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Synthesis, characterization and antimicrobial activity of novel acrylic materials

Dijit M. Patel, Mehdihasan I. Shekh, Kaushal P. Patel and R. M. Patel

Department of Advanced Organic Chemistry, P. D. Patel Institute of Applied Sciences, Charotar University of Science and Technology (CHARUSAT), Changa, Gujarat, India

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ABSTRACT

The copolymers from different feed composition of 2-(N-phthalimido)ethyl acrylate (NPEA) and 1-vinyl-2-pyrolidone (NVP) were synthesized using free radical polymerization using N,N'-dimethylformamide (DMF) as a solvent at 70±1ºC using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The monomer was characterized by ^{1}H-NMR and IR spectroscopic techniques. The copolymers were characterized by IR-spectroscopy. The copolymers composition were determined using ultraviolet (UV) spectroscopy. Reactivity ratio for NPEA and NVP was determined by using Fineman-Ross, and Kelen-Tudos methods. The polydispersities of copolymers suggest a strong tendency for chain termination by disproportionation. The thermal stability of the copolymers increases with increase in NPEA content. Antimicrobial activity of the homopolymer and copolymers were also investigated for various microorganisms such as bacteria, fungi and yeast.

Key words: 2-(N-phthalimido) ethyl acrylate, 1-vinyl-2-pyrolidone, Reactivity Ratio, Thermal Properties, Antimicrobial Activity

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INTRODUCTION

Acrylic copolymers have achieved prime importance in various avenues of application, such as films, fibers, binders, filament coatings, lithography, adhesives and printing inks [1-7]. The acrylate polymers also find applications in drugs as polymer supports which are easily degradable [8]. The use of polymeric system based on acrylic derivatives as biomaterials for clinical application has increased during the last two decades because of their excellent biocompability and long-term stability [9]. The determination of copolymer composition and reactivity ratio of the monomers is important in evaluating the specific application of the copolymer [10]. Free radical copolymerization is a valuable tool for tailoring the properties of polymeric materials for a wide scope of applications. For statistical copolymers, the monomer sequence distribution and compositional heterogeneity in and among the copolymer chains have a heavy influence on the physical attributes of the materials [11-17]. Copolymers containing the phthalimide derivatives have been used as optical brighting agents [18]. Polymer containing phthalimido groups are found to possess excellent heat resistance and transparency [19]. N-vinylpyrrolidone (NVP) exhibit good biocompatibility due to their hydrophilic nature and low cytotoxicity [20-22]. NVP based polymers find applications in plasma substitutes, soluble drug carriers, and UV-curable bio adhesives [23].The amide group of NVP has a high binding affinity for several small and large molecules that are known as good hydrogen-bond acceptors and has been copolymerized with a variety of monomers [24-28]. The composition of the copolymers depends on the degree of incorporation of the comonomers and also on their relative reactivity. Monomer reactivity ratio are very important to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. The accurate estimation of copolymer composition and determination of monomer reactivity ratio are significant for a tailor-made copolymer with required physical chemical properties and in evaluating the specific end application of copolymers. The monomer reactivity ratio were determined by linearization methods of Fineman-Ross [29] and Kelen-Tudos [30]. R. Jayakumar et al. synthesized the copolymer

of 2-(N-phthalimido) ethylacrylate and methyl methacrylate and the reactivity ratio determined [31]. It indicates that Methyl methacrylate is more reactive and ideal copolymerization. Mitesh. B. Patel et al. synthesized the copolymer of N-Vinylpyrrolidone and 2, 4-Dichlorophenyl methacrylate. They determined that the reactivity ratio of both the monomers is less than unity [32]. They have also determined the azeotropic composition of the copolymer. This article discusses the synthesis and characterization of the monomer and homopolymer and copolymers using different feed ratio. The copolymer composition were determined by ultraviolet (UV) spectroscopy and molecular weight were determined by gel permeation chromatography (GPC). Thermal analyses of polymers are also included. The antimicrobial activity of homopolymer and copolymers against microorganisms such as bacteria (*Escherichia coli, Bacillus subtilis, Staphylococcus citreus*), fungi (*Aspergillus niger, Sporotichum pulverulentum, Trichoderma lignorum*), and yeast (*Candida utilis, Saccharomyces cerevisiae, Pichia stipitis*) were determined.

EXPERIMENTAL SECTION

Materials

Phthalic anhydride, monoethanolamine, benzoyl chloride, acrylic acid, 1-vinyl-2-pyrolidone (NVP), trimethylamine and 2,2'-azobisisobutironitrile (AIBN) were obtained from Sigma-Aldrich chemical. The organic solvents such as N,N'-dimethylformamide, acetone, and chloroform were of AR Grade.

Synthesis of acryloyl chloride

Acryloyl chloride were prepared following the standard procedure given by Stempel [31].

Synthesis of 2-(N-phthalimido)ethyl acrylate (NPEA)

For synthesis of NHEP, Phthalic anhydride (0.1 mol) 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 mol) was added drop wise. The reaction was moderately exothermic hence cooled in an ice bath. The contents were stirred with a magnetic stirrer and refluxed at 130 ºC for 3 hrs. Excess DMF was removed by distillation and the contents were poured into ice-water mixture. The precipitated product, NHEP, was filtered off and recrystallized using rectified spirit as a solvent. The melting point of the product was 126 ºC and the yield was 88%. To a one liter three necked flask equipped with stirrer, thermometer and guard tube, DMF (200 ml) and triethylamine (0.1 mol) were added and the contents were stirred for 30 minutes. To this, NHEP (0.1 mol) was added and the reaction mixture was heated to 60 ºC for 30 minutes with stirring, cooled to room temperature and then to 0-5 ºC. Freshly prepared acryloyl chloride (0.11 mol) was added drop wise within 60 minutes to the cooled reaction mixture. The temperature was maintained around 0-5 ºC during the addition. After completion of the addition, the reaction mixture was stirred for 90 minutes and it was poured into crushed ice water mixture where light yellow colored solid (NPEA) product settled down. It was filtered and recrystallized from rectified spirit. The yield was 78% and the melting point was 106 ºC.
The reaction scheme for monomer synthesis is shown in Scheme 1.

The monomer was characterized using a Nicolet 6700 Fourier transform (FT) IR spectrophotometer and a FT-NMR spectrophotometer (400 MHZ). The IR spectrum of NPEA monomer is shown in Figure 1. **IR** (cm^{-1}): 3100 (aromatic C-H stretching), 2945 (C-H stretch due to alkyl group), 1773 (-CO-OR), 1723 (C=O stretching due to phthalimido group), 1637 (C=C stretching), 1600 and 1463 (aromatic C=C- stretching), 1194 (C-O-C asymmetric stretching), 1145 (C-O-C symmetric stretching), 999 and 673 (C-H out of plane bending).

The ^{1}H-NMR spectrum of NPEA is shown in Figure 2. The resonances are as follows. **^{1}H-NMR** (δ ppm) (400 MHz): 7.9-7.7 (4H) [aromatic protons], 6.4, 6.1 and 5.8(3H) [olefinic protons], 4.4(2H) [-CH_2-O-], 4.0(2H) [N-CH_2].

Copolymerization

Copolymers of NPEA with NVP having different composition were synthesized using free-radical polymerization using N,N'-dimethylformamide as a solvent using AIBN as a free-radical initiator. The feed composition monomer and comonomer is given in Table 1. Appropriate quantity of monomer, comonomer, N,N'-dimethylformamide, and AIBN (0.5% w/w based on total monomers 1 and 2) were taken in a polymerization tube equipped with reflux condenser. The reaction mixture was heated at 70 ºC for 5 hr with stirring. It was then cooled to room temperature and the resulting polymer solution were slowly poured in a large volume of acetone:water (50:50) with stirring, and the polymer precipitated out. It was filtered and wash with acetone:water (50:50). Solid polymers were purified by repeated precipitation using acetone: water (50:50) from solution in N,N'-dimethylformamide and finally dried. Scheme 2 show the reactions leading to the formation of NPEA monomer, homopolymer as well as copolymers of NPEA with NVP.

Measurements

IR spectra of the polymers were recorded using a Nicolet 6700 FT-IR spectrophotometer using the solid KBr pellet method. A Shimadzu 160-A recording UV-vis spectrophotometer was used to determine copolymer composition and reactivity ratio. Molecular weights of the polymers were obtained from a waters 410 gel permeation chromatography instrument equipped with a differential refractive index detector. Tetrahydrofuran was used as the eluent and polystyrene standards were employed for calibration. The intrinsic viscosity (η) of the copolymers were measured in toluene solvent at 25 ± 0.1 ºC using an Ubblelohde suspended-level Viscometer. Thermogravimetric traces were recorded in a nitrogen atmosphere using a DuPont 900 thermal analyzer. A heating rate of 10 ºC min^{-1} and sample size 10 ± 1 mg were used in each experiment.

Antimicrobial activity

The homopolymer and copolymers prepared were tested for their antimicrobial activity against bacterial strains (*Escherichia coli*, *Bacillus subtilis*, *Staphylococcus citreus*), fungal strains (*Aspergillus niger*, *Sporotichum pulverulentum*, *Trichoderma lignorum*), and yeast strains (*Candida utilis*, *Saccharomyces cerevisiae*, *Pichia stipitis*) using the experimental procedure have been reported elsewhere [33, 34].

RESULTS AND DISCUSSION

Copolymers of NPEA with NVP were synthesized by taking different mole fractions of the monomers in feed ranging from 0.2 to 0.8 (Table 1). The copolymers were found to be soluble in N,N'-dimethylformamide, chloroform, tetrahydrofuran, toluene, but insoluble in methanol, ethanol and n-hexane. The copolymers characterized by IR spectroscopy and the results are given in the following.

The IR spectrum of copolymer is shown in Figure 3. The peak at 3029-3025 cm^{-1} is due to the C-H stretching of aromatic ring. The peak at 2957 cm^{-1} is due to the C-H stretching vibration of methyl and methylene groups. The strong absorption peaks at 1777 cm^{-1} ester carbonyl stretching. The strong absorption peaks at 1711 cm^{-1} carbonyl stretching of the phthalimido group. The peaks at 1612 and 1394 cm^{-1} are assigned to the C=C stretching of the aromatic ring. The band at 1160 cm^{-1} is assigned to the C-O stretching of the ester group. The out of plane C-H bending of the alkyl ring is observed at 998 cm^{-1}. The out of plane C-H bending of the phenyl ring is observed at 876 and 720 cm^{-1}. The absence of an absorption at 1640 cm^{-1} in the polymers is indicative of the participation of the vinyl group in the polymerization.

Copolymer composition and reactivity ratio

The UV spectrum of each copolymer sample makes it possible to obtain the composition of the material. The assignment of the absorbance in UV spectrum important for accurate determination of the content of each kind of monomeric unit incorporated into the copolymers chains. The λ_{max} for poly(NPEA) was found at 294 nm. The UV-spectra of different composition of copolymers are shown in Figure 4. The agreement between the two concentrations were good. The composition of the copolymers of the NPEA and NVP were obtained from the UV-spectral data. From the monomer feed ratio and copolymer composition, the reactivity ratio of the NPEA and NVP were determined using Fineman-Ross method and Kelen-Tudos method. The values are shown in Table 1. The reactivity ratio obtained by these two methods agree well. The reaction time was selected in such a way that conversion was less than 10% in weight. This was done to satisfy the differential copolymerization equation for calculation of reactivity ratio. A plot of G verses F in F-R method was a straight line shown in Figure 5. The intercept at *y*-axis gives the value of $-r_2$ and the slope gives the value of r_1. Similarly, in K-T method, by plotting η against ξ, a straight line is obtained as shown in Figure 6, which when extrapolated to ξ = 0 and ξ = 1 gives $-r_2/\alpha$ and r_1, respectively. When r_1 and r_2 are less than 1, the system gives rise to azeotropic polymerization at a particular composition of the monomer, which is calculated using the Equation.

$$N_1 = \frac{(1-r_2)}{(2-r_1-r_2)} = 0.038 \qquad (1)$$

where N_1 is the mole fraction of NPEA in the feed.

When the mole fraction of the monomer NPEA in the feed is 0.038, the copolymer formed will have the same composition as that in the feed. When the mole fraction of NPEA in the feed is less than 0.038, the copolymer is relatively richer in this monomeric unit than the feed. When the mole fraction of the monomeric NPEA in the feed is above 0.038, the copolymer is relatively richer in NVP monomeric units.

Molecular weight and viscosity measurements

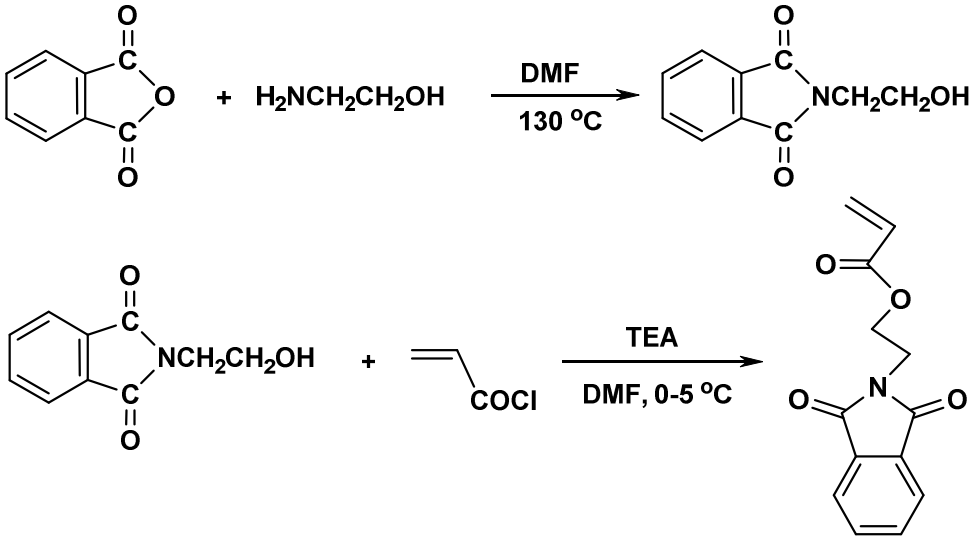
The number-average and weight-average molecular weights of the copolymers of NPEA with NVP were obtained from gel permeation chromatography. The value of the number-average and weight-average molecular weights range from 17877 to 19424 and from 25602 to 39644 respectively. The polydispersity index of homopolymer and copolymers varied in the range of 1.95-2.08. The intrinsic viscosities (η) lie in the range 0.218-0.239 dl g^{-1} are shown in Table 2. These data clearly indicated that as the NPEA content in the copolymer increases, the molecular weights and viscosity increases, while polydispersity index decreases.

Thermogravimetric analysis

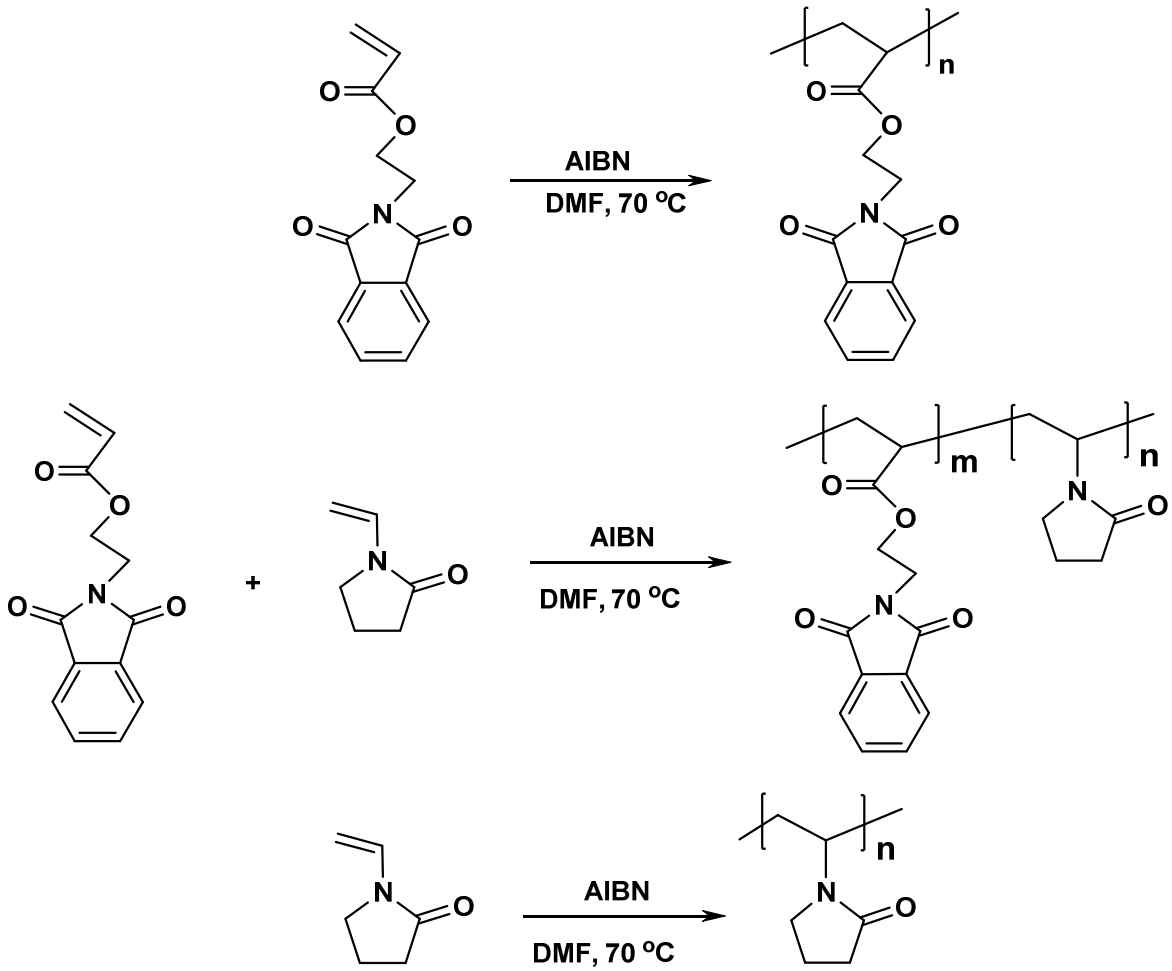
The results of thermogravimetric analysis of the homopolymers and copolymers of NPEA with NVP are shown in Table 3. It appears that all polymers except poly(NPEA) undergo decomposition in the temperature range 237-510 °C. The activation energy, calculated by Broido's method [35] lies in the range 33 to 51 kJ.mol^{-1}. The integral procedural decomposition temperature (IPDT) were calculated by Doyle's method [36]. The IPDT express the overall thermal stability of the polymer and it varies between 533 and 583 °C for these polymers. The homopolymer of NPEA is the stables thermally and poly (NVP) is the least stable. The copolymers as expected have stability between these two extremes.

Antimicrobial activity

The homopolymer and copolymers of the NPEA and NVP when tested for their response against microorganisms showed interesting results. Figures 7-9 provide a comparative account of the effect of the homopolymer and copolymers of the NPEA and NVP on the percentage growth of bacteria, fungi, yeast. Poly(NPEA) allowed about 46-51% growth of bacteria, 57-60% growth of fungi, and 53-56 growth of yeast, while for poly(NVP), 76-81 growth of bacteria, 68-69% growth of fungi and 63-66% growth of yeast were observed. However, in poly(NPEA-*co*-NVP) 56-76% growth of bacteria, 58-68% growth of fungi and 56-64% growth of yeast were observed. It was observed that poly(NPEA-*co*-NVP) is a stronger antimicrobial agent than the homopolymer of NVP. The phthalimido group content of the polymers has been said to play an important role in imparting antimicrobial properties. The homopolymer of NPEA has highest phthalimido group content amongst the polymers studied here. It is interesting to observe that this homopolymer has the strongest antimicrobial property. It is also seen, that as the NPEA content increases in the copolymers, the growth of microorganisms' decreases. It is also possible that the conformation of the polymers acquired under experimental conditions may also be a factor for their antigrowth activity. This study, however, is beyond the scope of this investigation.



Scheme 1



Scheme 2

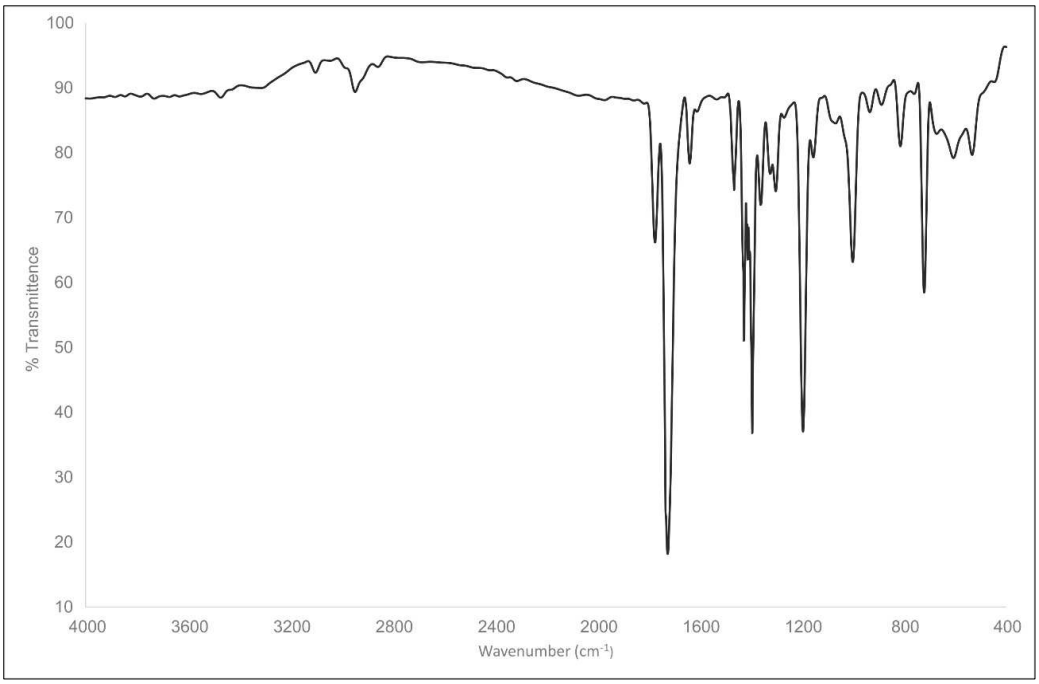


Figure 1. IR spectrum of NPEA monomer

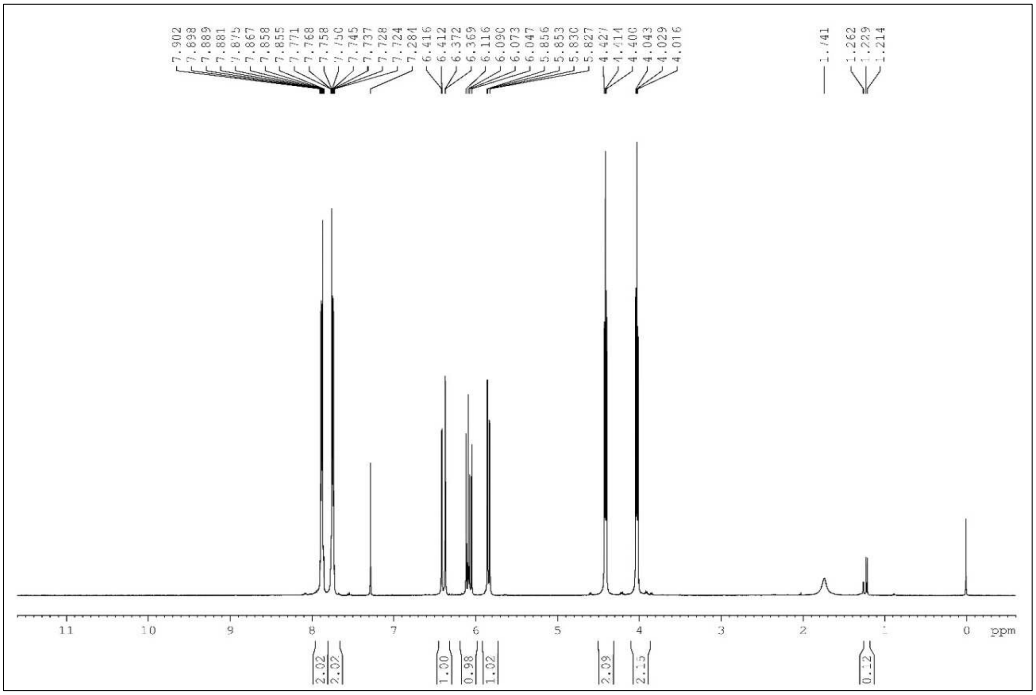


Figure 2. ^{1}H-NMR spectrum of NPEA monomer

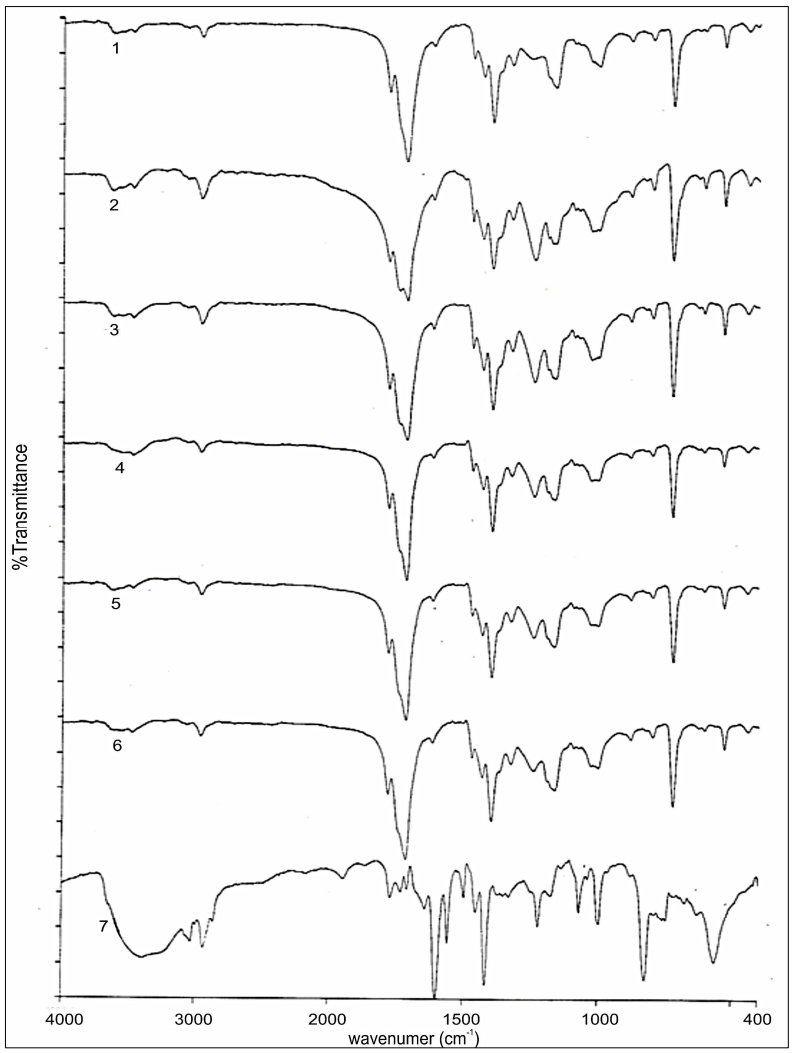


Figure 3. IR spectra oh homopolymer and copolymer of NPEA with NVP

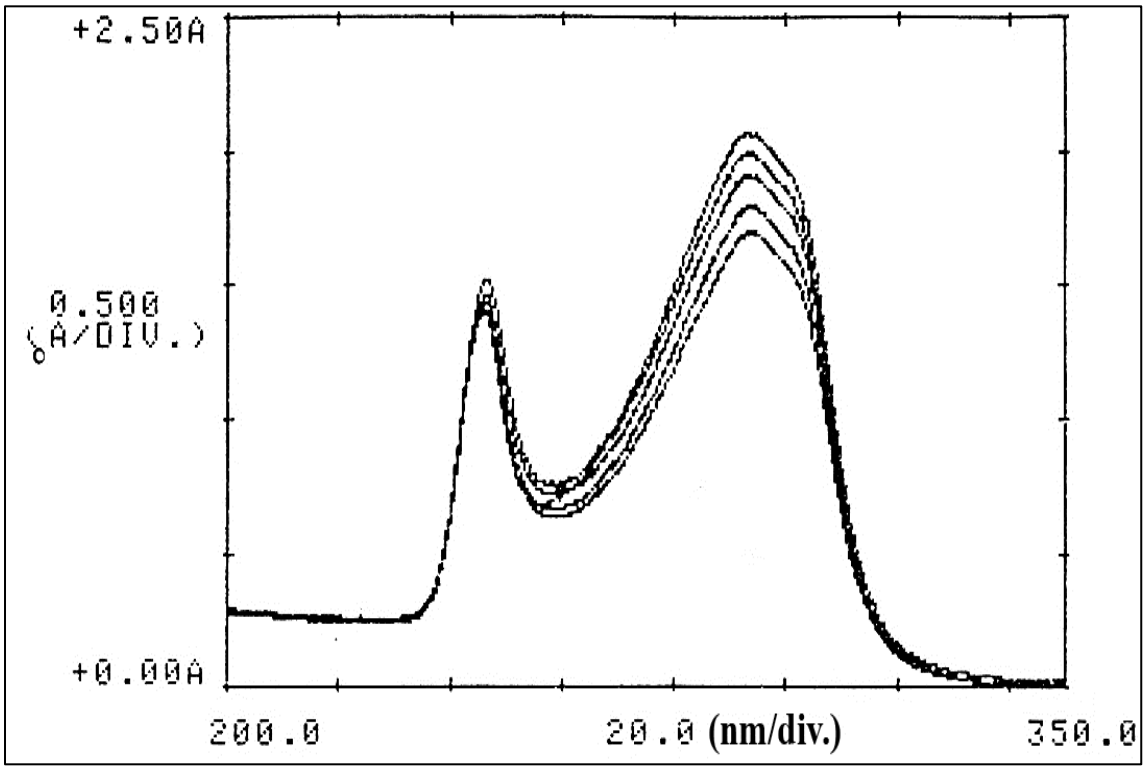


Figure 4. UV spectra of poly(NPEA-*co*-NVP) in chloroform at 294 nm

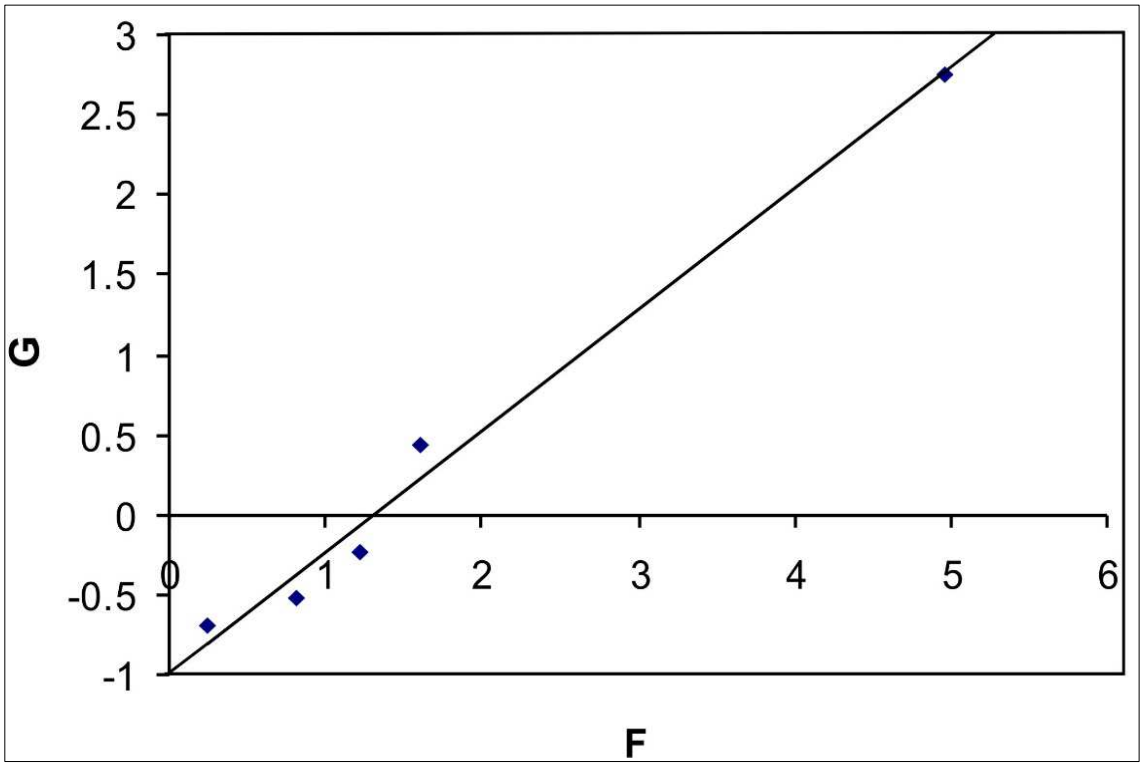


Figure 5. F-R plot for poly(NPEA-*co*-NVP)

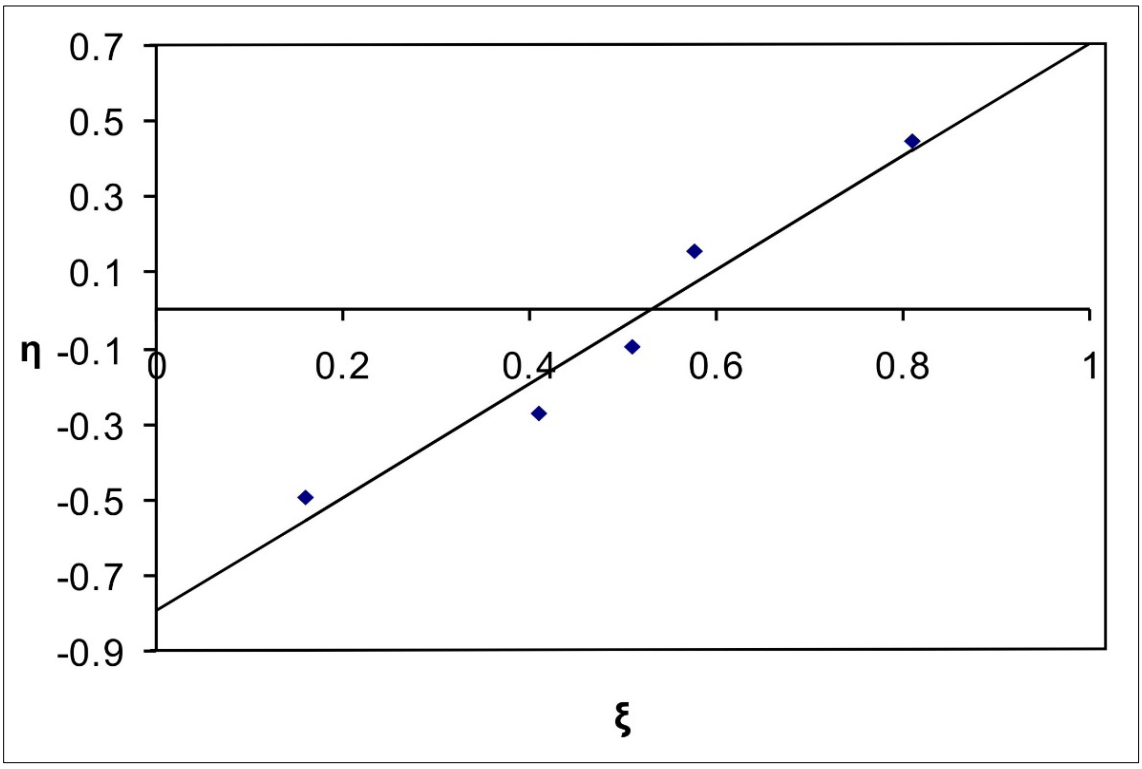


Figure 6. K-T plot for poly(NPEA-*co*-NVP)

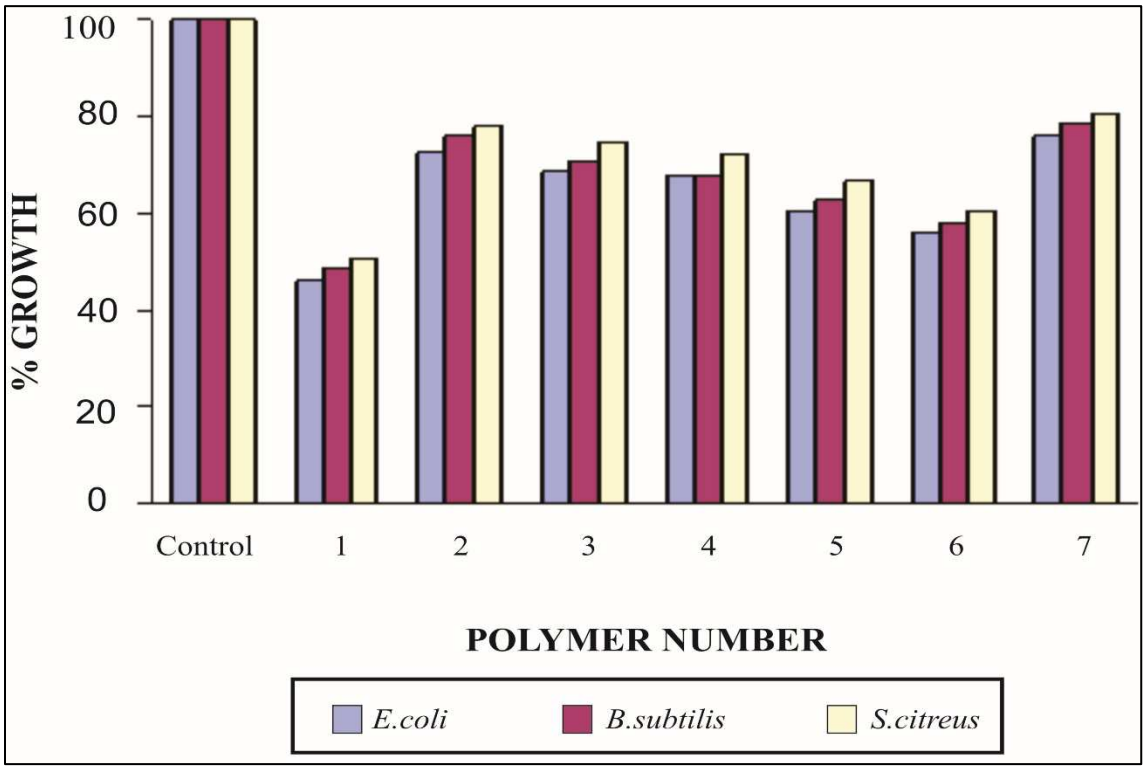


Figure 7. Effect of homopolymer and copolymers on percentage growth of bacteria

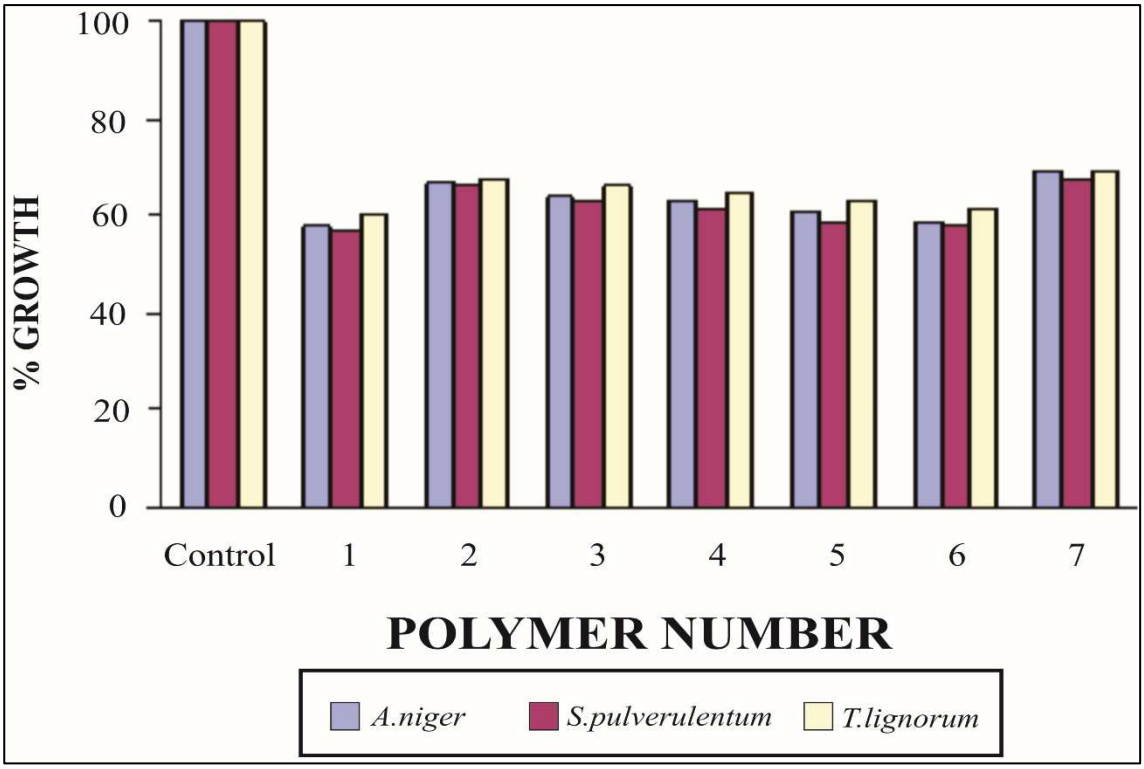


Figure 8. Effect of homopolymer and copolymers on percentage growth of Fungi

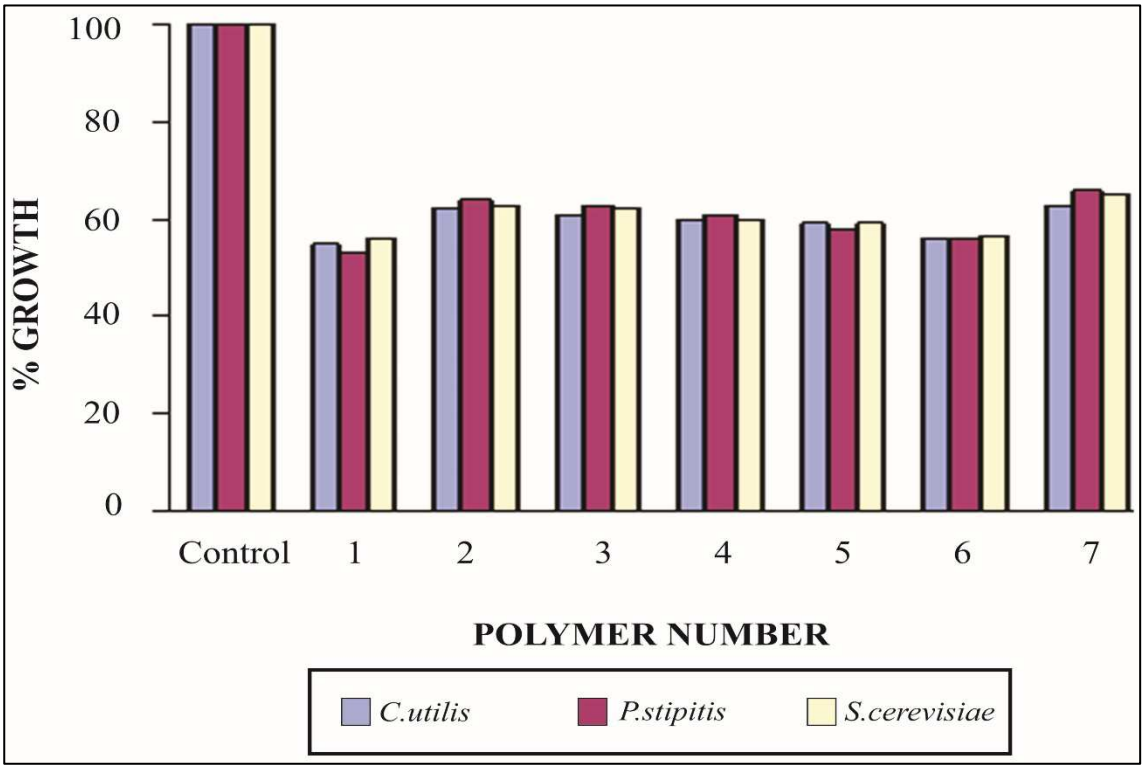


Figure 9. Effect of homopolymer and copolymers on percentage growth of yeast

Table 1. Copolymer composition and reactivity ratio of copolymers of NPEA and NVP

Sample code	Monomer feed composition		Conversion (%)	Composition of NPEA in the copolymer [m_1]	*X*	*Y*	*F*	*G*	*ξ*	*η*	*Reactivity ratio*			
	NPEA [M_1] (mol)	NVP [M_2] (mol)									Fineman -Ross		Kelen-Tudos	
											r_1	r_2	r_1	r_2
1	1.0	-									0.75	0.99	0.72	0.94
2	0.2	0.8	9.76	0.198	0.25	0.264	0.236	-0.696	0.161	-0.494				
3	0.4	0.6	10.22	0.356	0.67	0.552	0.813	-0.513	0.409	-0.273				
4	0.5	0.5	8.92	0.449	1.00	0.814	1.229	-0.230	0.511	-0.095				
5	0.6	0.4	8.27	0.584	1.50	1.401	1.609	0.430	0.578	0.154				
6	0.8	0.2	9.14	0.763	4.00	3.220	4.968	2.758	0.809	0.449				
7	-	1.0												

Where, $m_2=1-m_1$; $x=M_1/M_2$; $Y=m_1-m_2$; $F=X^2/Y$; $G=x(Y-1/Y)$; $\xi=G/\alpha+F$; and $\alpha=[F_M . F_m]^{1/2}$.

Table 2. GPC and viscosity data for homo- and copolymers of NPEA with NVP

Sample Code	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_z+1$	Polydispersity ($\bar{M}_w/\bar{M}_n$)	Intrinsic viscosity[η] (dl g^{-1})
1	19424	39644	64234	88103	2.04	0.213
2	12280	25602	48493	73788	2.08	0.218
3	13237	26871	49392	74845	2.03	0.223
4	14120	28324	50732	76119	2.00	0.227
5	16389	32450	54989	79756	1.98	0.232
6	18636	36474	58512	80523	1.95	0.239
7	17877	36006	57962	81526	2.01	0.210

Table 3. TGA data of homo and copolymers of NPEA and NVP

Sample Code	% Weight loss at various temperature (°C)			Decomposition Temperature Range (°C)	T_{max} (°C)[a]	T_{50} (°C)[b]	IPDT (°C)[c]	Activation Energy (E_a) (kJ.mol^{-1})[d]
	300	400	500					
1	4	89	97	269-498	371	370	547	51
2	11	82	96	237-417 417-519	380	365	539	39
3	10	82	97	242-421 421-518	376	366	533	39
4	9	83	98	252-451 451-511	372	368	583	40
5	8	84	98	252-449 449-509	370	369	581	42
6	7	85	98	253-417 417-498	368	362	535	45
7	31	94	98	154-358 358-485	336	323	536	33

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

CONCLUSION

The homopolymer and copolymers of the NPEA and NVP having various compositions were synthesized in solution by free-radical polymerization. The structure of the monomer was confirmed by IR and ^{1}H-NMR spectroscopic techniques. IR spectral data were employed to characterize the polymers. The copolymer compositions were obtained from UV spectral data. The reactivity ratio of NPEA (r_1) is less than that of NVP (r_2) and the product of the reactivity ratio were less than 1. This indicates that the monomers were distributed in the copolymer chain in a random manner. The gel permeation chromatography results show that the molecular weights of the copolymers increase as the NPEA content in the copolymers increases. Phthalimido group is important for antimicrobial property of the polymers under studies. The fact that amongst the polymers investigated, the homopolymer of NPEA is the most effective antimicrobial agent lends support to this view.

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