

Synthesis, characterization and antimicrobial activity of important heterocyclic acrylic copolymers

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Abstract. The acrylate monomer, 7-acryloyloxy-4-methyl coumarin (AMC) has been synthesized by reacting 7-hydroxy-4-methyl coumarin, with acryloyl chloride in the presence of NaOH at 0–5°C. Copolymers of 7-acryloyloxy-4-methyl coumarin (AMC) with vinyl acetate (VAc) were synthesized in DMF (dimethyl formamide) solution at 70±1°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The copolymers were characterized by Fourier transform infra red (FTIR) spectroscopy. The copolymer composition was evaluated by ¹H-NMR (proton nuclear magnetic resonance) and was further used to determine reactivity ratios. The monomer reactivity ratios for AMC (M_1)-VAc (M_2) pair were determined by the application of conventional linearization methods such as Fineman-Ross ($r_1 = 0.6924$; $r_2 = 0.6431$), Kelen-Tüdös ($r_1 = 0.6776$; $r_2 = 0.6374$) and extended Kelen-Tüdös ($r_1 = 0.6657$; $r_2 = 0.6256$). Thermo gravimetric analysis showed that thermal decomposition of the copolymers occurred in single stage in the temperature range of 263–458°C. The molecular weights of the polymers were determined using gel permeation chromatography. The homo and copolymers were tested for their antimicrobial properties against selected microorganisms.

Keywords: thermal properties, 7-hydroxy-4-methyl coumarin, ¹H-NMR, antimicrobial activity

1. Introduction

Copolymerization is one of the important techniques adopted in effecting systematic changes in the properties of the commercially important polymers. The copolymers of acrylic/methacrylic esters have been used for various industrial applications [1]. The chemical structure of a copolymer depends not only on the two-monomer units forming the macromolecule, but also on how such units are distributed along macromolecular chains. This distribution is a direct consequence of each monomer's reactivity in the copolymer molecule [2]. In case of radical copolymerization, the reactivity of a free radical depends on the nature of the side group linked to the radical carbon [3].

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 group. These groups provide an approach to a subsequent modification of the polymer for specific end application [4]. Czeh and coworkers synthesized acrylic pressure sensitive adhesives with the help of azo-prester radical initiators [5]. Pazhanisamy and coworkers synthesized copolymers of N-cyclohexylacrylamide/n-butyl acrylate. The resulting copolymers were characterized by FT-IR, NMR, DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis). Reactivity ratios of the monomers were also computed [6]. There are several reports on acrylic polymers for use in binding of pigments as well as for antimicrobial coatings in textile industry [7, 8].

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Coumarin polymers possessing antimicrobial activity have not received considerable attention in the literature. However the reported coumarin polymers possess variety of functions and appear to be interesting. Although there is a huge number of reports on monomeric coumarin derivatives, there are only a few reports on coumarin polymers. Vinylated coumarins are used as polymerizable fluorescent brightening agents and, when copolymerized with acrylonitrile and methyl acrylate, they faded more slowly than copolymers of acrylonitrile and methylacrylate [9].

A novel blue luminescent polymer bearing coumarin pendants was prepared by Lu *et al.* [10]. Its luminescent properties were determined indicating that it had strong blue fluorescent properties and good film formation ability. This novel polymer can be used as a blue organic electroluminescent material (OELM) in organic electroluminescent devices. Chen and co-workers have studied the radical copolymerization behaviour of styrene with coumarin or 7-acetoxy coumarin [11]. Lindsay and co-workers [12] synthesized the copolymer of coumarin methacrylate with isobornylmethacrylate. These polymers showed tremendous non linear optical properties.

Due to various physiological and biochemical properties of coumarin, our interest was to synthesize acrylic copolymers containing coumarin side groups. Present work focuses on synthesis and characterization of 7-acryloyloxy-4-methyl coumarin (AMC) and its copolymers with vinyl acetate (VAc). Reactivity ratio values of the monomers were determined by various linearization techniques. TGA and GPC results are also included. The prepared copolymers were tested for their antimicrobial activity against various bacteria, fungi and yeast.

2. Experimental

2.1. Materials

Vinyl acetate (VAc) was freed of inhibitor by washing with 5% NaOH and then with water several times. After being dried over anhydrous Na_2SO_4 , it was distilled under reduced pressure. 2,2'-Azobis (iso butyronitrile) (AIBN) was recrystallized twice from methanol. 7-hydroxy-4-methyl coumarin and acryloyl chloride were synthesized as

per reported procedure [13, 14]. Fractionally distilled solvents were used in the reaction.

2.2. Synthesis of 7-acryloyloxy-4-methyl coumarin (AMC)

7-hydroxy-4-methyl coumarin (0.1 mol) dissolved in absolute alcohol (250 ml), was placed along with sodium hydroxide (0.1 mol) in a two necked 500 ml flask. With continuous stirring of the reaction mixture at 0–5°C, freshly distilled acryloyl chloride (0.11 mol) was added slowly from an addition funnel. An hour after the completion of addition, the contents were stirred for 90 minutes and were poured into crushed ice water mixture where a white colored monomer was separated out. It was filtered, washed with cold water and dried. Further the monomer was recrystallized from methanol (yield: 89%, m.p.:122°C). The formation of the monomer was confirmed by FT-IR (Figure 1a) and $^1\text{H-NMR}$ spectra (Figure 1b).

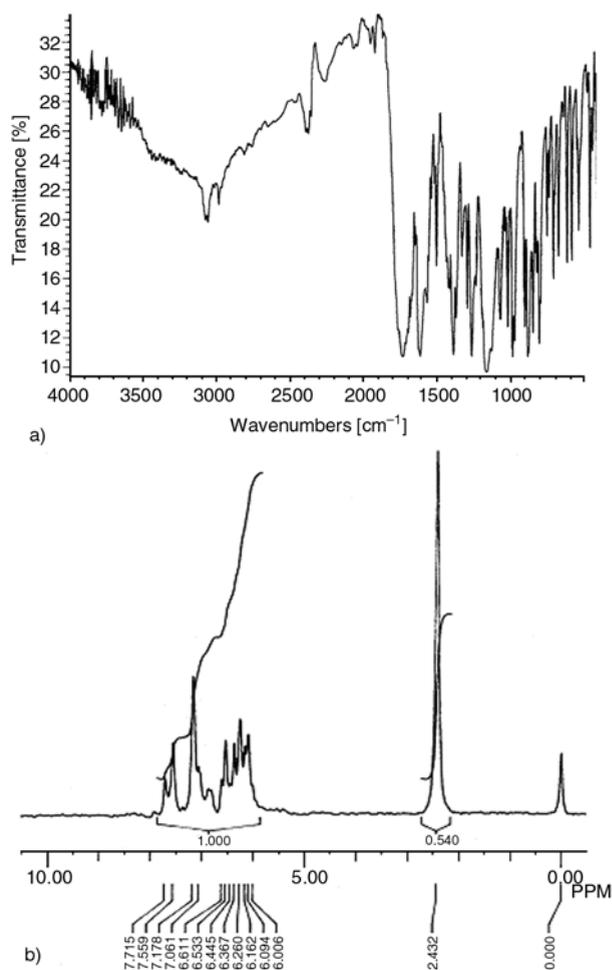


Figure 1. Characterization of AMC (a) FT-IR and (b) $^1\text{H-NMR}$

IR (KBr, cm^{-1}): 3073 (–CH stretching vibration of the aromatic ring), 2986 (–CH₃), 1737 (broad, C=O of acrylate and of coumarin moiety), 1630 (C=C), 1240 (asymmetric C–O–C), 1142 (symmetric C–O–C), 890 (–CH bending mode of vinyl group), 730 (rocking mode of vinyl group).

¹H-NMR (δ [ppm]) (60 MHz): 6.26 (1H, –CH=), 2.43 (3H, CH₃), 6.36 (2H, non-equivalent methylene protons), 7.06–7.72 (3H, aromatic protons).

2.3. Homopolymerization of AMC

This was carried out using solution polymerization technique. AIBN (1% wt of monomer) was added to 2 g of AMC dissolved in 10 ml of DMF taken in a polymerization tube. The content was degassed with nitrogen and kept at $70 \pm 1^\circ\text{C}$ in a water bath for 5 hours. The polymer was precipitated by pouring the contents of the polymerization tube into excess methanol. The resultant precipitate was filtered and dried in vacuum at 40°C .

2.4. Copolymerization of AMC with VAc

Copolymerization was carried out by solution polymerization technique using DMF as a solvent and AIBN as a free radical initiator at $70 \pm 1^\circ\text{C}$ under nitrogen atmosphere. Appropriate amounts of AMC, VAc, AIBN (1 wt% of the monomers) and DMF (Table 1) were mixed in a polymerization tube, degassed with nitrogen and kept in a thermostat ($70 \pm 1^\circ\text{C}$) for a definite period of time so as to

maintain the conversion below 10%. Then the contents were precipitated by pouring into excess methanol and filtered. The precipitate was purified by dissolving in dimethyl formamide and reprecipitated using methanol, filtered and dried in a vacuum oven at 40°C . Figure 2 shows the copolymerization of AMC with VAc.

2.5. Measurements

IR spectra of the monomer and polymers were recorded on Nicolet 400D FT-IR spectrometer using KBr pellets. ¹H-NMR spectra of the samples were run on a Hitachi-R-1500 permanent magnet 60 MHz spectrophotometer. TGA curves of the homo and copolymers were recorded on TA instrument (USA) 2690 thermogravimetric analyzer in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The number average and weight average molecular weight of the polymers were determined by gel permeation chromatography using polystyrene as standard and DMF is used as eluent at 1.0 ml/min flow rate.

2.6. Antimicrobial activity

The homo and copolymers obtained were tested against different bacterial strains (*Bacillus subtilis*, *Escherichia coli* and *Staphylococcus citreus*), fungal strains (*Aspergillus niger*, *Sporotichum pulveruleum* and *Trichocerma lignorum*) and yeast strains (*Candida utilis*, *Saccharomyces cerevisiac*

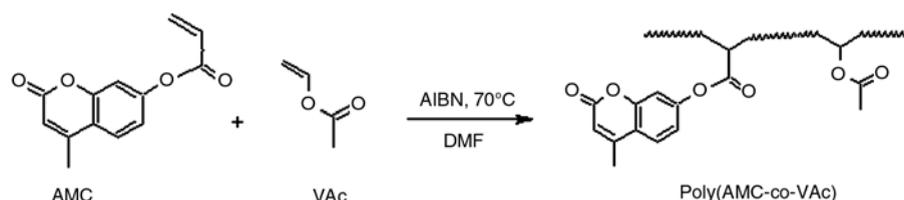


Figure 2. Reaction scheme of P(AMC-co-VAc)

Table 1. Copolymer composition data of AMC and VAc

Polymer No.	Mole fraction in feed		Intensities of protons		C	Mole fraction in copolymer	
	AMC (M ₁)	VAc (M ₂)	I _{arom}	I _{lip}		AMC (m ₁)	VAc (m ₂)
1	1.0	–	–	–	–	1.0	–
2	0.5	0.5	34.81	148.76	0.234	0.508	0.492
3	0.4	0.6	27.65	139.64	0.198	0.425	0.575
4	0.3	0.7	21.38	131.97	0.162	0.344	0.656
5	0.2	0.8	17.08	147.24	0.116	0.243	0.757
6	0.1	0.9	13.49	201.34	0.067	0.139	0.861
7	–	1.0	–	–	–	–	1.0

and *Pichia stipitis*). The details of the experimental procedures have been reported in our earlier publication [15, 16].

3. Results and Discussion

Different homo and copolymers were obtained by the free radical solution polymerization technique. The mole fractions of AMC ranging from 0.5 to 0.1 in the feed were studied in a wide composition interval. The reaction time was selected in trials to give conversions less than 10% in order to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in Figure 2. The data on the composition of the feed and copolymers are given in Table 1.

3.1. Characterization of polymers

3.1.1. Solubility

The homo and copolymers synthesized were soluble in chloroform, dimethyl formamide, dimethyl sulfoxide, toluene and tetrahydro furan. It is insoluble in n-hexane, acetone and hydroxyl group containing solvents such as methanol and ethanol.

3.1.2. Infrared spectra

The IR spectra of the homo and copolymers are shown in Figure 3. The two medium bands at 2966 and 2932 cm^{-1} may be attributed to the asymmetric and symmetric C–H stretching vibration of methylene group where as, absorption at 1455 cm^{-1} may be due to bending vibration of $-\text{CH}_2$ group. The strong absorptions at 1394 cm^{-1} may be traced due to in-plane bending vibrations of methyl and methylene groups. The broad band at 1736 cm^{-1} is assigned to C=O stretching vibration of ester group (due to presence of three carbonyl group in the monomer AMC and VAc) and sharp band at 1260 cm^{-1} and a broad band at 1148 cm^{-1} are assigned C–O stretching vibration of ester group. Two strong bands at 1502 and 1585 cm^{-1} are observed which the characteristic absorptions of phenyl ring. As the content of AMC in the copolymers decreases the intensities of these peaks also decreases. The absence of 1630 cm^{-1} absorption in the polymers is indicative of the participation of the vinyl group in the polymerization.

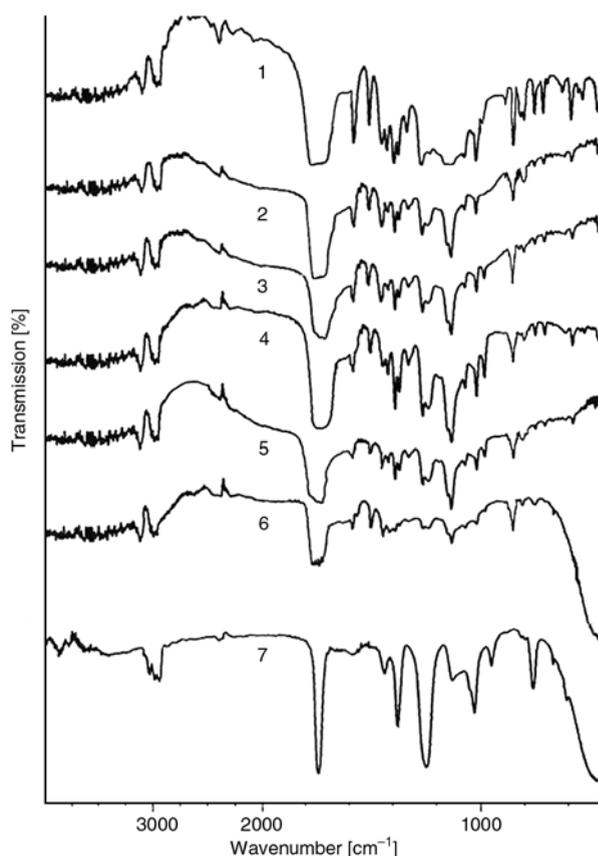


Figure 3. IR spectra of P(AMC), P(VAc) and copolymers

3.2. Copolymer composition and monomer reactivity ratio

The average compositions of the copolymer samples were determined by $^1\text{H-NMR}$ spectra. The assignment of the resonance peaks in the $^1\text{H-NMR}$ spectrum leads to accurate evaluation of each monomeric content incorporated into the copolymer chains. Thus, the mole fraction of AMC in the copolymer was calculated by measuring the integrated peak height of aromatic protons of AMC to that of total aliphatic protons in the copolymer as described in Equation (1):

$$\therefore C = \frac{\text{Intensity of aromatic protons}(I_{Ar})}{\text{Intensity of aliphatic protons}(I_{Al})} \quad (1)$$

The following expression (Equation (2)) is used to determine the composition of the copolymers. Let m_1 be the mole fraction of AMC and $1 - m_1$ be that of VAc. AMC contains three aromatic protons and seven aliphatic protons, and VAc contains six aliphatic protons (Equation (2)).

$$\therefore C = \frac{3m_1}{7m_1 + 6(1-m_1)} \quad (2)$$

This on simplification gives (Equation (3)):

$$\therefore m_1 = \frac{6C}{3-C} \quad (3)$$

Based on Equation (3), the mole fractions of AMC in the copolymers were determined by measuring the integral peak height of aromatic proton and aliphatic proton signals. Table 1 gives the values of C and the corresponding mole fractions of AMC in the copolymers.

From the monomer feed ratios and the copolymer composition, the reactivity ratios of AMC and VAc were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R) [17], Kelen-Tüdös (K-T) [18] and extended Kelen-Tüdös (Ext. K-T) [19]. The F-R and K-T parameters for the copolymers are presented in Table 2 and those for Ext. K-T are shown in Table 3. The reactivity ratios values obtained from F-R plot, K-T and Ext. K-T plots (Figures 4a, 4b and 4c) are presented in Table 4.

The reactivity ratio values indicate that the AMC radical favors its own monomer rather than VAc. Generally the neutral olefin molecules and those

Table 2. F-R and K-T parameters for copolymers of AMC with VAc

Polymer No.	AMC (M ₁) [mole]	VAc (M ₂) [mole]	Conversion (w) [%]	x	y	F	G	ξ	η
2	0.5	0.5	9.12	1.00	0.969	1.033	-0.033	0.799	-0.025
3	0.4	0.6	8.83	0.67	0.745	0.597	-0.228	0.697	-0.266
4	0.3	0.7	8.72	0.43	0.548	0.334	-0.353	0.563	-0.595
5	0.2	0.8	9.01	0.25	0.364	0.172	-0.436	0.398	-1.012
6	0.1	0.9	8.98	0.11	0.189	0.065	-0.476	0.20	-1.467

where, $x = M_1/M_2$; $y = m_1/(1 - m_1)$; $F = x^2/y$; $G = x[(y - 1)/y]$; $\alpha = \sqrt{F_M \cdot F_m} = 0.272$; $\xi = F/(\alpha + F)$; $\eta = G/\alpha + F$

Table 3. Extended K-T parameters for copolymers of AMC with VAc

Polymer No.	ζ ₂	ζ ₁	z	F	G	ξ	η
2	0.090	0.092	1.034	0.965	0.031	0.783	0.025
3	0.079	0.088	1.113	0.595	-0.234	0.690	-0.271
4	0.076	0.093	1.234	0.343	-0.385	0.563	-0.630
5	0.072	0.094	1.298	0.190	-0.523	0.416	-1.143
6	0.071	0.104	1.478	0.073	-0.567	0.216	-1.664

where, $\mu = \mu_2/\mu_1 = 0.374$; $\zeta_2 = w(\mu + x/\mu + y)$; $\zeta_1 = \zeta_2(y/x)$; $z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$; $F = y/z^2$; $G = (y - 1)/z$; $\alpha = \sqrt{F_M \cdot F_m} = 0.2669$; $\xi = F/(\alpha + F)$; $\eta = G/\alpha + F$

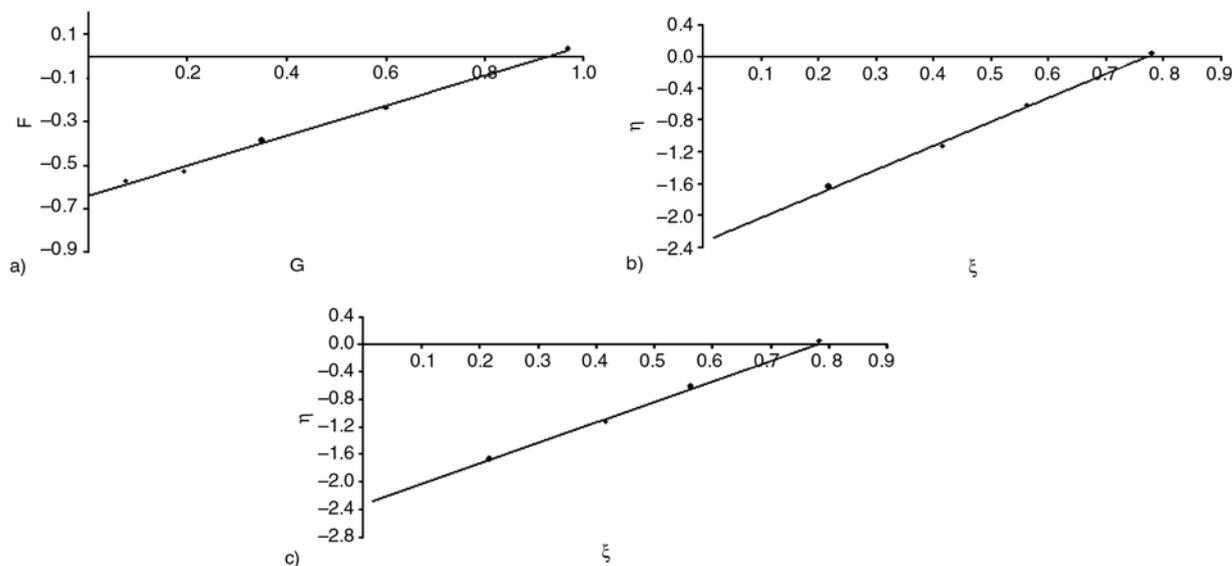


Figure 4. P(AMC-co-VAc) system (a) Finemann-Ross plot, (b) Kelen-Tüdös plot and (c) Extended Kelen-Tüdös plot

Table 4. Monomer reactivity ratio by different linearization methods

Method	r_1	r_2	r_1r_2
Fineman-Ross	0.6924	0.6431	0.6173
Kelen-Tüdös	0.6776	0.6374	0.6690
Extended Kelen-Tüdös	0.6657	0.6256	0.6530

r_1 and r_2 are the reactivity ratios of AMC and VAc, respectively

olefin molecules containing moderately electron-donating or electron-withdrawing groups favor free radical polymerization. VAc consists of electron withdrawing acetate group attached to olefin molecule while AMC consist of electron withdrawing phenyl group. But the net charge on AMC is less compared to VAc and thus is more reactive. Also steric effects and overall polarity of molecule plays a key role in relative reactivity of monomers. Since the r_1 and r_2 values are less than one, this system gives rise to azeotropic polymerization at a particular composition of the monomers which is calculated using Equation (4) [20]:

$$N_1 = \frac{(1-r_2)}{(2-r_1-r_2)} = 0.537 \quad (4)$$

When the mole fraction of AMC in the feed is 0.537, the copolymer formed will have the same composition as that of feed. When the mole fraction of the feed is less than 0.537 with respect to AMC, the copolymer is richer in this monomeric unit. When the mole fraction of AMC in the feed is above 0.537, the copolymer is relatively richer in VAc monomeric unit.

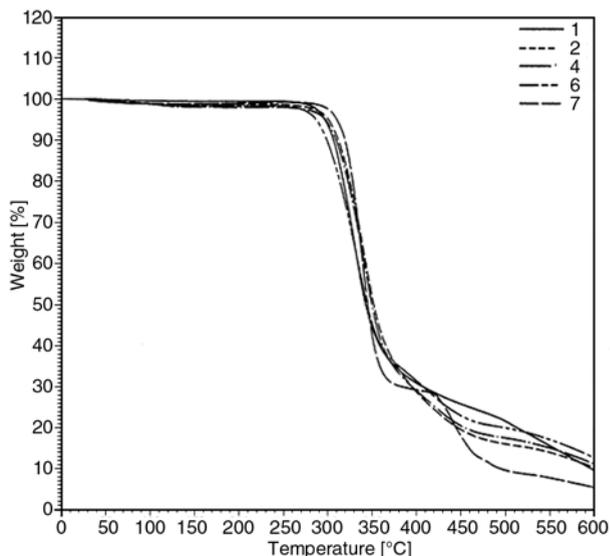


Figure 5. TG curves of P(AMC), P(AMC-co-VAc) and P(VAc)

3.3. Thermogravimetric analysis

TGA curves for P(AMC), P(VAc) and P(AMC-co-VAc) are shown in Figure 5. The thermograms clearly indicate that P(AMC) and P(AMC-co-VAc) undergoes single step degradation where as P(VAc) undergoes double step degradation. The decomposition temperature of different copolymers ranges between to 263–567°C. The activation energy found by Broido’s method [21] lies in the range of 38 to 50 kJ·mole⁻¹ whereas integral procedural decomposition temperature found by Doyle’s method [22] lies in the range of 348–358°C. The detailed result are shown in Table 5 and indicates that value of E_A and IPDT does not depend on AMC content in the copolymers i.e. it may increase or decrease randomly with decrease in AMC content.

Table 5. TGA, GPC and viscosity data for homo and copolymers of AMC with VAc

Polymer No.	Decomposition temperature range [°C]	T_{50}^a [°C]	IPDT ^b [°C]	Activation energy ^c (E_A) [kJ·mole ⁻¹]	\bar{M}_n	\bar{M}_w	\bar{M}_z	Poly dispersity index \bar{M}_w/\bar{M}_n	Intrinsic viscosity (η) [dl·g ⁻¹]
1	280–403	341	348	43	31230	47070	63470	1.507	0.212
2	280–450	351	355	40	30430	44590	59600	1.465	0.196
4	286–455	352	358	38	26060	37990	51250	1.458	0.168
6	263–458	343	348	39	21840	30320	40050	1.388	0.138
7	283–373 419–567	338	358	50	20580	27130	36380	1.318	0.108

^atemperature for 50% weight loss

^bintegral procedural decomposition temperature by Doyle’s method

^cby Broido’s method

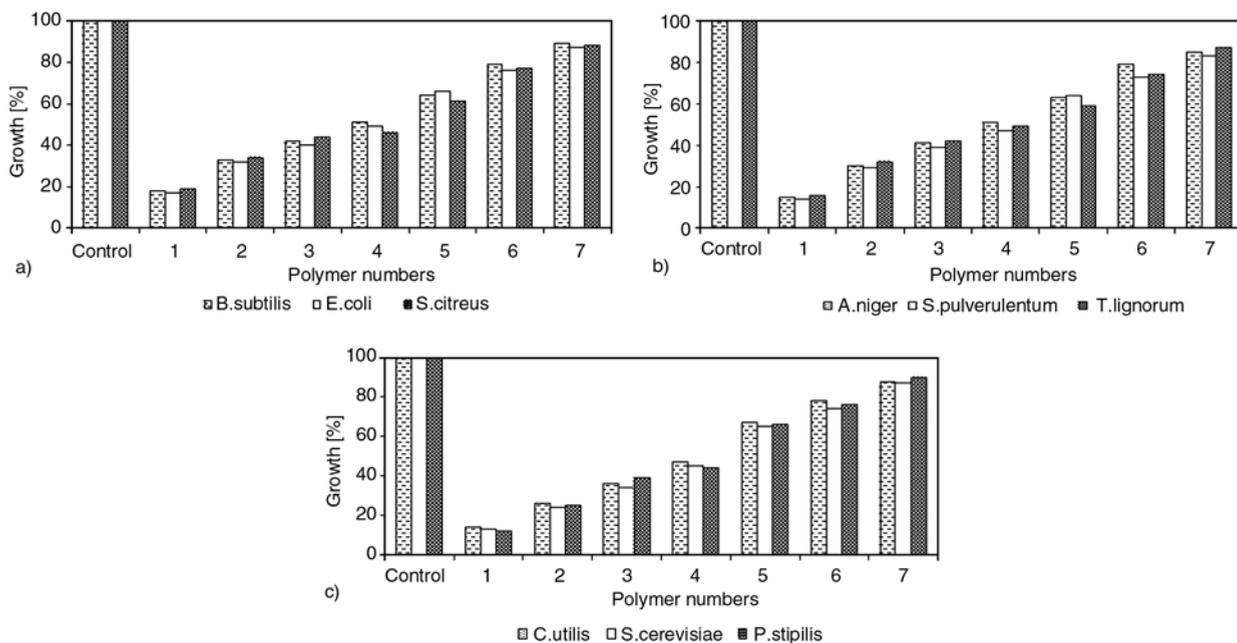


Figure 6. Effect of P(AMC), P(AMC-co-VAc) and P(VAc) on growth of (a) bacteria, (b) fungi and (c) yeast

3.4. Molecular weights

The number and weight average molecular weight of P(AMC) and P(AMC-co-VAc) were determined by gel permeation chromatography and are presented in Table 5. The polydispersity indices of different polymers lies in the ranges 1.318 to 1.507 respectively whereas intrinsic viscosity $[\eta]$ ranges from 0.108 to 0.196 dl·g⁻¹. The results indicate that with decrease in the AMC content in the copolymers, molecular weights, polydispersity and viscosity decreases to the considerable extent.

3.5. Antimicrobial activity

The results obtained for antimicrobial activity of the P(AMC), P(AMC-co-VAc) and P(VAc) are presented in Figures 6a, 6b and 6c. P(AMC) allows 17–19% growth of bacteria, where as its copolymers favors 24–78% growth. Fungi in presence of P(AMC) register around 14–16% growth, while 29–79% growth for fungi is observed in the copolymers. Yeast in presence of P(AMC) shows 12–14% growth, while 24–78% growth for yeast is observed in copolymers. The P(AMC) is found to be most effective in inhibiting the growth of microorganisms; these may be traced due to heterocyclic moiety of coumarin. As the percentage of monomer AMC increases in the copolymer the antimicrobial activity of the copolymers increases.

4. Conclusions

New acrylate based homo and copolymers were synthesized by free radical solution polymerization technique. The monomers and copolymers were characterized by spectroscopic methods. The reactivity ratio of AMC (r_1) is greater than VAc (r_2) and the product of r_1r_2 is less than one. This shows that the monomers were distributed in the copolymer chain in random fashion. Thermo gravimetric analysis showed that P(AMC) and P(AMC-co-VAc) undergoes single step decomposition where as P(VAc) undergoes double step decomposition. All the polymers showed moderate thermal stability. The number average molecular weight and weight average molecular weight were in the range of 20580 to 31230 and 27130 to 47070 respectively. Molecular weight increases with increase in content of AMC in copolymer. Presence of 4-methylcoumarin group in the polymer chain imparts antimicrobial properties to the polymers. The results of antimicrobial activity shows that the copolymers containing AMC shows excellent growth inhibition against all microorganisms and as AMC content in the copolymers increases the growth inhibition of microorganisms also increases.

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