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Novel acrylic copolymers: synthesis, characterization and antimicrobial studies.

*Hetal Patel, Mitesh Patel, Kirit Patel and Rajni Patel**

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India. Fax no.: +912692-236475. E-mail: khp293@yahoo.co.in,

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Abstract: The monomer 2,4-dichloro phenyl acrylate (2,4-DCPA) was synthesized from 2,4-dichlorophenol and characterized by conventional methods. The homopolymers of 2,4-DCPA and its copolymers with 8-quinolinyl methacrylate (8-QMA) in different feed ratio were prepared by free radical polymerization using dimethyl formamide (DMF) as a solvent and 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The resulting polymers were characterized by Infrared Spectroscopy. UV spectral data were employed to obtain the reactivity ratios of the monomers, 2,4-DCPA and 8-QMA. The results showed that 2,4-DCPA is more reactive than 8-QMA. Average molecular weights and intrinsic viscosities determined by Vapour pressure osmometer (VPO) lies in the range of 7900 to 10890 and 0.021-0.036 $dl.g^{-1}$ respectively. 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.

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].

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 [4]. However, they can have the limitation of residual toxicity even when suitable amounts of the agents are added [5].

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 [6]. Chlorine containing phenyl methacrylate and its polymers has been used as biocides in various applications [7, 8]. The use of polymeric system based on acrylic derivatives as biomaterials for clinical application has increased during last two decades because of their excellent biocompatibility and long term stability [9].

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 [10]. 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 end application of the copolymers. The main aim in commercial copolymerization is to achieve a desired product composition. Ibrahim Erol [11, 12] prepared new methacrylate monomers, their derivatives and copolymerized these monomers with various vinyl monomers. Reactivity ratios were calculated by applying conventional linearization methods of Fineman-Ross (F-R) and Kelen-Tudos (K-T). Vijayanand [13] and coworkers prepared copolymers with various contents of 4-nitro-3-methyl phenyl mehthacrylate and GMA in methyl ethyl ketone solvent using benzoyl peroxide as free radical initiator at 70°C. Characterization of the resulting polymers was done by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Reactivity ratios were calculated by F-R & K-T methods. Thermal analysis was also carried out for these polymers.

So far it was found that the presence of chlorine in the polymers enhances the antimicrobial property. This work has demonstrated that 8-quinoline moiety also has antimicrobial activity which is more than chlorine containing phenyl moiety. The antimicrobial activity of 8-quinoline moiety although known, not much systematic work has been carried out on copolymers derived from 8-quinoline methacrylate.

The present paper reports the synthesis, characterization, monomer reactivity ratios, thermal analysis and antimicrobial activity of homopolymers of 2,4-DCPA, 8-QMA and their copolymers.

Results and Discussion

The synthesized monomer structure of 2,4-DCPA was confirmed by IR and ^{1}H NMR techniques. All the expected signals for 2,4-DCPA were observed. HPLC result showed that the synthesized monomer is 99.85% pure.

IR of 2,4-DCPA (cm^{-1}): 3015(ν_{CAr-H}), 2978(ν_{-CH3}), 1756($\nu_{C=O}$), 1640($\nu_{C=C}$), 1230(asymmetric ν_{C-O-C}), 1150(symmetric ν_{C-O-C}), 890(-CH bending mode of vinyl group), 730 (rocking mode of vinyl group), 667 (ν_{C-Cl}) . The two absorption bands at 1593 and 1480 cm^{-1} may be assigned as the characteristic absorption of o-substituted phenyl ring.

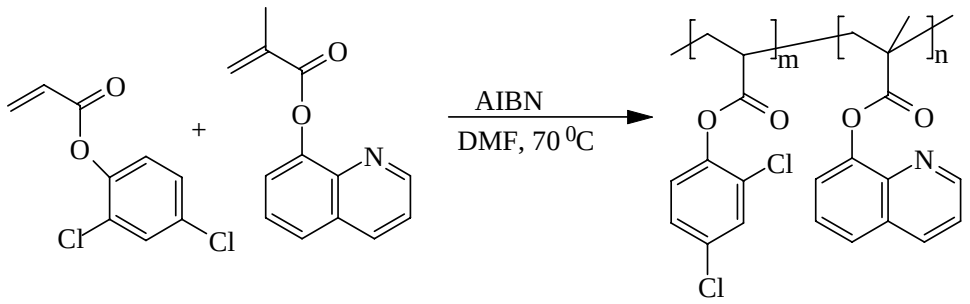
^{1}H-NMR of 2,4-DCPA (δ ppm) (60MHz): 5.98 (1H, -CH=), 6.36 (1H) and 6.53 (1H) (non-equivalent methylene protons), 7.16-7.43 (3H, aromatic protons).

The copolymerization of 2,4-DCPA with 8-QMA in DMF solution was studied in a wide composition interval with mole fraction of 2,4-DCPA ranging form 0.2 to 0.8 in

the feed as shown in Tab. 1. To satisfy the differential copolymerization equation for calculation or reactivity ratio, the reaction time was so selected as to obtain conversion less then 10% w/w. The scheme for synthesis of copolymers is presented in Fig. 1.

Tab.1. Copolymer Composition data and reactivity ratio of monomer (2,4-DCPA) and co monomer (8-QMA).

Sample code no.	Monomer feed composition		% Conversion (w/w)	Content of 2,4-DCPA in copolymer (mol/mol) [m_1]	Reactivity Ratio	
					F-R method	
	2,4-DCPA [M_1] mole	8-QMA [M_2] mole			r_1	r_2
1	1.0	-	-	-		
2	0.2	0.8	9.89	0.235		
3	0.4	0.6	9.75	0.428		
4	0.5	0.5	10.28	0.539	0.86	0.66
5	0.6	0.4	9.58	0.627		
6	0.8	0.2	8.90	0.790		
7	-	1.0	-	-		



2,4-DCPA 8-QMA Poly(2,4-DCPA-co-8-QMA)

Fig. 1. Reaction scheme for synthesis of copolymers.

The IR-spectra of the copolymers are shown in Fig. 2. The two medium bands at 2993 and 2947 cm^{-1} may be attributed to the asymmetric and symmetric stretching vibrations due to C-H of methylene moiety, where as strong absorption at 1471 cm^{-1} may be due to ν_{C-H} bending vibration of $-CH_2-$ group. Two sharp and distinct bands at 1770 and 1215 cm^{-1} may have contributions from $\nu_{C=O}$ and ν_{C-O} stretching vibration of ester group. The vibrations due to phenyl ring are assigned to strong absorptions at 1461 and 1582 cm^{-1}. The ν_{C-Cl} stretching frequency is assigned to the band at 670 cm^{-1}. The spectrum also show three strong bands at 1474, 1505 and 1605 cm^{-1} which are due to the characteristic absorption of the 8-o-substituted quinoline ring system.

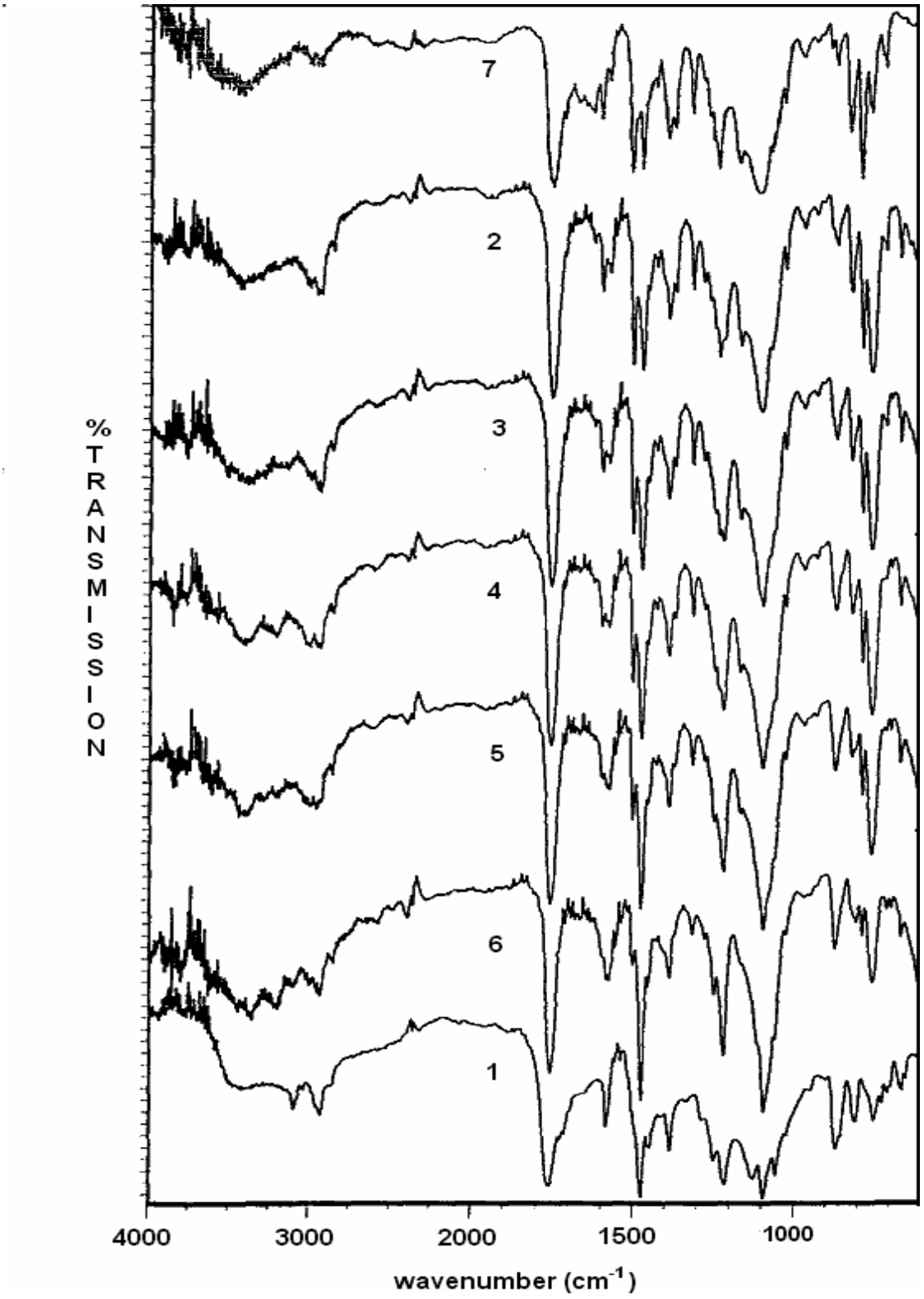


Fig. 2. FT-IR spectra of 2,4-DCPA-co-8-QMA homo and copolymers.

The average composition of each copolymer sample was determined from the corresponding UV-spectrum as shown in Fig. 3. The composition of each monomer in the polymer was obtained form measurement of absorption at λ_{max}=272 nm which is characteristic λ_{max} for 2,4-DCPA. From monomer feed ratios and copolymer compositions, the reactivity ratios of 2,4-DCPA and 8-QMA were determined using

Fineman-Ross method [14] and the results are presented in Tab. 1. The value of reactivity ratio for 2,4-DCPA (r_1) and 8-QMA (r_2) form F-R plot is 0.86 and 0.66 respectively. The value of r_1 is greater than r_2. 2,4-DCPA is found to be more reactive than 8-QMA. The product r_1r_2 is less than 1, thus the system gives rise to azeotropic polymerization at a particular composition of the monomer which is calculated using equation 1 [15].

$$N_1 = \frac{(1-r_2)}{(2-r_1-r_2)} \tag{1}$$

where N_1= mole fraction of monomer 2,4-DCPA in feed.

From above equation the value of N_1 is 0.701. When the mole fraction of the monomer 2,4-DCPA in the feed is 0.701, the copolymer formed will have the same composition as that of feed. When the mole fraction of feed is less than 0.701 with respect to 2,4-DCPA, the copolymer is richer in this monomeric unit. When the mole fraction of the monomer 2,4-DCPA in the feed is above 0.701, the copolymer is relatively richer in 8-QMA monomeric unit.

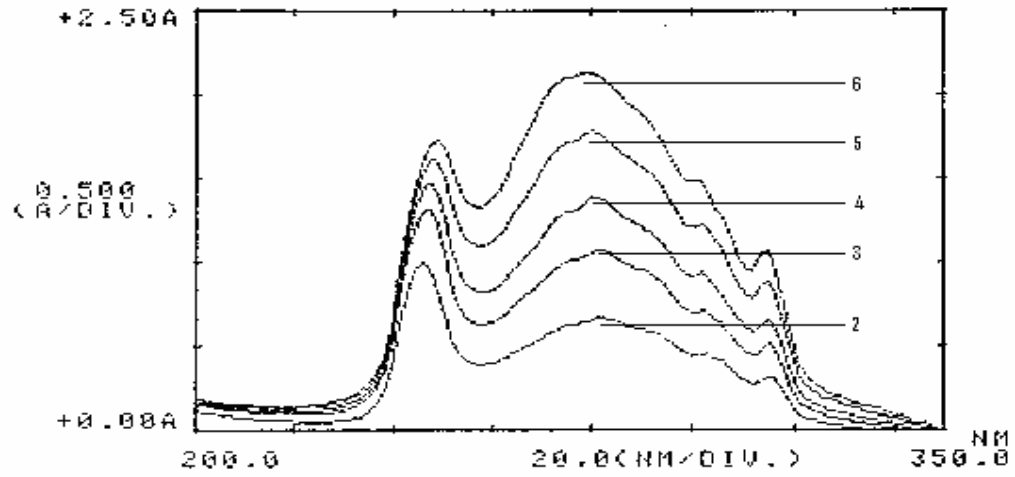


Fig. 3. UV spectra of poly(2,4-DCPA-co-8-QMA) in chloroform.

The number average molecular weights of poly(2,4-DCPA), poly(8-QMA), and five samples of copolymers were obtained from Vapor pressure osmometry using DMF as solvent at 90 °C. It is observed from data that value of number average molecular weight ranges from 7900 to 10800 where as intrinsic viscosity is in the range of 0.021-0.036 $dl.g^{-1}$. These data clearly indicates that as 8-QMA content in copolymer increases molecular weight and viscosity as well. The results are presented in Tab. 2.

Typical thermograms obtained by plotting percentage of residual weight against temperature for poly(2,4-DCPA), poly(8-QMA) and their copolymers are given in Fig. 4 and corresponding data are presented in Tab. 3. The data clearly indicate that all polymers undergo a two step decomposition. Homopolymer of 2,4-DCPA starts decomposing at 191°C while the copolymer containing 8-QMA begins to decompose at 128 °C. The decomposition temperature is lowered by the presence of 8-QMA. It has already been found that homo(8-QMA) has a lower decomposition temperature than homo(2,4-DCPA). In the copolymer, possibly 8-quinoline moiety starts to decompose first. Activation energy (E_A) and Integral procedural decomposition

temperature (IPDT) were determined by Broido's method [16] and Doyle's method [17] respectively. Thermal studies showed that the polymers undergo first step decomposition in the range of 128-340 °C and second step decomposition occurs in the range of 257-454°C.

Tab. 2. Average Molecular Weights and Intrinsic Viscosity data for poly(2,4-DCPA), poly(2,4-DCPA-co-8-QMA) and poly(8-QMA).

Sample Code No.	$\overline{Mn}$	Intrinsic Viscosity [η] ($dl.g^{-1}$)
1	7900	0.021
2	10500	0.034
3	10200	0.031
4	9600	0.029
5	9100	0.026
6	8500	0.025
7	10800	0.036

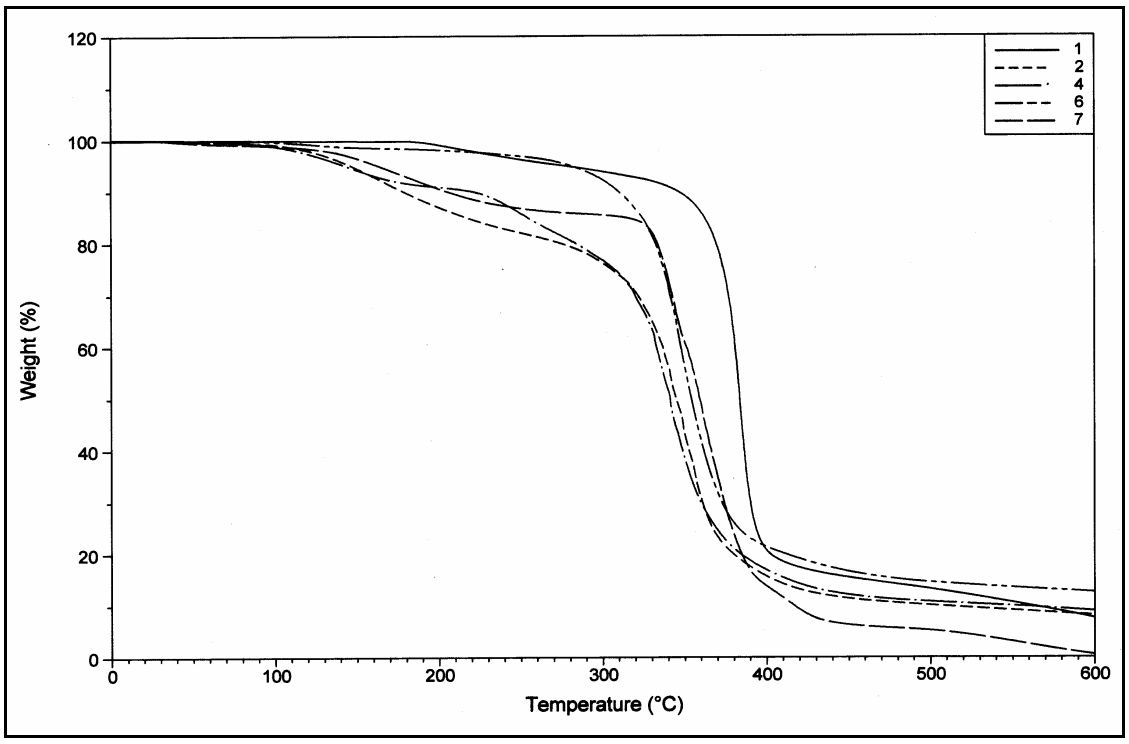


Fig. 4. TG thermograms of poly(2,4-DCPA), poly(8-QMA) and poly(2,4-DCPA-co-8-QMA).

Tab. 3. TGA data for homo- and copolymers of 2,4-DCPA with 8-QMA.

Sample Code No.	% Weight loss at various temperature (°C)					Decomp. Temp. Range (°C)	T_{max} [a] (°C)	T_{50} [b] (°C)	IPDT [c] (°C)	Activation Energy [d] (E_A) (kJ·mole^{-1})
	200	300	400	500	600					
1	1	6	79	87	92	191-340 341-424	389	383	403	75
2	13	24	84	90	92	128-282 283-438	343	335	369	56
4	9	23	83	89	91	138-256 257-442	348	342	372	58
6	2	8	79	85	87	284-454	355	353	374	63
7	9	15	86	95	100	140-322 323-445	364	358	375	68

[a] Temperature for maximum rate of decomposition
[b] Temperature for 50% weight loss
[c] Integral procedural decomposition temperature
[d] By Broido's method

Tab. 4. DTA data for homo- and copolymers of 2,4-DCPA with 8-QMA.

Sample Code No.	T_1 [a] (°C)	T_2 [b] (°C)	T_b [c] (°C)	Activation Energy [d] (E_A) (kJ·mole^{-1})	Reaction Order
1	385	440	412	76.44	1
2	348	442	380	59.80	1
4	342	450	372	55.81	1
6	350	455	384	64.40	1
7	352	422	403	65.52	1

[a] Starting Temperature of DTA trace
[b] Ending Temperature of DTA trace
[c] Peak maxima Temperature of DTA trace
[d] Activation Energy by Reich's method

The results of DTA for homo and copolymers are shown in Tab. 4. The activation energy for thermal degradation and reaction order were determined by Reich's method [18]. The activation energy for thermal degradation of polymers ranged form 56-76 K.J.mole^{-1}.

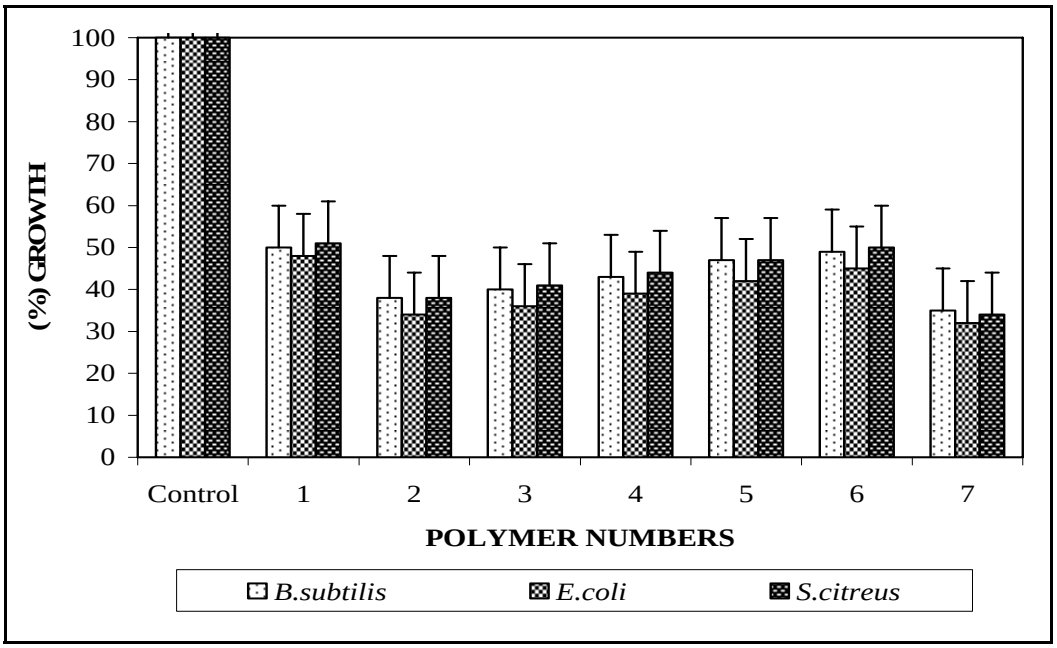


Fig. 5. Effect of 2,4-DCPA-co-8-QMA homo and copolymers on growth (%) of bacteria.

The microbial screening on the homo and copolymer of 2,4-DCPA and 8-QMA was carried out. The results obtained are presented in Fig. 5, 6 and 7. It is observed from these results that poly(2,4-DCPA) allows 48-51%, 43-48%, and 42-44% growth for bacteria, fungi and yeast respectively.

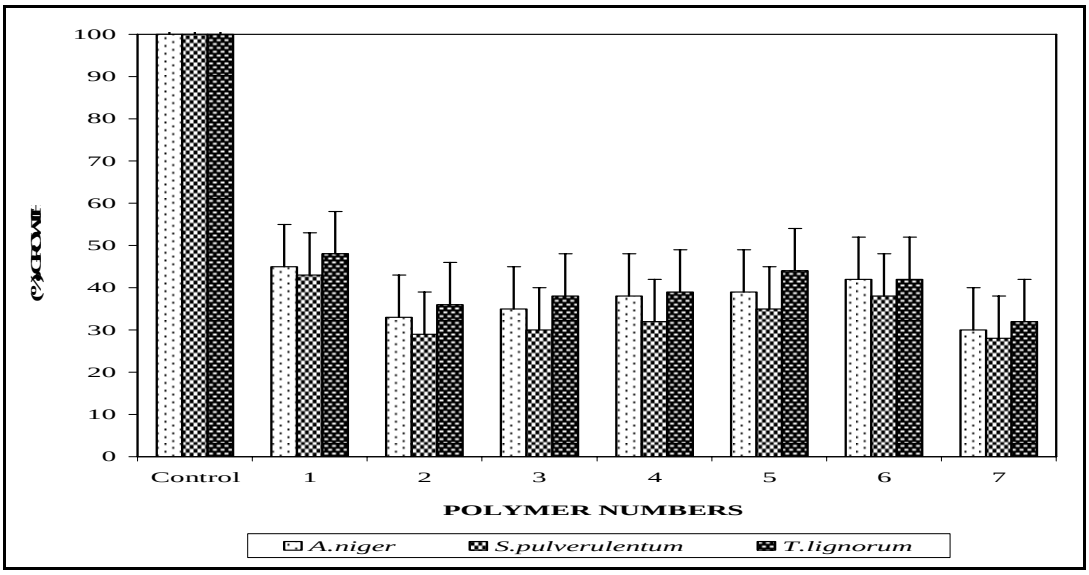


Fig. 6. Effect of 2,4-DCPA-co-8-QMA homo and copolymers on growth (%) of fungi.

Copolymers of 2,4- DCPA with 8-QMA allows 34-49% growth for bacteria, 29-46% growth for fungi and 29-41% growth for yeast, while poly(8-QMA) registers 32-35%, 28-32% and 27-28% growth for bacteria, fungi and yeast respectively. However, during this period control culture (without polymer) exhibited maximum growth (100%). All copolymer systems impart almost similar antimicrobial properties against

various microorganisms. As 2,4-DCPA content in copolymer increase antimicrobial activity decrease, this may be due to higher biological activity of quinoline moiety of 8-QMA compared to 2,4-dichlorophenyl group of 2,4-DCPA.

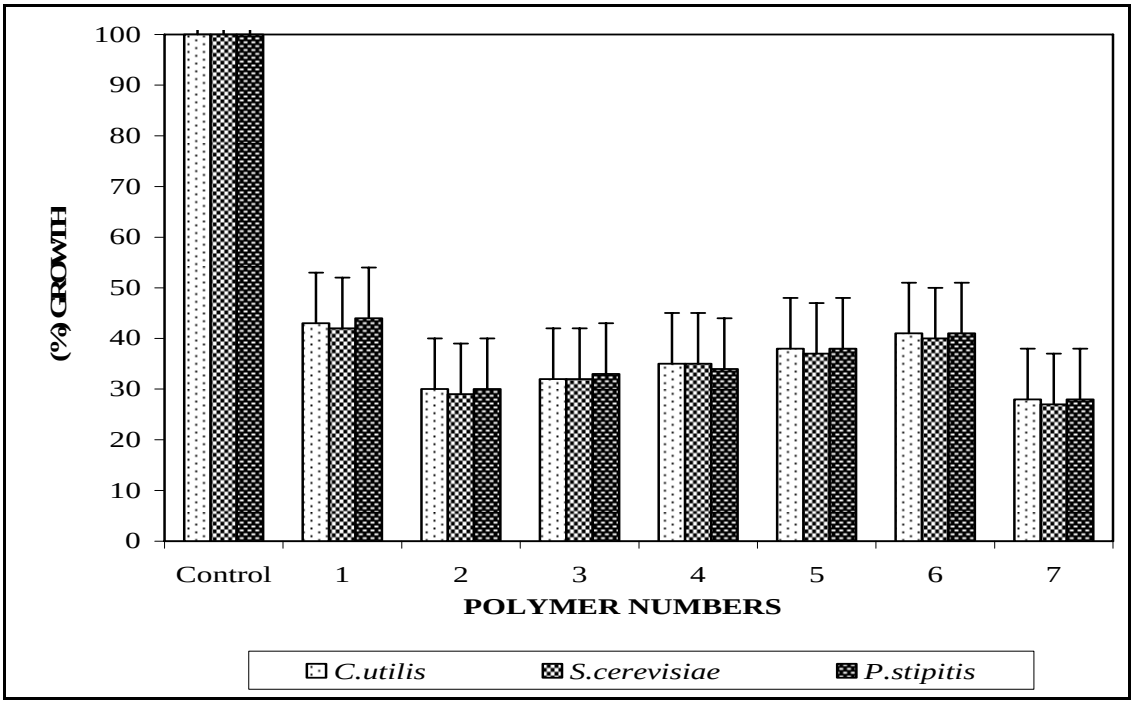


Fig. 7. Effect of 2,4-DCPA-co-8-QMA homo and copolymers on growth (%) of yeast.

Conclusions

The homopolymer and copolymers of 2,4-DCPA and 8-QMA having various compositions were synthesized in solution by free radical polymerization. The structure of the monomer was confirmed by FT-IR and ^{1}H-NMR spectroscopic techniques. The homopolymer and copolymers were characterized by FT-IR spectroscopy. The copolymer compositions were obtained by UV-spectroscopic technique. The reactivity ratio of 2,4-DCPA (r_1) is greater than 8-QMA (r_2). The product r_1r_2 is less than1. So the system gives rise to azeotropic polymerization at a particular composition of the monomer. The VPO results shows that the molecular weight of copolymers increases as the content of 8-QMA in copolymers increases. Thermogravimetric analysis indicated that the thermal stability of copolymers increases with increase in 2,4-DCPA. As 2,4-DCPA content in copolymers increases the antimicrobial activity decreases, this may be due to the higher biological activity of quinoline moiety of 8-QMA compared to 2,4-DCPA.

Experimental part

Materials

2,4-dichloro phenol (S.D.Fine chemicals), 8-hydorxy quinoline (Merck), 2,2'-azobisisobutyronitrile (Aldrich), Benzoyl chloride (S.D.Fine chemicals) were used as received. Solvents purified by fractional distillation were used in the reaction.

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

Acryloyl chloride was prepared as reported [19] and used for further reaction. The esterification was performed with acryloyl chloride and 2,4-dichloro phenol. 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 acryloyl 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 when a light brown color liquid settled down. It was extracted with ether. The ether layer was separated out and evaporated. The liquid monomer obtained after evaporation of ether was dried over anhydrous calcium chloride in vacuum desiccator. The product yield was 82%.

Synthesis of 8-quinolinyl methacrylate (8-QMA)

Synthesis and characterization of 8-QMA is already discussed in our earlier publication [20].

Copolymerization

The homo and copolymers were synthesized by free radical polymerization of 2,4-DCPA with 8-QMA using DMF as a solvent and AIBN as an initiator at 70 °C with constant stirring. The resulting polymer solution was slowly poured into large volume of methanol with stirring when the polymer was precipitated out. It was filtered and washed with methanol. Solid polymers were purified by repeated precipitation by methanol from solution in DMF and finally dried under vacuum. Tab. 1 indicates the reaction parameters for copolymerization.

Characterization

NICOLET 400_D FT-IR spectrophotometer was used to record the infrared spectrum of homo and copolymers on solid KBr pellets. Copolymer composition and reactivity ratios were determined using Shimadzu-160-A UV-visible spectrophotometer. KNAUR (Germany). Vapour pressure osmometer was used to determine the number average molecular weight. TA instrument (U.S.A.)-2960 thermo gravimetric analyzer was used to record the thermograms of polymers at a heating rate of 10 °C/min in nitrogen atmosphere. DTA trace was obtained with the TA instrument (U.S.A.)-2960 differential analyzer at a heating rate of 10 °C/min under nitrogen atmosphere.

Microbial Screening

The homo- and co-polymers thus obtained, were tested against different microorganism that is commonly employed for biodegradability tests. Bacterial strain (*Bacillus subtilis, Escherichia coli and Staphylococcus citreus*), fungal strain (*Aspergillus niger, Sporotichum pulveruletum and Trichocerma lignorum*) and yeast strain (*Candida utilis, Saccharomyces cerevisiac and Pichia stipitis*) were taken for the antimicrobial activity study.

The bacterial strains were grown in Nutrient broth (N-broth) and fungal strains were grown in Sabourand's dextrose broth. Yeast extract peptone dextrose (YEPD) was added to N-broth to grow yeast strains, with or without indicated polymers. The content of the flasks were incubated in a shaker at room temperature. At specific time

intervals (20-48 h), the absorbance was measured at 660 nm for bacteria and yeast cultures. % inhibition (*I*) is obtained from equation 2.

$$I = \frac{100(X - Y)}{X} \quad (2)$$

where X= absorbance of bacterial suspension in control set and Y= absorbance of bacterial suspension in test set.

The fungal cultures were harvested after 48 hr, and the dry cell mass was determined gravimetrically. The % inhibition (*I*) is obtained from equation 2 where X= Weight of dry fungal cell mass in control set and Y= Weight of dry fungal cell mass in test set. The details of experimental procedure have been reported elsewhere [21].

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