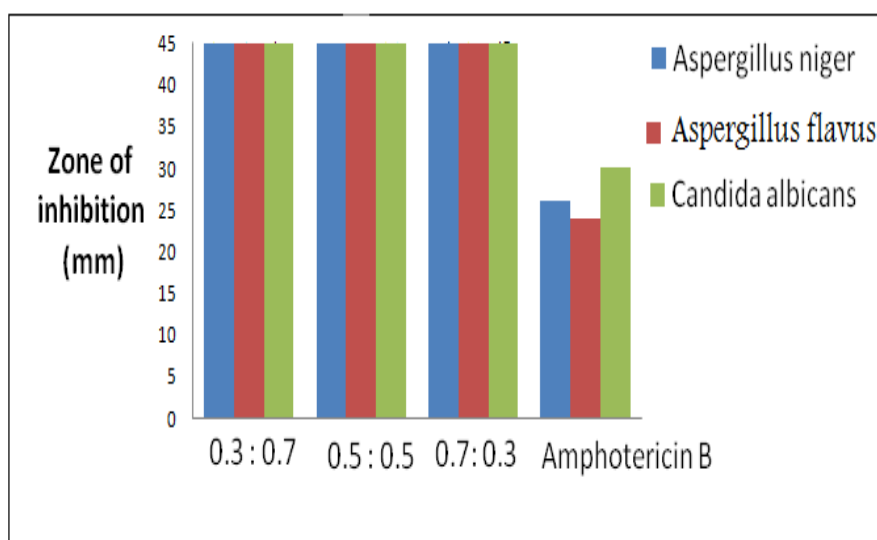
**Fig.4: Comparison of Zone of inhibition of Poly (NTA-co- QA) with bacteria.****Fig. 5: Comparison of Zone of inhibition of Poly (NTA-co- QA) with fungi.**



Fig. 6: Antimicrobial studies of Poly (NTA-co- QA).

4. CONCLUSIONS

The copolymers poly(N-tert-amylacrylamide –co- 8-quinolinylacrylate) was prepared by free radical polymerization technique at 60°C. The copolymer composition of monomers in the polymer was determined by ¹H-NMR spectral analysis. Subsequently the reactivity ratios are also determined by Fineman-Ross and Kelen-Tudos showed as $r_1 = 0.83$ and $r_2 = 2.0$. The synthesized copolymers showed good antimicrobial activity towards selected microorganisms.

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