Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2011, 2(6):112-128

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Novel acrylic copolymers derived from Paracetamol: Determination of reactivity ratio, microbial screening and thermal properties

Jignesh B. Dholakiya[1], Hetal J. Patel[1], Kirit H. Patel[1] and Rajni M. Patel[2*]

[1]*Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat INDIA*
[2]*Sophisticated Instrument Centre for Applied Research & Testing (SICART), Charutar Vidya Mandal, Vallabh Vidyanagar, Gujarat, INDIA*

ABSTRACT

The monomer p-acetamidophenyl methacrylate (PAPM) has been synthesized by reacting paracetamol with methacryloyl chloride using methanol as solvent. Homopolymers of PAPM, quinoline methaacrylate (QMA) and its copolymers were synthesized by free radical polymerization technique using 2,2'-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The prepared copolymers were characterized by FT-IR spectroscopy. The copolymer composition was evaluated by ^{1}H-NMR and was further used to determine reactivity ratios. The monomer reactivity ratios for PAPM (M_1)-QMA (M_2) pair were determined by using Fineman-Ross (F-R) (r_1 =0.66; r_2 =1.12), Kelen-Tudos (K-T) (r_1 = 0.66; r_2 = 1.12) and extended Kelen-Tudos (Ex.K-T)(r_1 = 0.65; r_2 = 1.13) methods. Thermogravimetry analysis (TGA) showed that thermal decomposition of the polymer occurred in a two step. The first step decomposition occurs in the ranges from 224°C to 350°C whereas second step ranges from 350°C to 503°C. TGA data also showed that activation energy of all poly(PAPM-co-QMA) are in range of 38-52 K.J.mole^{-1}.The values of integral procedural decomposition temperature (IPDT) calculated by Doyle's method for copolymers is in the range of 379°C -389°C. Activation energies (E_a) calculated by Broido's method are in the range of 41-52 K.J.mole^{-1} for poly(PAPM-co-QMA). The characteristic temperature and kinetic parameters for the homo and copolymers have been obtained from DTA traces using Reich's method. The molecular weights of the polymers were determined using gel permeation chromatography. All polymers were tested for their antimicrobial property against various microorganisms and found to possess significant antimicrobial activity. The composition of copolymers can be regulated to have materials of desired property.

Keywords: copolymers, reactivity ratio, thermal analysis, antimicrobial properties.

INTRODUCTION

Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties [1]. This kind of macromolecules possesses significant importance from both fundamental and applied point of view. Acrylic ester latex polymers are widely used as high quality paint binders because of their excellent durability, toughness, optical clarity, UV stability and color retention. These properties allow acrylics to find use as binder vehicles in all type of paints [2] and improve the flowability [3]. Copolymers of acrylics with acrylic/methacrylic acid can be used as thickners for textile coating formulation. Due to their exceptional resistance to environmental assaults such as UV radiation, ozone, heat, water, dry cleaning and aging, they are widely used in textile industry [4,5]. Acrylates are biocompatible and have been widely used in a synthesis of polymeric drugs [6]. Polymer-anti-inflammatory drug conjugation has been the major approach to reduce toxicity and increase therapeutic efficiency of the drug [7]. Antimicrobial agents have considerable use for their potential to provide quality and safety benefits to many materials. Contamination by microorganism is of great concern in areas such as medical devices and healthcare product, biocidal coating [8] and ion-exchange study [9]. It is known that 8-quinoline moiety has good antimicrobial and ion-exchange properties. The PAPM moiety is also expected to be capable to inhibit the growth of microbes, although 8-quinoline moiety has edge over PAPM in this area of activity. The thermal stability of these two components of the copolymer is also different. It was thought appropriate to prepare copolymers having different compositions of QMA and PAPM, so that polymers of desired property can be made. So, keeping this in view the main aim of present work is to modify methacrylic copolymer by incorporating paracetamol side groups into copolymer chain, so as to make them useful as antimicrobial agents. There are a huge number of reports on monomeric paracetamol and its derivatives, but its polymers have not received considerable attention in the literature. In this paper, we report the synthesis, characterization, thermal studies, and effect of PAPM/QMA copolymers on different micro-organisms. The formation of polymer has been established with the help of IR spectral data. Gel permeation chromatography was employed to determine the molecular weights of the synthesized polymers. The thermal stability of the polymers has been investigated using Broido method. Proton NMR spectroscopy has been employed to study the copolymers compositions and monomer reactivity ratios.

MATERIALS AND METHODS

Materials

Paracetamol, AIBN (Aldrich) was recrystallized twice from methanol. 8-Hydroxy-Quinoline and Methacryloyl chloride were synthesized using procedure previously described in the literature [10,11]. The solvents used were purified by using standard procedure [12].

Synthesis of p-acetamidophenyl methacrylate (PAPM)

To a one liter three necked flask equipped with stirrer, thermometer and guard tube, absolute alcohol (200 ml) and NaOH (0.1 mole) were added and the contents were stirred until all the NaOH dissolved. To this, paracetamol (0.1 mole) was added. The reaction mixture was heated to 60°C for 30 minutes with stirring, cooled to room temperature and then to 0-5°C. Freshly prepared methacryloyl chloride (0.11 mole) was added drop wise within 60 minutes to the cooled reaction mixture. The temperature was maintained around 0-5°C during the addition.

After completion of addition, reaction mixture was stirred for 90 minutes and it was poured into crushed ice water mixture where white colored solid was separated out. It was washed thoroughly with water and filtered. The solid mass was again dissolved in ethanol and poured into cooled distilled water. Solid mass was filtered and dried. (Yield: 83%, m.p.: 129°C). The formation of the monomer was confirmed by FT-IR (Figure 1a) and ^{1}H-NMR spectra (Figure 1b).

FT-IR (KBr, cm^{-1}): 1733 (C=O *str* due to ester group) [13], 1663 (C=O *str* in amide group), 1530 (N-H *bend*), 3308 (N-H *str*), 1198 (C-O *str* of ester group), 1607 (aromatic C=C *str*) 1641 (olefinic C=C *str*), 945 (C-H *bend* of geminal =CH_2).

^{1}H-NMR (DMSO-d6, δppm)(400 MHz): 10.0 (1H, -NH-), 7.6 (2H, Ar-H), 7.1 (2H, Ar-H), 6.3 & 5.9 (2H, =CH_2) 2.1 (3H, -$COCH_3$), 2.0 (3H, -CH_3).

Synthesis of Poly(PAPM)

Homopolymerization of PAPM was carried out in solution using free radical polymerization technique. Appropriate quantity of PAPM, dimethyl formamide (DMF) and AIBN (0.5 w/w of monomer) were taken in a flask equipped with reflux condenser. The reaction mixture was heated at 70±2°C for 5 hours with stirring. It was then cooled to room temperature and the resulting homopolymer was precipitated by pouring the reaction mixture into excess of methanol. Solid polymer obtained was purified by repeated precipitation using methanol from solution in DMF and finally dried. The yield of homopolymer obtained was 84%.

The formation of the homopolymer was confirmed by FT-IR (Figure 2a) and ^{1}H-NMR spectra (Figure 2b).

FT-IR (KBr, cm^{-1}): 1748 (C=O *str* due to ester group), 1673 (C=O *str* in amide group), 1548 (N-H *bend*), 3268 (N-H *str*), 1194 (C-O *str* of ester group), 1611 (aromatic C=C *str*).

^{1}H-NMR (DMSO-d6, δppm)(400 MHz): 10.0 (1H, -NH-), 7.5 & 7.0 (4H, Ar-H), 2.0 – 1.3 (methylene group in backbone).

Copolymerization

Copolymers of PAPM with QMA having different composition were synthesized by free radical polymerization in DMF solvent using AIBN as a free radical initiator. The reaction parameters and feed composition of monomer and comonomers are given in Table 1. Appropriate quantities of monomer, comonomer, DMF and AIBN (0.5% w/w based on total monomers) were taken in a polymerization tube equipped with reflux condenser. The reaction mixture was heated at 70±2°C for 5 hours with stirring. It was then cooled to room temperature and the resulting copolymer was slowly precipitated by pouring the contents into an excess of methanol, and purified by repeated reprecipitation from solution in DMF by methanol and finally dried. Figure 3 show the reaction leading to the formation of homopolymers as well as copolymers of PAPM with QMA.

Measurement

IR spectra of the monomer and polymers were recorded on Nicolet 400$_D$ FT-IR spectrometer, using KBr pellets. NMR spectra were obtained on Hitachi-R-1500 in $CDCl_3$ solution. The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 30ºC.

Molecular weights were determined by gel permeation chromatography (GPC) equipped with Jasco-PU 1580 pump and two PL gel column packed with styrene divinylbenzene bead. R.I. detector (RI-71 Shodex) was employed in these measurements. Dimethylformamide (DMF) at 1.0 mL/min flow rate was used as a mobile phase throughout the analysis. All the measurements were carried out at 30ºC. Thermogravimetric (TG) measurement was carried out with DuPont-951 thermal analyzer at a heating rate of 10ºC/min in nitrogen atmosphere. Differential thermal analysis (DTA) was done with DuPont-9900 differential thermal analyzer at heating rate of 10ºC/min in nitrogen atmosphere.

Microbial Screening

Homo and copolymers were screened for their effect on growth of various microorganisms, viz, their antimicrobial properties against bacteria (*B.subtilis, E.coli and S.citreus*), fungi (*A.nigar, S Pulveruletum and T. lingorum*) and yeast (*C.utilis, S.cerevisiac and P.stipitis*).

Screening of Acrylic copolymer for Antibacterial, Antifungal and Antiyeast activity (%Inhibition of Growth)

The detail experimental procedure to measure antimicrobial activity was given in our earlier communication [14] and percentage inhibition of microbial were calculated using the following formula.

I) Percentage inhibition of bacteria/yeast $= 100(X - Y)/X$

Where $X =$ optical density of bacteria/yeast suspension in control set, and

$Y =$ optical density of bacteria/ yeast suspension in test set.

II) Percentage inhibition of fungi $= 100(X - Y)/y$

Where $X =$ weight of dry fungal cell mass in control set, and

$Y =$ weight of dry fungal cell mass in test set.

RESULTS AND DISCUSSION

The copolymers of PAPM with QMA in DMF solution was studied in wide composition interval with mole fraction of PAPM ranges from 0.2 to 0.8 in the feed. The reaction time was selected to give conversion less than 10% weight to satisfy the differential copolymerization equation for calculation of reactivity ratio. The copolymers were found to be soluble in dimethylformamide, toluene, chloroform, acetone, tetrahydrofuran, dimethylsulfoxide but insoluble in hexane and hydroxyl containing solvents, such as methanol and ethanol.

Characterization of homopolymer and copolymers

The formation poly(PAPM) was confirmed by FT-IR and ^{1}H-NMR spectra. The disappearance of C-H of plane bending at 945 cm^{-1} and C=C stretching at 1641 cm^{-1} indicates polymerization, which is further supported from proton NMR data. The ^{1}H-NMR resonances due to vinyl protons at 6.3ppm and 5.9ppm are not seen in polymers. Further appearance of broad signals at 3.1ppm and between 2.0-1.0ppm indicates the presence of $-CH_2$ and CH_3 respectively in the polymer backbone.

Figure 4 shows the comparative FT-IR spectra of the copolymers of PAPM with QMA along with their respective homopolymers. The important IR frequencies and their assignments are tabulated in Table 2. The spectra(Figure 4) of copolymers show all the characteristic absorptions of the components of the copolymer system. FT-IR spectrum of poly(PAPM) shows two sharp absorption at 1748 and 1673 cm^{-1}due to $\upsilon_{C=O}$ of ester group and amide group respectively. The absorption at 1194 cm^{-1} is attributed to υ_{C-O} of ester group. The absorption at 1611 cm^{-1} is assigned to $\upsilon C_{=C}$ vibration of benzene ring. The sharp band at 1548 cm^{-1} has contribution from N-H bending of amide group and as expected, the relative intensity of this band decreases with decrease in PAPM content in the copolymers.

IR spectrum (Figure 4) of poly(QMA) has characteristic absorptions of 8-o-substituted quinoline ring at 1590, 1496 and 1469 cm^{-1}. The two bands at 1754 and 1221 cm^{-1} are assigned respectively $\upsilon_{C=O}$ and υ_{C-O} of ester group. In IR spectra of poly(PAPM-*co*-QMA), the absorptions at around 1590 and 1469 cm^{-1} due to 8-o-substituted quinoline ring, become stronger as the QMA content in the copolymer increases. It is also seen that the absorption due to C=O *str* of amide group at~1673cm^{-1} becomes weaker as the PAPM content in the copolymer chain decreases.

Copolymer Composition and Reactivity Ratios

Copolymer average monomer composition was determined from the corresponding proton NMR spectra using following procedure:

Let the reaction is

$$A + B \rightarrow P \text{------(1)}$$

Where A is the monomeric unit-1 and B is monomeric unit-2 while P is the resultant polymer.

The parameter C is defined as

$$C = \frac{\text{Intensity of aromatic protons } (I_{AROMATIC})}{\textit{Intensity of aliphatic protons } (I_{ALIPHATIC})} \text{-----(2)}$$

$$C = \frac{am_1 + bm_2}{cm_1 + dm_2} \text{------(3)}$$

Where

m_1 = mole fraction of monomer1
m_2 = mole fraction of monomer 2
a = number of aromatic protons in monomer 1
b = number of aromatic protons in monomer 2
c = number of aliphatic protons in monomer 1

and

d = number of aliphatic protons in monomer 2

$$AS \qquad m_1 + m_2 = 1$$

$$C = \frac{am_1 + b(1 - m_1)}{cm_1 + d(1 - m_1)} \text{ - - - - - - - - -(4)}$$

Hence

$$m_1 = \frac{b - Cd}{C(c - d) - (a - b)} \text{ - - - - - - - - -(5)}$$

The value of C is determined from the integration height of aromatic and aliphatic protons in the ^{1}H-NMR spectra shown in Figure 5. The composition of PAPM in homo and copolymer were obtained with the help of the above equation (5) and converted into the appropriate units. The results are shown in Table 1. The ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition, tacticity and sequence distribution because of its simplicity, rapidity and sensitivity [15-18].

Measurement of integration of aliphatic and aromatic protons, allows accurate evaluation of the content of each kind of monomeric unit incorporated into the polymer chains. From monomer feed ratio and copolymer compositions, the reactivity ratios of PAPM and QMA are obtained by (F-R) [19], (K-T) [20] and Ex.K-T [21] methods and these are shown in Table 3 and Table 4. The values of reactivity ratio, r_1 and r_2 of PAPM and QMA are 0.66 and 1.12, 0.66 and 1.12, 0.65 and 1.13 respectively, obtained from F-R, K-T and Ex.K-T plots shown in Figure 6. In poly(PAPM-*co*-QMA), the value of r_1 is less than 1 and that of r_2 is greater than 1, indicating the presence of higher amount of QMA units in the copolymer than in the feed. The value of the product r_1r_2 is greater than one, suggesting random distribution of monomers.

Molecular Weight Measurements

The values of average molecular weights, polydispersity obtained by GPC and intrinsic viscosity for copolymers of PAPM with QMA are presented in Tables 5 whereas comparative GPC curves are shown in Figures 7. It is observed from the GPC data of poly(PAPM) that the values of $\overline{Mn}$, $\overline{Mw}$, $\overline{Mz}$ and $\overline{Mw}/\overline{Mn}$ are 28870, 43980, 60130 and 1.52 respectively whereas intrinsic viscosity [η] is 0.28 dl.g^{-1}.In case of various poly(PAPM-*co*-QMA) (sample no. 2, 4, 6) the GPC data reveals that the values of $\overline{Mn}$, $\overline{Mw}$, $\overline{Mz}$ and $\overline{Mw}/\overline{Mn}$ which ranges from 19567 to 26424, 34046 to 43071, 53906 to 58639 and 1.63 to 1.74 respectively whereas intrinsic viscosity [η] ranges from 0.18 to 0.26 dl.g^{-1}. For poly(QMA) the values of $\overline{Mn}$, $\overline{Mw}$, $\overline{Mz}$ and $\overline{Mw}/\overline{Mn}$ is 17506, 32911, 51642 and 1.88 respectively and intrinsic viscosity [η] 0.16 dl.g^{-1}. The result reveals that molecular weight decreases and polydispersity index increases as the content of PAPM in the copolymer decreases.

Thermal Analysis

Thermal behavior of homo and copolymers was studied by TGA and DTA in nitrogen atmosphere.

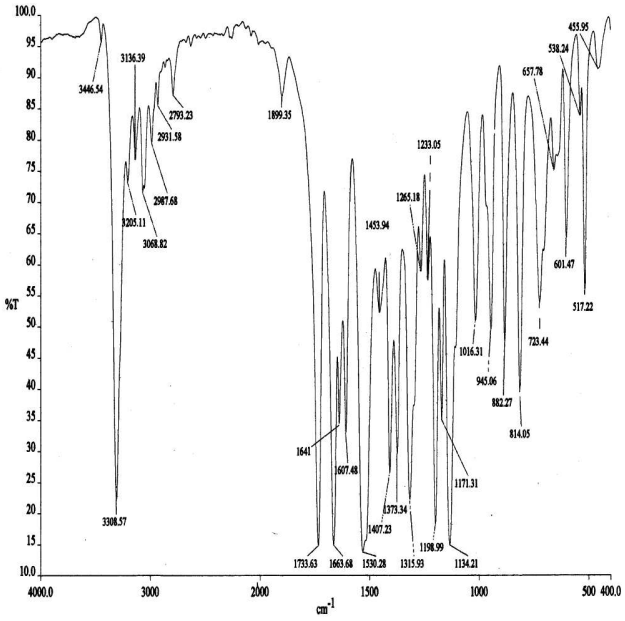

Figure 1a: FT-IR spectra of PAPM.

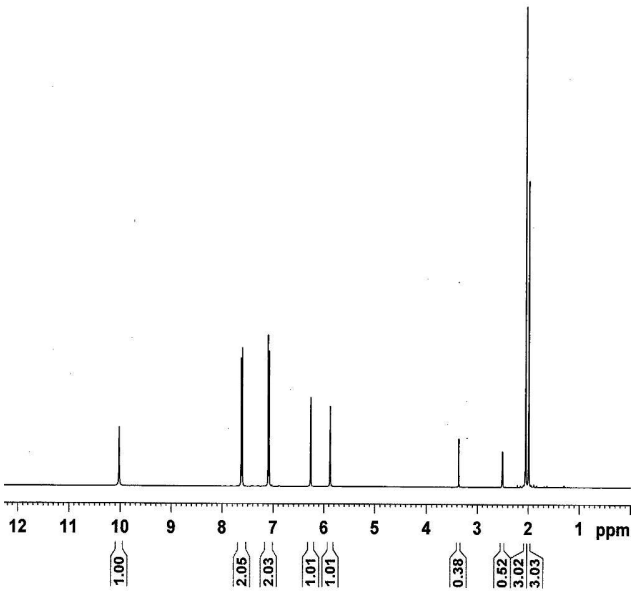

Figure 1b: ^{1}H-NMR spectra of PAPM.

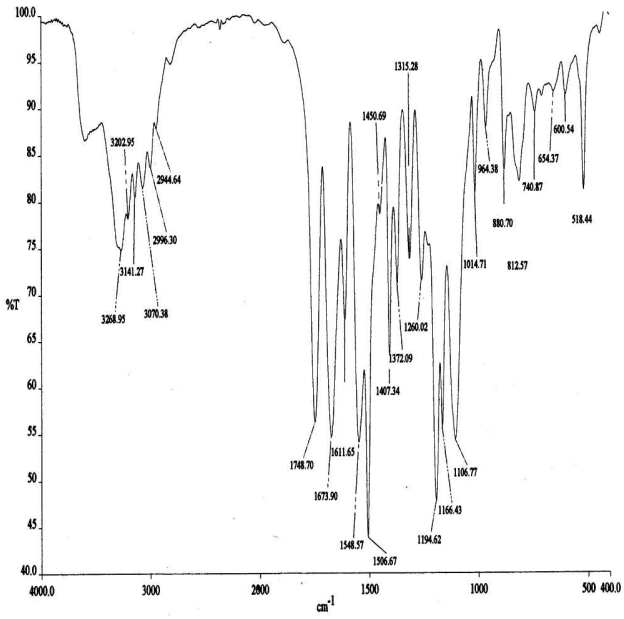

Figure 2a: FT-IR spectra of Poly(PAPM).

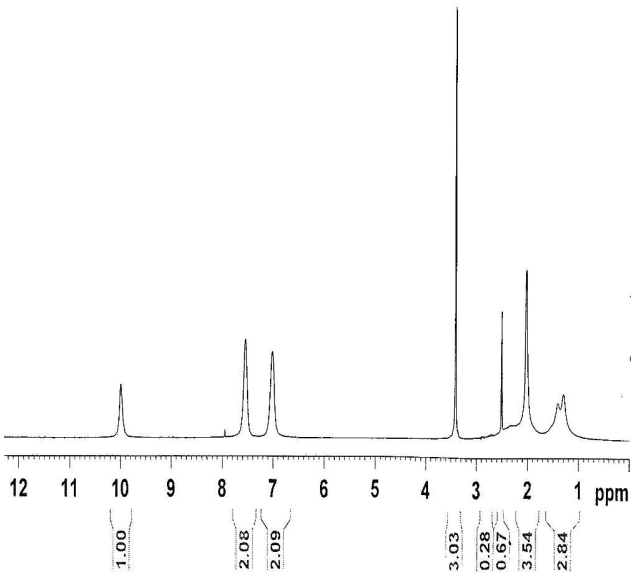

Figure 2b: ^{1}H-NMR spectra of Poly(PAPM).

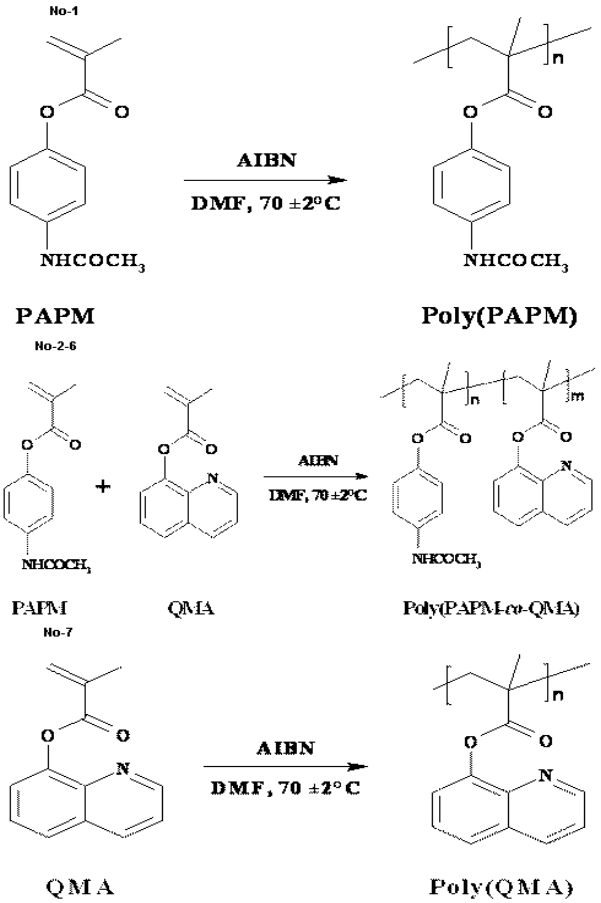

Figure 3: Reaction scheme.

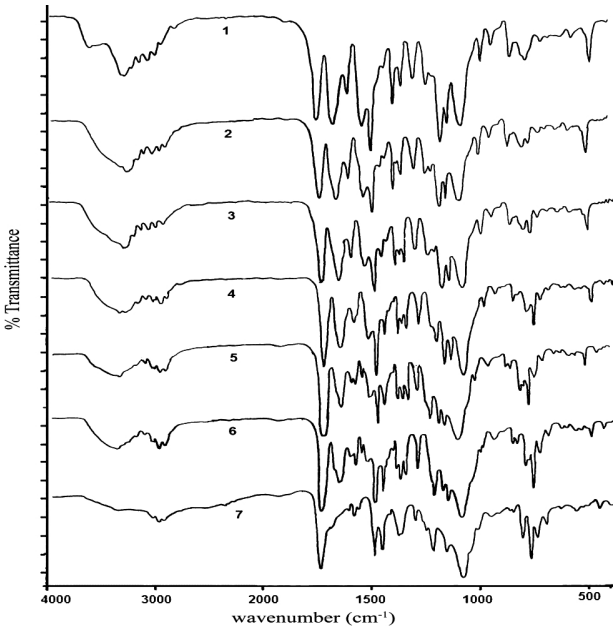

Figure 4: FT-IR spectra of Poly(PAPM), Poly(PAPM-co-QMA) and Poly(QMA).

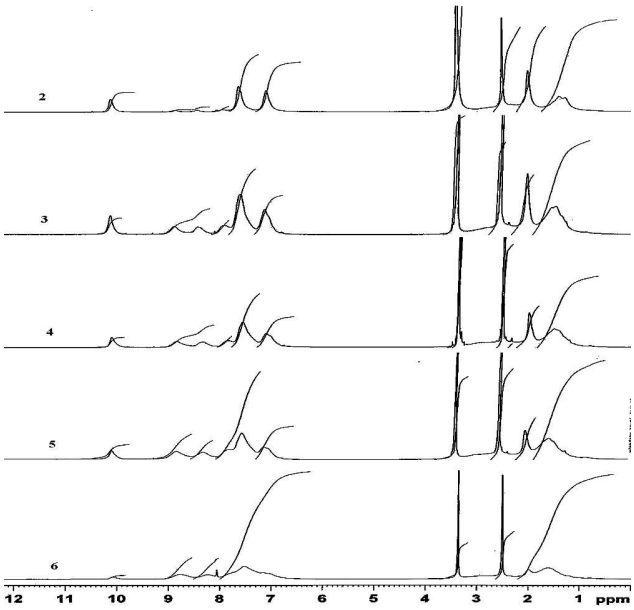

Figure 5: ^{1}H-NMR spectra of Poly(PAPM-co-QMA).

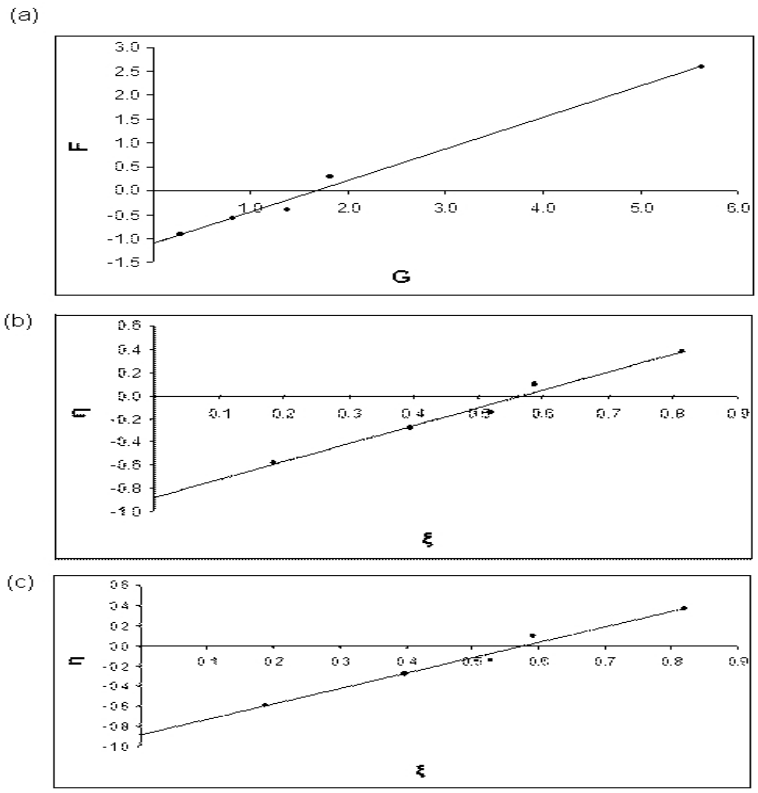

Figure 6: (a) F-R, (b) K-T and (c) Ex.K-T plots for Poly(PAPM-co-QMA).

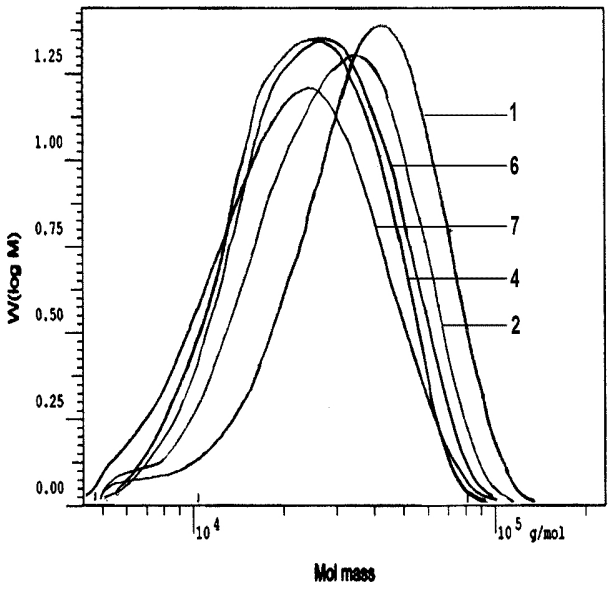

Figure 7: GPC curves for homo and copolymers of PAPM with QMA.

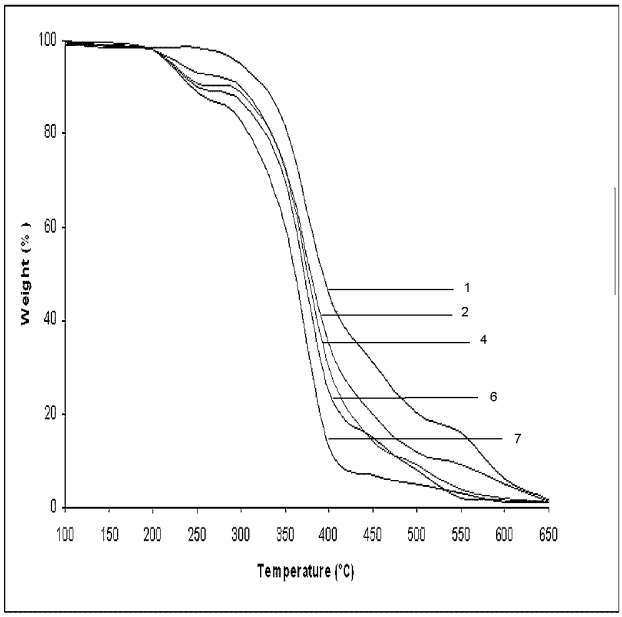

Figure 8: TG thermogram of Poly(PAPM), Poly(PAPM-co-QMA) and Poly(QMA).

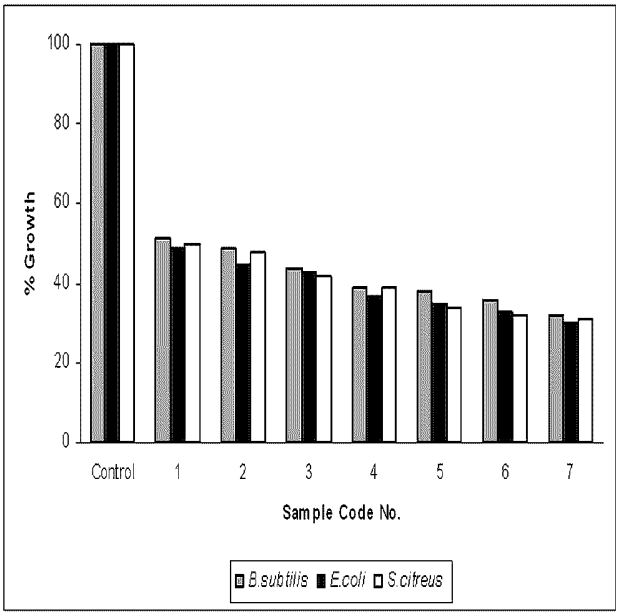

Figure 9: Effect of Poly(PAPM), Poly(PAPM-co-QMA) and Poly(QMA) on growth(%) of bacteria.

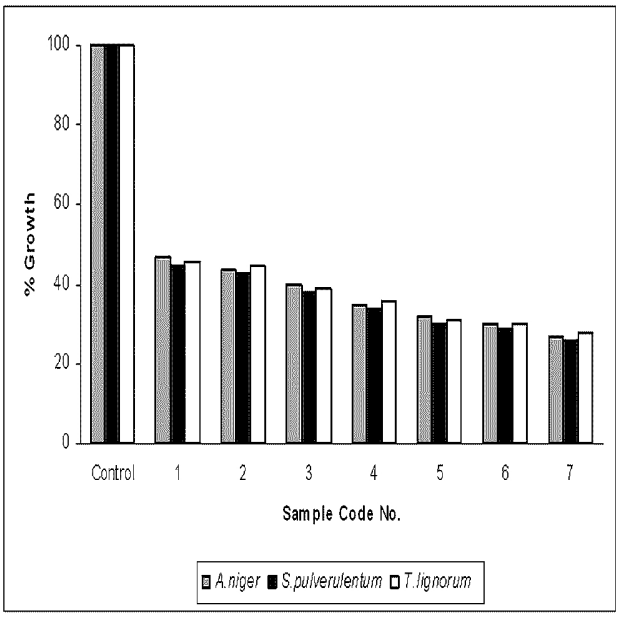

Figure 10: Effect of Poly(PAPM), Poly(PAPM-co-QMA) and Poly(QMA) on growth(%) of fungi.

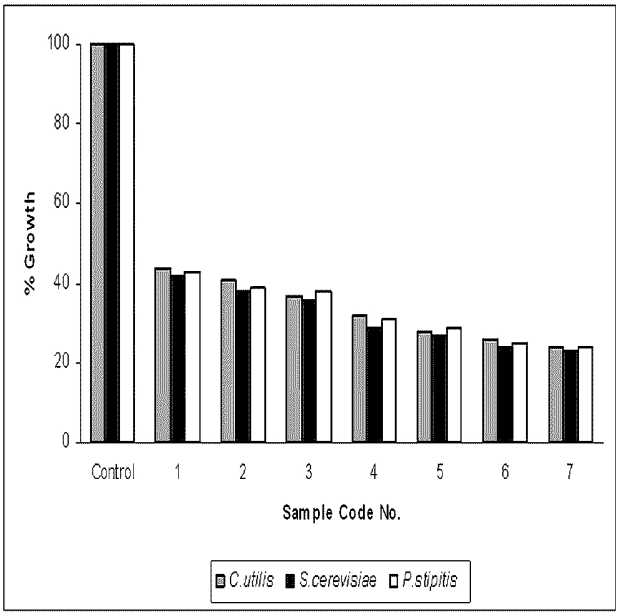

Figure 11: Effect of Poly(PAPM), Poly(PAPM-co-QMA) and Poly(QMA) on growth(%) of yeast.

Table 1: Reaction parameters and composition data for poly(PAPM-*co*-QMA).

Sample Code No.	Monomer feed composition				Integrated peak area of proton		Composition of PAPM in copolymer (m_1) Mole	% yield
	PAPM (M_1)		QMA (M_2)					
	Mole	Gms.	Mole	Gms.	I_{aro}	I_{ali}		
1	1.0	219	-	-	-	-	-	84
2	0.8	175	0.2	42	5.81	11.07	0.824	88
3	0.6	131	0.4	85	8.85	13.65	0.601	80
4	0.5	109	0.5	106	12.33	17.10	0.490	78
5	0.4	87	0.6	127	24.32	30.02	0.371	75
6	0.2	43	0.8	170	31.92	32.70	0.189	72
7	-	-	1.0	213	-	-	-	89

Solvent: DMF, Initiator: AIBN (0.5% w/w), Temp.: 70±2ºC, Reaction time: 5 hrs.

Thermogravimetry Analysis (TGA)

The TGA thermograms of homopolymers and copolymers of PAPM with QMA are shown in Figure 8. The TGA data shown in Table 6 indicates that thermal decomposition of the polymer occurred in two steps. The first step decomposition occurred in the range 224^0C to 350^0C, while second step is seen in the range 350^0C to 503^0C. The activation energies of all poly(PAPM-CO-QMA) obtained from TGA data using Broido's method [22] are found to be in the range 41-52 KJ/mol. The values of integral procedural decomposition temperature (IPDT) calculated by Doyle's [23] methods for copolymers are in the range of 379^0C-389^0C. It is observed that as the PAPM content in poly(PAPM-CO-QMA) decreases the thermal stability of the copolymers decreases. Poly(PAPM) is more stable. As amount of QMA increases thermal stability decreases. The energy of activation for thermal decomposition of poly(QMA) at 38 KJ/mol indicates that decomposes comparatively easily than poly(PAPM) having energy of activation for thermal decomposition at 49 KJ/mol.

Table 2: FT-IR spectral data for poly(PAPM), poly(QMA) and poly(PAPM-*co*-QMA)

Sample Code No.	$\upsilon_{C=O}$ stretching in ester group (cm^{-1})	$\upsilon_{C=O}$ stretching in amide group (cm^{-1})	N-H bending in amide group (cm^{-1})	υ_{C-O-C} stretching (cm^{-1})	υ_{C-C} stretching in aromatic ring (cm^{-1})	υ_{C-H} stretching in aromatic ring (cm^{-1})	υ_{C-H} stretching in alkyl group (cm^{-1})	$\delta_{sy}CH_3$ (cm^{-1})	υ_{C-O} stretching of 8-o-sub. quinolinoyl ring (cm^{-1})
1	1748	1673	1548	1194	1611	3141, 3070	2996, 2944	1372	-
2	1749	1673	1546	1194	1612	3141, 3070	2996, 2942	1371	1467
3	1748	1672	1545	1195	1611	3142, 3068	2995, 2944	1371	1467
4	1748	1672	1544	1195	1611	3142, 3066	2995, 2943	1370	1469
5	1749	1670	1543	1195	1613	3140, 3065	2998, 2944	1369	1470
6	1750	1670	1541	1195	1611	3139, 3065	3001, 2949	1368	1469,1496, 1596
7	1758	-	-	1221	1612	3010	2985, 2959	1387	1474,1500, 1605

Table 3: Composition data, F-R and K-T parameters for copolymers of PAPM with QMA

Sample Code No.	PAPM [M_1] Mole	QMA [M_2] Mole	% Conversion [w]	Composition of PAPM in copolymer [m_1] Mole	x	y	F	G	ξ	η
2	0.8	0.2	8.46	0.740	4.00	2.846	5.622	2.595	0.815	0.376
3	0.6	0.4	9.28	0.553	1.50	1.234	1.819	0.288	0.587	0.093
4	0.5	0.5	9.11	0.419	1.00	0.721	1.387	-0.387	0.520	-0.145
5	0.4	0.6	8.94	0.348	0.67	0.534	0.833	-0.582	0.394	-0.276
6	0.2	0.8	9.32	0.177	0.25	0.215	0.291	-0.912	0.185	-0.582

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

Table 4: Extended K-T parameters for copolymers of PAPM with QMA

Sample Code No.	ζ_2	ζ_1	z	$\bar{x}$	F	G	ξ	η
2	0.110	0.078	0.699	4.069	5.819	2.639	0.819	0.372
3	0.103	0.085	0.816	1.514	1.855	0.290	0.592	0.092
4	0.106	0.076	0.709	1.016	1.431	-0.392	0.528	-0.145
5	0.097	0.078	0.792	0.673	0.850	-0.588	0.399	-0.276
6	0.095	0.825	0.854	0.251	0.294	-0.919	0.187	-0.584

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

Table 5: GPC and viscosity data for homo and copolymers of PAPM with QMA

Sample Code No.	$\overline{M}n$	$\overline{M}w$	$\overline{M}z$	Polydispersity $\left(\overline{M}w/\overline{M}n\right)$	Intrinsic viscosity [η] dl.g-1
1	28870	43980	60130	1.52	0.281
2	26424	43071	58639	1.63	0.259
4	22104	37355	55342	1.69	0.218
6	19567	34046	53906	1.74	0.181
7	17506	32911	51642	1.88	0.156

Table: 6 TGA data for homo and copolymers of PAPM with QMA

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.mole^{-1})
	300	400	500	600					
1	7	49	79	92	315-470 470-635	370	400	393	49
2	10	65	88	95	248-349 349-503	378	374	389	46
4	11	70	91	99	231-345 345-494	375	370	381	52
6	13	75	92	99	224-347 347-462	369	361	379	41
7	17	87	95	99	215-322 322-445	364	358	375	38

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

Table 7: DTA data for homo and copolymers of PAPM with QMA

Sample Code No.	T_1 [a] (°C)	T_2 [b] (°C)	T_3 [c] (°C)	Activation Energy[d] (E_a) (K.J.mole^{-1})	Reaction Order
1	377 498	484 682	448 585	41 47	1 1.5
2	257 348	348 532	315 450	44 48	1 1
4	220 362	362 514	298 437	51 57	1 1
6	212 354	354 498	274 418	42 45	1 1
7	198 352	352 422	239 403	41 39	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

Differential Thermal Analysis (DTA)

Differential thermal analysis data of homo and copolymers were analyzed by Reich's [24] method and are presented in Table 7. It is observed that all the copolymers of PAPM with QMA show two endotherms. The activation energy for thermal degradation lies in the range 42-57 KJ/mol for poly(PAPM-CO-QMA) having different feed composition. The activation energy

(Ea) obtained by Broido's method (TGA) and Reich's method (DTA) compare well. Order of reaction for thermal decomposition of all the copolymers is one.

Microbial Screening

Antimicrobial activities of poly(PAPM), poly(QMA) and poly(PAPM-CO-QMA) on bacteria, fungi and yeast are shown in Figure 9, 10 and 11 respectively. All the polymers are good inhibitors for the growth of bacteria, fungi and yeast. Poly(PAPM) allows about 50% growth of bacteria,46% growth of fungi and 43% growth of yeast. Poly(QMA) allows about 32% growth of bacteria, 27% growth of fungi and 24% growth of yeast. It is thus apparent QMA has better antimicrobial property. It is gratifying to note that as the PAPM content in the copolymer decreases the inhibitory effect increases due the presence of higher amount of QMA.

CONCLUSION

The homopolymers of PAPM and 8-QMA and copolymers of PAPM and 8-QMA of various compositions were synthesized in solution by free radical polymerization. The structure of the monomers was confirmed by FT-IR and ^{1}H-NMR data. The homopolymers and copolymers were characterized FT-IR spectroscopy. The reactivity ratio of PAPM (r_1) is less than 1 and that of 8-QMA (r_2) is greater than 1 and the product r_1r_2 is greater than one, indicating random distribution of monomers in the copolymers. TGA analysis showed that thermal decomposition of the polymers occurred in two steps. All the polymers have moderate thermal stability. The GPC data showed that as the PAPM content in the copolymer decreases, molecular weight decreases and polydispersity index increases. Microbial screening showed that PAPM containing 8-QMA based acrylic polymers may be used as antimicrobial agent due to presence of higher content of bioactive group. As expected the potency of the antimicrobial activity of the copolymers is better than that of poly(PAPM) but less than that of poly(QMA).

REFERENCES

[1]C. Soykan, M. Ahmedzade and M. Coskun, *Euro Polym J*, **2000**, 36**,** 1667.
[2] CS. Chuang, KC. Tsai and MK. Wang, et al, *wood science and technology*, **2008**, 42, 593**.**
[3]H. I. Al-Shafey, A.I. Hashem, R. S. Abdel Hameed, E. A. Dawood, *Advances in Applied Science Research*, **2011**, 2, 5, 476.
[4]Robert V. Slone, Acrylic Ester Polymer. In: encyclopedia of polymer science and technology: *john wiley&sons, Inc*, **2010**.
[5]M. D. Teli, R. D. Kale, *Advances in Applied Science Research*, **2011**, 2, 4, 491.
[6]T O. Sang, K M. Byung, S H. Chang and J C. Won, *J Appl Polym Sci*, **1994**, 52, 5, 583.
[7]A. Gallardo, J S. Roman, *Polymer*, **1993**, 34**,** 394.
[8]S. K. Singh, A. Jain, D. Sharma, A. Dubey, *Der Chemica Sinica*, **2011**, 2,1, 111.
[9]D.T. Masram, K. P. Kariya, N. S. Bhave, *Advances in Applied Science Research*, **2011**, 2, 4,156.
[10]BS. Furniss, AJ. Hannaford, PWG. Smith, AR. Tatchell, Vogel's Textbook of Practical OrganicChemistry, 5th Ed, *Pearson Education Pvt*, Singapore, **1989**.
[11]GH. Stempel, RP. Cross, RP. Mareioll, *J Am Chem Soc*, **1950**, 72, 2299.
[12]D. Perrin, WLF. Armarego, Purification ofLaboratory Chemicals, *Pergamon*, New York, **1988**.

[13] P. Ghose, T. Das, *Advances in Applied Science Research*, **2011**, 2, 272.
[14] JN. Patel, MV. Patel, RM. Patel, *J Macromol Sci A Pure Appl Chem*, **2005**, 42,71.
[15] H. Satapathy, AK. Banthia, *Pigment and resin technology*, **2007**, 36, 335.
[16] KR. Kumar, SK. Feroz, PR. Rao, *Asian journal of chemistry*, **2010**, 22, 100.
[17] J. Patel, K. Patel, R. Patel , Colloid and polymer science, **2009**, 287,89.
[18] H. J. Patel, M. G. Patel, A. K. Patel, K. H. Patel, R. M. Patel, **2008** *eXPRESS Polymer Letters*, 10,727.
[19] M. Fineman, SD. Ross, *J Polym Sci: Polym Chem*, **1950**, 5, 259.
[20] T. Kelen, F. Tudos, *J Macromol Sci: Part A Pure and Appl Chem*, **1975**, 9, 1.
[21] T. Kelen, F. Tudos, B. Turesanyi, JP. Kennedy, *J Polym Sci: Polym Chem*, **1977**, 15, 3041.
[22] A. Broido, *J Polym Sci: Part A*, **1969**, 27, 1761.
[23] CD. Doyle, *Anal Chem*, **1961**, 33, 77-79.
[24] L. Reich, *Die Makromol Chem*, **1969**, 123, 42.