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N-cyclohexylacrylamide based copolymers –I : Synthesis and characterization of Poly (NCA-co-8QA)

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Abstract: A series of copolymers N-cyclohexylacrylamide(NCA) and 8-Quinolinylacrylate(QA) were prepared by free radical polymerization in methanol/Water medium at60^{0}C using AIBN as initiator. The copolymers were characterized by ^{1}H-NMR spectroscopy and the copolymer compositions were determined by^{1}H-NMR analysis. The reactivity ratios of monomers were determined by Fineman-Ross and Kelen- Tudos methods. The reactivity ratios of monomers determined by Fineman-Ross(r_1= 0.84 and r_2=2.86) , Kelen-Tudos (r_1=0.84 and r_2=2.82). The $r_1.r_2$=2.42 value indicates the formation of random copolymers. The thermal stability decreases with increasing mole % of 8QA. It shows antimicrobial activity. The activity of copolymers against Fungi (A.N and A.F) increases with increasing mole% of NCA.

Keywords: free radical polymerization , copolymer composition, reactivity ratios, antimicrobial activity.

Introduction

Many polymers with reactive functional groups are now being synthesized, tested and used not only for the macromolecular properties but also for the properties of functional groups. These functional groups provide an approach to a subsequent modification of the polymers for specific end application [1]. In recent years, some comprehensive work has been published on functional monomers and their polymers [2, 3].

The N-substituted acrylamides are used to prepare thermo sensitive polymers like poly(N-isopropylacrylamide)and copolymers of N-alkyl acrylamide and styrene [4]. Thermosensitive polymers have great potential in applications as drug delivery system [5] human gene vector [6] and biocatalysts [7].

The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific application of the copolymer [8]. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their value [9–11]. ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [12, 13].

Antimicrobials gained interest in both academic research and industry due to their potential to provide quality and safety benefits to many materials. Contamination by microorganism is of great concern in several areas such as medical devices, health care products, water purification systems, hospital and

dental equipments etc. One possible way to avoid the microbial contamination is to develop antimicrobial agents. Antimicrobial agents are those materials capable of killing pathogenic microorganisms. Antimicrobial agents of low molecular weight are used for the sterilization of water, as antimicrobial drugs, as food preservatives, and for soil sterilization [14]. However, they can have the limitation of residual toxicity even when suitable amounts of the agents are added [15].

The use of antimicrobial polymers offers promise for enhancing the efficacy of some existing antimicrobial agents and minimizing the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging the lifetime of the antimicrobial agents. Kenawy and coworkers discussed on the requirements of antimicrobial polymers, factors affecting the antimicrobial activities, methods of synthesizing antimicrobial polymers, major field of application, and future and perspectives in the field of antimicrobial polymers in their review article [16].

H.Patel et al., prepared the homopolymers of 2,4-DCPA and its copolymers with 8-quinolinyl methacrylate .The results showed that 2,4-DCPA is more reactive than 8-QMA. Thermal analysis shows that thermal stability of copolymers increases with the increase of 2,4-DCPA. The copolymers also showed antimicrobial activity which increased with increase in 8-QMA content[17]. The antimicrobial activity of 8-quinoline methacrylate although known, not much systematic work has been carried out on copolymers derived from N-cyclohexylacrylamide.

Present work focuses on synthesis and characterization of 8-quinolinyl acrylate and N-cyclohexylacrylamide copolymers. Reactivity ratio values of the monomers were determined by various linearization techniques. Thermal analysis results are also included. The prepared copolymers were tested for their antimicrobial activity against various fungi.

Experimental

Materials

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber coloured bottle and kept in the refrigerator at 5° C. Benzoyl proxide (BPO) was recrystallized from chloroform. N,N'-dimethylformamide(DMF) was dried in Megnesium Sulphate All the solvents were purified by distillation prior to their use.

Preparation of N-cyclohexylacrylamide (NCA)

The monomer N-cyclohexylacrylamide was prepared by the reaction of cyclohexanol with acrylonitrile. N-cyclohexylacrylamide was recrystallized in warm dry benzene. The white crystals have amp.115° C and the yield was -87%.[18] The monomer was confirmed by both ^{1}H-NMR and ^{13}C-NMR.

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer(JEOL, Tokyo,Japan) operating at 400 MHz respectively in $CDCl_3$. The following peaks appear in NCA spectrum; at 1.2- 1. 9 ppm for cyclohexyl CH_2 ,at 3.84 ppm for cyclohexyl methane , at 5.59-6.28 ppm for vinyl protons and at 7.27 ppm for N-H proton **(Figure 1)** .

^{13}C-NMR($CDCl_3$),δ(ppm) (Figure 2) :

δ 164.80(CH_2 = C(H)-CO-NH..);
δ 132.93(CH_2 =C(H)-CO-NH…);
δ 122.82(CH_2=C(H)-CO-NH..) ;
δ 49.82(cyclohexyl- C_1)
δ 32.84(cyclohexyl- C_2);
δ 26.19 cyclohexyl- C_3)
δ 26..17 cyclohexyl- C_4)

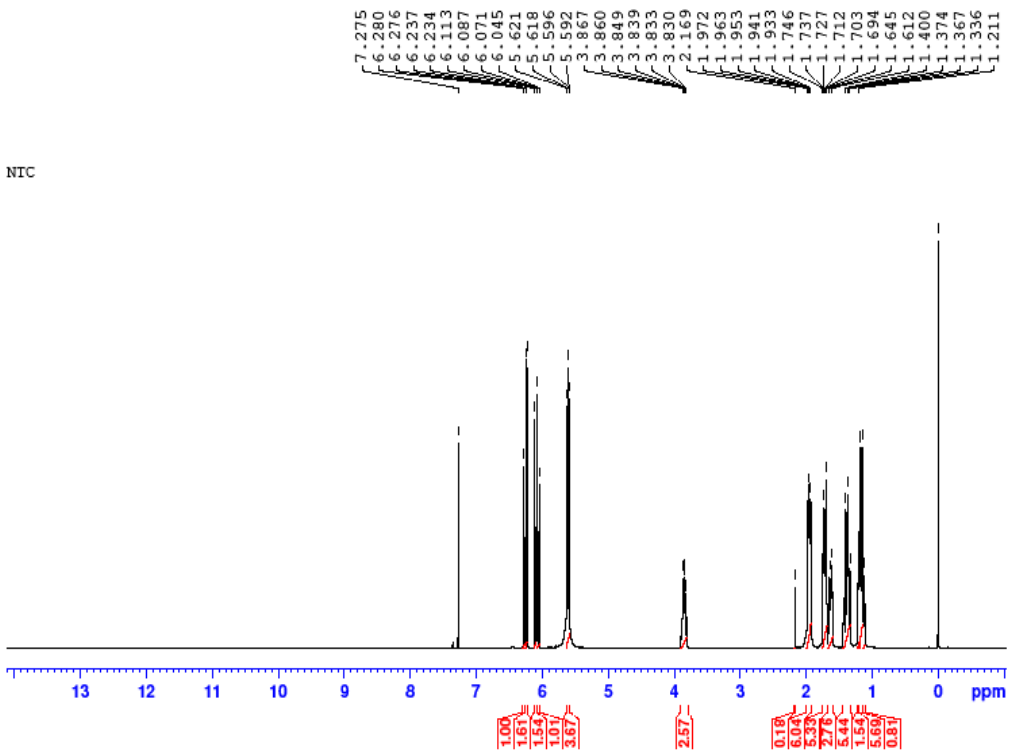

Figure 1. [1] H-NMR spectra of N-cyclohexylacrylamide

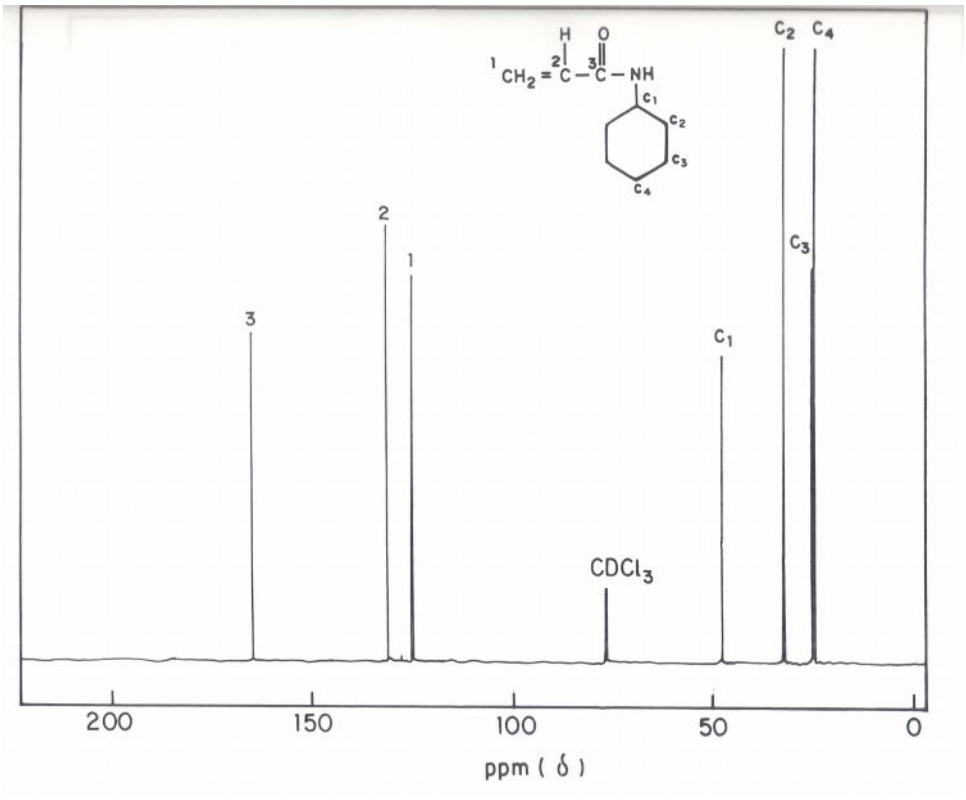

Figure 2 . [13] C-NMR spectra of N-cyclohexylacrylamide

Preparation of 8-Quinolinyl acrylate

The 8-Quinolinyl Acrylate comonomer was prepared by esterification of 8-Hydroxy quinoline and acrylolyl chloride. IR spectral analysis conformed the monomer formation **(Figure 3)** .

IR (KBr, cm^{-1}) : 1741 for C=O of ester group, 1634 for olefinic (C=C) stretching, 3066 C-H vibration of aromatic ring and 894 for –C-H bending mode of vinyl group.

Copolymerization

A total feed of 5 gm of monomers N-cyclohexylacrylamide , 8-Quinolinyl acrylate and 50mg of AIBN initiator were dissolved in 25ml of Methanol/ water (3:1) placed in a standard reaction tube to obtain a homogenous solution. The mixture was flushed with oxygen free dry nitrogen gas. The inlet and outlet of the reaction tube were closed by means of rubber tubing's and pinch cock. The reaction vessel is then immersed in a thermostatic water bath maintained at 60°C. The copolymerization reaction was allowed to proceed for an appropriate duration that would give a conversion below 10%. After the reaction vessel was removed from the thermostat and cooled under the tap. The solution poured in ice cold water to precipitate the copolymer and the copolymer washed with methanol. It was then dried in vacuum oven for 24 hours.

Instrumentation

The ^{1}H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer(JEOL, Tokyo,Japan) operating at 400 MHz respectively in $CDCl_3$. A DSC - Q200 V23 , Differential scanning calorimeter was used to study the thermal behavior of ionomers at a heating rate of 20°C /min under nitrogen atmosphere. Thermogravimetric analysis was carried out using TGA Q500 V-20 at a heating rate of 20°C /min under nitrogen atmosphere.

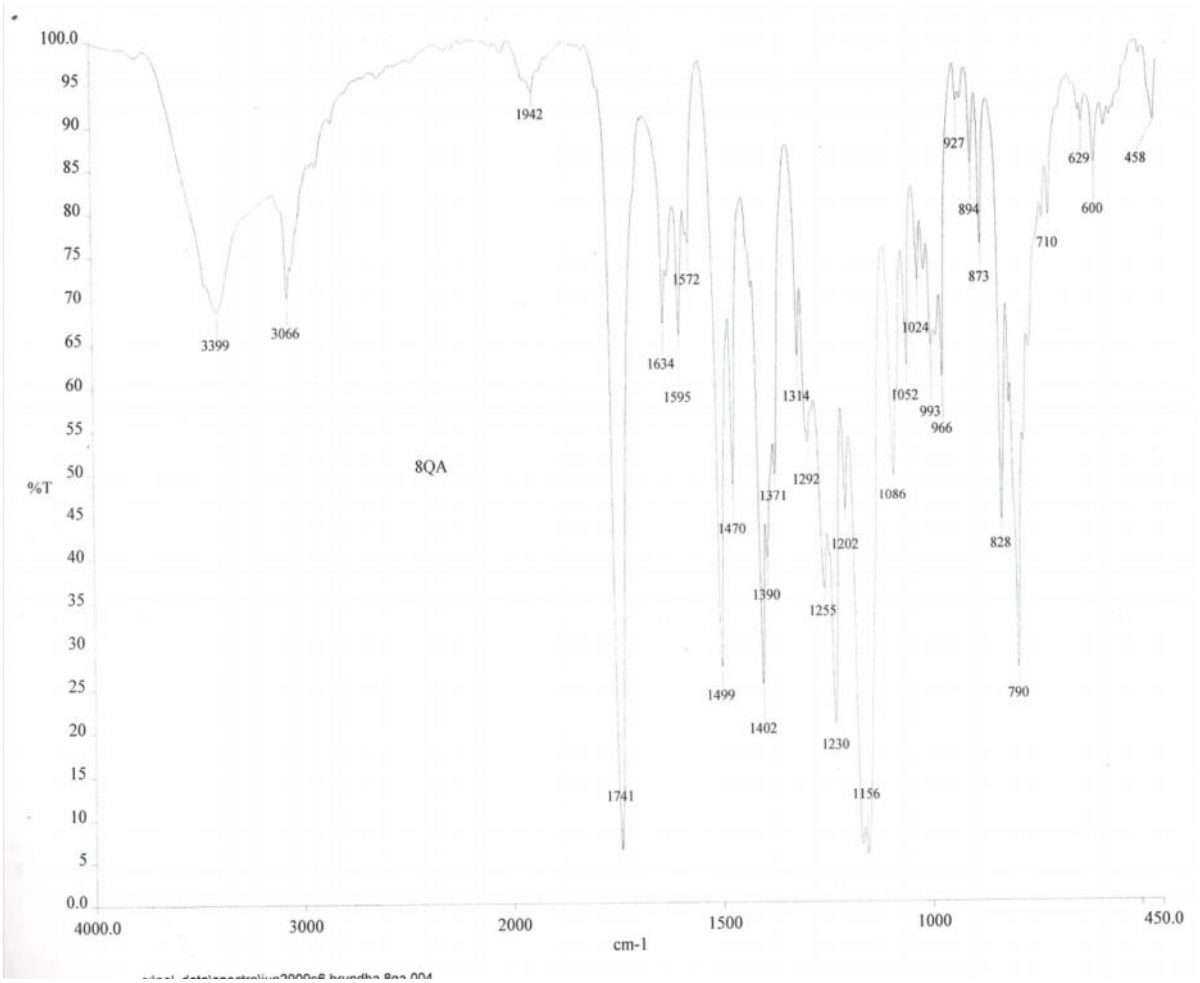

Figure 3. FT-IR spectra of 8-Quinolinyl acrylate

Antimicrobial activity

The synthesized compounds in the present investigation have been tested for antimicrobial activity by Cup-plate diffusion method. The organisms selected for the antifungal activity was carried out by using *Aspergillus niger* and *Aspergillus flavus.* The plates are prepared as per the standard methods[19-21]. The outcome is presented in Table-5.

Results and Discussion

Copolymerization

A series of copolymers N-cyclohexylacrylamide (NCA) and 8-Quinolinyl acrylate (8QA) were prepared by free radical polymerization in methanol/Water medium at 60^0C using AIBN as initiator The schematic representation of the copolymer is given bellow:

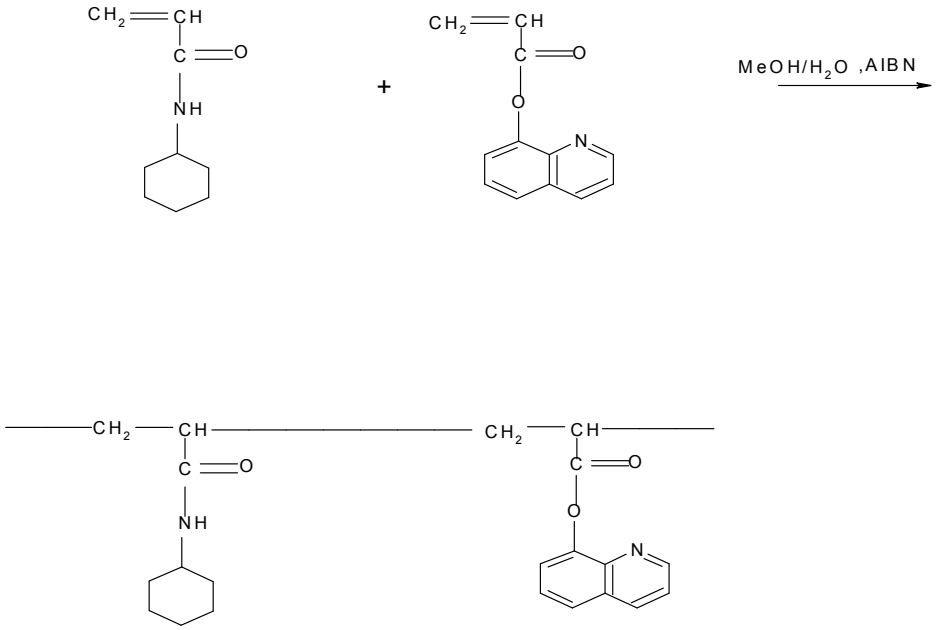

Figure 4: Copolymerization of NCA and 8QA

Characterization

The ^{1}H-NMR spectrum of copolymer , poly (8QA-co- NCA) (0.5 : 0.5) is shown in Figure 5 . The following peaks appear in the copolymer spectrum : at 1.03 -1.89 ppm for cyclohexyl CH_2 group , at 3.57 ppm for backbone CH_2 , at 7.11-8.7 ppm due to Quinolinyl aromatic protons.

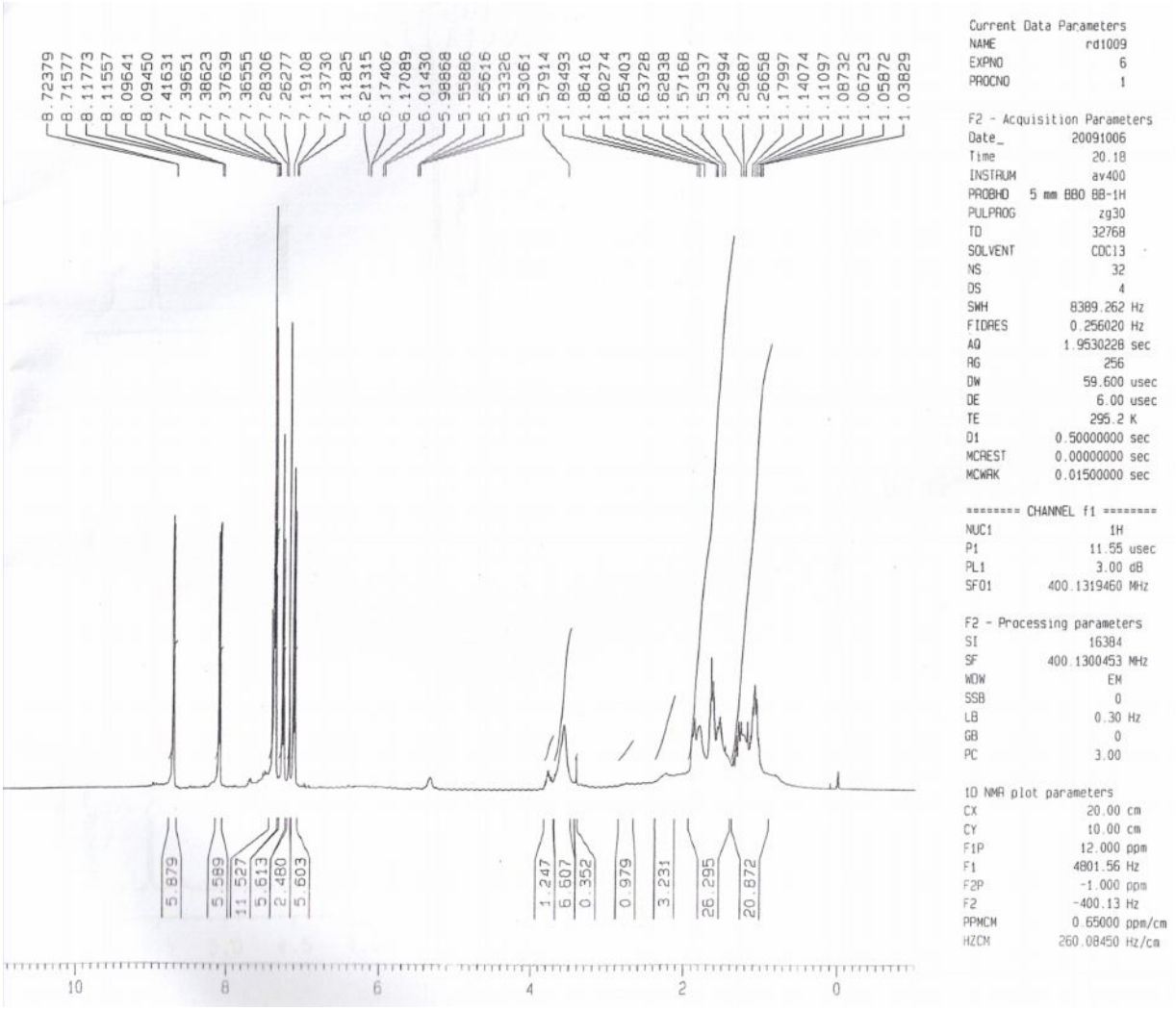

Figure 5 . ^{1}H-NMR spectrum of poly (8QA-co- NCA) (0.5 : 0.5)

Determination of copolymer composition

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

The quinolinyl peak area**[17]** is used to determine the copolymer composition. Resonance signal at 7.11-7.41 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

$$X_{8QA} = \frac{15\,A(\text{Quinolinyl})}{5A_{total} + 7A(\text{Quinolinyl})} \quad \ldots..(1)$$

Where X= mole fraction and A= peak area. Table 1. gives the values of the corresponding mole fractions in the copolymers.

Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (NCA) and monomer 2 ((8-QA) were evaluated by the methods of Fineman-Ross (FR) and Kelen- Tudos (KT).The significant parameters of F-R and K-T and equation are presented in Table 1 and Table 2 respectively. The reactivity ratios for NCA (r_1) and 8-QA (r_2) from the F-R plot (Figure 6) AND K-T plot are given in Table 3. The value(s) of r_1 is less than 1 and r_2 is greater than 1. r_1 shows that NCA favors cross-propagation as opposed to homopropagation and r_2 shows that 8QA favors homopropagation over cross-propagation. The value $r_1 . r_2 = 2.41$ showed that 8QA is generally more

reactive than NCA, hence the copolymers contain a higher proportion of 8QAunits.

Thermal analysis

The glass transition temperature (Tg) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The Tg depends on the morphology of the polymer and the Tg values are presented in Table 4 . The Tg of poly (N-cyclohexylacrylamide) homopolymer is 79.2°C. The Tg of corresponding copolymers are increases with increasing feed content of 8QA. The increase in Tg may due to a reduction in segmental mobility. The TGA data for the copolymers of NCA with 8QA are given in Table 5 . A typical TGA curve for poly(NCA-co-8QA) is shown in Figure 7 . From the Table 5, it was observed that the initial weight loss increases with increasing feed of 8QA . Hence the stability of the copolymers decreases with the increasing mol % 8QA. The maximum weight loss may be due to scission in aryl ring of 8QA monomeric units of copolymer. .

Antifungal activity

These polymer samples were tested against the fungi *Aspergillus niger* and *Aspergillus flavus* at various concentrations as mentioned in table 5. From the table it noticed that the activity of polymers against fungi increases with increasing mole % of NCA(Figure 8). These polymers are more active against both the fungi.

Table 1: Fineman-Ross parameters for the Copolymes of N-cyclohexylacrylamide and 8-Quinolinyl acrylate

Mole fraction of 8QA in feed ,M_1	Mole fraction of NCA in feed, M_2	Mole fraction of 8QA in copolymer, m_1	Mole fraction of NCA in copolymer, m_2	$F=M_1/M_2$	$F=m_1/m_2$	(f-1)/F	f/ F^2
0.2	0.8	0.2595	0.7405	0.250	0.3504	-2.5984	5.6064
0.3	0.7	0.4235	0.5765	0.429	0.7346	-0.6192	3.9990
0.4	0.6	0.5686	0.4314	0.667	1.3180	0.4770	2.9652
0.5	0.5	0.6891	0.6891	1.000	2.2165	1.2165	2.2165
0.6	0.4	0.7602	0.2398	1.500	3.1701	1.4467	1.4089
0.7	0.3	0.8606	0.1394	2.333	6.1736	2.2173	1.1340
0.8	0.2	0.9092	0.0908	4.000	10.0132	2.2533	0.6258

Table 2 . kelen- Tudos parameters for the Copolymes of N-cyclohexylacrylamide and 8-Quinolinyl Acrylate

$G =F(f-1) / f$	$H =F^2 / f$	$\eta =G /(\alpha + H)$	$\varepsilon = H / (\alpha + H)$
-0.4635	0.1784	-0.6507	0.2505
-0.1548	0.2500	-0.1975	0.3189
0.1608	0.3372	0.1846	0.3871
0.5488	0.4512	0.5571	0.4580
1.0268	0.7098	0.8256	0.5707
1.9553	0.8818	1.3812	0.6229
3.6005	1.5980	1.6889	0.7496

α= 0.5339

Table 3 . Copolymerization parameter, for the NCA (r_1) and 8QA (r_2) copolymer .

Methods	r_1	r_2	$r_1 . r_2$
Fineman-Ross (FR)	0.84	2.86	2.41
Kelen-Tudos (KT)	0.84	2.82	2.37

Table 4. TGA and DSC data for Poly(NCA-co-8QA)

Copolymers	Mole fraction of NCA ,in feed	Mole fraction of 8QA, in feed	Mole fraction of 8QA,in copolymer	(%Wt. loss) at 50-200 (°C)	(%Wt. loss) at 200-320 (°C)	(%Wt. loss) at 320-490 (°C)	(%Wt. loss) Above 490 (°C)	T_g (°C)
NCA-8QA	0.70	0.30	0.42	12.62	19.89	62.64	2.86	68.54
NCA-8QA	0.50	0.50	0.69	56.42	36.12	-	3.79	69.27
NCA-8QA	0.30	0.70	0.86	70.32	19.65	-	5.73	70.40
Poly-NCA		-	-	-	-			79.2

T_g : glass transition temperature

Table 5. Anti fungal activity of copolymers

S.No	Concentration (ppm)	3QC		5QC		7QC	
		A.F	A.N	A.F	A.N	A.F	A.N
1	1,00,000 ppm	2.90cm	3.25cm	1.00cm	1.75cm	0.75cm	0.90cm
2	10,000 ppm	2.40cm	2.3cm	1.80cm	1.25cm	0.50cm	0.70cm
3	1,000 ppm	1.85cm	1.25cm	1.20cm	0.70cm	0.40cm	0.65cm
4	100 ppm	0.75cm	0.65cm	0.60cm	0.30cm	0.15cm	0.40cm
5	10 ppm	0.30cm	0.25cm	0.25cm	0.10cm	0.10cm	0.20cm
	DMSO solvent	No Zone of Inhibition					

A. F : Aspergillus flavus ; A.N : Aspergillus niger
3QC : 30 mol% 8QA& 70 mol% NCA ; 5QC: 50 mol% 8QA& 50 mol% NCA&
7QC: 70 mol% 8QA& 30 mol% NCA

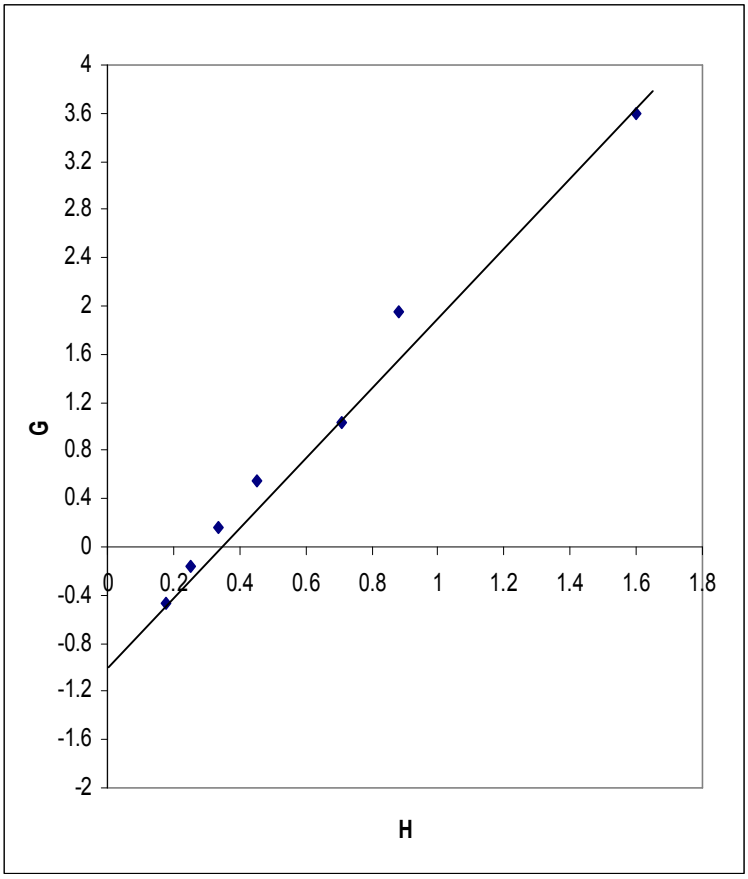

Figure 6 . Fineman-Ross Plot

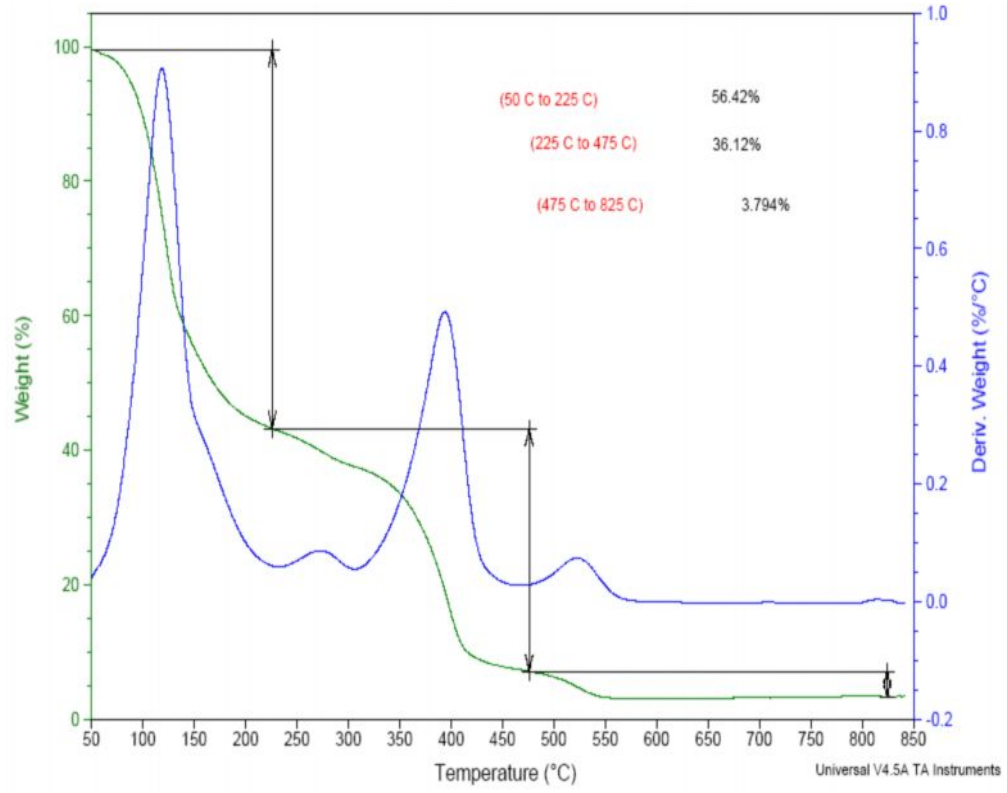

Figure 7. TGA curve of poly (8QA-co- NCA) (0.5 : 0.5) .

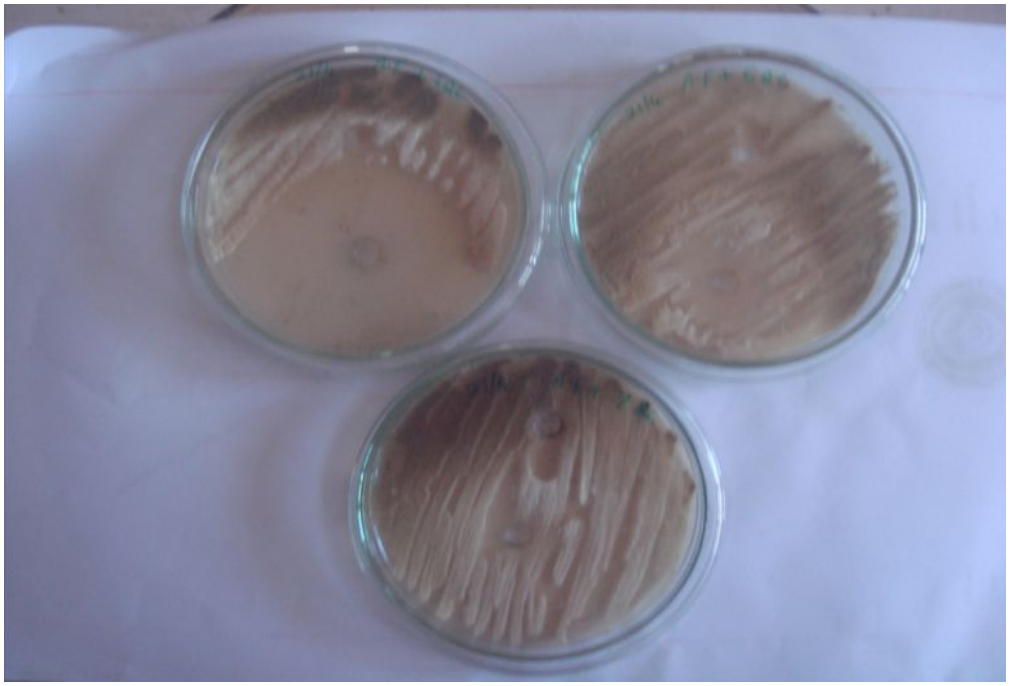

Figure 8. Anti fungal activity of copolymers 10000ppm of A.F (a)Top Left 2QC (b) Top right 5QC (c) Bottom 3QC

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