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Research Article

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Copolymers of phthalimide moiety containing 2-(N-phthalimido) ethyl methacrylate (NPEMA) with p-acetamidophenyl methacrylate (PAPMA): Synthesis, characterization, thermal properties and antimicrobial activity

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ABSTRACT

Different functional group/moiety containing methacrylate copolymers are synthesized via free radical solution polymerization in N,N-dimethylformamide at 70 °C using 2,2-azo-bisisobutyronitrile (AIBN) as initiator. The monomers and copolymers are characterized by spectroscopic techniques. The compositions of the copolymers were determined by using UV spectroscopy. The reactivity ratios of the monomers were obtained from linear methods. Using these linear methods, average r_1= 0.9 and r_2= 1.09 were obtained. The mean sequence length is determined by statistical method using average values of r_1 and r_2. Thermal characteristics of the homo and copolymers of NPEMA with PAPMA were evaluated by using thermogravimetric analysis (TGA). The thermal degradation kinetic parameters of homo and copolymers of NPEMA with PAPMAare quantitatively evaluated using namely Broido method. The antimicrobial screening of homo and copolymers of NPEMA with PAPMA is determined by quantitative method.

Key words: Free radical polymerization, reactivity ratio, mean-sequence length,Thermal properties, Antimicrobial screening

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INTRODUCTION

Polymers are macromolecules which are made from the single or two different types of repeating units joined together by covalent bond. Polymers are used in various fields of industries, biomedical, agriculture and daily life because of their macromolecular properties. Various types of polymers are synthesized and characterized by researchers. Because of valuable properties like optical clarity, weather resistance, transparency, crystalinity, solubility, permeability, elasticity, dyeability and adhesion the acrylates or methacrylates polymers are most valuable polymers for preparation of adhesions, UV-Curing coatings, binders in paints, in oil extractions, biomedicals devises, food packaging, used as modifier in polymer concrete and many more [1-11]. Copolymers are macromolecules having diverse property than individual monomers and which made from two or three different types of monomers via different types of polymerization process. In polymerization process free radical polymerization process is one of the versatileprocesses to prepare acrylate or methacrylate homo and copolymers. The copolymers of acrylate or methacrylates are used for their diverse properties, as well as they are also used for their functional group properties [11-15]. Phthalimide moiety containing polymers are used for to improve therapeutic drug profiles, semiconductor in solar cells, optical brightening agents and ion-exchanging polymer stabilizers [16-18]. Macromolecular derivatives of drugs can be prepared by the chemical transformation of the drug

into a reactive derivative suitable for polymerization or by binding the drug into an existing natural or synthetic polymer [19-21]. Copolymer properties are depends on two monomers properties and as well as depends on distribution of two monomeric units in copolymer structure. To find the distribution of the monomericunits in copolymers,several spectroscopic techniques such as ^{1}H-NMR, UV spectroscopy are used [22-23]. Reactivity ratios are determined from F-R and Inverted F-R [24], K-T [25] and Extended K-T [26] methods using the data obtained from spectroscopic techniques.Thermal stability is one of the important properties of polymers. Thermal gravimetric analysis (TGA), differential scanning colorimetriy (DSC), deferential thermal analysis (DTA) and many more techniques are available to determine the thermal stability of polymers, but thermal gravimetric analysis is one of the most useful techniques to determine the thermal stability of polymers.Polymers having antimicrobial properties are used in antifouling paints, in cosmetics, herbicides, insecticides and many more.Present paper, describes the synthesis of monomers N-(2-Hydoxyethyl) phthalimide (NHEP), p-acetamidophenyl methacrylate (PAPMA) and their homopolymers and copolymers prepared using free radical solution polymerization technique. The characterization of monomers, homopolymers and copolymers are using conventional spectroscopic tools. Our main objectives were to find out to thermal stability, kinetics of thermal degradation of synthesized homopolymers and copolymers of NPEMA/PAPMA. UV spectral data were employed to obtain reactivity ratios of the monomers by F-R, Invrt. F-R,K-T and Ext. K-T methods. In addition, the distributions of the monomer sequence along the copolymer chain were determined by using a statistical method based on the average reactivity ratios obtained. TGA traces illustrated the thermal stability of the polymers. The parameters indicated above were obtained for the polymers from the thermal data using broidometjod. The antimicrobial screening is adopted for synthesized homo and copolymers of NPEMA/PAPMA against bacteria, yeast and fungi.

EXPERIMENTAL SECTION

2.1 Materials

Analytical grade N, N-Dimethyl formamide (DMF), Methanol, Phthalic anhydride, Ethanol amine, Benzoyl chloride, Methacrylic acid, Hydroquinone, Triethyl amine (TEA) and 2,2-azobisisobutyronitrile (AIBN) are purchased from Lobachemie. Pvt. Ltd. (India). The chemicals were used without purification.

2.2 Synthesis

2.2.1 Synthesis of starting materials

Methacryloyl chloride (MAC) was synthesized as reported by Stempel [27]. The monomers N-(2-Hydoxyethyl) phthalimide (NHEP), 2-(N-Phthalimido) ethyl methacrylate (NPEMA) and p-acetamidophenyl methacrylate (PAPMA) were prepared as reported [28, 29].

FT-IR data of NPEMA (KBr) : 3059 cm^{-1} (due to the aromatic =C-H stretching), 2977 & 2962 cm^{-1} (due to the –C-H stretching of alkyl group), 1749cm^{-1} (due to the C=O stretching of ester group), 1714 cm^{-1} (due to the C=O stretching of amide group), 1631 cm^{-1} (due to the olifinic C=C stretching), between 1400-1600 cm^{-1} (due to the aromatic C=C stretching), 1466 cm^{-1} (due to the overlay bands of $\delta_{scissoring}$ and δ_{asymm}bending vibration of $–CH_2$ and $–CH_3$ groups), 1366 cm^{-1} (due to the δ_{sym}bending vibration of $–CH_3$), 1173 cm^{-1} (due to the -C-O stretching vibration of ester group), 720 cm^{-1} (due to the rocking vibration of methylene group).

^{1}H-NMR data of NPEMA ($CDCl_3$, δ ppm):=7.5-7.8(4H,m,Ar-CH),5.9 (1H ,d, vinylic-H) , 5.5 (1H , d, vinylic-H), 4.3 (2H , t,$-CH_2$-O),3.9 (2H, t, $-CH_2$-N),1.9 (3H, s, CH_3).

FT-IR data of NPEMA (KBr): 3136 & 3068 cm^{-1} (due to the aromatic =C-H stretching), 2987 & 2931 cm^{-1} (due to the –C-H stretching of alkyl group), 1733 cm^{-1} (due to the C=O stretching of ester group), 1663 cm^{-1} (due to the C=O stretching of anilide group), 1530 cm^{-1} (due to the N-H bending vibration in anilide group), 3308 cm^{-1} (due to the secondary N-H stretching in anilide group), 1198 cm^{-1} (due to the -C-O stretching vibration of ester group), between 1400-1600 cm^{-1} (due to the aromatic C=C stretching), 1641 cm^{-1}(due to the olifinic C=C stretching), 1373 cm^{-1}(due to the δ_{sym} bending vibration of $–CH_3$).

^{1}H-NMR data of PAMA(DMSO, 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, $-CH_3$).

2.2.2 Synthesis of homo and copolymers

Homo and copolymers of NPEMA with PAPMA having different composition were synthesized by free-radical polymerization in DMF using AIBN as a initiator. The feed composition of monomers is given in Table 1. The procedure followed for synthesis of homo and copolymers of NPEMA with PAPMA is reported in reference [30]. Figure 1 shows the reactions leading to the formation of homopolymers as well as copolymers of NPEMA with PAPMA.

2.3 Characterization

The IR-spectra of solid samples in KBr pallets were obtained from Nicolet 6700 FTIR spectrophotometer. Copolymer compositions and reactivity ratios were determined by spectroscopic data from UV-Visible-NIR Schimadzu-3600 spectrophotometer. Average molecular weights of the polymers were obtained by gel permeation chromatography equipped with a 410-RI detector, calibrated with polystyrene used as standards. Thermal analysis was done in nitrogen atmosphere at 10°C/min heating rate by Mettlertoledo thermo gravimetric analyzer for TGA/DSC.

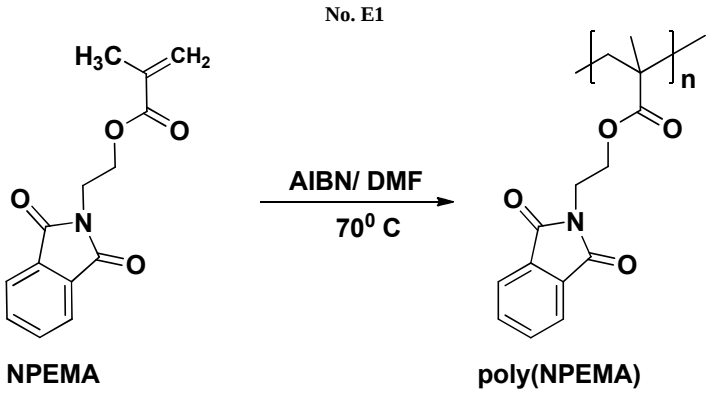
2.4 Antimicrobial screening

The homo and copolymers of NPEMA/PAPMA are tested against different microorganisms which are commonly employed for biodegradability test such as bacteria (*Escherichia coli*, *Bacillus subtilis*and*Staphylococcus citreus*), fungi (*Sporotichumpulverulentum*, *Aspergillusniger*and *Trichodermalignorum*) and yeast (*Candida utilis*, *Pichia stipites* and *Saccharomyces cerevisiae*) known protocol [30] of antimicrobial screening by quantitative method is followed.

RESULTS AND DISCUSSION

3.1 FT-IR spectrum of polymers

The IR spectra of Homo and Copolymer of NPEMA and PAPMA are given in Figure 2. Absence of C=C stretching (1667-1640 cm^{-1}) in Poly-(NPEMA) and copolymers of NPEMA with PAPMA indicate polymer formation. The strong absorptions between 1770-1740 cm^{-1} and 1720-1700 cm^{-1} in all the polymers are attributed to the C=O stretching vibrations of ester moiety and phthalimide group respectively. The band of C=O stretching of amide group is between 1670-1700 cm^{-1}in all copolymers and homopolymers of PAPMA. The medium band at 1455 cm^{-1} has contributions from bending of CH_2 and CH_3 groups. Symmetrical CH_3 bending is assigned in the region 1370-1380 cm^{-1}. Breathing vibrations of aromatic ring are attributed to absorptions between1600-1400 cm^{-1} in these polymers. The band between 1540-1555 cm^{-1} is assigned for bending vibration of N-H in acetanilide group. The C-O-C stretching of ester was traced to absorptions in the range 1210-1163 cm^{-1}. The rocking vibration of methylene group was assigned at 720 cm^{-1} whose intensity decreases as amount of NPEMA in copolymer decreases.



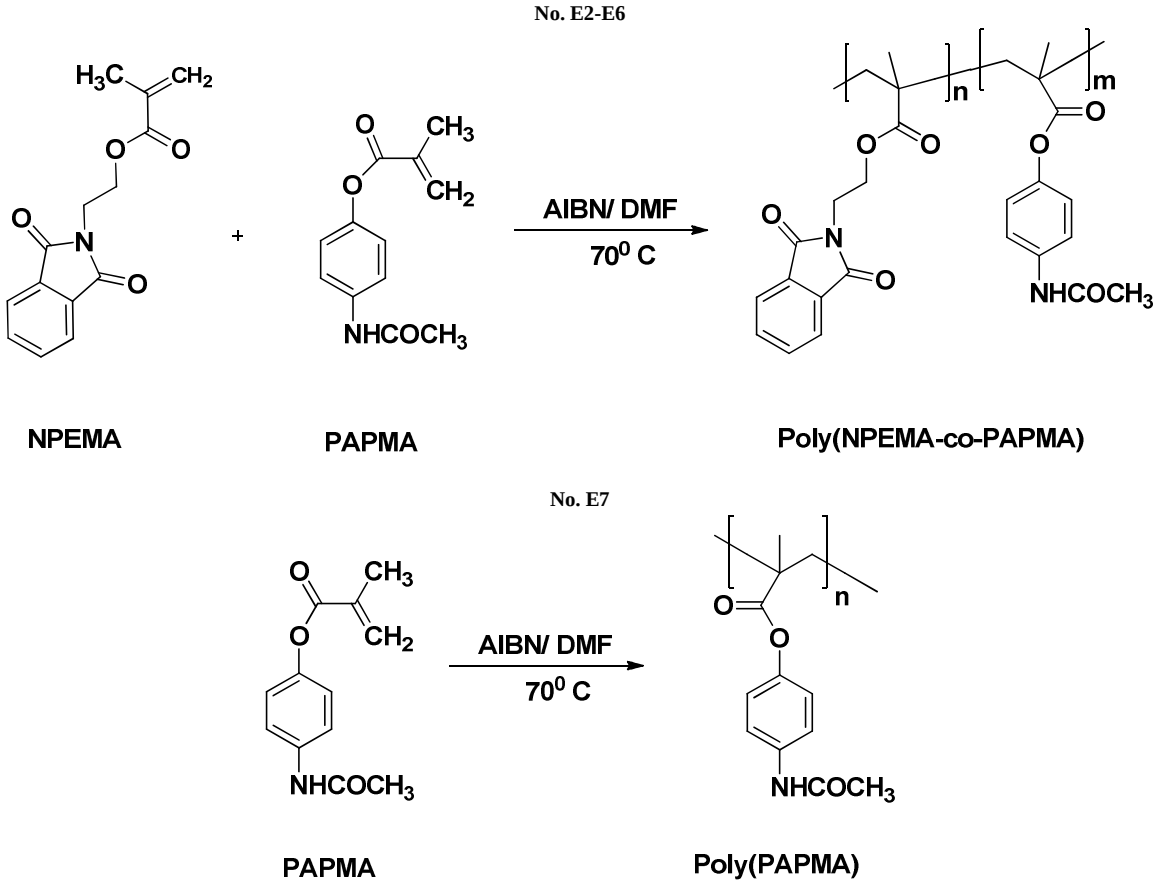


Figure 1: Reaction scheme of formation of homo and copolymers of NPEMA with PAPMA

3.2 Copolymer composition and reactivity ratio

The compositions of monomeric units in copolymer are determined using UV-spectroscopy. The peak maximum for NPEMA is 294 nm. From the standard curve of concentration versus absorbance at 294 nm wascurve employed to find the concentration of NPEMA monomeric units in copolymers. Data obtaining from the UV spectroscopy is use to determine the reactivity of NPEMA and PAPMA monomers from the linear method like Fineman-Rose (F-R), Inverted Fineman-Rose (Inv. F-R), Kelan-Tudos (K-T) and Extended Kelen-Tudos (Ext.K-T) methods. The graphical plotting of linear methods is shown in Figure 3.

If r_1 is less than 1 and r_2 is greater than 1 then, NPEMA favored cross-propagation as opposed to homopropagation and PAPMA favored homopropagation over cross-propagation. The values of r_1 and r_2 aretabulated in Table 2. From the values of r_1 and r_2;thePAPMA was generally more reactive than NPEMA. From the values of $1/r_1$ and $1/r_2$, it is possible to find the ends of growing radical chain weather it is NPEMA unit or PAPMA unit. As the $1/r_1 > 1/r_2$ it can be concluded that there was more growing radicals with NPEMA ends than PAPMA ends due to $r_1 < r_2$. The product of r_1 and r_2 is nearly 1 indicating that the formation of a random copolymer system.

3.2.1 Mean sequence length

The mean sequence lengths μ_{NPEMA} and μ_{PAPMA}were calculated using equation reported in elsewhere [31]. At $[M_1]$ =20.0% and $[M_2]$ =80.0% (Table 3) each copolymer segment with M_2 units was approximately five times longer than its adjoining segment with M_1 units. The sequence may be expressed as NPPPPPN when P stands for PAPMA and N is for NPEMA. The number of NPEMA units in copolymer increases with increasing concentration of NPEMA in the feed. The results of mean sequence length and values of $1/r_1$ and $1/r_2$compare each other very well,$1/r_1$ is greater than $1/r_2$, and as expected in copolymers the homopropagation of PAPMA decreased with decreasing of PAPMA in monomer feed, while cross-propagation of monomeric units increased with increasing concentration of NPEMA in monomer feed.

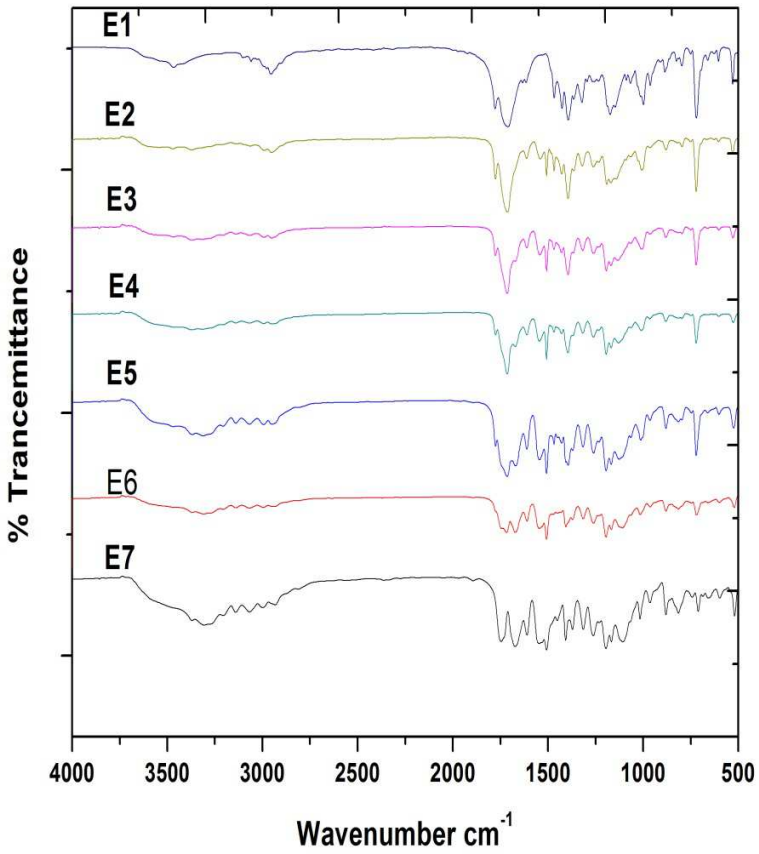


Figure 2: FTIR spectra of homo and copolymer of NPEMA/PAPMA

3.3Average molecular weights

The average molecular weights namely $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ and polydispersity are shown in **Table 4**. The molecular weights of homo and copolymers of NPEMA withPAPMA randomly increases ordecreases as NPEMA in copolymer decreased. The polydispersity of homo and copolymers varied between 1.19-1.45. The polydispersity of homopolymers and copolymers were nearly 1.5, indicating termination of growing chain by radical combination [28].

3.4 Thermal analysis

TGA plays an important role in determining thermal stability of the material. The decompositions of homo and copolymers of NPEMA/PAPMA are illustrated in Figures 4. The decompositions were completed in two steps. The percentage weight loss at different temperatures, decomposition range, integral procedural decomposition temperature (IPDT), T_{max}, T_{50} are tabulated in Table 5 for homopolymers and copolymers of NPEMA/PAPMA. The first step of decomposition in TGA trace corresponded to the breaking of the ester linkages of polymeric chain having small molecular weight and second step which span over a wide range (shown in Table 5) might be due to bond scission of main polymeric chain (-C-C-). It was concluded from the TGA data that the homopolymer of PAPMA is more stable than homopolymer of NPEMA and copolymers of NPEMA/PAPMA. With the increasing amount of PAPMA monomer in the feed ratio the stability of copolymers of NPEMA/PAPMA follow a regular trend. The temperature peak maxima of homopolymer of NPEMA and copolymers of NPEMA/PAPMA also shifts to higher temperature as the PAPMA monomer feed in copolymer increases. The integral procedural decomposition temperature (IPDT) was calculated by Doyle's method[32].

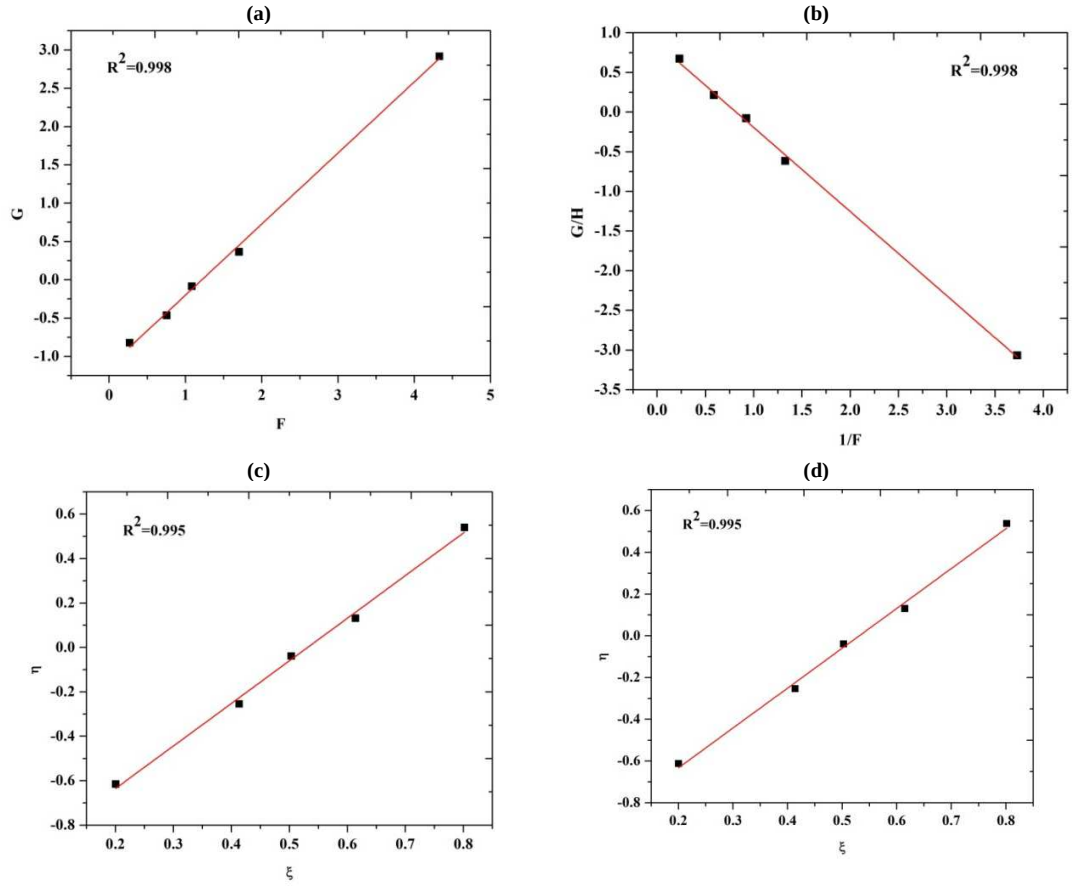


Figure 3: Graphical plotting of (a) F-R method, (b) Invrt. F-R method, (c) K-T method and Ext. K-T method

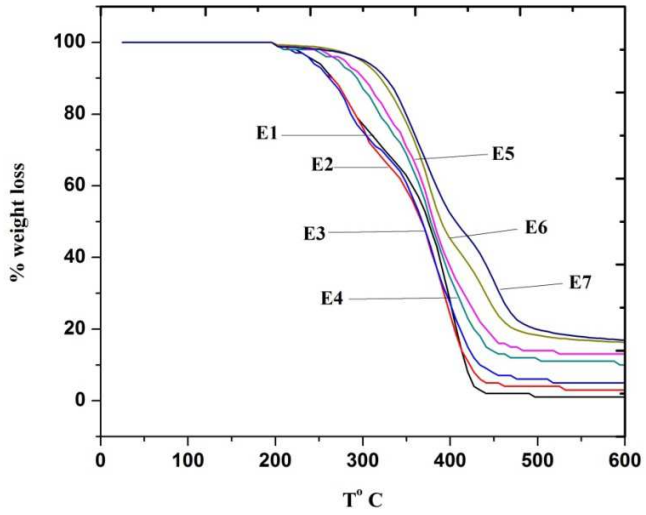


Figure 4: TGA graph of homo and copolymers of NPEMA/PAPMA

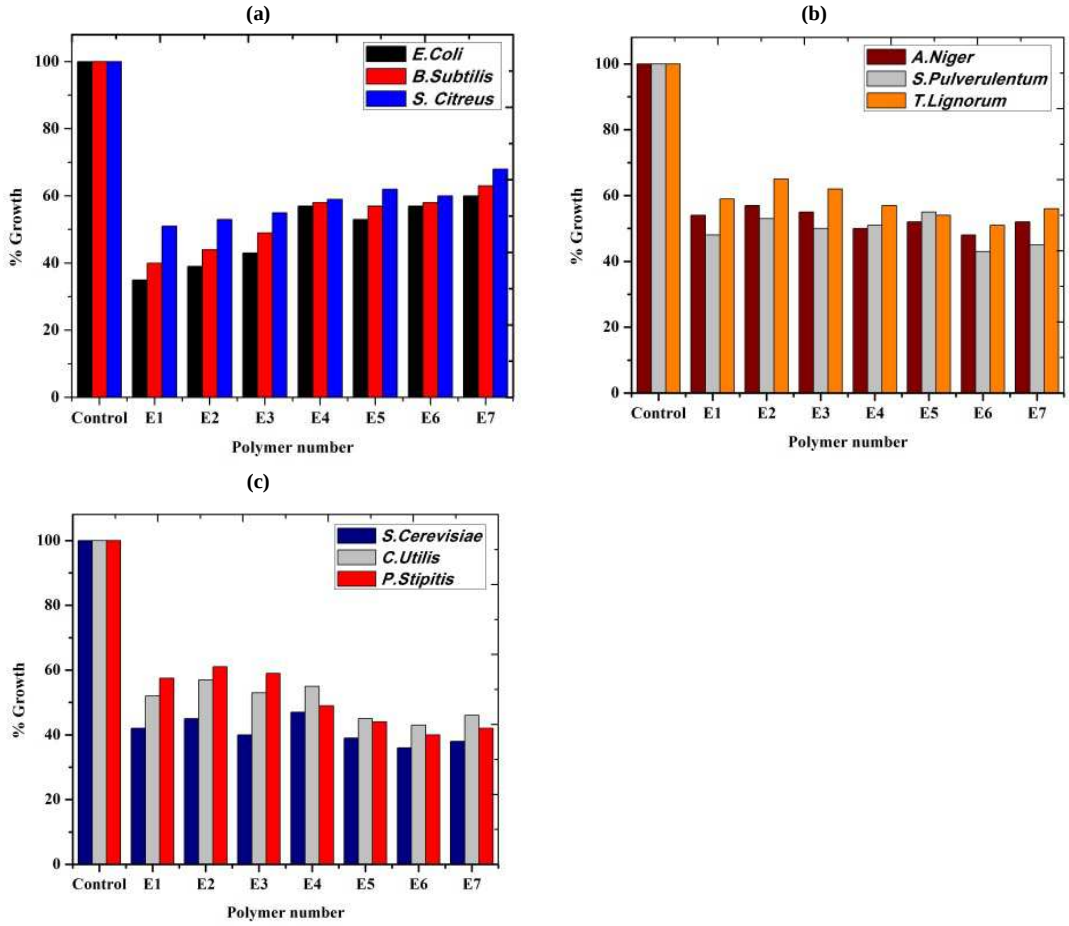


Figure 5: Antimicrobial screening of homo and copolymers of NPEMA/PAPMA against different microorganisms (a). Bacteria (b).Fungi and (c). Yeast

Table 1:Reaction parameters for homo and copolymers of NPEMA with PAPMA

Sample No.	Monomer feed composition						Composition of NPEMA monomer in copolymer (%)	% yield
	NPEMA			PAPMA				
	Mole	Gms.	%	Mole	Gms.	%		
E1	0.1	25.9	100	-	-	-	100	80
E2	0.08	20.72	80	0.02	4.38	20	78	77
E3	0.06	15.54	60	0.04	8.76	40	64	78
E4	0.05	12.95	50	0.05	10.95	50	47	81
E5	0.04	10.36	40	0.06	13.14	60	39	69
E6	0.02	5.18	20	0.08	17.52	80	21	84
E7	-	-	-	0.1	21.9	100	-	70

Table 2: Monomer reactivity ratio of NPEMA/PAPMA Copolymers by F-R, Inv. F-R, K-T and Ext. K-T methods

Method	Reactivity Ratio				
	r_1	r_2	r_1*r_2	$1/r_1$	$1/r_2$
F-R	0.92	1.13	1.04	1.09	0.88
Inve. F-R	0.87	1.06	0.92	1.15	0.94
K-T	0.91	1.09	0.99	1.10	0.92
Ext. K-T	0.89	1.09	0.97	1.12	0.92
Average	**0.90**	**1.09**	**0.98**	**1.11**	**0.92**

Table 3:Mean sequence length of monomeric units in copolymers

Sample No.	Monomer Feed		μNPEMA	μPAPMA	μNPEMA:μPAPMA	μNPEMA/μPAPMA	Distribution
	M1	M2					
E2	0.8	0.2	4.60	1.2725	4:2	3.615	NNNNPPNNNN
E3	0.6	0.4	2.35	1.726667	2:2	1.361	NNPPNN
E4	0.5	0.5	1.90	2.09	2:2	0.909	NNPPNN
E5	0.4	0.6	1.60	2.635	2:3	0.607	NNPPPNN
E6	0.2	0.8	1.23	5.36	1:5	0.229	NPPPPPN

μ_N= NPEMA (N); μ_p= PAPMA (P)

3.6 Kinetics of Thermal Decomposition

The Kinetics parameters of thermal degradation were evaluated from theBroido [33] method. In this method the plot of ln [ln (1/y)] vs 1/T gives a straight line, activation energy (Ea) was obtained from the slope and from the intercept the Pre-exponential factor (A) was calculated. In this calculations y= $(W_t - W_\alpha) / (W_0 - W_\alpha)$ where W_t is the weight at temperature T °k, W_0 is initial weight and W_α is the weight at end of pyrolysis.

The activation energy of first decomposition step was lower than that of second step. It has already been stated that the energy required for first step was less than that required for breaking of polymeric chain in second decomposition step. The value of Activation Energy of homopolymers and copolymers of NPEMA/PAPMA randomly increased or decreased for both the decomposition steps. The Pre-exponential factor was small for both steps indicating that the decomposition of polymer was slow. The values of (R^2), correlation coefficient (Table 6) derived from plots of Broidowas nearly 1 for both steps indicating a good correlation for the decomposition steps.

The values (Tables 6) of Ea, ΔH, ΔS and ΔG are calculated [34] employing Broido method. The positive value of Enthalpy change (ΔH) indicated the endothermic nature of thermal degradation of polymer. The lower the value of ΔH signified the formation of activated complex was easily favored and hence degradation process was faster. The lower activation entropy (ΔS) suggests that formation of activated complex is slow and consequently degradation process is slow and vice versa. The negative value of ΔS and positive value of ΔG for a decomposition process indicate that steps are non-spontaneous. As the values of ΔG increases the process of formation of activated complex is slow which means thermal degradation process is slower and vice versa. The results indicate that homopolymer of NPEMA was less stable than homopolymer of PAPMA and copolymers of NPEMA/ PAPMA. It is seen that the values ofEa, ΔH and ΔG (Tables 6) for first decomposition steps are lower than those of second decomposition steps, suggesting that the first decomposition step was faster than that of second step. This was also proved from the higher value of ΔS for first decomposition step. Consequently first degradation is relatively easier.

3.5 Antimicrobial screening

The results of microbial screening against different microbial organisms were presented in Figure 5. Poly-(NPEMA) allowed 30-45% growth for bacteria, while Poly-(PAPMA) permitted 55–65% growth for bacteria. The copolymers favored 30–60% growth. In case of antifungal screening results showed that poly-(PAPMA) is less effective on fungi than Poly-(NPEMA) and copolymers. Poly-(PAPMA) tolerated around 40–50% growth of yeast, 40–55% growth of the same was observed in the copolymers. Both homo and copolymers are moderately effective in inhibiting the growth of microorganisms. As the percentage of PAPMA in the copolymers increased, the effectiveness of the copolymers to inhibit the growth of microorganisms randomly increased or decreased.

Table 4

Sample No	Average molecular weights				Polydispersity
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_{z+1}$	
E1	18310	26613	37812	50279	1.45
E2	14178	19687	28991	41877	1.37
E3	12812	18551	29538	43266	1.45
E4	15870	19320	27272	39456	1.22
E5	21372	25403	37543	45859	1.19
E6	31622	40202	49247	57888	1.37
E7	26031	31945	37880	43358	1.23

Table 5: TGA data of homo and copolymer of NPEMA/PAPMA

Sample No	% weight loss at different temperature					Decomposition step		Tmax		IPDT
	200	300	400	500	600	step-I	step-II	step-I	step-II	
E1	1.74	21.85	64.98	99.51	100	172-318	318-430	281	405	351
E2	3.59	27.14	78.39	99.34	99.93	162-328	328-459	299	395	360
E3	5.1	29.01	76.35	98.23	99.23	181-318	318-480	279	376	366
E4	6.09	17.82	70.09	93.43	94.58	217-333	333-490	314	377	357
E5	7.66	17.09	69.07	93	94.38	198-334	334-488	319	377	364
E6	7.64	12.4	61.41	88.64	90.7	227-412	412-524	377	441	358
E7	6.22	9.93	52.31	84.91	88.07	221-418	418-556	399	449	361

Table 6: Kinetic parameter of thermal degradation of homo and copolymers of PEMA/PAPMA by Broido method

sample No.	Step	Range	R^2	E*	A	Δs*	ΔH*	ΔG*
E1	I	172-318	0.991	55.97	1.16E-03	-248.84	51.36	189.22
	II	318-430	0.952	82.85	8.97E-05	-271.79	77.21	261.48
E2	I	162-328	0.989	63.57	3.66E-04	-258.69	58.81	206.78
	II	328-459	0.961	85.97	4.39E-05	-277.61	80.42	265.86
E3	I	181-318	0.97	66.44	1.68E-06	-303.15	83.28	250.62
	II	318-480	0.955	87.87	8.52E-04	-252.71	61.04	225.05
E4	I	217-333	0.954	59.74	1.01E-03	-250.48	54.86	201.89
	II	333-490	0.91	57.71	3.78E-03	-240.33	52.31	208.52
E5	I	198-334	0.979	64.63	4.40E-04	-257.44	59.70	212.11
	II	334-488	0.955	65.16	1.08E-03	-250.78	59.75	222.76
E6	I	227-412	0.959	54.30	6.69E-03	-235.59	48.90	202.03
	II	412-524	0.97	75.31	5.50E-04	-257.14	69.37	252.97
E7	I	221-418	0.981	59.78	3.59E-03	-241.04	54.19	216.17
	II	418-556	0.984	84.42	1.52E-04	-267.93	78.42	271.86

CONCLUSION

The monomers NPEMA and PAPMA have been used for preparation of polymers. The monomers and copolymers were characterized primarily from IR data and ^{1}H-NMR data.The $r_1<r_2$ that means the reactivity of PAPMA is more than NPEMA that means more units of PAPMA is present in copolymers and from the data of mean sequence length also prove that the PAPMA units is more in copolymers. The thermal stability of poly(PAPMA) is more than poly(NPEMA) and their copolymers. The kinetic parameter of thermal degradation is also prove that the poly(PAPMA) is more stable than other homo and copolymers.The homo and copolymers of NPEMA and PAPMA could inhibit microorganisms in the order bacteria > yeast > Fungi.

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