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Research Article

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Novel Acrylic Copolymers Derived from 4-Chloro-3,5-Dimethyl Phenol: Synthesis, Characterization and Antimicrobial Screening

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ABSTRACT

A series of methacrylate polymers derived from 4-chloro-3,5-dimethyl phenyl methacrylate (CDMPMA) with comonomer tetrahydrofurfuryl methacrylate (THFMA) were synthesized via free radial polymerization technique. The copolymers were characterized by fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (^{1}H-NMR), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). All polymers were thermally stability up to 200^{o}C under nitrogen atmosphere. The reactivity ratio of monomers in copolymer was obtained by different linearization methods using ^{1}H NMR data. Antimicrobial activities of the homopolymers and copolymers were investigated for various microorganisms such as bacteria, fungi and yeast.

Keywords: Methacrylate polymers; Reactivity ratio; Thermogravimetric analysis; Antimicrobial activity

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INTRODUCTION

Contamination by microorganisms is of great concern in a variety of applications such as medical devices, healthcare products, hospitals, dental office equipment, water purification systems, food packaging, food storage, household sanitation, etc. Bacterial contamination of biomedical devices, for example, permanent catheters or implants, is a major problem in those medical disciplines employing biomaterials [1-3]. The use of polymeric system based on acrylic derivatives as biomaterials for clinical application has increased during the last two decades because of their excellent biocompability and long-term stability [4]. Various studies have identified the properties of polymeric systems based on heterocyclic methacrylates for clinical applications [5-7] such as drug delivery [8] and cartilage [9,10] or bone repair materials, blood filters, tubing connector, syringes, surgical trays, blood-pump housing and surgical-blade-dispensers[5-7]. Chlorine containing phenyl methacrylate and its polymers has received considerable attention in recent years due to their varied applications. These chemicals find application as biocides. These are also useful in electro photoconductive layers for colour proofing, high colour filters for liquid-crystal display devices and solid-state image pick up device [11-13], films, packaging materials, food stuffs, sanitary application and many others [14,15]. In this investigation, the homopolymers of 4-chloro-3,5-dimethyl phenyl methacrylate (CDMPMA) and tetrahydrofurfuryl methacrylate (THFMA) and their copolymers were prepared by free radial polymerization technique. The polymers were characterized by FTIR, ^{1}H-NMR, TGA and gel permeation chromatography (GPC). The determination of copolymer composition and reactivity ratio of the monomers is important in evaluating the specific application of the copolymer [16]. ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [17-21]. The polymers were screened for antimicrobial activities against bacteria, fungi and yeast.

EXPERIMENTAL SECTION

Materials

p-chloro-m-Xylenol was obtained from Merck. Tetrahydrofufuryl methacrylate was purchased from Sigma-Aldrich and purified via vacuum distillation. 2,2'-azobisisobutironitrile was purchased from S.D. Fine chemicals. Benzoyl chloride and methacrylic acid were procured from Loba chemical and used without any further purification.

Synthesis of methacryloyl chloride

Methacryloyl chloride was prepared according to the process reported in the literature [22]. A mixture of methacrylic acid (1 mole), benzoyl chloride (2 mole) and hydroquinone (0.0025 mole) was distilled at fairly high rate through an efficient column. The distillate was collected in a receiver containing hydroquinone (0.0025 mole). The crude product obtained at temperature between 85-100°C was redistilled through the same column at 95-96°C. The product yield was 70%.

Synthesis of 4-chloro-3,5-dimethylphenyl methacrylate

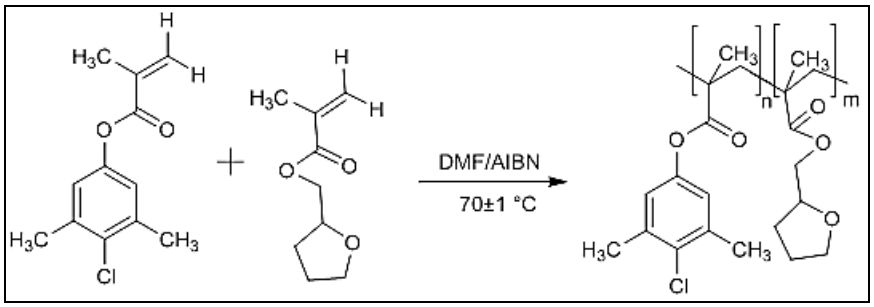
4-chloro-3,5-dimethylphenyl methacrylate was prepared following the standard procedure given in the patent [23].

Homopolymerization

Homopolymers of monomers CDMPMA and THFMA were synthesized by free radical polymerization in DMF solvent using AIBN as a free radical initiator. The polymers were purified by repeated precipitation by methanol from DMF and then filtered and dried until a constant weight was attained.

Copolymerization

Copolymers of CDMPMA with THFMA having different composition were synthesized by free-radical polymerization technique using AIBN as free radical initiator and N,N'-dimethylformamide as a solvent. The feed composition monomer and comonomer is given in Table 1. Appropriate quantities of monomer, comonomer, N,N'-dimethylformamide and AIBN (0.5% w/w based on total monomers 1 and 2) were taken in a polymerization tube equipped with reflux condenser. The reaction mixture was heated at 70ºC for 5 hrs with stirring. It was then cooled to room temperature and the resulting polymer solution was slowly poured in a large volume of methanol with stirring when the polymer precipitated out. It was filtered and washed with methanol. Solid polymers were purified by repeated precipitation using methanol from solution in N,N'-dimethylformamide and finally dried. Scheme 1 shows the reactions leading to the formation of copolymers of CDMPMA with THFMA.



Scheme 1: Synthesis of poly(CDMPMA-*co*-THFMA)

Table 1: Composition data for free radical copolymerization of CDMPMA (1) with THFMA (2) in DMF solution at 70 °C

Sample code	M_1	Conversion (%)	Intensity of protons		m_1
			I_{Aro}	I_{Ali}	
R2	0.8	5.8	2.97	17.63	0.9
R3	0.6	6.12	2.81	23.13	0.71
R4	0.5	4	2.69	27.87	0.58
R5	0.4	10.4	2.47	35.41	0.43
R6	0.2	4	1.25	33.25	0.24

M_1 and m_1 are the mole fraction of CDMPMA in the feed and copolymer respectively.

Characterization technique

Infrared spectra of the solid sample of monomer and polymers were recorded in the range from 4000 to 400 cm^{-1} using Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer by solid KBr pellet method. The composition of the monomers in the copolymers was obtained by Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) in solvents $CDCl_3$ and DMSO on a Bruker 400MHz. ^{1}H NMR was employed to

determine the reactivity ratio by methods of Fineman-Ross (F-R), Inverted F-R, Kelen-tudos (K-T) and Extended K-T [24-26]. Molecular weights of the polymers were obtained from a waters 410 gel permeation chromatography instrument equipped with a differential refractive index detector. Tetrahydrofuran was used as the eluent and polystyrene standards were employed for calibration. The measurements were taken at 30°C with tetrahydrofuran as the mobile phase on columns (Waters Styragel HR 4). The thermogravimetric analysis (Mettler Toledo TGA/DSC) of the Polymer carried out under a nitrogen atmosphere in the temperature range from 25 to 700°C. The heating rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

Characterization of monomer and polymers

The IR spectrum of monomer CDMPMA is shown in Figure 1. The important absorptions (cm^{-1}) are:
2928 (νCH_3), 1736 (νC=O), 1634 (νC=C), 1287 (asymmetric νC-O-C) and 1261 (symmetric νC-O-C), 960 (-CH bending mode of vinyl group), 705 (νC-Cl), 1600 and 1467 (bands due to phenyl ring). The copolymers characterized by IR spectroscopy and the IR spectra of copolymers are shown in figure below. The copolymers have absorptions in the range 2984-2930 cm^{-1} which are attributed to the C-H stretching vibrations of methyl and methylene groups. The strong bands at 1392 and 1452 cm^{-1} are assigned to symmetric and asymmetric bending vibrations of -CH_3 group. The band ~1450 has contribution from -CH_2 bending vibration also. The strong absorption at 1729 cm^{-1} and medium absorption between 1264-1240 cm^{-1} have respectively contributions from $\nu_{C=O}$ and ν_{C-O} stretching vibrations of ester group. The band at 1150 has predominate contribution from C-O stretching in the tetrahydrofuran ring. The band at 892 cm^{-1} is due to ν_{C-H} out of plane bending in phenyl ring. The sharp band at 1602 cm^{-1} is traced to benzene ring breathing. Interestingly the relative intensity of this band decreases with decrease in CDMPMA content in the copolymers. The peak at 1460 cm^{-1} has contribution from C-C stretching in aromatic ring. The band around 1298 cm^{-1} is due to ν_{C-O-C} stretching of the ester moiety; interestingly the relative intensity of this band decreases with decrease in CDMPMA content in the copolymers. As the content of CDMPMA in poly(CDMPMA-*co*-THFMA) increases band intensity at 705 cm^{-1} due to ν_{C-Cl} also increases. The absence of absorption at 1634 cm^{-1} in the polymers is indicative of the participation of the vinyl group in the polymerization. The NMR spectrum of CDMPMA is shown in Figure 2.
The resonance are: ^{1}H-NMR (δ ppm) (400MHz) 1.99 (3H) (methyl protons), 2.50 (6H) (methyl protons), 5.90 (1H) and 6.26 (1H) (nonequivalent methylene protons), 7.05 (2H) (aromatic protons).
The ^{1}H - NMR spectrum of a typical copolymer of CDMPMA with THFMA (0.8:0.2) is shown in Figure 3. The aromatic protons (δ ppm) are seen at ~ 6.7 and the resonances due to aliphatic proton appear in the region 1.1 to 4.0 (Figure 4).

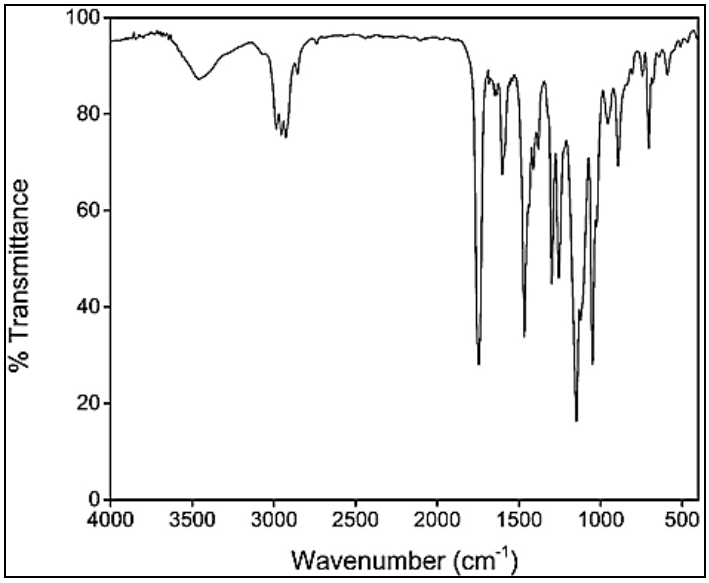


Figure 1: IR spectrum of CDMPMA

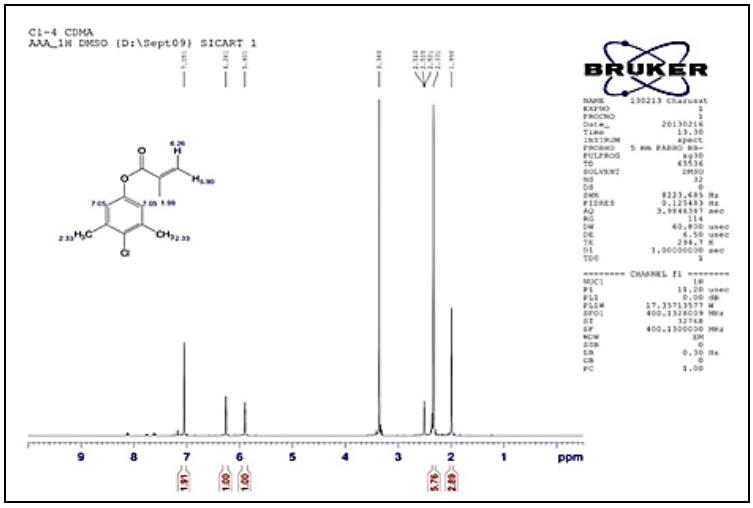


Figure 2: ^{1}H NMR spectrum of CDMPMA

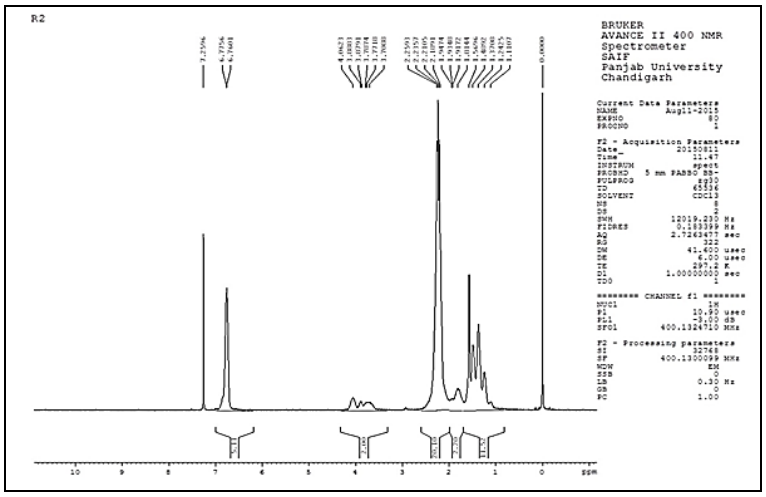


Figure 3: ^{1}H NMR spectrum of poly(CDMPMA-*co*-THFMA) (sample code-2)

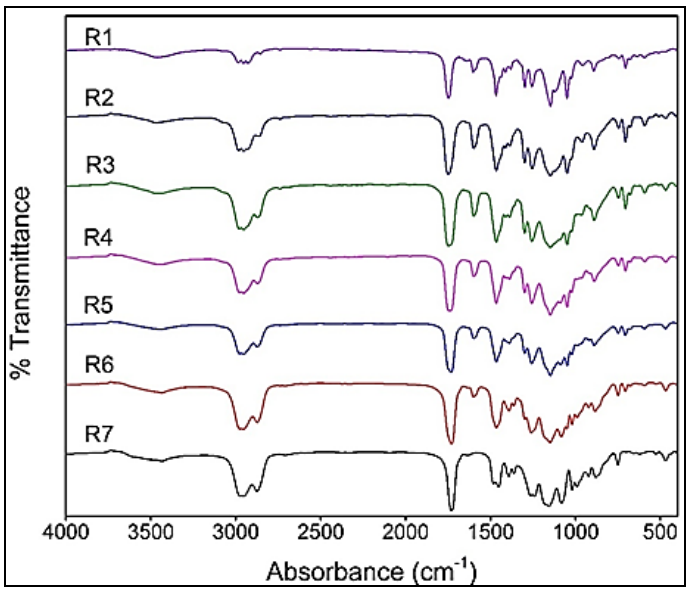


Figure 4: IR spectrum of homo and copolymer of CDMPMA with THFMA

Copolymer composition and reactivity ratio

Copolymers of CDMPMA with THFMA were synthesized by taking different mole fractions of the monomers in feed ranging from 0.2 to 0.8 (Table 1). The copolymers were found to be soluble in N,N-dimethylformamide, chloroform, tetrahydrofuran, toluene, but insoluble in methanol, ethanol and n-hexane. The structures of

copolymers are represented in Scheme 1. The compositions of the copolymer samples were determined from the ^{1}H-NMR spectrum. The ^{1}H-NMR data also lead to the evaluation of reactivity ratios. Thus, the mole fraction of CDMPMA in the copolymer chain was calculated by measuring the integrated intensities of aromatic protons and aliphatic protons in the copolymers. Following expression is used to determine the composition of copolymers. Let m_1 be the mole fraction of CDMPMA and (1-m_1) be that of THFMA. CDMPMA contains 2 aromatic protons and 11 aliphatic protons and THFMA contains 14 aliphatic protons.

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Inensities of aliphatic protons } (I_{Ali})}$$

$$= \frac{2m_1}{14-3m_1} \text{----- (1)}$$

Which on simplification gives the following equation:

$$m_1 = \frac{14C}{2+3C} \text{----- (2)}$$

From Eq. (2), the mole fraction of CDMPMA in the copolymers was determined by measuring the intensity of aromatic proton and aliphatic protons signals. Table 1 gives the value C and corresponding mole fractions of CDMPMA in the copolymers. The plot of mole fraction of CDMPMA (M_1) in the feed vs. that in the copolymer (m_1) is shown in Figure 5. It indicates that the system can form random polymerization. Figure 3 showed that ^{1}H-NMR spectrum of poly(CDMPMA-*co*-THFMA) (sample code- R2). From the monomer feed ratios and the copolymer composition, the reactivity ratios of CDMPMA and THFMA were determined by application of the Fineman-Ross (F-R) [24], Inverted Fineman-Ross (F-R), Kelen- Tudos (K-T) [25], and Extended Kelen-Tudos (Ext K-T) [26], methods. Tables 2 and 3 showed the parameters for F-R, Int. F-R, K-T and Ext. K-T in copolymers of CDMPMA with THFMA. The values of r_1 and r_2 obtained from the plot F-R, Int F-R, K-T and Ext K-T plots (Figure 6) are presented in Table 4. The product r_1r_2 was less than 1 indicating that the system had strong tendency to form random copolymers.

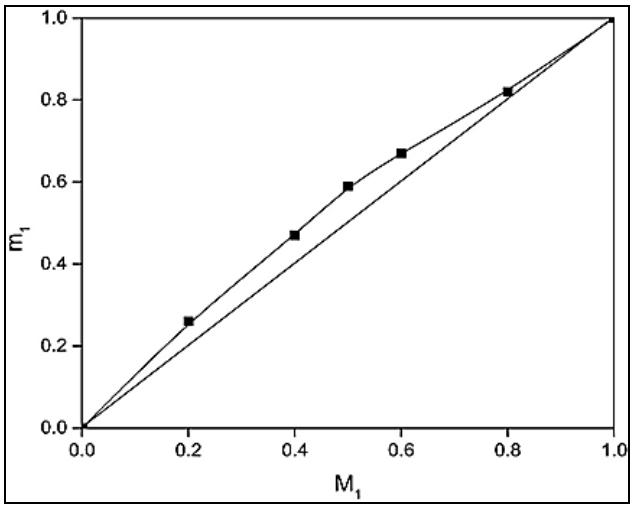


Figure 5: Copolymer composition diagram of poly(CDMPMA-*co*-THFMA)

Table 2: Composition data, F-R, Int. F-R and K-T parameters for copolymers of CDMPMA with THFMA

Sample Code No.	M_1	M_2	w	m_1	m_2	F	G	ξ	η	1/F	G/F
R2	0.8	0.2	5.8	0.82	0.18	3.51	3.12	0.82	0.73	0.28	0.89
R3	0.6	0.4	6.12	0.67	0.33	1.11	0.76	0.58	0.4	0.9	0.69
R4	0.5	0.5	4	0.59	0.41	0.69	0.31	0.47	0.21	1.44	0.44
R5	0.4	0.6	10.4	0.47	0.53	0.5	-0.09	0.39	-0.07	2	-0.17
R6	0.2	0.8	4	0.26	0.74	0.18	-0.46	0.18	-0.48	5.62	-2.59

Where, $m_2 = 1-m_1$; $x = M_1/M_2$; $y = m_1/m_2$; $F = X^2/Y$; $G = x(y-1/y)$; $\xi = F/\alpha+F$; $\eta = G/\alpha+F$ and $\alpha = [F_M \bullet F_m]^{1/2}$

Table 3: Ext. K-T parameters for copolymers of CDMPMA with THFMA

Sample Code No.	ζ_2	ζ_1	Z	$\bar{x}$	F	G	ξ	η
R2	0.05	0.06	1.14	1.14	3.49	3.11	0.82	0.73
R3	0.05	0.07	1.37	1.35	1.09	0.75	0.58	0.4
R4	0.03	0.05	1.45	1.44	0.68	0.3	0.47	0.21
R5	0.09	0.12	1.35	1.33	0.49	-0.08	0.38	-0.07
R6	0.04	0.05	1.42	1.41	0.18	-0.46	0.18	-0.48

Where, $\mu = \mu_2/\mu_1$; $\varsigma_2 = w(\mu + x/\mu + y)$; $\varsigma_1 = \varsigma_2(y/x)$; $z = \log(1-\varsigma_1)/\log(1-\varsigma_2)$; $\bar{x} = y/z$; $F = y/z^2$; $G = (y-1)/z$; $\alpha = [F_M * F_m]^{1/2}$; $\xi = F/(\alpha+F)$; $\eta = G/\alpha+F$

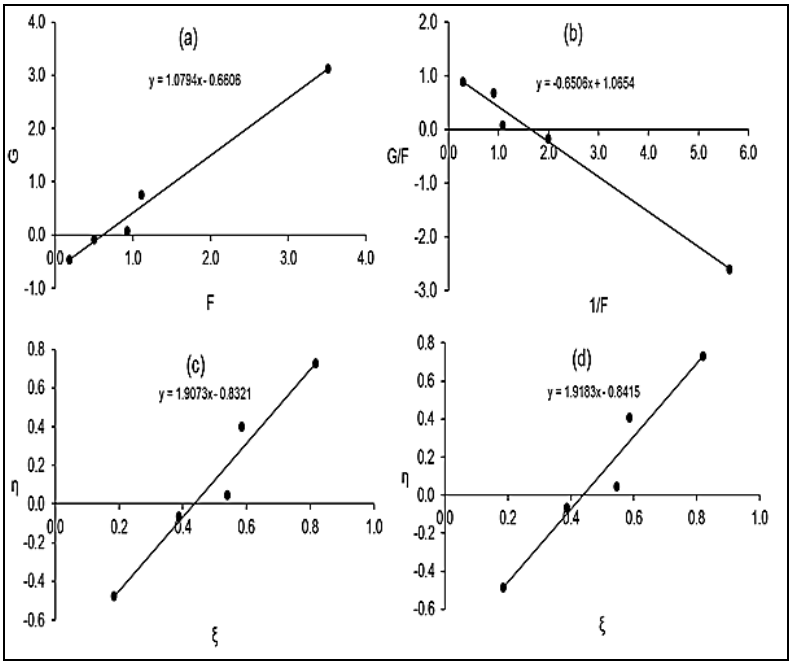


Figure 6: (a) F-R, (b)Int. F-R, (c) K-T and (d) Ext. K-T plot for poly(CDMPMA-*co*-THFMA) system

Table 4: Reactivity data of poly (CDMPMA-*co*-THFMA)

Method	Reactivity ratio		
	r_1	r_2	r_1r_2
F-R	1.05	0.53	0.55
Int. F-R	1.23	0.67	0.82
K-T	1.14	0.62	0.7
Ex. K-T	1.14	0.62	0.7

Molecular weights of polymer

The number-average and weight-average molecular weights of the copolymers of CDMPMA with THFMA were obtained from gel permeation chromatography. The number-average and weight-average molecular weights range from 2.1×10^{-4} to 2.7×10^{-4} and from 3.3×10^{-4} to 4.8×10^{-4} respectively. The poly dispersity index of homopolymer and copolymers varied in the range of 1.3-1.8 and are shown in Table 5. These data clearly indicated that as the CDMPMA content in the copolymer increases, the molecular weights decrease, while polydispersity index also decreases.

Thermogravimetric analysis

Themogravimetric analysis is one of the commonly used techniques for rapid evolution of the thermal stability of different materials, and also demonstrates the decomposition of polymers at various temperatures. Figure 7 shows the TGA thermograms of homo and copolymers of CDMPMA with THFMA form 25 to 700°C in nitrogen atmosphere with 10°C/min. The rate of weight loss decreases with decreasing value of CDMPMA. Figure 8 shows weight loss characteristic of the CDMPMA with various THFMA contents. The thermal stability of poly (CDMPMA-*co*-THFMA) decreased with decreasing of THFMA contents. The integral procedures of decomposition temperature (IPDT) [27] have been correlated for all the polymers and were used for estimating the inherent thermal stability of polymeric materials.

Table 5: Molecular weight data for homo and copolymers of CDMPMA and THFMA

Sample code	Mw × 10^{-4}	Mn × 10^{-4}	Mw/Mn
R1	4.8	2.7	1.8
R2	3.3	2.1	1.6
R3	3.3	2.2	1.5
R4	3.4	2.3	1.5
R5	3.3	2.4	1.4
R6	3.5	2.5	1.4
R7	3.4	2.6	1.3

The IPDT values (Table 6) indicated that the polymers are moderately stable. The polymers decomposed in the temperature range 180-480°C. The activation energy, calculated by Broido's method [28] were found to be in the range 92 to 153 $kJ.mol^{-1}$ and are shown in Figure 9. The activation energy was found to increase linearly

with increase in THFMA content in the copolymers. This suggested that polymers with higher content of THFMA will be thermally more stable. Consequently, homopolymer of CDMPMA is the least stable and poly (THFMA) is thermally most stable.

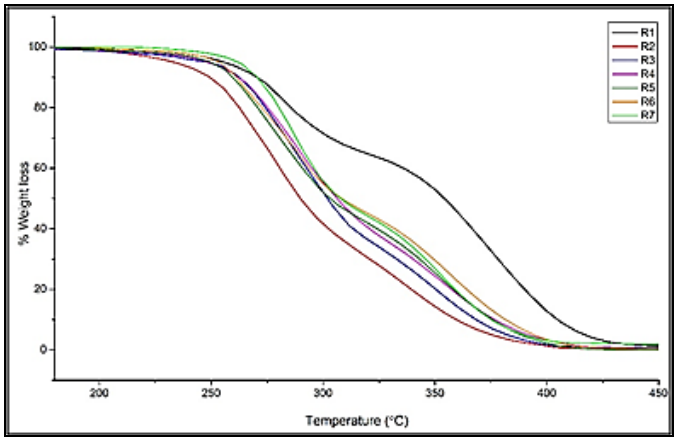


Figure 7: TGA themograms of homo and copolymer of CDMPMA with THFMA

Table 6: TGA data for homo and copolymer of CDMPMA with THFMA

Sample Code No.	Decomposition Temperature Range (°C)		Tmax (°C)	IPDT (°C)
R1	180-322	322-431	377	337
R2	200-300	300-434	373	345
R3	200-353	353-410	374	373
R4	201-340	340-411	381	362
R5	199-360	360-424	382	353
R6	210-388	388-438	388	373
R7	214-321	321-418	375	350

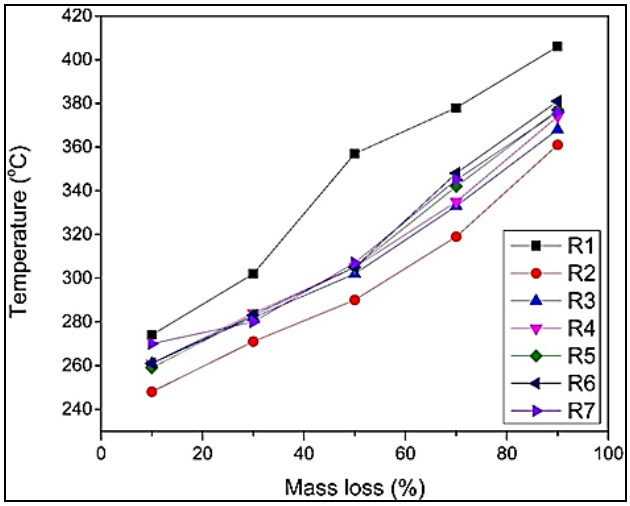


Figure 8: The weight loss temperature vs. weight loss for homo and copolymer of CDMPMA with THFMA

Antimicrobial activity

The homopolymer and copolymers prepared were tested for their antimicrobial activity against bacterial strains (*Escherichia coli, Bacillus subtilis, Staphylococcus citreus*), fungal strains (*Aspergillus niger, Sporotichum pulverulentum, Trichoderma lignorum*), and yeast strains (*Candida utilis, Saccharomyces cerevisiae, Pichia stipitis*) using the experimental procedure reported elsewhere [29,30]. The homopolymer and copolymers of the CDMPMA and THFMA when tested for their response against microorganisms showed interesting results.

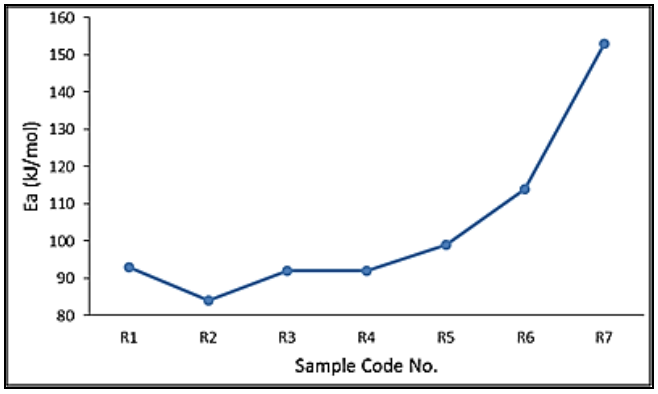


Figure 9: The plot of activation energy, ΔE (kJ/mol), of homo and copolymer of CDMPMA with THFMA by Broido's method

Figures 10-12 provide a comparative account of the effect of the homopolymers and copolymers of CDMPMA and THFMA on the percentage growth of bacteria, fungi, yeast. Poly (CDMPMA) allowed about 18-20% growth of bacteria, 14-16% growth of fungi, and 12-14% growth of yeast, while for poly(THFMA), 81-83% growth of bacteria, 77-79% growth of fungi and 75-77% growth of yeast were observed. However, in poly (CDMPMA-*co*-THFMA**)** 30-74% growth of bacteria, 27-70% growth of fungi and 25-68% growth of yeast were observed. It was observed that poly (CDMPMA-*co*-THFMA) is a stronger antimicrobial agent than the homopolymer of THFMA. The chlorine group content of the polymers played an important role in imparting antimicrobial properties. The homopolymer of CDMPMA has the highest chlorine content amongst the polymers studied here. It is interesting to observe that this homopolymer has the strongest antimicrobial property. It is also seen, that as the CDMPMA content increases in the copolymers, the growth of microorganisms decreases. It is also possible that the conformation of the polymers acquired under experimental conditions may also be a factor for their antigrowth activity. This study however is beyond the scope of this investigation.

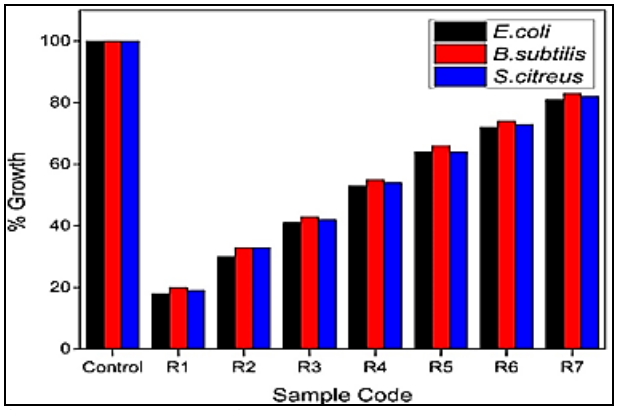


Figure 10: Effect of homo and copolymers of CDMPMA with THFMA on percentage growth of bacteria

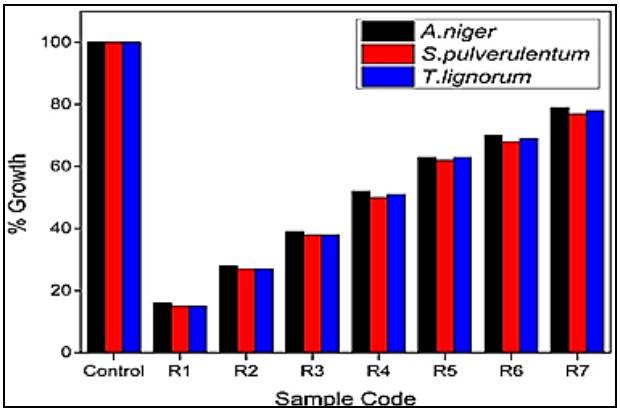


Figure 11: Effect of homo and copolymers of CDMPMA with THFMA on percentage growth of fungi

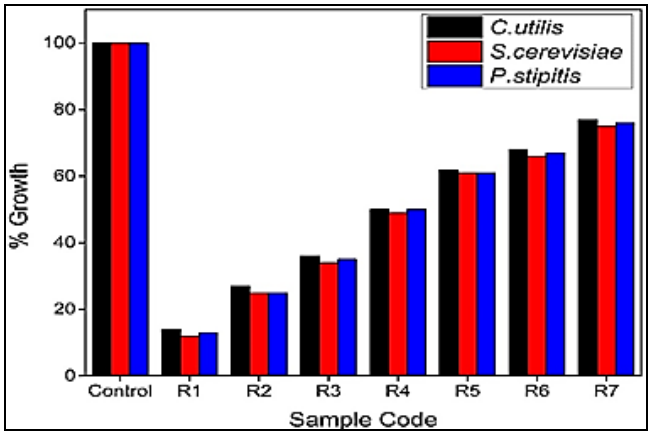


Figure 12: Effect of homo and copolymers of CDMPMA with THFMA on percentage growth of yeast

CONCLUSION

The homopolymers of CDMPMA and THFMA and their copolymers having various compositions were synthesized in solution by free-radical polymerization. The structure of the monomer was confirmed by IR and ^{1}H-NMR spectroscopic techniques. IR spectral data were employed to characterize the polymers. The copolymer compositions were derived from ^{1}H-NMR data. The reactivity ratio of CDMPMA (r_1) is higher than that of THFMA (r_2) and the product of the reactivity ratios was less than 1. This indicated that the monomers were distributed in the copolymer chain in a random manner. The gel permeation chromatography results showed that the molecular weights of the copolymers increased as the THFMA content in the copolymers increased. Chlorine group is important for antimicrobial property of the polymers. The fact that amongst the polymers investigated, the homopolymer of CDMPMA was the most effective antimicrobial agent lends support to this view.

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