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Synthesis, Characterization and Antimicrobial Studies of N-cyclohexylacryl amide and 2, 4-dichlorophenyl acrylate Copolymers

KEYWORDS: free radical polymerization, copolymer composition, reactivity ratios, antimicrobial activity

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ABSTRACT *A series of copolymers N-cyclohexylacrylamide(NCA) and 2,4-dicholorophenyl acrylate(2,4-DCPA) were prepared by free radical polymerization. The copolymer compositions were determined by 1H-NMR analysis. The reactivity ratios of monomers were determined by Fineman-Ross and Kelen- Tudos methods. The reactivity ratios r1.r2 = 0.4 value indicates the formation of random copolymers. Tg found to increase with increasing feed content of DCPA. The antimicrobial studies showed that the copolymers are active against both Bacteria and Fungi. Moreover these copolymers showed excellent antifungal activity.*

Introduction

The synthesis and development of antimicrobial polymers is one of the leading frontiers of research in polymer science. With this view, in our earlier work N-cyclohexylacrylamide was copolymerized with 8-quinolinyl acrylate[1], 2,4-DCPMA[2]. Copolymers with different feed ratio were prepared and characterized by ^{1}H-NMR spectroscopy. The reactivity ratios of monomers were determined by Fineman-Ross , Kelen-Tudos and ext-Kelen-Tudos . The $r_1.r_2$value indicates the formation of random copolymers. It shows antimicrobial activity. In the present work, the synthesis of N-cyclohexylacrylamide and 2,4-dichlorophenylacrylate copolymers in different feed ratio by free radical polymerization was undertaken. The prepared copolymers were characterized by ^{1}H-NMR spectroscopy. Copolymer composition was obtained from ^{1}H-NMR data monomer reactivity ratios were determined by Fineman-Ross[3], Kelen-Tudos[4] and ext.Kelen-Tudos[5] methods.

Experimental

Preparation of N-cyclohexylacrylamide (NCA)

The monomer N-cyclohexylacrylamide[6] 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%. The monomer was confirmed by both ^{1}H-NMR and ^{13}C-NMR.

Preparation of 2,4-dichlorophenyl acrylate (2,4-DCPA)

The 2,4-dichlorophenyl acrylate was prepared by the reactions of 2,4-dichlorophenol with Acryloyl chloride. Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride. Absolute ethanol (400ml) and NaOH (0.2 mol) were added to a three-necked flask that was equipped with stirrer, condenser and thermometer. The flask was placed in a water bath and the contents were stirred until all the NaOH was dissolved. 2,4-dichlorophenol (0.2 mol) was added to the reaction mixture, which was then heated to room temp. and then cooled to 0-5°C by ice. Freshly prepared acryloyl chloride (0.2 mol) was added drop wise to the cooled reaction mixture and stirred for 90 min. The mixture was then poured in to a crushed-ice. Light yellow colored precipitate separated out. The product was filtered, washed thoroughly with cold water and recrystallized from petroleum ether.

Copolymerization

Copolymers of N-cyclohexylacrylamide (NCA) and 2,4 dichlorophenylacrylate (2,4 - DCPA) were prepared by free radical polymerization in methanol/Water medium at 60^{0}C using AIBN as initiator (Scheme-1).

Characterization of Copolymer

The ^{1}H-NMR spectrum of copolymer, poly (NCA-co-DCPA) is shown in Figure 1 and the following peaks are appear in the copolymer spectrum : at 1.34 – 2.47 ppm for cyclohexyl CH_2 group , at 3.71ppm for backbone CH_2 , at 6.9 – 7.5 ppm due to DCPA aromatic protons.

Determination of copolymer composition

The copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymer.. The 2,4-dichloro phenyl peak area[7] is used to determine the copolymer composition. Resonance signal at 6.9-7.5 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

$$X_{DCPA} = \frac{15A\ (aryl)}{3A_{total} + 7A(aryl)} \qquad ----\ (1)$$

where X= mole fraction and A= peak area.

Determination of reactivity ratio of Poly (NCA-co-DCPA)

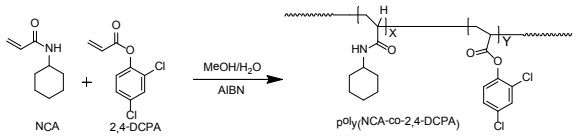
Monomer reactivity ratios provide a tool for estimating the average compositions of copolymers and the relative placement of reactive or functional monomers along the polymer chain[8]. The significant parameters of F-R and K-T equation are presented in Table-1 and extended K-T parameters in Table-2. The reactivity ratios for NCA (r_1) and DCPA (r_2) from the F-R plot (Figure 2) , K-T plot (Figure 3),and extended K-T plot (Figure 4) are given in Table-3. The value of r_1 is less than 1 and r_2 is greater than 1. DCPA is found to be more active than NCA. The system is lying in the range $0< r_1$. $r_2>1$. The nature of the copolymer sequence is random. The r_1. r_2 = 0.4 value indicates the formation of random copolymers, but it is closer to zero than to unity. The more the diverse from unity, the less random the distribution will be[9].

Thermal Studies

Thermal behaviours of Poly(NCA-co-DCPA) is shown Table-4. It is observed that all the copolymers undergo double stage decomposition. Initial weight loss may be due to moisture content. The decomposition at stage-1 occurs in the region 200-390°C due to scission of ester/amide linkages and stage-2 at 390-480°C occurs due to main chain degradation and breakdown of the polymer backbone. Weight loss at stage-2 increases as the mole fraction of DCPA increases. T_g also found to increase with increasing feed content of DCPA.

Volume : 4 | Issue : 1 | Jan 2014 | ISSN - 2249-555X

The increase in T_g may be due to reduction in segmental mobility.



Scheme 1 : Copolymerization of NCA and 2,4-DCPA

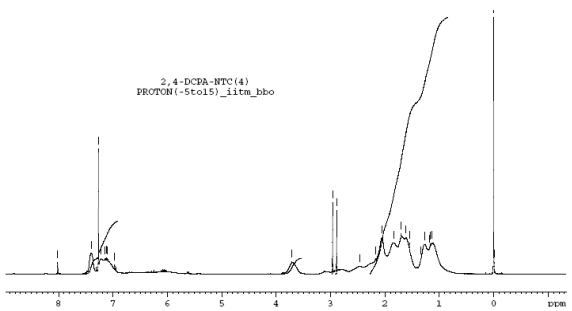


Figure 1 : ^{1}H-NMR spectrum of poly (NCA-co-DCPA) (0.5 : 0.5)

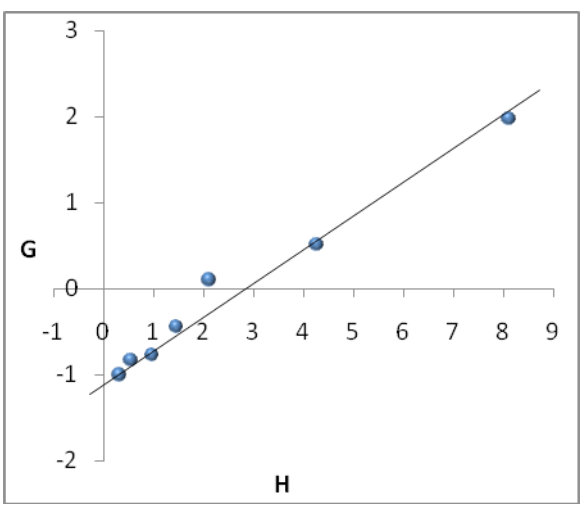


Fig 2 : F-R plot for Poly (NCA-co-DCPA)

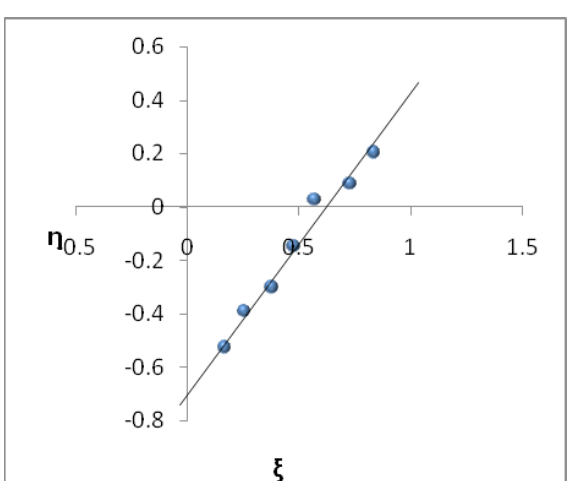


Fig 3 : K-T plot for Poly (NCA-co-DCPA)

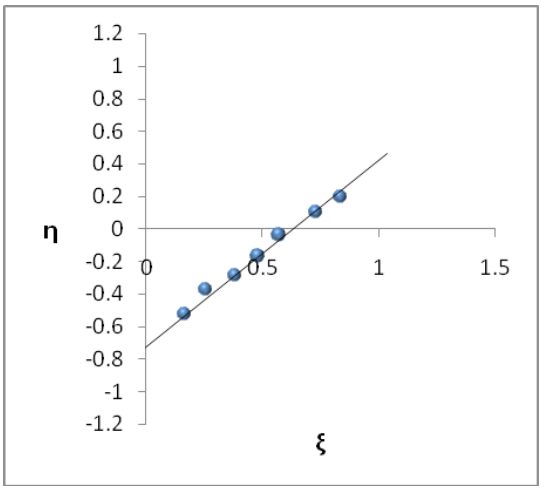


Fig 4 : ext. K-T plot for Poly (NCA-co-DCPA)

Table 1: Fineman-Ross and Kelen – Tudos parameters for the Copolymers of N-cyclohexylacrylamide and 2,4-DCPA

G = F(f-1)/f	H=F²/f	η=Γ/(α+H)	ξ=H/(α+H)
-1.0056	0.3139	-0.5268	0.1644
-0.8344	0.5386	-0.3911	0.2524
-0.7723	0.9601	-0.3022	0.3757
-0.4486	1.4486	-0.1473	0.4759
0.1019	2.0971	0.0276	0.5681
0.5081	4.2575	0.0868	0.7274
1.9741	8.1037	0.2035	0.8355

$$\alpha = \sqrt{H_{min} \cdot H_{max}} = 1.5949$$

Table 2: Extended Kelen-Tudos parameters for copolymers of NCA and2,4- DCPA

NCA : DCPA	ζ_2	ζ_1	Z	F	G	η=G/(α+F)	ξ=F/(α+F)
0.2 : 0.8	2.9862	2.4105	0.8042	0.3120	-0.9925	-0.5259	0.1653
0.3 : 0.7	2.8147	2.3206	0.8135	0.5344	-0.7944	-0.3756	0.2533
0.4 : 0.6	2.9558	2.1559	0.7088	0.9683	-0.7244	-0.2848	0.3806
0.5 : 0.5	3.6104	2.376	0.6739	1.4482	-0.5073	-0.1677	0.4789
0.6 : 0.4	4.392	2.6566	0.6601	2.0822	-0.1404	-0.0383	0.5693
0.7 : 0.3	3.5349	2.0316	0.5613	4.2557	0.6071	0.1041	0.7298
0.8 : 0.2	4.2075	2.03	0.4926	7.9532	1.8877	0.1981	0.8346

Where, $\mu = \mu_2 / \mu_1 = 1.4183$; $\zeta_2 = w(\mu+x) / (\mu+y)$; $\zeta_1 = \zeta_2(y/x)$; $z = \log(1-\zeta_1) / \log(1-\zeta_2)$

$$\alpha = \sqrt{H_{min} \cdot H_{max}} = 1.5752$$

Table 3 : Copolymerization parameter for the NCA (r_1) and 2,4-DCPA(r_2) copolymer.

Methods	r_1	r_2	$r_1.r_2$
Fineman-Ross	0.4	1.12	0.44
Kelen-Tudos	0.43	1.11	0.47
Extended Kelen-Tudos	0.42	1.13	0.47

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Table 4: TGA data for Poly(NCA-co-2,4-DCPA)

Mole fraction of 2,4-DCPA in feed	% weight loss at				IDT	T_1	T_2	T_f	T_g °C
	Initial	Stage-1	Stage-2	Re-sidual					
0.3	2.20	51.5703	39.93	6.1951	130	200-385	385-400	725	76.68
0.5	2.50	50.3774	48.42	-	165	200-390	390-480	895	78.38
0.7	6.30	24.98	67.32	-	160	250-370	370-480	890	140.42
Poly NCA									079.20

Table 5 : Anti bacterial activity of Poly (NCA-co-DCPA)

S.No	Copolymers	Escherichia coli	Staphy-lococcus aureus	Pseu-domonas aerugi-nosa
1	0.3 NCA : 0.7 DCPA	20 mm	18 mm	02 mm
2	0.5 NCA : 0.5 DCPA	16 mm	20 mm	03 mm
3	0.7 NCA : 0.3 DCPA	15 mm	20 mm	02 mm
4	Ciprofloxacin	27 mm	17 mm	20 mm

Table 6 : Anti fungal activity of Poly (NCA-co-DCPA)

S.No	Compounds	Aspergillus niger	Candida albicans	Candida kefyr
1	0.3 NCA : 0.7 DCPA	15 mm	15 mm	16 mm
2	0.5 NCA : 0.5 DCPA	25 mm	13 mm	18 mm
3	0.7 NCA : 0.3 DCPA	20 mm	14 mm	17 mm
4	Ketoconazole	15 mm	14 mm	15 mm

Antimicrobial studies

The polymers were tested against selected fungus and bacteria by standard agar well diffusion method. The plates are prepared as per the standard method[10-12]. The results are mentioned in Table-5 and Table-6. DMSO was used as solvent control. Ciprofloxacin was used as reference antibacterial agent . Ketoconazole was used as reference antifungal agent. The tests were carried out in triplicates. The antimicrobial studies showed that the copolymers are active against both Bacteria and Fungi. Moreover these copolymers showed excellent antifungal activity. So that the copolymers may be used as good antifungal agent. The comparative studies are shown in Figure 5 and Figure 6.

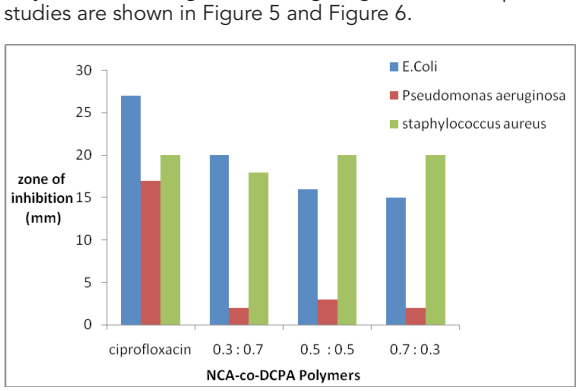


Figure 5 : Comparison of Zone of inhibition of Poly(NCA-co-2,4-DCPA)with bacteria

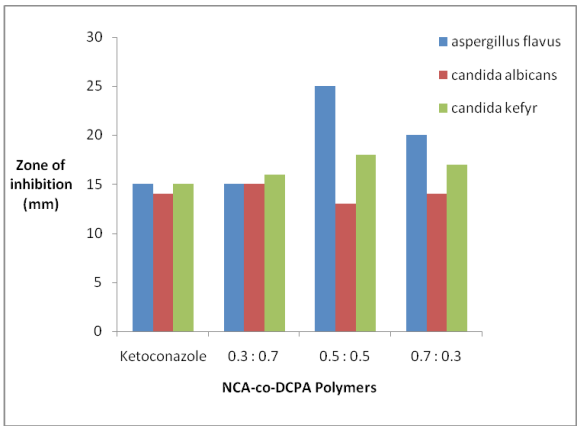
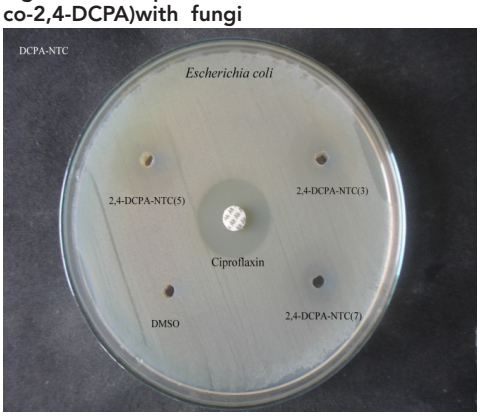


Figure 6 : Comparison of Zone of inhibition of Poly(NCA-co-2,4-DCPA)with fungi



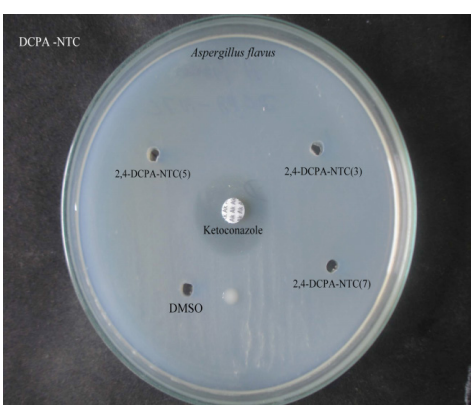


Figure 7 : Selected pictures of antimicrobial study of Poly(NCA-co-2,4-DCPA)

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Volume : 4 | Issue : 1 | Jan 2014 | ISSN - 2249-555X

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