Synthesis, Characterization and Antimicrobial Activity of Novel Acrylic Copolymers

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ABSTRACT: Copolymers of monomers 4-chloro-3-methyl phenyl methacrylate (CMPM) and methyl methacrylate (MMA) were synthesized with different monomer feed ratios using 2,2'-azobisisobutyronitrile (AIBN) as initiator in toluene at 70 °C. The copolymers were characterized by IR-spectroscopy and their compositions were determined by ultraviolet (UV) and ¹H NMR spectroscopy. The linearization method of Fineman–Ross and Kelen–Tudos were employed to calculate the monomer reactivity ratio. Average molecular weight and polydispersity index were obtained by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA and DTA) of copolymers were carried out under a nitrogen atmosphere. Antimicrobial effects of the homo and copolymers were also investigated for various microorganisms such as bacteria, fungi and yeast. [DOI 10.1295/polymj.38.159]

KEY WORDS Antimicrobial Activity / Copolymerization / Reactivity Ratio / Thermal Properties / Gel Permeation Chromatography (GPC) /

Many polymers with reactive functional groups are now being synthesized, tested and used not only for their macromolecular properties but also for the properties of functional groups. These groups provide an approach to a subsequent modification of the polymer for specific end applications.¹ Acrylic and methacrylic esters are readily polymerized or copolymerized with a wide range of other monomers. The copolymers of acrylic and methacrylic esters have found use in various applications.^{2–4} Due to their varied applications, chlorine containing phenyl methacrylate and its polymers have received considerable attention in recent years.^{5,6} These chemicals find application as biocides also. Many chlorine containing polymers possessing antimicrobial property have been reported.^{7,8} Phenyl acrylate polymer are relatively newly developed materials compared to the commercial polymers such as vinyllic, acryl amides, alkyl acrylates etc. Phenyl acrylates are considered as reactive monomers primarily because of the presence of the aromatic ring.⁹ The copolymers of phenyl acrylate and methacrylate exhibit good adhesive characteristics.¹⁰ Incorporation of photosensitive group is expected to enhance the usage of methyl methacrylate copolymers in microlithography due to improvement in the mechanical properties without affecting thermal performance.¹¹

Erol and coworkers have prepared new methacrylate monomers, their derivatives and polymers. These authors have also investigated biological activity of these polymers and they showed good biological activity.^{12,13}

Reactivity ratios are among the most important parameters for determination of copolymer composition

and they offer information about the relative reactivity of monomer pairs. Many reports have been published on the correlation between the reactivity ratio of vinyl monomers and extent of radical polymerization and copolymerizations.^{14,15} The distribution of protons in the two units is an important means of distinguishing monomers in the copolymerization. The aliphatic protons of both the monomers are almost indistinguishable. Narsinhaswamy¹⁶ *et al.* proposed a method for the determination of copolymer composition in the copolymer of phenyl methacrylate and glycidyl methacrylate from ¹H NMR data.

In continuous to our work on copolymers of CMPM and 8-Quinolinylnyl methacrylate,¹⁷ it was thought appropriate to synthesize copolymers of CMPM with MMA and examine their bioactivity. This investigation will help to understand the role of moieties other than chlorine in imparting antimicrobial activity to a polymer. We report here the synthesis and characterization of monomers CMPM and MMA, their homo polymers and copolymers using different feed ratio. The copolymer composition was obtained by UV and ¹H NMR data. The reactivity ratio of monomers was obtained by Fineman–Ross and Kelen–Tudos method. Molecular weight was determined by gel permeation chromatography. The monomer and polymers were characterized from their IR data. The results of thermal analysis on polymers are also included in this paper. Homo and copolymers were also tested for their antimicrobial properties against microorganisms such as bacteria (*Bacillus subtilis*, *Escherichia coli* and *Staphylococcus citreus*), fungi (*Aspergillus niger*, *Sporotrichum pulverulentum* and *Trichoderma ligno-*

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rum) and yeast (*Candida utilis*, *Saccharomyces cerevisiae* and *Pichia stipitis*).

EXPERIMENTAL

Materials

4-chloro-3-methyl phenol and methyl methacrylate (S.D. fine chemicals), 2,2'-azobisisobutyronitrile (AIBN, Aldrich), methacrylic acid and benzoyl chloride (chiti chem.) have been used without any further purification. Solvents were purified by fractional distillation.

Synthesis of Methacryloyl Chloride

Methacryloyl chloride was prepared following the standard procedure given by Stempel.¹⁸

Synthesis of 4-Chloro-3-methyl Phenyl Methacrylate (CMPM)

The esterification was performed with methacryloyl chloride and 4-chloro-3-methyl phenol (CMP). Absolute alcohol (400 mL) and NaOH (0.2 mol, 8.0 g) were added to a three necked flask, equipped with a stirrer, condenser and thermometer. The flask was placed in a water bath. The contents of the flask were stirred until all the NaOH dissolved. CMP (0.2 mol, 42.1 g) was added to this. The reaction mixture was 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, 20.5 mL) was added drop wise within 60 min to the cooled reaction mixture. The reaction temperature (0–5 °C) was maintained through out the addition. It was then stirred for 90 min and poured into crushed ice-water mixture, where a light yellow color liquid product settled down. That was extracted with ether. The lower aqueous layer is separated. The remaining solution is transferred to a petry dish to allow evaporation of ether at room temperature and then dried over anhydrous calcium chloride in vacuum desiccator. The boiling point of this monomer was found to be 230 °C. Yield 75%.

Characterization of Monomers CMPM

The monomer was characterized by FTIR and ¹H NMR spectroscopy. IR spectra of monomer was recorded using NICOLET 400D FT IR spectrophotometer. ¹H NMR spectra of monomer was recorded on HITACHI-R-1500 FT NMR spectrophotometer (60 MHz) using CDCl₃ as solvent and tetramethylsilane as an internal standard.

IR Data of Monomer CMPM

The IR spectrum of monomer CMPM is shown in Figure 2a. The important absorptions in cm⁻¹ are:

2925 (ν_{CH_3}), 1743 ($\nu_{\text{C=O}}$), 1642 ($\nu_{\text{C=C}}$), 1232 (asymmetric $\nu_{\text{C-O-C}}$) and 1160 (symmetric $\nu_{\text{C-O-C}}$), 980 (–CH bending mode of vinyl group), 720 (rocking mode of vinyl group), 670 ($\nu_{\text{C-Cl}}$), 1590 and 1488 (bands due to phenyl ring).

¹H NMR (δ ppm) (60 MHz) Data of Monomer CMPM

The NMR spectrum of CMPM is shown in Figure 2b. The resonances are:

¹H NMR (δ ppm) (60 MHz): 2.275 (6H) (methyl protons), 6.494 (1H) and 6.533 (1H) (non-equivalent methylene protons), 7.080–7.217 (3H) (aromatic protons).

Copolymerization

Copolymers of CMPM with MMA having different feed composition were synthesized by free radical polymerization in toluene using AIBN as free radical initiator. The feed composition of both the monomer and comonomer is given in Table I. Appropriate quantities of monomer, comonomer, toluene (10 mL), and AIBN (0.5% of total monomers) were mixed in a round bottom flask equipped with mechanical stirrer and reflux condenser. The reaction mixture was heated to 70 °C for 5 h 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 then filtered and washed with methanol. Solid polymers were purified by repeated precipitation by methanol from solution in DMF and finally dried. Reaction scheme (Figure 1) shows the reaction leading to the formation of homopolymer as well as copolymers of CMPM with MMA. The yield of copolymers varies from 80 to 89%.

Characterization of Polymers

Infrared spectra of solid samples in KBr pellets were recorded with a NICOLET-400D FTIR spectrophotometer. Shimadzu-160-A recording UV–vis spectrophotometer was used to determine copolymer composition and reactivity ratios. HITACHI-R-1500 FT NMR spectrophotometer (60 MHz) was also used to determine copolymer composition. Molecular weights of the polymers were obtained by gel permeation chromatography (Waters 600 E) equipped with a 410-RI detectors calibrated with polystyrene standards. Thermogravimetric analysis was performed with Du Pont-951 thermal analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. Differential thermal analysis (DTA) traces were obtained with Du Pont-9900 differential thermal analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. A heating rate of 10 °C/min and a sample size of 10 ± 1 mg were used in each experiment. Intrinsic viscosity

Table I. Copolymer composition and reactivity ratios of copolymers of CMPM and MMA

Sample code no.	Monomer feed composition		Conversion (%)	Composition of CMPM in the copolymer [m ₁]	$F = \frac{M_1}{M_2}$	$f = \frac{m_1}{m_2}$	$H = \frac{F^2}{f}$	$G = \frac{F(f-1)}{f}$	$\eta = \frac{G}{\alpha + H}$	$\xi = \frac{H}{\alpha + H}$	Reactivity ratio			
	CMPM [M ₁]	MMA [M ₂]									F-R		K-T	
	(mole)	(mole)									r ₁	r ₂	r ₁	r ₂
M-1	1.0	—	—	—	—	—	—	—	—	—	r ₁	r ₂	r ₁	r ₂
M-2	0.2	0.8	8.72	(0.246)*, 0.225	0.25	0.290	0.216	−0.612	−0.493	0.174				
M-3	0.4	0.6	9.12	(0.375)*, 0.389	0.67	0.636	0.706	−0.383	−0.221	0.408				
M-4	0.5	0.5	8.83	(0.483)*, 0.468	1.0	0.88	1.136	−0.136	−0.063	0.526	0.75	0.88	0.70	0.82
M-5	0.6	0.4	7.86	(0.571)*, 0.573	1.5	1.342	1.677	0.382	0.142	0.621				
M-6	0.8	0.2	8.42	(0.775)*, 0.767	4.0	3.292	4.860	2.785	0.473	0.826				
M-7	—	1.0	—	—	—	—	—	—	—	—				

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

*Value in parenthesis are obtained from ¹H NMR data.

(a)

(b)

(c)

Figure 1. Synthesis scheme of (a) Homo CMPM (b) Homo MMA (c) Poly(CMPM-co-MMA).

(η) of the copolymers were measured in toluene at 25 ± 0.1 °C using an Ubbelohde suspended level viscometer.

Antimicrobial Activity

The homo and copolymers prepared were tested for their antimicrobial activity against bacterial strain

Figure 2. (a) IR spectrum of monomer CMPM (b) ^1H NMR spectrum of monomer CMPM.

(*Bacillus subtilis*, *Escherichia coli* and *Staphylococcus citreus*), fungal strain (*Aspergillus niger*, *Sporotrichum pulverulentum* and *Trichoderma lignorum*) and yeast strain (*Candida utilis*, *Saccharomyces cerevisiae* and *Pichia stipitis*). These microorganisms were grown in Nutrient broth (N-broth), Subourand's dextrose broth and yeast extract peptone dextrose (YEPD) media with or without indicated polymer respectively. The content of the flasks were incubated in a shaker at room temperature. At specific time intervals (20–48 h), the optical density was measured at 660 nm for bacterial and yeast cultures. The fungal cultures were harvested after 48 h and the dry cell mass was determined gravimetrically. The details of experimental procedure have been reported elsewhere.^{17,19}

RESULTS AND DISCUSSION

Five copolymers of CMPM with MMA were synthesized by taking different mole fraction of the monomers in the feed ranging from 0.2 to 0.8 (Table I). In order to satisfy the differential copolymerization equation, the reaction time was so selected as to have less than 10 wt % conversion. The copolymers are characterized by IR technique and the results are discussed here.

The IR spectra of copolymers shown in Figure 3 exhibit expected characteristic group frequencies. The medium bands in the range of 2928 and 2855 cm^{-1} may be due to C–H stretching vibrations of methyl and methylene groups respectively. Bands at

Figure 3. IR Spectra for copolymers of CMPM with MMA.

1410 and 1456 cm^{-1} could be assigned respectively to symmetric and asymmetric methyl group bending vibration.²⁰ The latter could be due CH_2 bending also. Interestingly as the CMPM content increases in the copolymer, the intensity of absorption at 1770 (due to $\text{C}=\text{O}$ stretching vibration in phenyl ester) also increases and the intensity of 1730 (due to $\text{C}=\text{O}$ stretching vibration in MMA ester) decreases as MMA content decreases. The aromatic ring breathing vibrations in these polymers are assigned at approximately 1600 and 1500 cm^{-1} . The $\text{C}-\text{O}-\text{C}$ stretching vibrations are attributed to the strong absorption in the region $1300\text{--}1250\text{ cm}^{-1}$ and the sharp band at 670 cm^{-1} is assigned to $\text{C}-\text{Cl}$ stretching.²¹ The absence of absorptions at 980 and 1642 cm^{-1} in the polymers indicates that the vinyl group has taken part in polymerization.

Copolymer Composition and Reactivity Ratios

The average composition of each copolymer sample was determined from the corresponding UV-spectrum. The assignment of the absorption in the UV-spectrum allows accurate determination of the content of each kind of monomeric unit incorporated into the copolymer chains. The λ_{max} for poly(CMPM) was found at 270 nm, while that of poly(MMA) was observed at 250 nm. The UV-spectra of different composition of copolymers are shown in Figure 4a and that of poly(MMA) is shown in Figure 4b. The composition of the copolymers of CMPM and MMA was obtained from the UV-spectral data. The reactivity ratios of CMPM and MMA were obtained from Fineman–Ross method²² and are shown in Table I. The reactivity ratios were also obtained by Kelen–Tudos^{23,24}

Figure 4. (a) UV Spectra for copolymers of CMPM with MMA. (b) UV Spectrum of poly(MMA).

method. These values are also shown in Table I. The reactivity ratios obtained by these two methods agree well. The reaction time was selected in such a way that conversion was less than 10% in weight. This was done to satisfy the differential copolymerization equation for calculation of reactivity ratio.²² A plot of G vs. H in F-R method was a straight line as shown in Figure 6a.

The intercept at Y-axis gives the value of $-r_2$ and the slope gives the value of r_1 . Similarly in K-T method, plot of η against ξ gives a straight line shown in Figure 6b which when extrapolated to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 respectively. When r_1 and r_2 are less than one, the system gives rise to azeotropic polymerization at a particular composition of the monomer, which is calculated using the equation²⁵

$$N_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} = 0.324 \text{ (by F-R method)} \quad (1)$$

Where N_1 is the mole fraction of CMPM in the feed. When the mole fraction of the monomer CMPM in the feed is 0.324 the copolymer formed will have the same composition as that in the feed. When the mole fraction of CMPM in the feed is less than 0.324 the copolymer is relatively richer in this monomeric unit than the feed. When the mole fraction of the monomeric CMPM in the feed is above 0.324 the copolymer is relatively richer in MMA monomeric units.

The composition of each of copolymer samples was determined from the corresponding ^1H NMR spectra also. The ^1H NMR spectra of the copolymers are giv-

Figure 5. ^1H NMR Spectra of poly(MMA) and copolymers of CMPM with MMA.

en in Figure 5. The peaks around 6.9 to 7.2 ppm are due to aromatic protons. The peak at 3.61 ppm is assigned to $-\text{OCH}_3$ group. The remaining resonances are due to other aliphatic protons. The composition of the copolymers was calculated by comparing the intensities of the aromatic protons and the total ali-

phatic protons of the copolymer.

The copolymer composition was obtained in the following way. Let m_1 be the mole fraction of CMPM and m_2 be the mole fraction of MMA. CMPM contains 3 aromatic protons and 8 aliphatic protons. MMA unit has 8 aliphatic protons.

(a)

(b)

Figure 6. (a) F-R plot for poly(CMPM-co-MMA). (b) K-T plot for poly(CMPM-co-MMA).

A parameter K is defined as

$$K = \frac{\text{Intensities of aromatic protons}}{\text{Intensities of aliphatic protons}} = \frac{3m_1}{8m_1 + 8m_2} \quad (2)$$

It is also known that,

$$m_1 + m_2 = 1 \quad (3)$$

Combining eqs (2) and (3)

$$m_1 = \frac{8K}{3} \quad (4)$$

The results of these calculations are shown in Table I. The compositions obtained from ^1H NMR and UV data compare well.

Table II. Average molecular weights by GPC data for the copolymers of CMPM with MMA

Sample code no.	M_n	M_w	Polydispersity (M_w/M_n)	Intrinsic viscosity $[\eta]$ dl·g ⁻¹
M-1	44011	67821	1.541	0.210
M-2	35421	51892	1.465	0.178
M-4	38945	57833	1.485	0.186
M-6	44487	69310	1.558	0.196
M-7	45609	74069	1.624	0.230

Molecular Weight and Viscosity Measurement

The number and weight average molecular weight of poly(CMPM), poly(MMA) and five samples of copolymers were obtained using gel permeation chromatographic technique. The polydispersity index of homo and copolymers varied in the range of 1.465–1.624. The intrinsic viscosities (η) were obtained by extrapolating $\eta_{\text{sp}}C^{-1}$ vs. C to zero concentration. Molecular weights and viscosities are presented in Table II.

Thermal Analysis

The thermal stability of the polymers were identified by estimating the percentage weight loss of the polymer on thermal decomposition. The decomposition temperature of the copolymers depends on the composition of the constituent monomeric units in the copolymer. The results of TGA analysis of poly(CMPM), poly(CMPM-co-MMA) (20:80, 50:50, 80:20 monomer feed ratio) and poly(MMA) are presented in Table III. The data clearly indicate that all copolymers of CMPM undergo two step decomposition while homo polymers of both the monomers show one step decomposition in the temperature range of 210–472 °C. The activation energy (E_A) calculated

Table IV. DTA data for poly(CMPM), poly(MMA) and their copolymers

Sample code no.	T_1^a (°C)	T_2^b (°C)	T_p^c (°C)	Activation energy ^d (E_A) (K·J·mol ⁻¹)	Reaction order
M-1	400	540	445	103	1
M-2	295	418	340	110	1
	418	497	442	113	1
M-4	290	381	336	107	1
	381	490	440	112	1
M-6	299	380	335	105	1
	380	488	439	107	1
M-7	398	520	438	102	1

^aStarting temperature of DTA. ^bEnding temperature of DTA trace. ^cPeak maxima temperature of DTA trace. ^dActivation energy by Reich's method.

by Broido's method,²⁶ lies in the range of 102–115 K·J·mol⁻¹. The integral procedural decomposition temperature (IPDT) was calculated by Doyle's method.²⁷ IPDT expresses the overall thermal stability of the polymer and it varies between 360–394 °C for these polymers.

DTA data of poly(CMPM), poly(CMPM-co-MMA) (20:80, 50:50, 80:20 monomer feed ratio) and poly(MMA) are presented in Table IV. It is observed that as the CMPM content in the polymer increases, the thermal stability also increases. This may be attributed to the increase in the number of aromatic rings. As expected homopolymer of CMPM has the highest thermal stability here. The activation energy for thermal degradation and reaction order were obtained by Reich's method.²⁸ The activation energy for thermal degradation of polymers ranged from 102–113 K·J·mol⁻¹.

Table III. TGA data for poly(CMPM), poly(MMA) and their copolymers

Sample code no.	% Weight loss at various temperature (°C)				Decomposition temperature range (°C)	T_{Max}^a (°C)	T_{50}^b (°C)	IPDT ^c (°C)	Activation energy ^d (E_A) (K·J·mol ⁻¹)
	250	350	450	550					
M-1	0.98	7.27	87.20	89.41	270–472	399	396	394	102
M-2	7.28	47.55	93.95	98.88	227–330 330–443	375	360	363	113 115
M-4	2.87	45.86	97.58	99.20	219–330 330–439	370	359	360	105 103
M-6	11.97	43.79	93.28	95.05	222–325 325–439	369	357	360	105 103
M-7	2.60	20.12	98.35	99.02	210–428	390	386	385	101

^aTemperature for maximum rate of decomposition. ^bTemperature for 50% weight loss. ^cIntegral procedural decomposition temperature. ^dBy Broido's method.

Figure 7. Effect of homo- and copolymers on percentage growth of bacteria.

Antimicrobial Activity

The antimicrobial activity of homo and copolymers of CMPM and MMA was investigated. The results obtained are presented in Figures 7, 8 and 9. It has been suggested that presence of chlorine in a compound is of prime importance for its antimicrobial activity.^{29,30} All the copolymers systems showed almost similar antimicrobial properties against bacteria, fungi and yeast. Poly(CMPM) allowed about 18–23% growth of bacteria whereas its copolymers favored 35–51% growth. Poly(CMPM) allowed 20–25% growth of fungi whereas its copolymers favored 37–53% growth. Yeast however in the presence of poly(CMPM) registered around 21–24% growth whereas 39–55% growth for yeast was observed in the copolymers. It was observed that copolymers of CMPM and MMA show strong inhibitory effect (Figures 7–9) against tested microorganisms than the homopolymer of MMA. Interestingly the homopolymer of MMA shows antimicrobial property to very less extent. It appears that polymers having no chlorine might also demonstrate antimicrobial activity, although presence of chlorine enhances this activity many fold. It is concluded that as the percentage of CMPM in the copolymers increases, the effectiveness of the copolymers to inhibit the growth of microorganisms increases and as expected the homopolymer of CMPM shows maximum growth inhibition. Although the chlorine content

of polymers appeared to be most important for imparting antimicrobial properties, it is to be noted that other moieties also possess antimicrobial activity. The copolymers of CMPM with 8-Quinolinylnyl methacrylate¹⁷ are more potent antimicrobial agents than the copolymers of CMPM and MMA. It thus appears that 8-Quinoline moiety also might have some role to enhance antimicrobial activity. Such role of other moieties needs to be systematically studied. The study of the mechanism of activity is beyond the scope of the paper. However, we may attempt a tentative mechanism. All the micro-organisms contain $\text{RNH-CH}_2\text{-COOH}$ molecule. The moiety

will possibly react with the amino acid and HCl will be evolved.

CONCLUSIONS

New methacrylate based homo and copolymers were synthesized by free radical solution polymerization technique. The monomers and copolymers were

Figure 8. Effect of homo- and copolymers on percentage growth of fungi.

Figure 9. Effect of homo- and copolymers on percentage growth of yeast.

characterized by spectroscopic methods. The reactivity ratio of CMPM (r_1) is less than that of MMA (r_2) and the product of reactivity ratio was less than one. This shows that the monomers were distributed in the copolymer chain in a random fashion. The number average molecular weight (M_n) and weight average molecular weight (M_w) were in the range of 35421 to 45609 and 51892 to 74069 respectively. Thermal analyses showed that all copolymers of CMPM undergo two step decomposition and homo polymers decompose in a single step. The chlorine content of the polymers appears to be the most important component to enhance antimicrobial activity. It is hoped that such chlorine containing copolymers will find use as antimicrobial agents.

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