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Effect of the Acrylate/Methacrylate Monomer Compositions on Copolymer's Thermal Stability and Biocidel Activity

Umesh Patel[1], Mehdihasan Shekh[2] and Rajnikant Patel[2*]

[1]Department of Chemistry, Sardar Patel University, Vallabh Vidhyanagar, Gujarat, India
[2]Department of Advanced Organic Chemistry, PD Patel Institute of Applied Sciences, Charotar University of Science Technology, Changa, Gujarat, India

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ABSTRACT

Both monomers 8-quinolinyl methacrylate (8-QMA) and 2-(N-phthalimido) ethyl acrylate (NPEA) are biologically active and their possible applications are in the field of the biomedical and membrane science. In this study, copolymers of NPEA and 8-QMA of various compositions were prepared using free radical solution polymerization technique. The composition of the copolymers was determined by Ultra-Violet (UV) spectroscopy. The reactivity ratios of the monomers were calculated using the conventional linear methods. The value r_2 is slightly higher than r_1 which suggest that monomeric units of NPEA and 8-QMA in copolymers were negligibly varied. Gel permeation chromatography is employed to evaluate the average molecular weights of the copolymers. Thermal stability of the copolymers was confirmed from the thermogravimetric analysis (TGA). To confirm antimicrobial properties of copolymers, they are assessed on various microorganisms. It is found that as increases of 8-QMA content in the copolymers, copolymers were more effective on growth of microorganisms.

Keywords: Free radical polymerization; Acrylate/methacrylate monomers; Copolymer composition; Thermal stability; Biocidal activity

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INTRODUCTION

Acrylic polymers were most useful due to their materialistic properties which are mainly weather durability, film forming ability, thermal stability, sparking crystal clarity and inflammability. They are mostly useful to prepare adhesives, coating materials, food packaging materials, dental materials, drug delivery materials, adsorbent materials, optoelectronic materials and many more [1-11]. By copolymerizing technique, two individual monomers having different properties were combines and forms copolymers. These copolymers have different properties than their individual monomers or hompolymers. In this article, we are showed the effect of monomer composition in copolymers which affects the thermal stability and antimicrobial properties. There are various copolymerization techniques are reported. These polymerization techniques were mainly bulk polymerization, emulsion polymerization, suspension polymerization, atom transfer free radical polymerization, reversible addition-fragmentation chain-transfer polymerization and free radical solution polymerization [12-17]. Among these techniques, free radical solution polymerization technique is easy to handle and cost effective. However, it has few disadvantages but these are negligible. In this article, copolymers of NPEA with 8-QMA (having different composition of monomers) was prepared through free radical solution polymerization technique.

It is interestingly notify that functional polymers were most useful due to presence reactive functional groups and also for their macromolecular properties. There were number of studies has been carried out by researchers in these area. Functional polymers were mainly useful for antimicrobial coatings or antimicrobial agents. Fluorinated acrylate copolymers are mostly useful for dental applications [18]. Phthalimide moiety containing acrylate polymers

are used for optical brightening agents, have good heat resistance and transparency [19,20]. Coumarine and phthalimide moiety containing acrylate or methacrylate copolymers possess good biocidal activities [21]. From these points keeping in minds, we take 8-QMA and NPEA as monomers and prepared the copolymers. However, only functionality of monomer is not effective for desirable application but distribution in copolymer chain is most important factor to obtain polymer with adequate application. So, the reactivity ratio of the monomers can important factor in free radical polymerization technique. The reactivity ratios of monomers pairs have been investigated by various research groups [22-26]. It was easy to predict the copolymer microstructure and copolymer properties from the values of reactivity ratios. In this article, we found the reactivity ratios of monomers (i.e., NPEA and 8-QMA) and these reactivity ratios are used to predict the copolymer microstructure.

This article covers the synthesis of monomers NPEA and 8-QMA from their respective starting materials. The copolymers having different monomer feed ratios which have been synthesized through free radical solution polymerization techniques. Monomers and copolymers were characterized through spectroscopic techniques. Thermal stability and Antimicrobial study of the homo and copolymers were confirms from the thermogravimetric analysis (TGA) and quantitative methods, respectively.

EXPERIMENTAL SECTION

Materials

The chemicals like, phthalic anhydride, acrylic acid, methacrylic acid, hydroquinone, 8-hydroxy quinoline, N, N-dimethyl formamide (DMF), methanol, 2, 2-azobis isobutyronitrile (AIBN) are purchased from the Loba Chem. Pvt. Ltd., India. All chemicals are analytical grade and no further purification is carried out.

Synthesis

Synthesis of acryloyl chloride (AC) and methacyloyl chloride (MAC):

Acryloyl chloride and methacryloyl chloride are synthesized by previously reported procedure [27]. Acrylic acid (0.1 mole) or methacrylic acid (0.1 mole) taken in to round bottom flask (RBF). Add the benzoyl chloride (0.21 mole) and hydroquinone (0.0025 mole) in RBF. Put RBF into oil bath and connect the flask with distillation essambly. Heat reaction mixture and maintain the temperature below 98^{o}C. Collect the product at their respective boiling points. The range of boiling points of acryloyl chloride and methacryloyl chloride are 72-76°C and 90-95°C, respectively. Both AC and MAC are distilled two times and then used for further reaction.

Synthesis of N-(2-hydroxyethyl) phthalimide (NHEP):

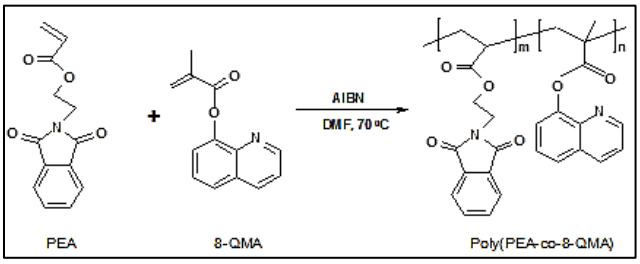
Following procedure was adopted for synthesis of NHEP [28]. Firstly, Phthalic anhydride (0.1 mole) was dissolved (with stirring) in 50 ml of DMF in two necked RBF. Cooled the above mixture at 10^{o}C and then add dropwise monoethanol amine in it. Then after reaction mixture was refluxed at 130^{o}C for 3 hrs. Excess DMF was distilled out and the contents were poured in ice-water mixture. White product is follow out and filtered off. The product is recrystallized using rectified spirit as a solvent. The melting point of the product was 126°C and the yield was 88%.

Synthesis of NPEMA and 8-QMA:

Synthesis of monomers, NPEA and 8-QMA were reported in our earlier publication [28,29]. In one liter three necked flask, DMF (200 ml) and tri-ethyl amine (0.1 mole) were added and the contents were stirred. After 30 minutes, NHEP (0.1 mole) was added and 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 acryloyl 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 then it was poured into crushed ice water mixture where light yellow colored solid product settled down. It was filtered and recrystallised from rectified spirit. The yield was 78% and the melting point was 106°C.

Same procedure was followed for synthesis of 8-QMA by changing the starting material like NHEP to 8-hydroxy quinoline (8-HQ) and acryloyl chloride to methacryloyl chloride. 8-QMA is solid, light yellow colour product and has 47-50°C of melting point range. The yield was 62%. Both monomers were characterized by ^{1}H-NMR spectroscopy (Bruckner 400 MHZ FT NMR spectrophotometer) and Fourier-Transform Spectroscopy (FT-IR) (Nicolet 6700 FT-IR spectrophotometer).

Copolymer synthesis:



Scheme 1: Copolymer synthesis of NPEA with 8-QMA

Copolymers of NPEA with 8-QMA were prepared as follow; Copolymers having different compositions of monomers NPEA and 8-QMA were synthesized by free radical polymerization using AIBN as a free radical initiator in DMF solvent. The feed composition of monomer and comonomers are given in Table 1. Appropriate quantities of monomer, comonomer, solvent (10 ml) 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°C for 5 hours with stirring. It was then cooled to room temperature and the resulting polymer solution was slowly poured in a large volume of methanol as a non-solvent with stirring for all copolymer system Solid polymers were purified by repeated precipitation and finally dried. Scheme 1 shows the reaction leading to the formation of copolymers of NPEA with 8-QMA. The structures of the copolymers were confirms from the FT-IR spectra whereas UV spectroscopy is adopted to confirm the copolymer composition and reactivity ratios. The average molecular weights of the copolymers were found using gel permeation chromatography (GPC). Thermal stability of the copolymers were confirms from the thermogravimetric analysis (TGA) (Mettlertoledo thermogravimetric analyzer and Heating rate: 10°C/min.).

Table 1: Monomer feed composition for copolymer preparation

Sample No.	Monomer feed ratio						NPEA concentration in copolymer	% yeild
	NPEA			8-QMA				
	Mole	Gms.	% wt	Mole	Gms.	%wt		
1	1	245	100	-	-	-	100	84
2	0.2	49	20	0.8	170.4	80	34.55	72
3	0.4	98	40	0.6	127.8	60	51.08	62
4	0.5	122.5	50	0.5	105.5	50	65.37	81
5	0.6	147	60	0.4	85.2	40	77.58	69
6	0.8	196	80	0.2	42.6	20	91.21	65
7	-	-	-	1	213	100	-	79

Biocidel Activity

Biocidel activities of the copolymers were assessed on various microorganisms. The procedure of biocidel activity was reported in elsewhere [29,30]. The copolymers were tested on bacteria (*Escherichia coli*, *Bacillus subtilis* and *Staphylococcus citreus*), fungi (*Sporotichum pulverulentum*, *spergillus niger* and *Trichoderma lignorum*) and yeast (*Candida utilis*, *Pichia stipites* and *Saccharomyces cerevisiae*).

RESULTS AND DISCUSSION

^{1}H-NMR Spectroscopy

Proton NMR spectral data of the monomers NPEA and 8-QMA were as follow:

In NPEA, two doublet of doublets is observed at 7.9 and 7.7 δ ppm which is corresponds to four aromatic protons. Three vinyl hydrogen gives three different multiplates at downfield is observed at 6.4, 6.1 and 5.8 δ ppm. Another two methylene multiplates were observed at 4.4 δ ppm and 4.0 δ ppm which is corresponds to methylene group attached to oxygen and nitrogen, respectively. While in 8-QMA, the aromatic protons of quinolinyl ring's gives three different multiplates having 8.5, 8.1 and 7.9 δ ppm values. The two vinyl hydrogen gives two different signals at 5.9 and 6.4 δ ppm. The singlet is observed near 2.1 δ ppm is corresponds to methyl proton.

Fourier Transform Infrared Spectroscopy (FT-IR)

In this article, only copolymers FT-IR spectrums are shown in Figure 1. The FT-IR spectrums of NPEA and 8-QMA shows the two new peaks in the range of 1730-1755 cm^{-1} and 1630 cm^{-1} which confirms that acryloyl chloride and methacryloyl chloride is successfully attached to the NHEP and 8-HQ. Former one is due to the C=O stretching in ester group and latter one is corresponds to the C=C stretching. In NPEA, another band is observed ~1720 cm^{-1} which is corresponds to the C=O stretching in amide group while sharp strong band near 719 cm^{-1} (rocking vibration of methylene group) is confirms the presence of methylene group in NPEA. Few more bands are observed which are common for both monomers and they are ring breathing vibration of C-C stretching between 1450-1600 cm^{-1}, C-O-C bending (in vinyl esters) vibrations between 1300-1210 cm^{-1} and 1190-1140 cm^{-1} and two peaks near 876 cm^{-1} and 815 cm^{-1} is corresponds to the C-H out of plane bending in benzene ring. In case of Copolymers, one of the band near 1630 cm^{-1} is disappeared which confirms the monomer is converted into polymer. All corresponding bands of C=O stretching in esters and amides; ring breathing vibration of C-C, $-CH_2$ rocking vibration, C-O-C bending vibration and C-H out of plane bending vibrations are observed at same wave numbers. Few are slightly shifts but these shifting are negligible. However, the intensity of band around 1232 cm^{-1} decreases as decrease in the 8-QMA content in the copolymer (due to C-O-C stretching of 8-QMA moiety).

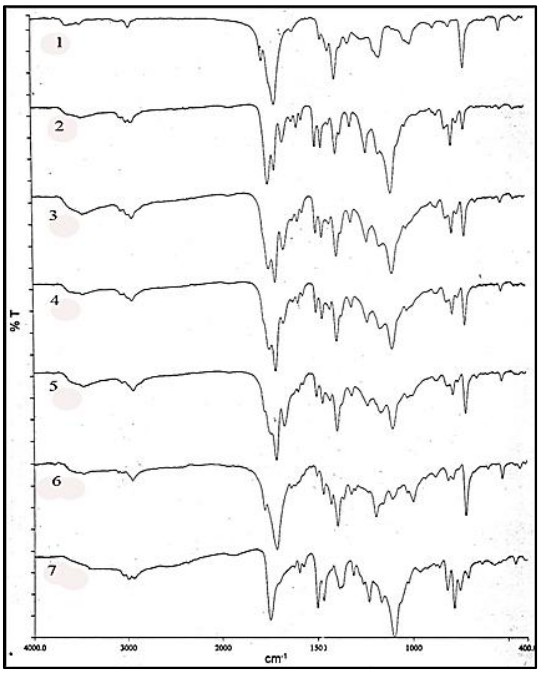


Figure 1: FT-IR spectra of NPEA-co-8-QMA homo and copolymers

Gel Permeation Chromatography

Table 2: GPC and viscosity data for homo- and copolymers of NPEA with 8-QMA

Sample No	Average molecular weights (in Dalton)				Polydispersity (Đ)
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_z$	
A1	19424	39644	64234	88103	2.04
A2	16635	33290	53510	75768	2
A4	14983	29465	48093	70847	1.96
A6	14293	28205	46690	68789	1.97
A7	18704	35308	55226	76016	1.88

The different average molecular weights of the homo and copolymers of the NPEA with 8-QMA was illustrated in Table 2. The GPC data reveals that the values of $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ and polydispersity index which ranges from 14293 to 16635, 28205 to 33290, 46690 to 53510, 68789 to 75768 and 1.96 to 2.0 respectively. For poly (8-QMA) the values of Mn, Mw, Mz, M_{z+1} and polydispersity index is 18704, 35308, 55226, 76016 and 1.88 respectively. The result reveals that molecular weight and polydispersity index changes randomly as the NPEA content increase in copolymer.

Copolymer Composition and Reactivity Ratio

It is easy to predict the properties of the copolymers from the copolymer composition. The copolymer composition is found from the UV spectroscopy (UV-Visible-NIR Schimadzu-3600 spectrophotometer). The procedure is illustrated in our earlier publication [30]. The maximum absorbance wavelength (λmax) of the NPEA was 294 nm. From the copolymer composition, reactivity ratio of the monomers can be easily calculated using linear methods which are mainly Finmann-Ross method (F-R method) [31] and Kelen-Tudos method (K-T method) [32]. The values of r_1 (NPEA) and r_2 (8-QMA) are tabulated in Table 3.

Table 3: Reactivity ratio values for poly (NPEA-co-8-QMA)

Method	Reactivity ratio	
	$\mathbf{r_1}$	$\mathbf{r_2}$
F-R	0.9	1
K-T	0.9	1

In poly (NPEA-co-8-QMA), the value of r_1 is less than r_2, so that 8-QMA is slightly more reactive than NPEA, Which confirms the more 8-QMA monomeric units are present in copolymers. The values of r_1 and r_2 are less than 1, the system gives rise to azeotropic polymerization at particular composition of monomer. Azeotropic mixture of monomers in copolymers was calculated using following equation;

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

From equation 1 the value of N_1 is 0.333. When the mole fraction of the monomer NPEA in the feed is 0.333, the copolymer formed will have the same composition as that of the feed. When the mole fraction of NPEA is below 0.333, the copolymer will be richer in NPEA monomeric unit. When the mole fraction of NPEA in the feed is above 0.333, the copolymer will be richer in 8-QMA monomeric unit.

Mean Sequence Length

Mean sequence length of copolymers can be calculated from the following equations [33],

$$\mu_{\mathrm{NPEMA}} = 1 + \mathrm{r}_1\left(\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\right) \quad (2)$$

$$\mu_{\mathrm{CMPMA}} = 1 + \mathrm{r}_2\left(\frac{[\mathrm{M}_2]}{[\mathrm{M}_1]}\right) \quad (3)$$

Where, M_1 and M_2 are concentrations of NPEMA and CMPMA respectively. Using above equations, obtained sequence of monomeric units in copolymers are shown in Table 4. From the mean sequence length's results, it's easy to predict the monomer alteration or distribution in copolymer chain. The results reveals that, as increases of NPEA from 0.4 mole to 0.6 mole, the monomeric units of NPEA in copolymers are equal to the monomeric units of 8-QMA. This is because of the negligible difference in the values of the r_1 and r_2. While in case of 0.2 mole of NPEA and 0.8 mole of 8-QMA, the monomeric units of 8-QMA are more in copolymers compared to the NPEA. Overall, the values of r_1 and r_2 are well correlate to the monomeric unit's distribution in copolymer chains.

Table 4: Mean sequence length of monomers NPEA and 8-QMA in copolymers

Sample No.	Monomer Feed		μ_{NPEA}	$\mu_{8\text{-}QMA}$	μ_{NPEA}:$\mu_{8\text{-}QMA}$	$\mu_{NPEA}/\mu_{8\text{-}QMA}$	Distribution
	$\mathbf{M_1}$	$\mathbf{M_2}$					
2	0.2	0.8	1	5	03:01	3.7	$N(Q)_5N$
3	0.4	0.6	2	2	02:02	1.4	NNQQNN
4	0.5	0.5	2	2	02:02	0.9	NNQQNN
5	0.6	0.4	2	2	01:03	0.6	NNQQNN
6	0.8	0.2	5	1	01:06	0.3	$(N)_5Q(N)_5$

Note: N=NPEA and Q=8-QMA units

Thermogravimetric Analysis (TGA)

TGA curves of poly (NPEA-co-8-QMA) shown in Figure 2. The % weight loss at different temperature, T^{50}, Decomposition range, and activation energies of copolymers are shown in Table 5. TGA curves depicts that the thermal degradation of the copolymers occur in two steps. First step is due to the small molecular weight containing chains while second one is due to the scission of main polymeric chain. The first step decomposition range for copolymers is varied between 110 to 398°C while second step is varied to 385-520°C. However, poly (NPEA)

shows single step thermal degradation while poly(8-QMA) shows two step degradation. The Tmax, and T^{50} for homo and copolymers of NPEA with 8-QMA are change between 320 to 375°C, and 275-370°C, respectively.

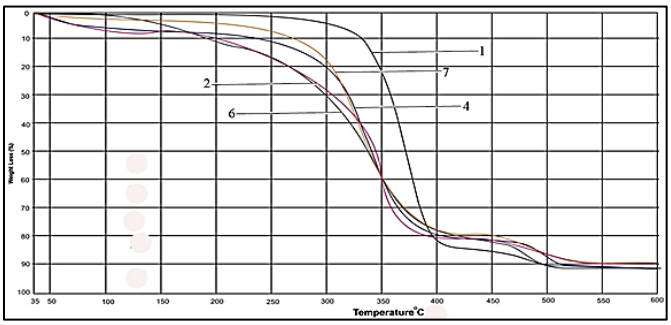


Figure 2: TGA traces of homo and copolymers of NPEA with 8-QMA

Table 5: TGA data for homo- and copolymers of NPEA with 8-QMA

Sample No.	% Weight loss at various temperature (°C)					Decomposition Range (°C) Temperature		Tmax[a] (oC)	T50[b] (oC)	Ea (KJ.mole-1)[c]
	200	300	400	500	600	Step-I	Step-II			
1	2	4	89	97	100	269-498		371	370	51
2	13	25	89	99	100	128-385	385-497	330	329	23
4	8	21	86	95	98	139-389	389-515	336	338	29
6	13	37	85	98	100	135-387	387-498	351	330	32
7	4	18	78	86	98	112-275	275-406	323	275	21

Note: [a] Temperature for maximum rate of decomposition; [b] Temperature for 50% weight loss; [c] By Broido's method

The activation energies of polymers are calculated using Broido method [34]. More activation energy means more energy is required to degradation. The activation energy of poly (NPEA) is more than poly(8-QMA) and their copolymers which reveals that the copolymers and poly(8-QMA) are less stable than poly(NPEA). It is also seen from the data as decreases of NPEA content in copolymers, the activation energy also decreases. Overall, activation energies of homo and copolymers shows that poly (NPEA) is more stable than poly(8-QMA) and poly(NPEA-co-8-QMA). From the thermal properties, it is found that as increases of 8-QMA monomeric units in the copolymers, the thermal stability of the polymers is decreases and vice versa. The results of reactivity ratios, mean-sequence length and TGA analysis are well correlating each other.

Biocidal Activity

The % growth of the microorganisms survives after 24 hours has been shown as Bar graph (Figure 3). From the results, poly (NPEA) permits 46%, 49% and 51% of growth of the bacteria namely, *E.coli*, *B.subtilis*, and *S.citreus*, respectively. Whereas poly (8-QMA) shows 34%, 35% and 31% of the same. The copolymers of NPEA with 8-QMA were permits 36-45%, 39-48%, 38-49% growth of *E.coli*, *B.subtilis,* and *S.citreus*, respectively. While in case of fungi, Poly (NPEA) permit the 58%, 57% and 60% whereas poly(8-QMA) permits 31%, 29% and 32% of growth of *A.niger, S.pulverulentum* and *T.lignorum*, respectively. The copolymers confirms the 36-50%, 33-49% and 38-53% of growth *A.niger, S.pulverulentum* and *T.lignorum*, respectively. For yeast, in the presence of homopolymers of NPEA and 8-QMA % growth observed in the range of 53-55% and 42-47% for all three yeast while copolymers can permit the 42-59% of the % growth of yeasts after 24 hours.

Overall, poly (8-QMA) can inhibit more growth of microorganisms than poly (NPEA) and their copolymers. The copolymers are moderately inhibiting the microorganisms. As increases of 8-QMA content in copolymers the inhibition is also may increases but this is not happens because the difference between the reactivity ratios of the both monomers is negligible. So, negligible difference is also observed in % growth of microorganisms. *-QMA is itself more active towards all microorganisms because of the heterocyclic ring. It is easily attaché to the DNA and affects the replication and cause death of microorganisms.

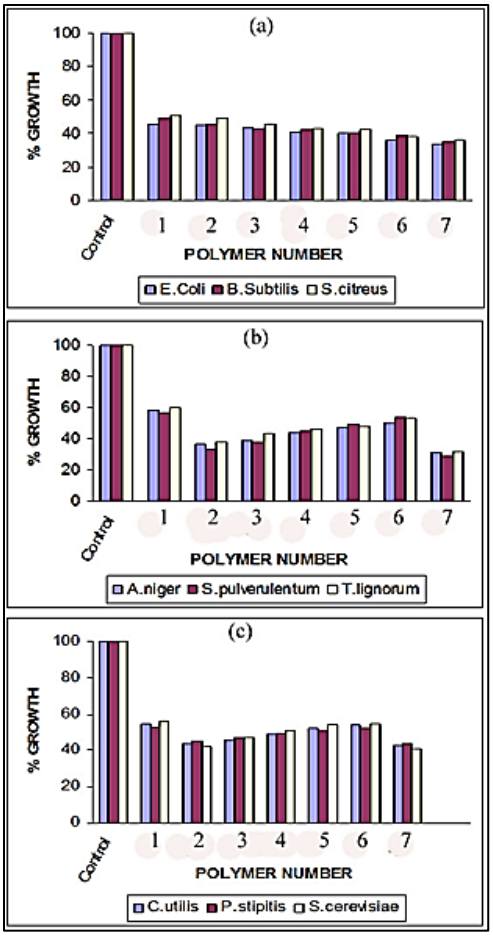


Figure 3: Effect of homo and copolymers of NPEA and 8-QMA on % growth of (a) bacteria; (b) fungi and (c) yeast

CONCLUSION

The FT-IR spectroscopy and ^{1}H-NMR spectroscopic data confirms the monomers and their copolymers are successfully synthesized. UV spectroscopic data confirms that theoretical and practical monomer feeds are almost equal. This is due to the negligible difference between reactivity ratios of the two monomers. Almost same monomeric concentration in copolymers can affects the thermal stability of the polymers and mostly on the activation energies of the copolymers which have negligible difference in the values of activation energies. Poly (NPEA) have 51 kJ/mole of activation energy while poly (8-QMA) have 21 kJ/mole. The difference between activation energies of both homopolymers is almost half while their copolymers have negligible difference. This may be due to the equal distribution of the monomeric units in the chains. Same observation is observed in antimicrobial properties of homo and copolymers. Poly (8-QMA) is effectively inhibiting the % growth of inhibition while poly (NPEA) moderately inhibits the growth of microorganisms. Overall, order of inhibition is Bacteria=Fungi>Yeast.

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