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Copolymerization of N-Tert-Butylacrylamide (Ntb) And 2-Methyl-N-1, 3-Thiazole-2-Acrylamide (Tma): Synthesis, Characterization And Antimicrobial Activity

KEYWORDS: Copolymerization, monomer reactivity ratios, thermal properties, antimicrobial activity

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ABSTRACT *The Acrylamide based monomer, N-tert-butylacrylamide (NTB) and 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA) was synthesized and characterized by NMR spectroscopy. Copolymerization of NTB with TMA in different feed ratio was carried out in 1, 4-dioxane at 60±1oC using AIBN as initiator. The resulting copolymers were characterized by 1H-NMR spectroscopy and the copolymer compositions were determined by 1H-NMR data. Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods were employed to calculate the reactivity ratios of monomers. Mean sequence lengths of copolymers were estimated from r1 and r2 values. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with increases in the mole fraction of NTB in the copolymers. The obtained copolymers were tested for their antimicrobial activity against selected micro-organisms.*

Introduction

Drugs and disinfectants based on copolymers with functional groups have received much attention in recent years. With this view, in our earlier work N-tert-butylacrylamide was copolymerized with 7-acryloyloxy-4-methyl coumarin[1], 2, 4-dichlorophenyl methacrylate[2], and 8-quinolinyl acrylate[3] which shows antimicrobial activity. The present work focuses on synthesis and characterization of N-tert-butylacrylamide (NTB), 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA) monomers and their copolymers. The obtained copolymers were tested for their antimicrobial activity against various bacteria and fungi.

Experimental

Preparation of N-tert-butylacrylamide (NTB)

The Monomer N-tert-butylacrylamide[4] was prepared by the reaction of t-butyl alcohol with acrylonitrile. N-tert-butylacrylamide was recrystallized in warm dry benzene. The white crystals have a mp. 94°C and the yield was 87 %. The monomer was confirmed by both ^{1}H-NMR and ^{13}C-NMR spectroscopy.

^{1}H-NMR Spectroscopy CDCl$_3$, δ (ppm)
The following peaks appear in the NTB spectrum; at 1.42 ppm for tert-butyl protons, at 5.59 - 6.28 ppm for vinyl protons and at 7.27 ppm for N-H proton.

CDCl$_3$), δ (ppm): The ^{13}C-NMR spectral values of N-tert-butylacrylamide is as follows δ 164.80(CH$_2$ = C(H)-$\underline{\mathrm{CO}}$-NH..), δ 132.93(CH$_2$ =$\underline{\mathrm{C}}$(H)-CO-NH…), δ 122.82($\underline{\mathrm{CH_2}}$=C(H)-CO-NH..), δ 51.37(-$\underline{\mathrm{C}}$(CH$_3$)$_3$), δ 28.77 (-C ($\underline{\mathrm{C}}$H$_3$)$_3$).

Preparation of 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA)

Methacryloyl chloride was prepared by reacting methacrylic acid with benzoyl chloride. 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA)[5] comonomer is prepared by Esterification of 2-amino thiazole with methacryloyl chloride. The comonomer (TMA) obtained is proved by ^{1}H-NMR spectroscopy (Figure 1).

^{1}H-NMR Spectroscopy CDCl$_3$, δ (ppm)
The following peaks appear in the TMA spectrum; at 2.0 ppm for methyl protons, at 5.6 – 6.2 ppm for Non – equivalent methylene protons, at 7.0 – 7.5 ppm due to aromatic protons, at 10.0 ppm for N-H protons.

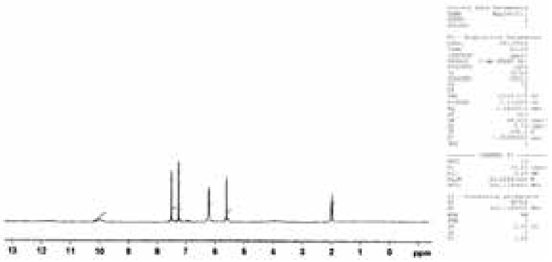
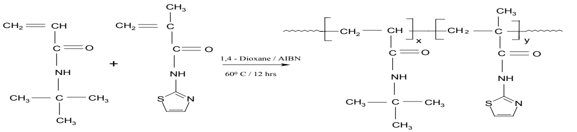


Figure 1: ^{1}H-NMR spectrum of 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA)

Copolymerization

A different feed ratio of series of copolymers, N-tert-butylacrylamide (NTB) and 2-methyl-N-1, 3-thiazole-2-acrylamide (TMA) were prepared by free radical polymerization in 1, 4 dioxane at 60±1°C using AIBN as initiator (scheme 1).



Scheme 1. Copolymerization of NTB with TMA

^{1}H-NMR spectra of Poly (NTB-co-TMA)

The ^{1}H-NMR spectra of copolymers, Poly (NTB-co-TMA) are shown in Figure 2 and the following peaks appear in the copolymer spectrum: at 1.1 -1.4 ppm for tert-butyl group, at 1.56 ppm for CH$_3$ group, at 1.6 – 1.8 and 2.9 ppm & 3.7 ppm for CH group and backbone –CH$_2$ group, at 7.0 -7.5 ppm due to aromatic protons and at 8.0 & 10.5 ppm for N-H proton.

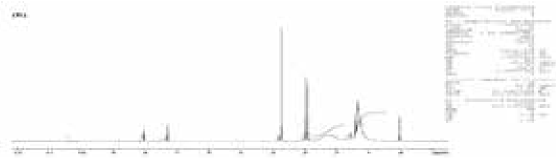


Figure 2:^{1}H-NMR spectra of Poly (NTB-co-TMA) (0.5:0.5)

Determination of copolymer composition

The **N-tert-butyl** peak intensity is used to determine the copolymer composition. Resonance signals at 1.1 -1.4 ppm

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corresponds to tert-butyl 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

$$X_{(NTB)} = \frac{8\,A_{(t-butyl)}}{9\,A_{(total)} - 5\,A_{(t-butyl)}} \quad \ldots\ldots (1)$$

Where X = mole fraction and A = peak area. Table 1 gives the values of the corresponding mole fraction in the copolymers. Plotting the mole fraction of TMA in comonomer feed (M_2) against copolymer feed (m_2) indicates that composition of TMA in the copolymer is lower than that in feed composition[6] (Figure 3).

Determination of Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer (NTB) and comonomer (TMA) are evaluated by Fineman–Ross (F-R)[7], Kelen-Tudos (K-T)[8] and Extended Kelen-Tudos (Ext. K-T)[9,10] methods. The significant parameters of F-R, K-T and Ext. K-T equation are presented in Table 2 and Table 3. The reactivity ratios for NTB (r_1) and TMA (r_2) from the F-R plot (Figure 4), K-T plot (Figure 5) and Ext. K-T plot (Figure 6) are shown in the Table 4. The value(s) of $r_1 > 1$ and $r_2 < 1$, it shows that NTB is generally more reactive than TMA units, hence the copolymer contains a higher proportion of NTB units. The product value of $r_1.r_2 = 1.75$ indicates that the copolymers are weakly order with predominantly a random distribution of monomeric unit in the polymer chain[11].

Table 1: Composition data for free radical polymerization of NTB with TMA

Mole fraction of NTB in feed (M_1)	Mole fraction of TMA in feed (M_2)	Mole fraction of NTB in copolymer (m_1)	Mole fraction of TMA in copolymer (m_2)	$F=M_1/M_2$	$f=m_1/m_2$
0.2	0.8	0.3383	0.6617	0.2500	0.5113
0.3	0.7	0.4491	0.5509	0.4286	0.8152
0.4	0.6	0.5425	0.4575	0.6667	1.1858
0.5	0.5	0.6713	0.3287	1.0000	2.0423
0.6	0.4	0.7640	0.2360	1.5000	3.2373
0.7	0.3	0.8400	0.1600	2.3333	5.2500
0.8	0.2	0.9050	0.0950	4.0000	9.5263

Table 2: F-R and K-T parameter for the copolymers of N-tert-butylacrylamide and methyl-N-1, 3-thiazole-2-acrylamide

$G = F(f-1)/f$	$H=F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
-0.2390	0.1222	-0.4155	0.2125
-0.0972	0.2253	-0.1433	0.3322
0.1045	0.3748	0.1262	0.4528
0.5104	0.4896	0.5415	0.5194
1.0367	0.6950	0.9031	0.6054
1.8889	1.0370	1.2677	0.6960
3.5801	1.6796	1.6788	0.7876

$\alpha = (H_{max}.\ H_{min})^{1/2} = 0.4530$

Table 3: Extended K-T parameter for the copolymers of N-tert-butylacrylamide and 2- methyl-N-1, 3-thiazole-2-acrylamide

TMA (M_2) (mole fraction)	W	ζ_2	ζ_1	Z	F	G	ξ	η
0.8	4.8	4.0724	8.3289	1.7744	0.1624	-0.2754	0.2640	-0.4477
0.7	5.0	4.0468	7.6970	1.7068	0.2798	-0.1083	0.3819	-0.1478
0.6	5.2	4.0745	7.2470	1.6312	0.4457	0.1139	0.4961	0.1268
0.5	5.1	3.4669	7.0805	1.9987	0.5112	0.5215	0.5303	0.5410
0.4	5.4	3.2918	7.1044	2.1810	0.6806	1.0258	0.6005	0.9051
0.3	5.9	3.2372	7.2838	2.2825	1.0077	1.8620	0.6900	1.2749
0.2	6.0	2.9124	6.9361	2.7468	1.2626	3.1041	0.7360	1.8095

Where, $\mu = \mu_{2\,(TMA)} / \mu_{1\,(NTB)} = 1.2126$, $\zeta_2 = W(\mu + F/\mu + f)$, $\zeta_1 = \zeta_2 (f/F)$, $Z = \log(1 - \zeta_1) / \log(1 - \zeta_2)$, $F = f/Z^2$, $G = (f-1)/Z$, $\xi = F/\alpha + F$, $\eta = G/\alpha + F$, $\alpha = (F_{max}.\ F_{min})^{1/2} = 0.4528$,

Table 4: Reactivity ratios of Poly (NTB-co-TMA)

Methods	r_1	r_2	$r_1.r_2$
Fineman–Ross (F-R)	2.5	0.7	1.75
Kelen- Tudos (K-T)	2.5	0.7	1.75
Extended Kelen- Tudos (Ext. K-T)	2.5	0.7	1.75

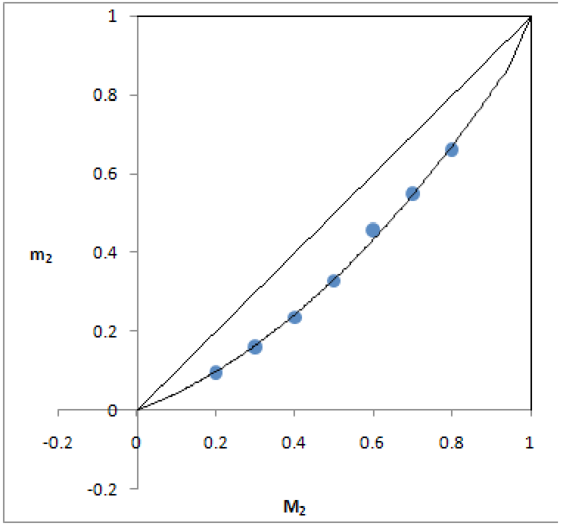

Figure 3: Copolymer composition curve of Poly (NTB-co-TMA)

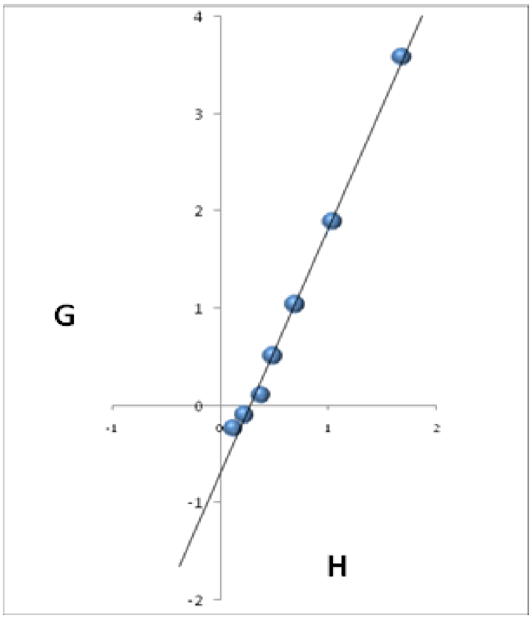

Figure 4: Fineman-Ross plot of Poly (NTB-co-TMA)

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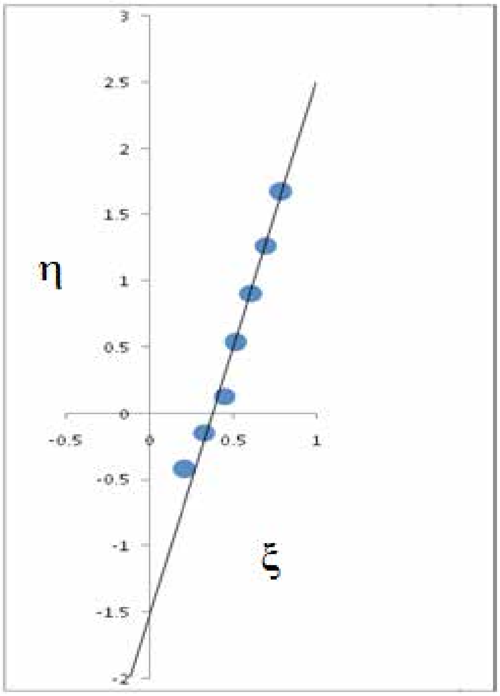

Figure 5: Kelen –Tudos plot of Poly (NTB-co-TMA)

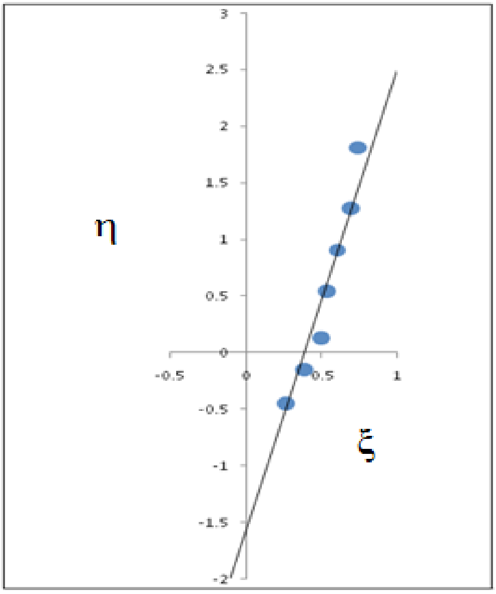

Figure 6: Extended Kelen –Tudos plot of Poly (NTB-co-TMA)

Determination of Mean sequence lengths

The mean sequence lengths[12] are determined using the pertinent equation:

$$l_1 = r_1 \frac{M_1}{M_2} + 1 \qquad \text{....... (2)}$$

$$l_2 = r_2 \frac{M_2}{M_1} + 1 \qquad \text{....... (3)}$$

Where r_1 and r_2 are the reactivity ratios and $[M_1]$ and $[M_2]$ represents the concentration of NTB and TMA in the monomer feed respectively. The mean sequence lengths of copolymer are given in Table 5. It is significant to note from the Table 5, that the TMA units decreases in a linear fashion in the polymer chain as the concentration of TMA decreases in the monomer feed. In other words, the NTB units increases in a linear fashion in the polymer chain as the concentration of NTB increases in the monomer feed. This suggests that the copolymers are becoming weakly ordered and predominantly random in nature.

Thermal studies

Thermal behaviors of copolymers are shown in Figure 7 the values are indicated in Table 6. It is observed that all the copolymers undergo three stages degradation. The initial weight loss < 100°C is observed due to moisture content. Weight loss at stage 1 (100–225°C) occurs due to degradation of partial amide linkages. Weight loss at stage 2 (225–420°C) indicates the scission in the amide linkages and / or other reactions of side chain units. Weight loss at stage 3 (above 420°C) occurs due to main chain degradation and breakdown of the polymer backbone[11, 13, 14]. T_g values found to increases with increasing feed content of NTB. The increase in T_g may be due to reduction in segmental mobility[15].

Table 5: Mean sequence lengths of copolymers of Poly (NTB-co-TMA)[a]

TMA in feed M_2 (mole fraction)	l_1	l_2	l_1: l_2	Distribution[b]
0.8	1:63	3:8	2:4	NNTTTTNN
0.7	2:07	2:63	2:3	NNTTTNN
0.6	2:67	2:05	3:2	NNNTTNNN
0.5	3:50	1:70	4:2	NNNNTTNNNN
0.4	4:75	1:47	5:1	N_5TN_5
0.3	6:83	1:30	7:1	$(N)_7T(N)_7$
0.2	11:00	1:18	11:1	$(N)_{11}T(N)_{11}$

[a] r_1 = 2.5 and r_2 = 0.7, [b] (N = NTB, T = TMA)

Table 6: TGA and DSC data of Poly (NTB-co-TMA)

Copolymers	Mole fraction of TMA in feed	% weight loss at various temperature (°C)						$T_{50\%}$	T_{max}	T_g	T_f
		100	200	300	400	500	600				
NTB-TMA	0.3	8	15	28	88	94	98	360	382	85.4	750
NTB-TMA	0.5	7	15	32	86	94	97	362	380	82.5	740
NTB-TMA	0.7	4	14	37	73	82	84	362	381	70.6	748

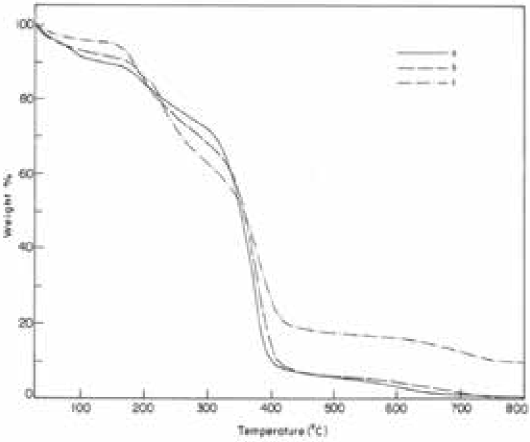

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Figure 7: TGA curves of Poly (NTB-co-TMA) in the mole fraction of a) 0.7:0.3, b) 0.5:0.5, c) 0.3:0.7

Antimicrobial studies

The synthesized copolymers were tested against selected bacteria and fungi, by well diffusion method and the plates were prepared as per the standard methods[16-18]. Antimicrobial activity was evaluated by measuring the zone of inhibition in mm against the microorganisms. DMSO was used as solvent control. Ciprofloxacin was used as reference antibacterial agent. Ketoconazole was used as reference antifungal agent. The results are summarized in Table 7.

The activity of polymers against bacteria like Escherichia coli and Klebsiella pneumonia are almost same except Pseudomonas aeruginosa. For antifungal activity, the zone of inhibition against Aspergillus flavus and Candida albicans are almost same except Cryptococcus neoformans (Figure 8 and Figure 9).

Table 7: Antibacterial and Antifungal activity of Poly (NTB-co-TMA)

S.No	Organisms (Bacteria)	Zone of Inhibition (mm)				
		Ciprofloxacin (10)	Control (DMSO)	3TMA -NTB	5 TMA -NTB	7 TMA -NTB
1.	Escherichia coli	21	No zone	6	8	8
2.	Pseudomonas aeruginosa	22	No zone	6	13	10
3.	Klebsiella pneumonia	28	No zone	4	5	4
	Organisms (Fungi)	Ketoconazole				
1.	Aspergillus flavus	23	No zone	4	5	4
2.	Candida albicans	15	No zone	6	8	9
3.	Cryptococcus neoformans	13	No zone	12	15	11

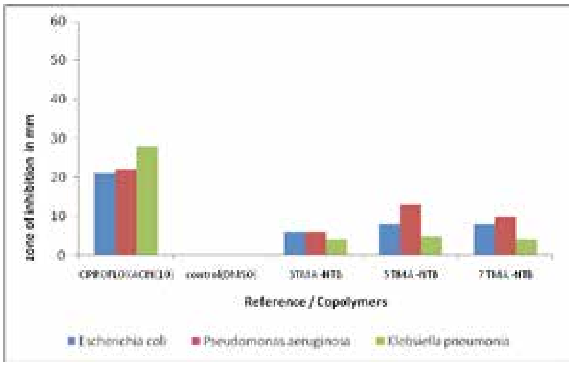

Figure 8: Graphical representation of Antibacterial activity of Poly (NTB-co-TMA)

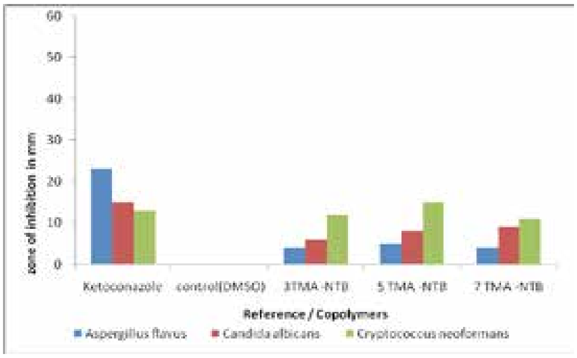

Figure 9: Graphical representation of Antifungal activity of Poly (NTB-co-TMA)

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