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Synthesis and investigation of chemically modified Phthalimide based copolymers and their Antimicrobial activity

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ABSTRACT

A novel phthalimide based monomer 2-(N-phthalimido)ethyl acrylate (NPEA) was synthesized by reacting N-(2-hydroxyethyl)phthalimide (NHEP) with acryloyl chloride and was further copolymerized with styrene (STY). Copolymers of NPEA with STY at different feed composition were prepared by free radical solution polymerization at 70±2°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator and dimethylformamide (DMF) as a solvent. The monomer and copolymers thus synthesized were characterized by Fourier transform infrared spectroscopy (FT-IR) and ^{1}H-NMR. Copolymer composition was obtained using FT-IR and UV spectroscopy. The reactivity ratios of the monomers were determined by Fineman-Ross (r_1 = 0.67, r_2 = 0.79) and Kelen-Tudos (r_1 = 0.68, r_2 = 0.81) methods. Gel permeation chromatography (GPC) was employed to find molecular weights and polydispersity index which increases as the NPEA content increases in the copolymer. Thermogravimatric analysis (TGA) in nitrogen atmosphere showed that thermal stability of the copolymer decreases as the NPEA content increases. The activation energy (Ea), calculated by Broido's method lies in the range 52-58 KJ/mole. As the NPEA content in the copolymer decreases the activation energy increases. Antimicrobial activity of the polymers was also investigated against various microorganisms like bacteria (Bacillus subtilis, Escherichia coli and Staphylococcus citreus), fungi (Aspergillus niger, Sporotichum pulveruletum and Trichocerma lignorum) and yeast (Candida utilis, Saccharomyces cerevisiac and Pichia stipitis). The antimicrobial activity of the copolymer increases as the content of NPEA increases in the copolymer. This demonstrates that phthalimide moiety plays very important role as antimicrobial agent.

Keywords: Phthalimide, Styrene, Copolymer, Reactivity ratios, Antimicrobial activity.

INTRODUCTION

It has been well documented that copolymerization is one of the important techniques used in affecting systematic changes in the properties of the commercially important polymers, for example, the copolymers of acrylic/methacrylic esters have been used for various applications [1,2]. Acrylate homopolymers along with their copolymers are used in various fields such as films, fibers, filaments, coating, lithography, lacquers, adhesives, printing inks and binders [3-5]. The incorporation of two different monomers in the same polymer chain in varying proportions leads to formation of new materials. Acrylic polymers are a class of reactive polymers that finds extensive applications due to the presence of electron attracting

groups in the aromatic ring [6]. Reactivity ratios are amongst the most important parameters for determination of copolymer composition and they offer information about relative reactivity of the monomer pairs. Many reports have been published on the correlation between the reactivity ratio of vinyl monomers and extent of radical polymerization and copolymerization [7,8]. The anhydride groups, in the polymer chain, make the STY polymer very reactive, and therefore, it is commonly used in various fields, as discussed elsewhere [9,10]. The anhydride moiety constitutes a nice handle to modify the polymer [11]. One can modify the polymer via addition of low molecular weight compounds such as water, alcohols, or amines because of the high reactivity of the anhydride group, as discussed by Bruch et al. [12]. The chemical modification of synthetic polymers allows the control of their mechanical and thermal properties [13] and expands their applicability [14-16]. Polymers containing phthalimide groups are found to possess excellent heat resistance and transparency. Copolymers containing phthalimide derivatives have been used as optical brightening agents, as discussed by Jayakumar et al. [17]. The incorporation of the phthalimide group remarkably enhanced the thermal stability of polymers. Polymers bearing the phthalimide group as a pendant group will exhibit relatively high thermal stability and good solubility [18, 19].

The synthesis and development of antimicrobial polymers is one of the leading frontiers of research in polymer science. With this view, the synthesis of NPEA and its copolymerization with STY by free radical solution polymerization was under taken. The prepared monomers and polymers were characterized by FT-IR and ^{1}H-NMR spectroscopy. Copolymer composition was obtained from UV spectroscopic data and monomer reactivity ratios were determined by Fineman-Ross [F-R] [20] and Kelen-Tudos [K-T] [21] methods. The molecular weight and polydispersity index were obtained by GPC. The thermal properties of the polymers were investigated by TGA. Antimicrobial activity of the homo and copolymers was carried out against selected microorganisms like bacteria, fungi and yeast.

MATERIALS AND METHODS

All the reagents were obtained commercially and used with further purification. Solvents used were of analytical grade. All melting points were taken in open capillaries and are uncorrected. Thin-layer chromatography (TLC, on aluminum plates coated with silica gel 60 F_{254}, 0.25 mm thickness, Merck) was used for monitoring the progress of reactions. The FT-IR spectra were recorded using potassium bromide disc on a Shimadzu FTIR 8401 spectrophotometer and only the characteristic peaks are reported in cm^{-1}. ^{1}H-NMR spectra were recorded in DMSO-d_6 on a Bruker Avance 400 (MHz) spectrometer using solvent peak as internal standard at 400 MHz. Shimadzu-160A-recording UV visible spectrophotometer was utilized to obtain UV spectra. GPC instrument equipped with Jasco-PU 1580 pump, multisolvent delivery system, manual injector and series connected two PL gel column packed with styrenedivinylbenzene bead and R.I. detector (RI-71 shodex made) was employed. TA instrument (U.S.A.)–2960 thermogravimetric analyzer was used in the present study to record the thermograms of polymer samples. NOVA Melt Flow Index Tester (Extrusion Plastometer) was employed to measure the MFI.

Synthesis of acryloyl chloride: A mixture of acrylic acid (1 mole), benzoyl chloride (2 mole) and hydroquinone (0.0025 mole) was distilled at a fairly high rate through an efficient column. The distillate was collected in a receiver containing hydroquinone (0.0025 mole). The product was obtained at a temperature between 85-100˚C. The crude product was redistilled through the same column.

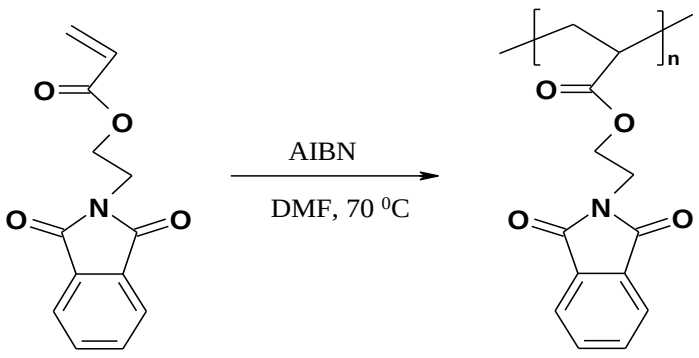
Synthesis of N-(2-hydroxyethyl) phthalimide (NHEP): For synthesis of NHEP [17], Phthalic anhydride (0.1 mole) and 50 ml N,N'-dimethyl formamide (DMF) was taken in a two-necked round bottom flask fitted with a reflux condenser and thermometer. The contents were stirred till phthalic anhydride dissolved. To this mixture monoethanol amine (0.1 mole) was added dropwise. The reaction was moderately exothermic hence cooled in an ice bath. The contents were stirred with a magnetic stirrer and refluxed at 130˚C for 3 hrs. Excess DMF was distilled out and the contents were poured in ice-water mixture. The precipitated product, NHEP, was filtered off and recrystallised using rectified spirit as a solvent.

Synthesis of 2-(N-phthalimido) ethyl acrylate (NPEA): To a one liter three necked flask fitted with stirrer, thermometer and guard tube, DMF (200 ml) and tri-ethyl amine (0.1 mole) were added and the contents stirred for 30 minutes. NHEP (0.1 mole) was added to this mixture in the flask and the contents were heated to 60˚C for 30 minutes with stirring, then cooled to room temperature and finally 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 and 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.

IR (cm^{-1}): 3041 (C-H stretching in olefinic & aromatic ring), 2947 (-C-H stretching vibration due to alkyl group), 1773 (υC=O due to ester group), 1725 (υC=O due to phthalimide group), 1637 (υC=C), 1192 (asymmetric υC-O-C), 1152 (symmetric υC-O-C), Two strong absorptions at 990 and 910 cm^{-1} are seen in this type of vinyl moiety due to out of plane bending of C-H. The out of plane C-H bending in aromatic is ~730 cm^{-1}. ^{1}H-NMR (ppm) (400MHz); 5.84 (m, 1H, -C<u>H</u>=), 5.89 and 6.26 (dd, 2H, non equivalent methylene <u>H</u>), 4.42 (t, 2H, –C<u>H</u>$_2$-O-), 4.01 (t, 2H, -N-C<u>H</u>$_2$-) and 7.79 (m, 4H, aromatic <u>H</u>).

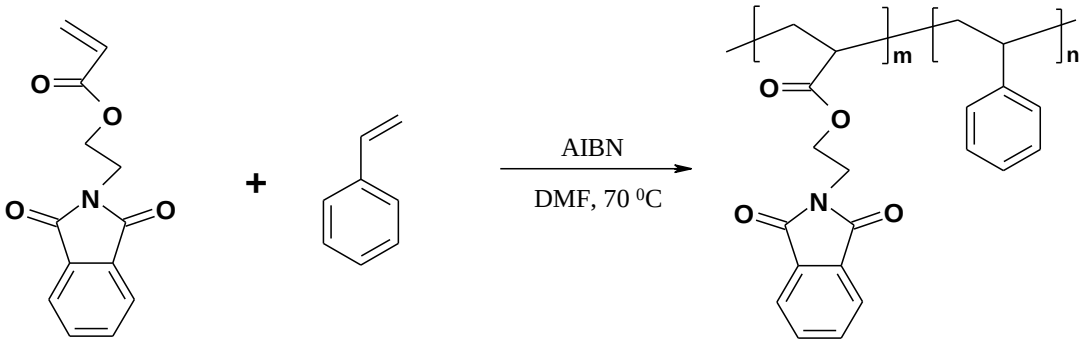
Copolymerization: The copolymers were synthesized by free radical solution polymerization. Appropriate quantities (Table 1) of NPEA, STY, DMF and AIBN were placed in a polymerization tube equipped with reflux condenser. The reaction mixture was heated at 70±2˚C with stirring in air. The polymerization time was carefully controlled to obtain low conversion (less than 10%) in order to follow the copolymer equation. After the specific time, the reaction mixture was cooled to room temperature and the resulting polymer solution was slowly poured in an excess of methanol. The solid polymers thus obtained were purified by continuous re-precipitation by methanol from solution in DMF and finally dried. The proposed reaction pathway is described in Scheme 1 shows the reaction leading to copolymerization of NPEA with STY.

No. 1



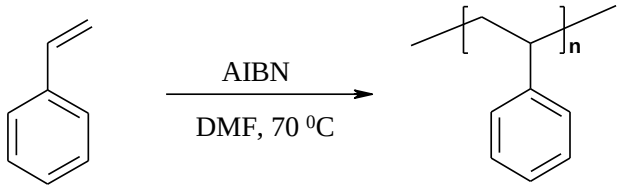
NPEA Poly(NPEA)

No. 2-6



NPEA STY Poly(NPEA-co-STY)

No. 7



STY Poly(STY)

Reaction Scheme of (1) poly(NPEA), (2-6) poly(NPEA-co-STY) and (7) poly(STY).

Determination of the NPEA content in the copolymers: A dilute solution of each copolymer, containing unknown amount of NPEA, was prepared by dissolving exact amount of the polymer into the chloroform. The weight of the polymer sample taken should be such that the concentration of NPEA in the resulting solution remains within the concentration range of the calibration curve. The absorbance of each solution was recorded, at λmax of NPEA (294nm), using chloroform as solvent. By using these absorption values, the corresponding concentration values for NPEA in the copolymers were determined using calibration plot. The values of NPEA content in the copolymer were converted into the appropriate units.

Antimicrobial activity: Homo and copolymers synthesized by different experimental conditions were tested for their effect on the growth of various microorganisms. Also their interactive role with bacteria (*Bacillus subtilis, Escherichia coli and Staphylococcus citreus*), fungi (*Aspergillus niger, Sporotichum pulveruletum and Trichocerma lignorum*) and yeast (*Candida utilis, Saccharomyces cerevisiac and Pichia stipitis*) was investigated. The details of the experimental procedure have been reported elsewhere [22,23].

RESULTS AND DISCUSSION

Synthesis of Polymers: Poly(NPEA) and its copolymers with STY were synthesized by free radical solution polymerization technique with different mole fractions of NPEA in the feed ranging from 0.2 to 0.8 mole shown in table 1.

Table 1: Monomer feed composition and composition of NPEA in the copolymers.

Sample No.	Monomer feed composition						% of NPEA in copolymer	Yield (%)
	NPEA			STY				
	Mole	Gms.	%Wt.	Mole	Gms.	%Wt.		
1	1.0	245.0	100	-	-	-	100.00	84
2	0.2	49.0	20	0.8	83.32	80	36.12	77
3	0.4	98.0	40	0.6	62.49	60	49.02	68
4	0.5	122.5	50	0.5	52.01	50	63.81	62
5	0.6	147.0	60	0.4	41.66	40	79.58	69
6	0.8	196.0	80	0.2	20.83	20	89.12	72
7	-	-	-	1.0	104.15	100	-	79

Copolymer Composition: The average composition of monomer units in the copolymer chain was determined from the corresponding UV-visible spectrophotometer [24]. UV absorption values of standard solution of NPEA in chloroform measured at 294 nm (characteristic λmax of NPEA in chloroform). These absorption values are plotted against known concentration of NPEA, which gives straight-line working curve. Using the absorption values of each copolymer solution at 294 nm, the corresponding concentration of NPEA was determined using plot. Each value was converted into the % of NPEA in the copolymers are presented in Table 1.

Characterization of Polymers: The FT-IR spectrum of respective copolymers is shown in Figure 1. In the spectrum of poly(NPEA), the medium band at 2954 cm^{-1} is attributed to the υC-H stretching vibration of alkyl group and strong absorption at 1467 cm^{-1} is due to bending vibration of $–CH_2$ group. Two sharp and distinct bands at 1770 $cm^{-1}$and 1248 cm^{-1} are assigned respectively to υC=O and υC-O stretching vibration of ester group, while one sharp band at 1712 cm^{-1} is the υC=O stretching ration in phthalimide moiety. The spectrum of poly(NPEA) also shows two strong bands at 1550,1480 cm^{-1} which are the characteristic absorptions of phenyl ring. One medium band observed at 1428 cm^{-1} is attributed to scissoring vibration of -N-C=O group. A strong peak at ~750 cm^{-1} is assigned to υC-H out of plane bending in aromatic moiety.The poly(STY) spectrum shows bands due to $-CH_2-$ group and mono substituted benzene ring. The bands at 1452 cm^{-1} may be due to the $-CH_2-$ bending vibration of methylene group. The band between 3100-3000 cm^{-1} may be assigned to the C-H stretching vibration of aromatic ring where as three bands at 1492 cm^{-1}, 1583 cm^{-1} and 1601 cm^{-1} are due to C=C stretching vibration of aromatic ring. The bands at 760 cm^{-1} and 698 cm^{-1} have contribution from υC-H out of plane bending vibration of mono substituted aromatic ring. It is observed from IR spectra of poly(NPEA-co-STY) that, the intensity of the peak at 698 cm^{-1} (due to C-H out of plane bending in mono substituted phenyl ring of styrene) decreases and the intensity of the peak at 730 cm^{-1} (due to C-H out of plane bending in phenyl moiety of NPEA) increases as the NPEA content in the copolymer increases.

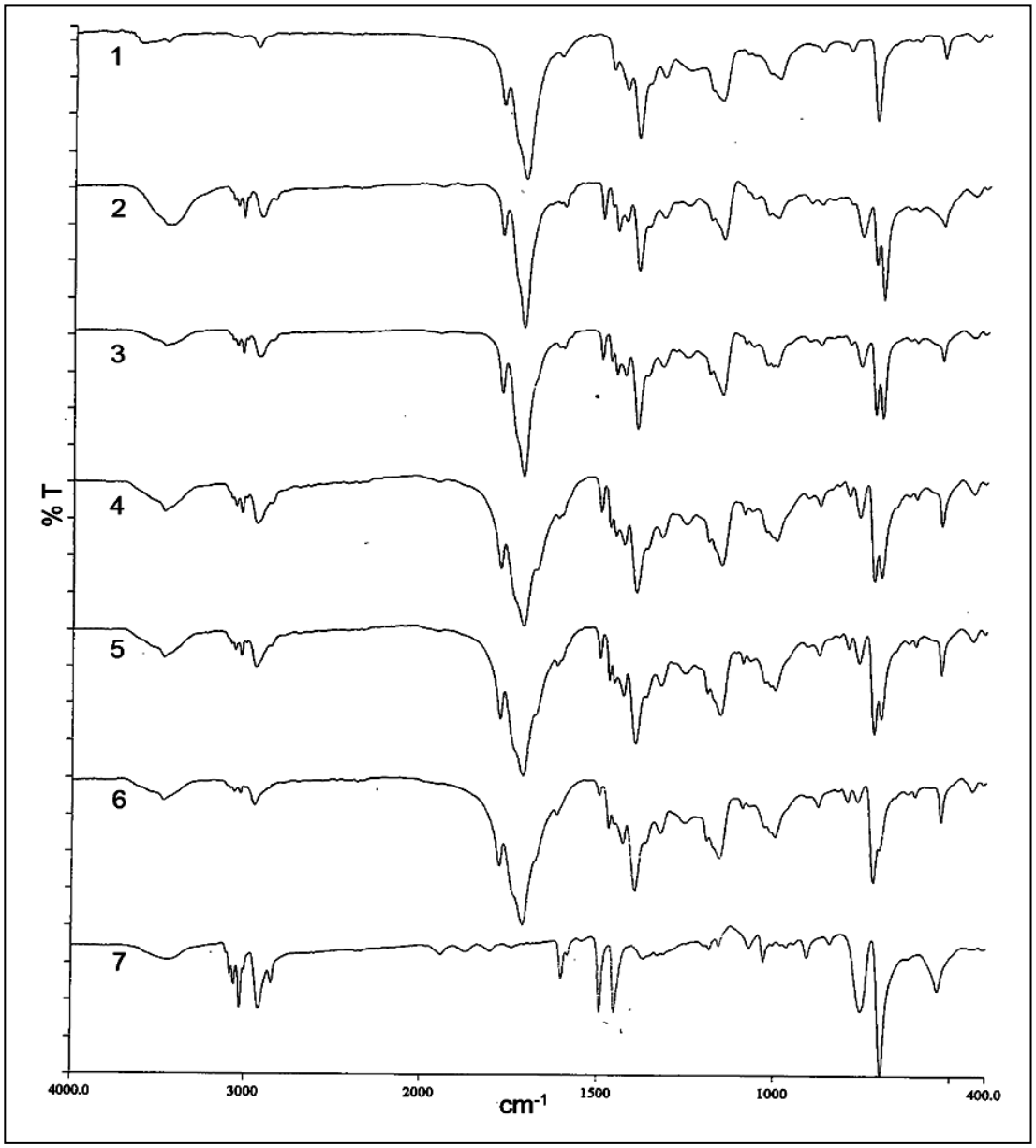


Figure 1: FT-IR spectra of (1) poly(NPEA), (2-6) poly(NPEA-co-STY) and (7) poly(STY).

Reactivity ratios: The monomer reactivity ratios were calculated by the application of linearization methods, such as F-R and K-T. The values of reactivity ratios are presented in Table 2. The r_1 and r_2 values obtained from F-R and K-T methods are in well agreement with each other. Since the value of r_1 is less than r_2. STY is found to be more reactive than NPEA. The values of r_1 and r_2 is less than 1, so the system gives rise to azeotropic polymerization at a particular composition of the monomer which is calculated using equation given below [25]. From equation (1) the value of N_1 is 0.338. When the mole fraction of NPEA in the feed is 0.338, the copolymer formed will have the same composition as that of feed. When mole fraction of feed is less than 0.388 with respect to NPEA, the copolymer is relatively richer in this monomeric unit.

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

Table 2: Reactivity ratio values for Poly(NPEA-co-STY)

Method	Reactivity Ratio	
	r_1	r_2
F-R	0.67	0.79
K-T	0.68	0.81

Molecular weights: The number average and weight average molecular weight and polydispersity index values of poly(NPEA) and poly(NPEA-co-STY) (Polymer no. 2,4 and 6) were estimated by GPC. The data presented in Table 3 shows that the values of $\overline{Mn}$, $\overline{Mw}$ and polydispersity index ranges from 19424 to 15361, 39644 to 27396 gm/mole and 2.04 to 1.78 respectively; whereas intrinsic viscosity ranges from 0.198 to 0.221 dl/gm. The data suggests that molecular weights and viscosity change randomly, where as polydispersity index decrease slightly as the NPEA content increases in copolymer.

Table 3: GPC and viscosity data for poly(NPEA) and poly(NPEA-co-STY)

Sample No.	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mz}$	$\overline{Mz}$ +1	Polydispersity Index	Intrinsic Viscosity [η] dl.g^{-1}
1	19424	39644	64234	88103	2.04	0.198
2	16390	29777	47248	68559	1.81	0.216
4	18833	33877	53313	75398	1.80	0.221
6	18780	33745	52994	74322	1.79	0.219
7	15361	27396	42827	63795	1.78	0.213

Thermogravimetric analysis (TGA): Thermal behaviors of polymers were investigated with TGA. The results of thermal analysis are shown in Table 4. Poly(NPEA), poly(NPEA-co-STY) and poly(STY) are undergo single step degradation. The copolymers undergo decomposition in the range 259-443˚C. The activation energy (Ea), calculated by Broido's method [26] lies in the range 52-58 KJ/mole. As the NPEA content in the copolymer decreases the activation energy increases. The integral procedural decomposition temperature (IPDT) was calculated by Doyle's method [27]. The IPDT tells the overall thermal stability of the polymers and it varies between 532-544˚C.

Table 4: TGA data for homo and copolymers of NPEA with STY

Sample Code No.	Decomposition Temperature Range (˚C)	T_{max}[a] (˚C)	T_{50}[b] (˚C)	IPDT[c] (˚C)	Activation Energy[d] (E_A) (KJ.mole^{-1})
1	269-498	371	370	547	51
2	259-404	381	374	542	58
4	269-403	375	372	532	53
6	276-443	369	373	544	52
7	267-398	397	373	543	66

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

Antimicrobial activity: The antimicrobial activity of homo and copolymers of NPEA with STY was investigated. The results obtained are presented in Figures 2, 3 and 4. All the copolymer systems showed almost similar antimicrobial behavior against bacteria, fungi and yeast. Poly(NPEA) allowed about 49% growth of bacteria, whereas its copolymers favored 65-83% growth. Poly(STY) allows 86% growth of bacteria. Poly(NPEA) allowed 58% growth for fungi whereas its copolymers favored 63-78% growth. Poly(STY) allows 81% growth of fungi. Yeast however in presence of Poly(NPEA) registered 55% growth, while 62-79% growth for yeast was observed in the copolymers. Poly(STY) registered 83% growth of yeast. It is seen from these data that presence of NPEA inhibits the growth of microorganism.

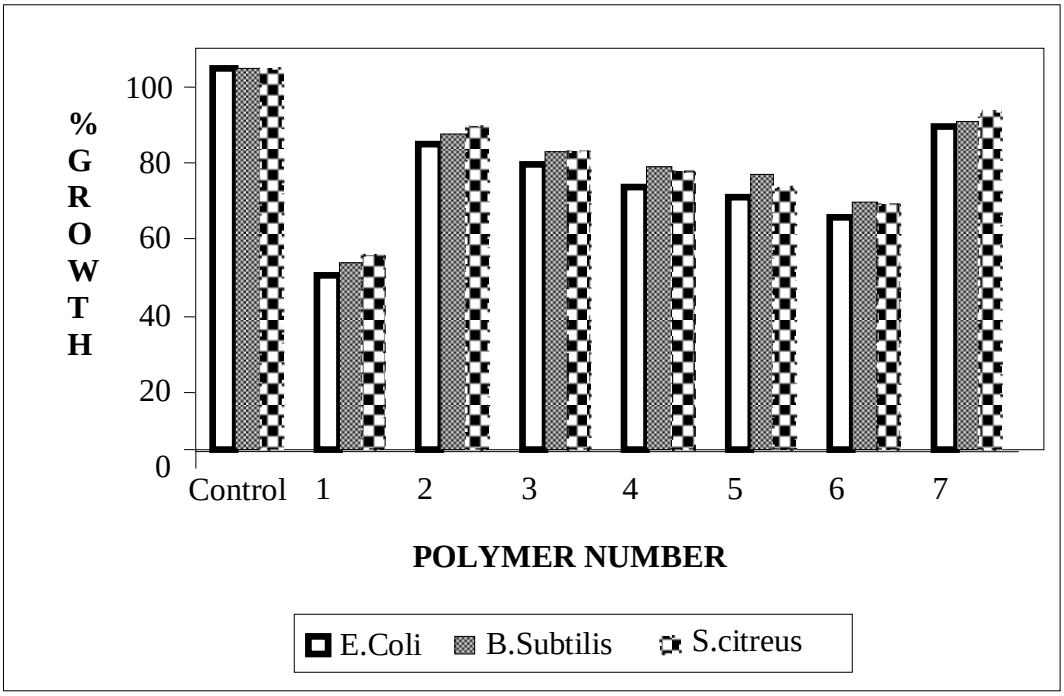


Figure 2: Effect of NPEA-co-STY homo and copolymers on growth (%) of bacteria.

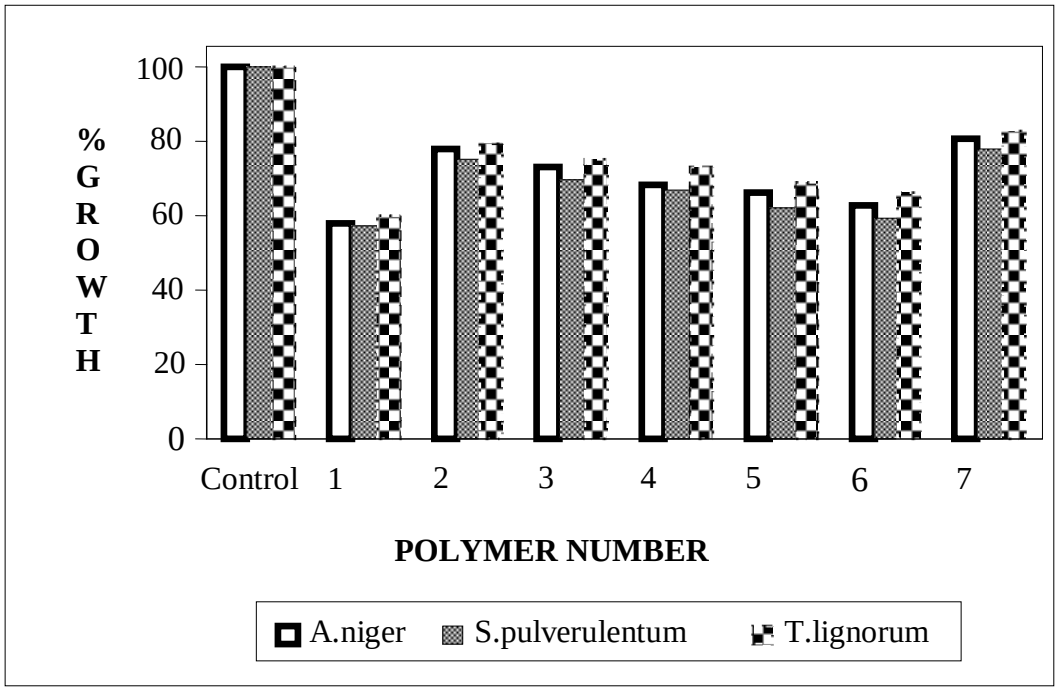


Figure 3: Effect of NPEA-co-STY homo and copolymers on growth (%) of fungi.

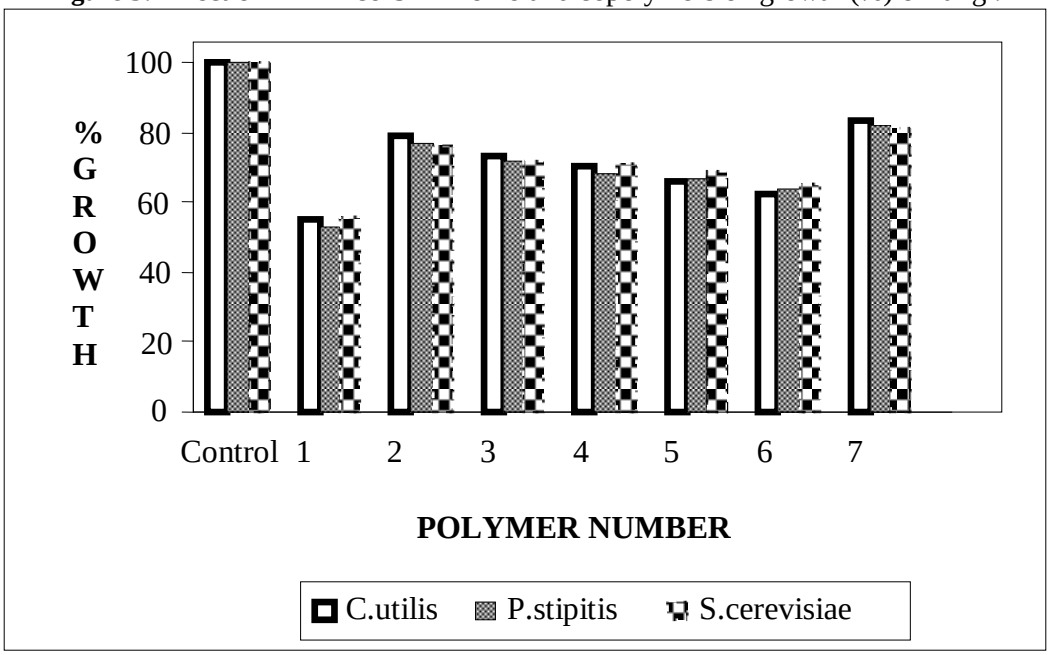


Figure 4: Effect of NPEA-co-STY homo and copolymers on growth (%) of yeast.

APPLICATIONS

This study suggests that, Polymers containing phthalimide groups are found to possess excellent heat resistance and transparency. The incorporation of the phthalimide group remarkably enhanced the thermal stability of polymers. This study also suggests that, NPEA containing acrylic copolymers can be used as an effective antimicrobial agent.

CONCLUSIONS

Poly(NPEA) and copolymers of NPEA with STY were synthesized by free radical solution polymerization. The homo and copolymers were characterized by FT-IR. The copolymers were soluble in chloroform, DMF, dimethyl sulfoxide and toluene while insoluble in n-hexane and hydroxyl group containing solvents such as methanol and ethanol. The copolymer composition was determined by UV-spectoscopic data. The reactivity ratios of the monomers obtained from the F-R and K-T methods were in good agreement with each other. The r_1 value is less than r_2 and as the product of r_1 and r_2 is less than 1, the system gives rise to azeotropic polymerization at a particular composition of monomer. The GPC data shows that molecular weights and viscosity change randomly, where as polydispersity index decreases slightly as the NPEA content increases in copolymer. Results of thermal analysis show that all the polymers undergo single step degradation. It is seen that as the NPEA content in the copolymers increases, inhibition to the growth of microorganisms increases.

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