

COPOLYMERIZATION OF N-CYCLOHEXYLACRYLAMIDE WITH 2,4-DICHLOROPHENYL METHACRYLATE: SYNTHESIS, CHARACTERIZATION, REACTIVITY RATIOS AND ANTIMICROBIAL ACTIVITY

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ABSTRACT

Copolymers of N-cyclohexylacrylamide (NCA) and 2,4-Dichlorophenyl methacrylate (DCPMA) were synthesized by the free radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The copolymers were characterized by ¹H-NMR spectroscopy and the copolymer compositions were determined by ¹H-NMR analysis. The reactivity ratios of monomers were determined using linear methods like Fineman-Ross ($r_1 = 0.38$ and $r_2 = 1.07$) and Kelen-Tudos ($r_1 = 0.38$ and $r_2 = 1.08$). The value $r_1 \cdot r_2 = 0.4$ showed that DCPMA is more reactive than NCA. Hence the copolymers contain a higher proportion of DCPMA units. Mean sequence lengths of copolymers were estimated from r_1 and r_2 values. It showed that the DCPMA units increases in a linear fashion in the polymer chain as the concentration of DCPMA increases in the monomer feed. The copolymers were tested for their antimicrobial properties against selected microorganisms.

Keywords: Dichlorophenyl methacrylate, NCA, Reactivity ratio, mean sequence length, Antimicrobial activity.

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INTRODUCTION

Acrylic polymers are a class of reactive polymers that finds extensive applications due to the presence of electron attracting groups in the aromatic ring¹. Phenyl acrylate polymers are relatively newly developed materials compared to commercial polymers such as vinyllic, acrylamides, alkyl acrylates etc., Phenyl acrylates are considered as reactive monomers primarily because of presence of aromatic ring². Kadir and co-workers prepared copolymers from phenyl methacrylate and methylmethacrylate. The copolymers were characterized by IR, ¹H-NMR and ¹³C-NMR techniques³.

The polymers having antimicrobial properties are suitable in a variety of applications such as films, packaging materials, food stuffs, sanitary application and many others^{4,5}. The presence of chlorine has been suggested to impart an antimicrobial property to a compound^{6,7}. Many acrylic polymers containing chlorine possess an antimicrobial property have also been reported.^{8,9}

Patel et al., prepared the homopolymers of 2,4-DCPA and its copolymers with 8-quinoliny methacrylate. The results showed that 2,4-DCPA is more reactive than 8-QMA. Thermal analysis showed 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 content¹⁰. They also prepared the polymers of 2, 4-DCPA and its copolymers with 2-Hydroxyethylmethacrylate (HEMA). The results showed that 2, 4-DCPA is less reactive than HEMA. Thermal analysis shows that thermal stability of copolymers increases with the increase of 2,4-DCPA. The result indicated that chlorine content is important to impart antimicrobial activity in the polymers¹¹.

The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific application of the copolymer¹². The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been

attempted to determine their value¹³⁻¹⁵. ¹H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition^{16,17}.

Pazhanisamy et al.,¹⁸ studied the Copolymerization of N-cyclohexylacrylamide (NCA) and n-butyl acrylate (BA) was carried out in Dimethylformamide at 55±1°C using azobisisobutyronitrile as a free radical initiator. The copolymers were characterized by ¹H-NMR spectroscopy and the copolymer compositions were determined by ¹H-NMR analysis. The reactivity ratios of the monomers were determined by both linear and non-linear methods. Mean sequence lengths of copolymers are estimated from r_1 and r_2 values. It showed that the BA units increase in a linear fashion in the polymer chain as the concentration of BA increases in the monomer feed.

The synthesis and development of antimicrobial polymers is one of the leading frontiers of research in polymer science. With this view, in our earlier work¹⁹ N-cyclohexylacrylamide was copolymerized with 8-quinoliny acrylate. Copolymers with different feed ratio were prepared and characterized by ¹H-NMR spectroscopy. 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.

In the present work, the synthesis of N-cyclohexylacrylamide and 2,4-dichlorophenyl methacrylate copolymers in different feed ratio by free radical polymerization was undertaken. The prepared copolymers were characterized by ¹H-NMR spectroscopy. Copolymer composition was obtained from ¹H-NMR data monomer reactivity ratios were determined by Fineman-Ross²⁰ and Kelen-Tudos²¹ methods.

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 CaCl₂. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber colored bottle and kept in the refrigerator at 5° C. The initiator AIBN was recrystallized from chloroform. All the solvents were purified by distillation prior to their use.

Preparation of 2,4-Dichlorophenyl methacrylate (DCPMA)

Reported method²² was followed to synthesize 2,4-dichlorophenyl methacrylate(DCPMA).The methacrylate monomer, 2,4-dichlorophenyl methacrylate (DCPMA), was synthesized by reacting of 2,4-dichlorophenol with methacryloyl chloride. Absolute alcohol (400 ml) and NaOH (0.2 mol) were added to a three necked flask, equipped with stirrer, condenser and thermometer and the contents were stirred until all NaOH dissolved. 2,4-dichloro phenol was added to this reaction mixture and heated to 60 °C for 30 min with stirring, cooled to room temperature and then to 0-5°C by ice. Freshly prepared methacryloyl chloride (0.21 mol) was added drop wise to the cooled reaction mixture and stirred for 90 min. It was then poured into crushed ice-water mixture where a powder product separated out. It was filtered, washed thoroughly with cold water and dried.

Preparation of N-cyclohexylacrylamide (NCA)

The monomer N-cyclohexylacrylamide was prepared by the reaction of cyclohexanol with acrylonitrile²³. N-cyclohexylacrylamide was recrystallized in warm dry benzene. The white crystals have mp.115° C and the yield was -87%. The monomer was confirmed by both ¹H-NMR and ¹³C-NMR.

¹H-NMR spectroscopy

The ¹H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz respectively in CDCl₃. The following peaks appear in NCA spectrum; at 1.2- 1.9 ppm for cyclohexyl CH₂, at 3.84 ppm for cyclohexyl methine, at 5.59-6.28 ppm for vinyl protons and at 7.27 ppm for N-H proton. The following peaks are appeared in DCPMA(Fig.-

1): at 2.1 ppm for =C(CH₃) methyl protons, at 5.8-6.4 for vinylic protons and at 7.1-7.6 ppm for aryl protons.

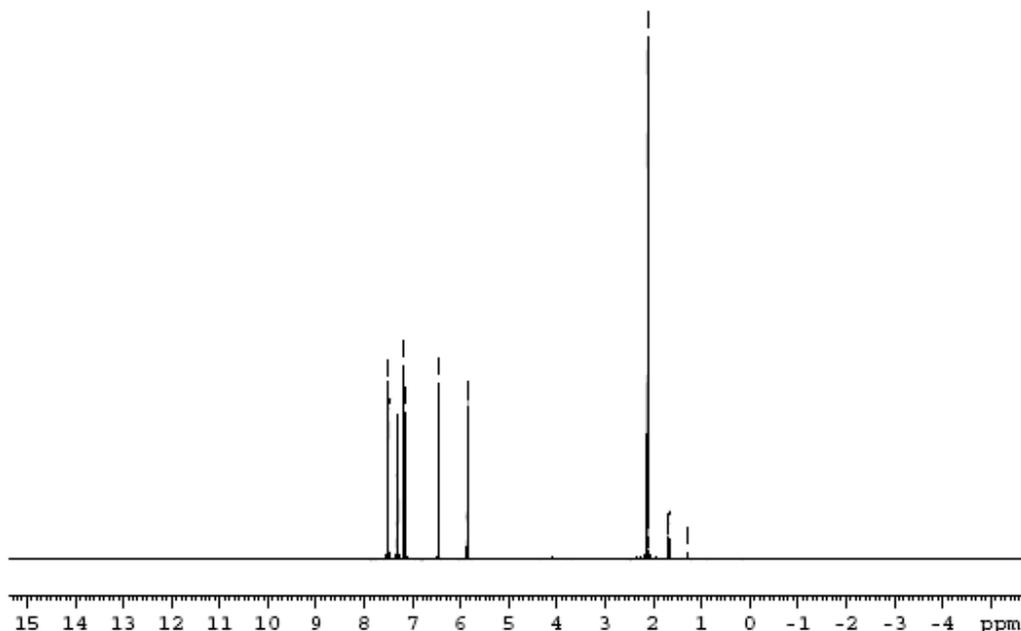


Fig.-1: ¹H-NMR Spectrum of DCPMA

RESULTS AND DISCUSSION

Copolymerization

Copolymerization of N-cyclohexyl acrylamide (NCA) with DCPMA carried out in methanol/Water medium at 60^oC using AIBN as initiator. The schematic representation of the copolymers is given below-

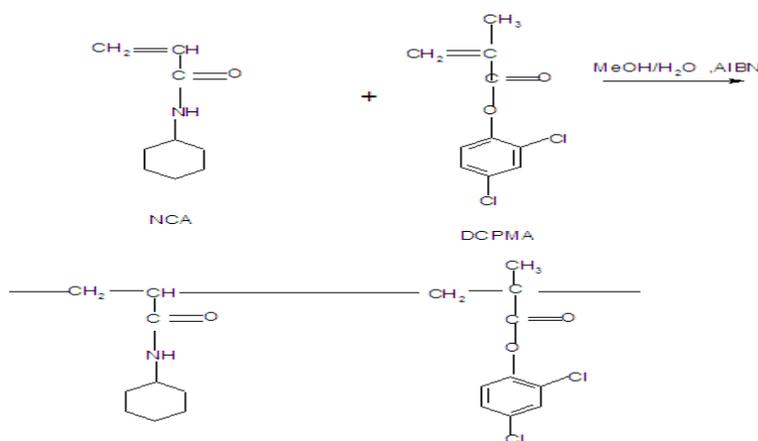


Fig.-2: Copolymerization of NCA and DCPMA

Characterization of Copolymer

The ¹H-NMR spectrum of copolymer is shown in Figure 2 and the following peaks appear in the copolymer spectrum : at 1.03 -1.89 ppm for cyclohexyl CH₂ group (backbone methyl protons overlapped) ,at 3.57ppm for backbone CH₂ , at 6.9-7.6 ppm due to DCPMA aromatic protons.

Determination of copolymer composition

The copolymer composition was determined by $^1\text{H-NMR}$ spectral analysis of the copolymer. The assignment of the resonance peaks in the $^1\text{H-NMR}$ spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain. The 2,4-dichloro phenyl peak area²⁴ is used to determine the copolymer composition.

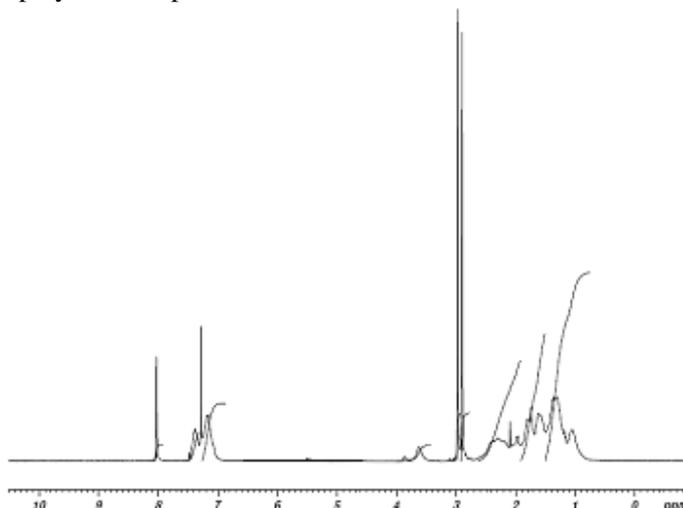


Fig.-3: $^1\text{H-NMR}$ spectrum of poly (NCA-co-DCPMA) (0.5: 0.5)

Resonance signal at 6.9-7.6 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 the equation-

$$X_{\text{DCPMA}} = 15A(\text{Aryl}) / 3A_{\text{total}} + 7A(\text{Aryl}) \quad (1)$$

Where X= mole fraction and A= peak area.

The kinetic behavior was determined by plotting the mole fraction of DCPMA in the feed against that in the copolymer (Figure 3).

Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (NCA) and monomer 2 (DCPMA) 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. The reactivity ratios for NCA (r_1) and DCPMA (r_2) from the F-R plot (Figure 4) and K-T (Figure 5) plot are given in Table 2. The value 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 DCPMA favors homopropagation over cross-propagation. The $r_1 \cdot r_2 = 0.4$ value indicates the formation of random copolymers. The more the diverse from unity, the less random the distribution will be¹⁶.

Mean sequence length

The mean sequence length¹⁸ can be determined using the pertinent equations;

$$l_1 = r_1 (M_1/M_2) + 1 \quad (2)$$

$$l_2 = r_2 (M_2/M_1) + 1 \quad (3)$$

Where r_1 and r_2 are the reactivity ratios and M_1 and M_2 represent the concentration of NCA and DCPMA respectively, in the monomer feed. The mean sequence lengths of copolymers are given in Table 4. It is significant to note from table 4 that the DCPMA units increases in a linear fashion in the polymer chain as the concentration of DCPMA increases in the feed.

Table-1: Fineman-Ross and Kelen-Tudos parameters for the Copolymers of NCA and DCPMA

Mole fraction of NCA in feed, M_1	Mole fraction of DCPMA in feed, M_2	Mole fraction of DCPMA in copolymer, m_2	$F=M_1/M_2$	$f=m_1/m_2$	$G = F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
0.2	0.8	0.8321	0.25	0.2018	-0.9888	0.3097	-0.5172	0.1619
0.3	0.7	0.7387	0.429	0.3537	-0.7802	0.5154	-0.3684	0.2433
0.4	0.6	0.6727	0.667	0.4865	-0.704	0.9144	-0.2797	0.3633
0.5	0.5	0.6031	1.000	0.6581	-0.5195	1.5195	-0.1664	0.4867
0.6	0.4	0.5243	1.500	0.9073	-0.1532	2.4799	-0.0375	0.6074
0.7	0.3	0.4272	2.333	1.3408	0.5929	4.0594	0.1047	0.7169
0.8	0.2	0.3413	4.000	1.9299	1.9273	8.2906	0.1948	0.838

$$\alpha = (H_{\min} \times H_{\max})^{1/2} = 1.6023$$

Table-2: Copolymerization parameter for the NCA (r_1) and DCPMA (r_2) copolymer

Methods	r_1	r_2	r_1, r_2
Fineman-Ross (FR)	0.38	1.07	0.406
Kelen-Tudos (KT)	0.38	1.08	0.410

Table-3 : Mean sequence lengths in (NCA-co-DCPMA)

Mole fraction of DCPMA in feed M_2	l_1	l_2	$l_1 : l_2$	Distribution
0.8	1.09	5.28	1 : 5	N (D) ₅ N
0.7	1.16	3.50	1 : 4	NDDDDN
0.6	1.25	2.61	1 : 3	NDDDN
0.5	1.38	2.07	1 : 2	NDDN
0.4	1.57	1.71	2 : 2	NNDDNN
0.3	1.88	1.45	2 : 1	NNDNN
0.2	2.52	1.26	3 : 1	NNNDNNN

Table-4: Thermal behavior of Poly (NCA-co-DCPMA)

Copolymers	Mole fraction of NCA in feed	Mole fraction of DCPMA in feed	Mole fraction of DCPMA in copolymer	IDT (°C)	T ₅₀ (°C)	T _f (°C)	T _g (°C)
NCA-DCPMA	0.3	0.7	0.7387	325	450	600	75.2
NCA-DCPMA	0.5	0.5	0.6031	150	450	600	74.4
NCA-	0.7	0.3	0.4272	225	450	525	66.1

DCPMA							
Poly-NCA							79.2

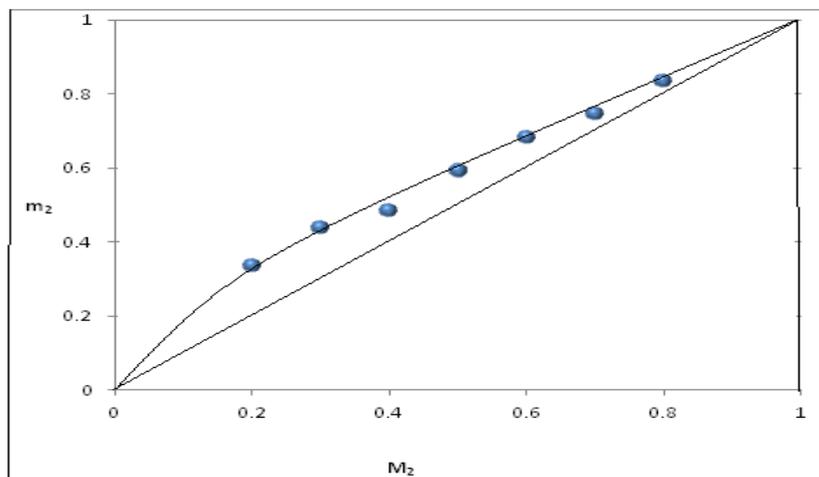


Fig.-4: Copolymer composition diagram of Poly (NCA-co-DCPMA)

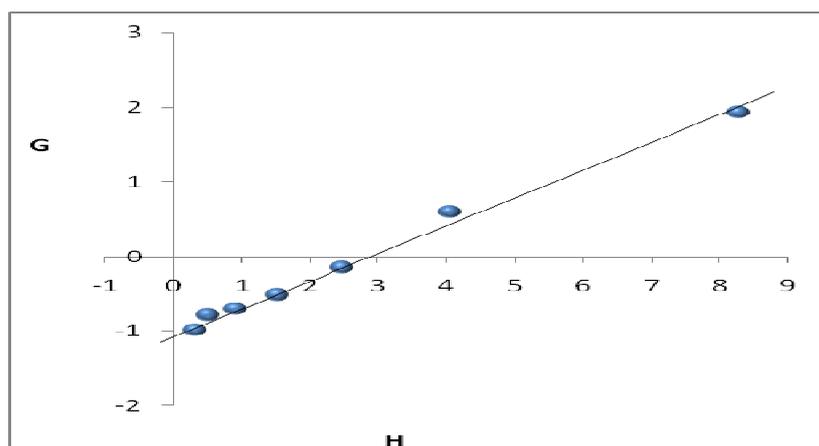


Fig.-5 : Fineman--Ross plot of Poly(NCA-co-DCPMA)

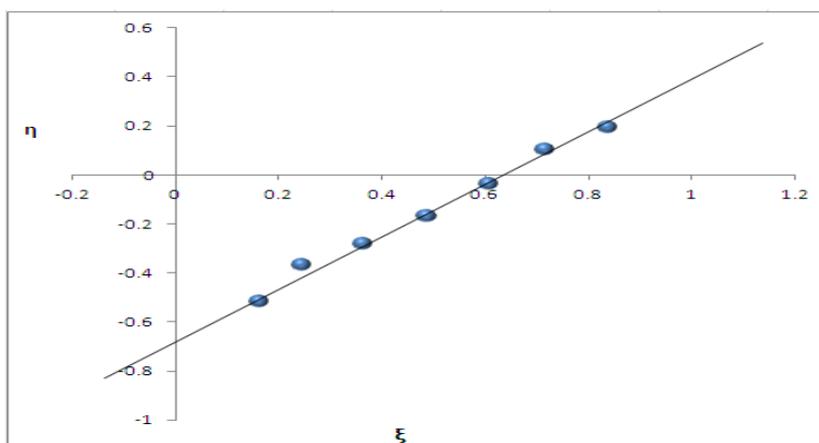


Fig.-6 : Kelen-Tudos plot of Poly(NCA-co-DCPMA)

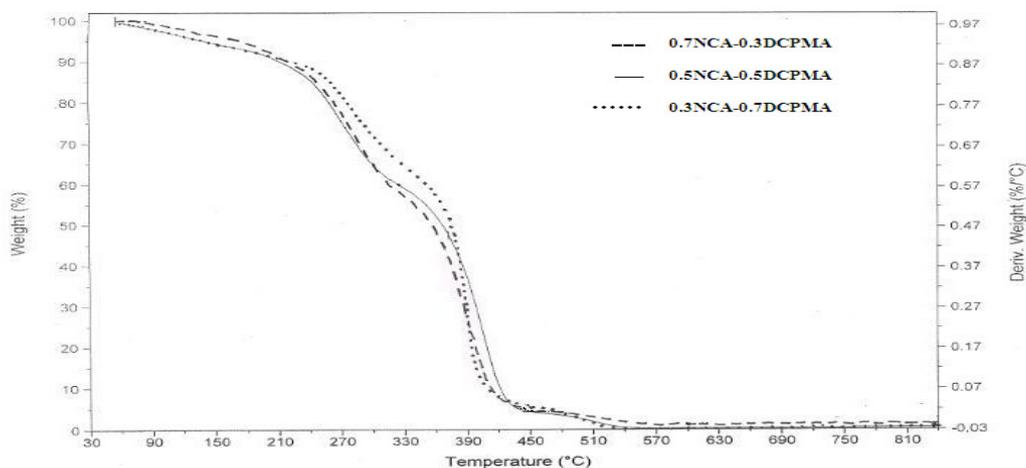


Fig.-7 : TG thermograms of Poly (NCA-co-DCPMA) (0.7:0.3) (0.5:0.5) (0.3:0.7)

Thermal studies

Thermal behaviors of polymers were studied using TG and DSC traces. The thermogram is shown in Figure 7 and the measured values are in Table 4. The copolymers undergo decomposition in the range 150-600 °C. The stability of the copolymer increases with the increasing feed content of DCPMA.

Table-5 : Antimicrobial studies on selected organisms

S.No	Organisms (Bacteria)	Zone of Inhibition (mm)			
		CONTROL (DMSO)	0.7NCA : 0.3DCPMA	0.5 NCA : 0.5DCPMA	0.3 NCA: 0.7DCPMA
1	<i>Staphylococcus aureus</i>	No zone	10	09	07
2	<i>E. coli</i>	No zone	17	12	06
3	<i>Pseudomonas aeruginosa</i>	No zone	15	13	07
	Organisms (Fungi)				
4	<i>Aspergillus niger</i>	No zone	11	12	05
5	<i>Candida tropicalis</i>	No zone	18	22	13
6	<i>Candida albicans</i>	No zone	17	19	11

Antimicrobial Activity

The synthesized compounds in the present investigation have been tested for antimicrobial activity by well diffusion method. The organisms selected for the antifungal activity was carried out by using *Aspergillus flavus*, *Candida albicans* and *Candida tropicalis*. The organisms selected for the antibacterial activity was carried out by using *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. The plates are prepared as per the standard methods²⁵. It was observed that the copolymers prepared using NCA and DCPMA showed strong inhibitor effect towards the microorganism tested (Table 5). It was observed that as the NCA content increases antibacterial activity increases and the antifungal activity was higher at equal monomer feed content.

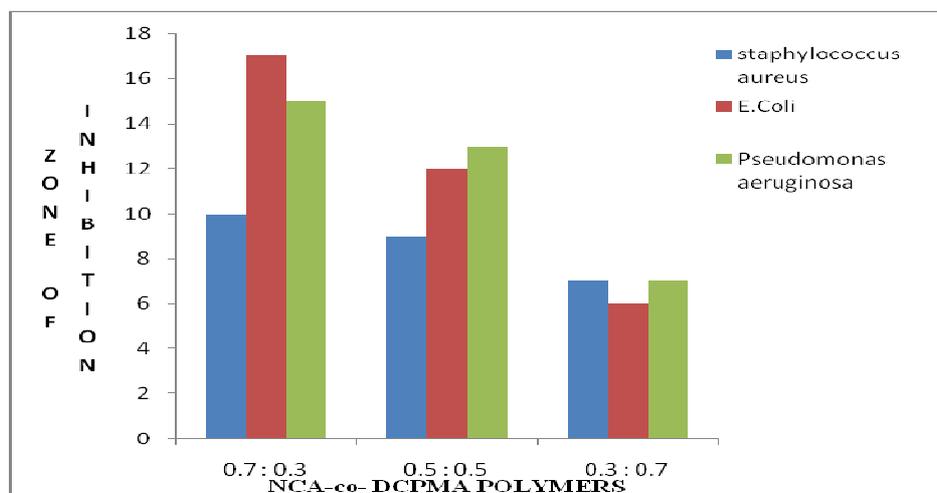


Fig.-8 : Antibacterial activity of Poly(NCA-co-DCPMA)

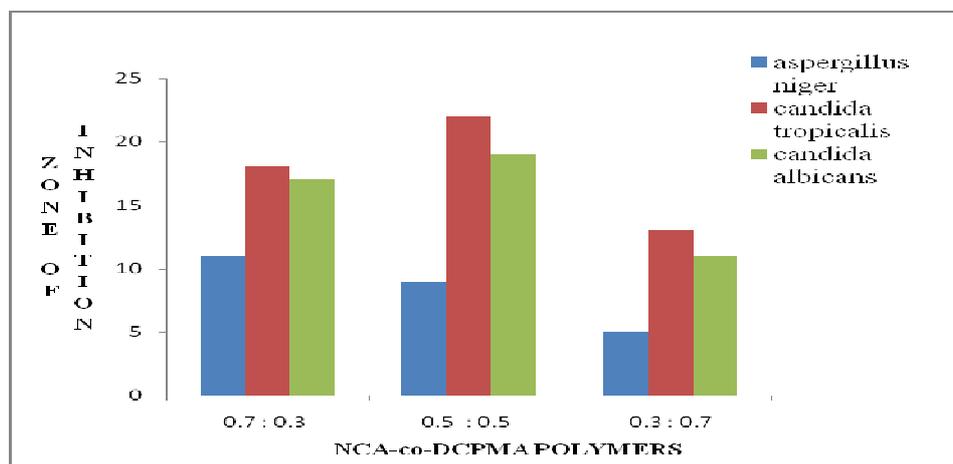


Fig.-9 : Antifungal activity of Poly(NCA-co-DCPMA)

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