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# Chelation ion-exchange properties of terpolymer resin-I derived from p-hydroxybenzaldehyde, terephthalic acid and ethylene glycol

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# ABSTRACT

Ion-exchange resin abbreviated as HPEG-I was synthesized by polycondensation in the presence of polyphosphoric acid as a catalyst using monomers p-hydroxybenzaldehyde (0.1M), terephthalic acid (0.1M) and ethylene glycol (0.3M) at  $120^{9}$ C. The terpolymer resin was characterized by elemental analysis, the number average molecular weight, UV-Visible, IR and <sup>1</sup>H NMR spectrum. Chelating ion-exchange properties of HPEG-I terpolymer was studied for Sb<sup>3+</sup>, Bi<sup>3+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup> ions by the batch equilibrium method. The metal ions were estimated spectrophotometrically. The study was carried out over a wide pH range and in media of various ionic strengths. The terpolymer resin can be used as a selective ion exchange resin for Bi<sup>3+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup> ions.

Keywords: Polycondensation, Ion-exchange, Polymerization, Rate of metal ion uptake, Resins, Terpolymer

# INTRODUCTION

Removal and optimization trace heavy metals have been attracting much attention as far as environmental issues are concerned. For this purpose high selective and precise analytical techniques have to be developed to subside the problem of metal pollution. The literature survey revealed that many ion-exchangers with varying selectivities were developed for separation and removal of inorganic pollutants from the waste and industrial effluents. The existence of heavy metals in the environment has been a basis of concern due to their sensitive and long term toxicity. Ion-exchanges have been usually used in analytical chemistry, hydrometallurgy, antibiotic purification, separation of radioisotopes; discover great application in water treatment and pollution control [1- 2]. Therefore, interest has been developed in the synthesis of ion exchange polymer resin.

Gurnule et al synthesized terpolymer resins by condensation of 2-hydroxyacetophenone-oxamide-formaldehyde [3-4], 4-hydroxyacetophenone-oxamide-formaldehyde [5], 4-hydroxyacetophenone-biuret-formaldehyde [6-7], 8-hydroxyquinoline-melamine and formaldehyde [8], salicylic acid–melamine–formaldehyde [9]. They studied ion-exchange properties of terpolymers for  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions over the pH range 1.5-6.5 and in media of various ionic strengths. They reported that the polymer showed a higher selectivity for  $Fe^{3+}$  ion over any other ion.

Hiwase et al synthesized PHBRF-I and PHBRF-II polymers by condensation of p-hydroxyacetophenone-hexamine-formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers [10]. They studied ion-exchange properties of terpolymers for  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  ions over the pH range 3.0-6.0. They reported that the polymer showed that the rate of metal uptake of PHBRF-II > PHBRF-I for metal under study and terpolymeric resins show high selectivity for  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Co^{2+}$  as compared to  $Ni^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ .

Rahangdale et al synthesized 2, 4-dihydroxyacetophenone-dithiooxamide-formaldehyde terpolymer and chelating ion-exchange properties was studied employing the batch equilibrium method. It was employed to study selectivity

of metal ion uptake over a wide pH range and in the media of different ionic strength. The overall rate of metal uptake was found to follows the order:  $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} = Zn^{2+}$  [11].

Pancholi et al synthesized polymer by condensation of 2-hydroxy-4-methoxyacetophenone-thiourea-trioxane and studied ion-exchange properties of terpolymers for ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $UO_2^{2+}$  ions over the pH range 3.5-5.5 and in media of various ionic strengths. They reported that the polymer showed a higher selectivity for  $Cu^{2+}$ ,  $Fe^{2+}$  and  $UO_2^{2+}$  ions over any other ion [12].

The present communication deals with the systematic study of synthesis, characterization and ion-exchange properties of HPEG-I terpolymer resin derived from p-hydroxybenzaldehyde, terephthalic acid and ethylene glycol by the batch equilibrium method.

## MATERIALS AND METHODS

## 2.1 Materials:

All chemicals were AR grade or chemically pure grade, p-hydroxybenzaldehyde, terephthalic acid, ethylene glycol and polyphosphoric acid were procured from s.d. fine chemicals, India.

## 2.2 Synthesis of HPEG-I terpolymer:

A terpolymer resin abbreviated as HPEG-I was synthesized by polycondensation of monomers phydroxybenzaldehyde, terephthalic acid and ethylene glycol in the presence of polyphosphoric acid. To a wellstirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.1M), terephthalic acid (0.1M) and ethylene glycol (0.3M), polyphosphoric acid (PPA) was added slowly with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 30 minutes then heated on oil bath at  $120^{\circ}C \pm 2^{\circ}C$  for 5.30 hrs. The reaction mixture was cooled, poured on crushed ice and left over night [13-14]. Light reddish brown solid was separated. The crude product was squeezed with ether so as to remove terephthalic acid-glycol copolymer which might be formed along with HPEG-I. The HPEG-I terpolymer was further purified by dissolving in 0.1N NaOH solution and precipitated by dropwise addition of 1:1 HCl with constant stirring. The product was washed several times with hot water and cold water. The product was air dried and kept in vacuum over silica gel. Yield was found to be 82%. The scheme of synthesis of HPEG-I is shown in figure 1.



Figure 1 Scheme of synthesis of HPEG-I terpolymer resin

## 2.3 Ion exchange experimental procedures

The ion-exchange property of the HPEG-I terpolymer resin was determined by the batch equilibrium method. Estimation of metal carried out using a spectrophotometer.

#### 2.3.1 Procedure for determination of the effect of electrolyte on metal uptake

The resin sample (25 mg) was suspended in an electrolyte solution of required concentration (25 ml) for 24 hrs. The pH of the solution was to 6.0 using 0.1M HNO<sub>3</sub> or 0.1M NaOH. To this solution 5 ml of 0.1M metal nitrate solution added at room temperature and pH was adjusted to the required value. The mixture was stirred again at room temperature for 24 hrs and filtered. Solids were washed and washings were quantitatively combined with the filtrate. The metal content was determined by a spectrophotometer. The amount of metal exchanged was determined from the difference between blank and reading in actual experiments [15-16]. The amounts of metal ion in mg per gm of resin were calculated in the presence of NaCl, NaNO<sub>3</sub>, NaClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> electrolyte for metal ions Sb<sup>3+</sup>, Bi<sup>3+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup>.

## **2.3.2 Procedure for evaluation of rate of metal ion uptake**

In order to determine optimum time required to reach the equilibrium the experiments were performed as above but here metal ion uptake was estimated as a function of time in hrs in the presence of 1.5 M NaNO<sub>3</sub> solution (25 ml). It was assumed that the equilibrium state was established within 24 hrs. The rate of metal uptake was expressed in terms of percent metal uptake related to a state of equilibrium by the formula (1) [17-18].

% metal uptake =  $\frac{mg \ of \ metal \ sorbed \ in \ given \ time}{mg \ of \ metal \ sorbed \ in \ 24hrs} \times 100 \ \dots \dots (1)$ 

## 2.3.3 Procedure to study the effect of pH on metal uptake

The resin sample 25 mg was allowed to swell for 24 hrs in  $1.5 \text{ M NaNO}_3$  solution. The pH was adjusted to the required value as above. 5mL of 0.1 M metal nitrate solution was added. The pH was maintained again and stirred for 24 hrs. Metal was estimated by a spectrophotometer to determine the distribution ratio (D) between polymer phase and solution phase [19-20]. The distribution ratio was calculated by the formula (2),

$$D = \frac{weight (mg) of metal ions taken up by 1gm of polymer}{weight (mg) of metal ions present in 1ml of solution} \dots (2)$$

### **RESULTS AND DISCUSSION**

HPEG-I terpolymer resin was Light reddish brown in color and soluble in DMSO and NaOH solution where as insoluble in acids and common organic solvents.

## 3.1 Elemental analysis and molecular weight determination (Mn)

Elemental analysis has been carried out in CIMFR unit, Nagpur, by analytical functional testing Vario MICRO CHN elemental analyzer (Germany). The elemental analysis data of HPEG-I terpolymer are tabulated in table 1.

Table 1	Elemental	analysis	data o	of HPEG-I	terpolymer
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% C		% H		Mol Formula repeat unit	
Calc.	Found	Calc.	Found	Mor. Formula repeat unit	
68.48	68.40	5.43	5.39	$(C_{21}H_{20}O_6)_n$	

The number average molecular weight (Mn) was determined by non-aqueous conductometric titration in DMSO using 0.1M KOH in absolute alcohol as titrant [21].

From the figure 2, graph of specific conductance against miliequivalents of KOH, first and last breaks were noted. The degree of polymerization ( $\overline{Dp}$ ) and the number average molecular weight ( $\overline{Mn}$ ) have been calculated using equations (3) and (4),

$$\overline{Dp} = \frac{Total \quad Meq. \quad of \quad base \quad required \quad for \quad last \quad break}{Meq. \quad of \quad base \quad required \quad for \quad first \quad break} \dots (3)$$

The repeating unit weight was obtained from elemental analysis. The molecular weight determination data of HPEG-I terpolymer are tabulated in table 2.



Figure 2 Graph of specific conductance against miliequivalents of KOH

Table 2 Molecular weight determination	n data of HPEG-I terpolymer
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Meq. Of KOH/100gm of resin for first Break	Meq. Of KOH/100gm of resin for last Break	$\overline{Dp}$	Molecular Weight of Repeat Unit	Molecular Weight $(\overline{Mn})$
600	7240	12	368	4416



Figure 3 IR specta of HPEG-I terpolymer resin

## 3.2 IR spectra

IR spectrum of HPEG-I terpolymer was recorded at department of pharmacy, RTM Nagpur University, Nagpur, using FT-IR spectrophotometer, Shimadzu, model No-8101A. FT-IR spectrum of HPEG-I terpolymer is shown in figure 3.

A broad absorption band appeared in the region 3440 cm<sup>-1</sup> was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. The presences of the peaks at 2930 cm<sup>-1</sup> and 2820 cm<sup>-1</sup> were due to the -C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1680 cm<sup>-1</sup> was due to C=O stretch (ester). A peak at 1650 cm<sup>-1</sup> assigned to the C=O band (an aldehyde). The presence of peak at 1601 cm<sup>-1</sup> was due to aromatic-ring. A peak appeared at 1480 cm<sup>-1</sup> due to ethylene bridge coupled with aromatic ring. Peak appeared at 1424 cm<sup>-1</sup> was assigned to in plane bending vibration of phenolic -OH. Peak at 1350 cm<sup>-1</sup> was due to aldehyde C-H bend. The broad band displayed at 1230 cm<sup>-1</sup> was due to the C-O stretch in ester group. 1170 cm<sup>-1</sup> was due to O-C-C band stretch. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned to the peaks at 1113 and 947 cm<sup>-1</sup>. The presence of peak at 833 cm<sup>-1</sup> was due to the -CH<sub>2</sub>- (wagging) [22-23].

Table 3 FT-IR spect	trum data of	HPEG-I	terpolymer
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Observed frequency (cm <sup>-1</sup> )	Assignment
3440 (b)	-OH bonded (phenolic)
2930 (w), 2820 (w)	C-H stretches in aldehyde (doublet due to Fermi resonance)
1680 (w)	C=O stretch (ester)
1650 (w)	C=O band (an aldehyde)
1601 (s)	Aromatic-ring
1480 (w)	CH <sub>2</sub> bending
1424 (w)	-OH bending (phenol)
1350 (w)	Aldehydic C-H bonds
1230 (b)	C-O stretch in ester group
1170 (w)	The O-C-C band stretch
1113 (w), 947 (b)	1,2,3,5 tetra substituted aromatic ring
833 (w)	-CH <sub>2</sub> -wagging

## 3.3 <sup>1</sup>H NMR Spectrum

<sup>1</sup>H NMR spectrum of HPEG-I terpolymer using DMSO-d<sup>6</sup> solvent was scanned on NMR spectrophotometer SAIFNM100820A, at Sophisticated Test and Instrumentation Center (STIC), Cochin University, Kerala, India. The <sup>1</sup>H NMR spectrum of HPEG-I terpolymer is shown in figure 4.



Figure 4 <sup>1</sup>H NMR spectra of HPEG-I terpolymer resin

The  $\delta$  in the range 1.3 ppm was of -CH<sub>2</sub>- in HPEG-I. The signal at 2.5  $\delta$  ppm was due to DMSO solvent. Signal at 3.9  $\delta$  ppm was attributed to CH-OH moiety. The signal at 6.8  $\delta$  ppm was due to aromatic ring protons in HPEG-I. The signal at 8.0  $\delta$  ppm was due to the aldehydic proton [24].

HPEG-I resin Chemical shift $\delta$ ppm	Nature of proton assigned
1.3	-CH <sub>2</sub> -
2.5	DMSO solvent
3.9	СН-ОН
6.8	Aromatic proton (Aromatic- <b>H</b> ) (asymmetrical substitution pattern)
8.0	-CHO

Table 4 <sup>1</sup>H NMR Spectrum data of HPEG-I terpolymer resin

## 3.4 UV-Visible spectrum

UV-Visible spectrum of HPEG-I terpolymer in DMSO solvent recorded by UV-Visible double beam spectrophotometer, Schimadzu, model-1800 at the department of nanotechnology, Shivaji Science College, Nagpur. The electronic spectrum of the HPEG-I terpolymer is shown in figure 5.



Figure 5 UV-Visible spectra of HPEG-I terpolymer

The copolymer sample displayed two characteristic broad bands at 250 - 280 and 290 - 342 nm. These observed positions for the absorption bands indicate the presence of a carbonyl group (ketonic) having a carbon - oxygen double bond which is in conjugation with the aromatic nucleus. The latter band (more intense) was assigned for

\* transition while the former bond (less intense) was due to  $n-\Box^*$  electronic transition. The bathochromic shift (shift towards longer wavelengths) from the basic values of the C=O group such as 320 and 240 nm respectively, may be due to the combined effect of conjugation and phenolic hydroxyl group (auxochromes). A peak at 279.5 nm was assigned to \* due to aromatic ring and peak at 341.5 nm was assigned to n- \* due to >C=O linkage [25].

## **3.5 Ion-exchange properties**

To ascertain the selectivity of HPEG-I, we studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the resin and solution. The results of the batch equilibrium study carried out with the HPEG-I terpolymer resin are presented in table 5-6 and in graph figure 6. Estimation of metal carried out using a spectrophotometer.

## 3.5.1 Effect of electrolytes on the metal Uptake

Effect of electrolyte on metal uptake is summarized in Table 5. The inspection of the data reveals that the amount of metal ions taken up in the presence of NaNO<sub>3</sub> is larger than NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub>. For the metal ions Sb<sup>3+</sup>, Bi<sup>3+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, the exchange capacity increases with increases in the concentration of NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup>, whereas it decreases with increases in concentration of SO<sub>4</sub><sup>2-</sup>. This is due to the fact that metal ions under study form kinetically more inert compound with respect to SO<sub>4</sub><sup>2-</sup> as compared to metal-resin interaction. On a contrary increases in the metal exchange capacity of metal resin in the presence of NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> attributed to high kinetically inert metal-resin interaction as compared to metal-electrolyte interactions [26].

Matalian	Electrolyte (Mol/l)	Wt. Of metal ion (in mg) per gm of HPEG-I resin taken up in the presence of				
Wietai ion		NaC1	Na <sub>2</sub> SO <sub>4</sub>	NaClO <sub>4</sub>	NaNO <sub>3</sub>	
	0.25	9.21	20.19	11.20	13.93	
	0.50	10.89	17.72	12.65	14.36	
Sh3+	0.75	13.25	15.31	14.17	16.66	
30	1.00	15.90	13.03	15.58	19.29	
	1.25	19.22	11.80	17.18	21.49	
	1.50	21.51	10.95	20.01	23.40	
	0.25	7.65	14.53	5.50	9.94	
	0.50	9.64	14.11	6.82	10.83	
D; <sup>3+</sup>	0.75	10.77	12.82	8.69	12.10	
DI	1.00	12.07	10.94	9.48	13.52	
	1.25	13.32	9.64	11.09	15.19	
	1.50	15.17	7.73	13.34	15.94	
	0.25	4.73	7.91	5.47	5.17	
	0.50	4.92	7.70	6.40	5.59	
$M a^{2+}$	0.75	5.31	7.32	7.04	6.01	
Mg	1.00	5.82	6.40	7.67	7.83	
	1.25	6.87	5.80	8.13	8.53	
	1.50	8.03	5.02	8.45	9.04	
	0.25	0.34	7.88	1.05	2.27	
$Zn^{2+}$	0.50	3.26	7.50	3.77	4.23	
	0.75	5.35	7.21	5.95	6.55	
	1.00	7.24	6.78	7.91	8.50	
	1.25	8.77	6.14	9.44	9.69	
	1.50	9.61	5.91	10.07	10.18	

Table 5 Evaluation of the effect of different electrolytes on the uptake of several metal ions on HPEG-I resin

 $\begin{array}{l} \textit{Metal nitrate solution} = 0.1 \textit{ Mol/l}, \textit{ 5ml}; \textit{ Electrolyte} = \textit{NaNO3}, 1.5 \textit{ M}, 25 \textit{ ml}; \textit{ Equilibrium state} = 24 \textit{hrs}; \textit{ Wt. of resin=25 mg}; \textit{ Temperature} = \textit{Room Temperature}; \textit{ Error} = \pm 1.5 \%; \textit{ The metal ions were estimated spectrophotometrically.} \end{array}$ 



#### Figure 6 Comparison of the rate of metal ion uptake

#### 3.5.2 Rate of Metal Uptake

From the graph present in figure 6, Initially the rate of metal uptake was steeply increased, become gradual and finally remain constant as the time passes for all metal ions. For  $Bi^{3+}$ ,  $Sb^{3+}$  and  $Mg^{2+}$  the equilibrium was reached within 7 hrs where as for  $Zn^{2+}$ , time required to reach equilibrium was 6 hrs. The rates of metal uptake for trivalent metal ions ( $Bi^{3+}$  and  $Sb^{3+}$  ions) were higher than divalent metal ions ( $Mg^{2+}$  and  $Zn^{2+}$  ions). The rate of metal ion uptake decreases in order  $Bi^{3+} > Sb^{3+} > Zn^{2+} > Mg^{2+}$ .

## 3.5.3 Distribution ratio of metal ions at different pH

The effect of pH on a distribution ratio of metal ions between resin and solution phase can be explained by revealing the data given in table 6. The study was carried out in the limit of higher pH in order to prevent hydrolysis of metal ions [27]. Distribution ratios for  $Mg^{2+}$  and  $Zn^{2+}$  ions were found to increase with increases in pH values. However reverse effect of pH was observed on distribution ratios for  $Sb^{3+}$  and  $Bi^{3+}$  ions.

HPEG-I resin shows the order of distribution ratio decrease as  $Bi^{3+} > Mg^{2+} > Sb^{3+} > Zn^{2+}$  at pH 4. At pH 5, the order of distribution ratio as  $Zn^{2+} > Mg^{2+} > Sb^{3+} > Bi^{3+}$ . The order of the distribution ratio (D) decreases as  $Mg^{2+} > Zn^{2+} > Sb^{3+} > Bi^{3+}$  at pH 6 and at pH 7, the order of distribution ratio was  $Mg^{2+} > Zn^{2+} > Sb^{3+} > Sb^{3+}$ .

Table 6 Distribution ratio (D) of different metal ions as a function of the pH on HPEG-I resin

mII.	Distribution ratio (D) of the metal ions on HPEG-I resin					
рн	Sb <sup>3+</sup>	Bi <sup>3+</sup>	Mg <sup>2+</sup>	$Zn^{2+}$		
4	139	657.3	172	100		
5	148	98.3	188	204		
6	151	78.8	389	327		
7	5	56.8	448	432		

 $\begin{array}{l} \textit{Metal nitrate solution} = 0.1 \textit{ Mol/l}, \textit{ 5ml; Electrolyte} = \textit{NaNO3}, \textit{ 1.5 M}, \textit{ 25 ml; Equilibrium state} = \textit{24hrs; Wt. of resin=25 mg; Temperature} = \textit{Room Temperature; Error} \pm 1.5 \%; \textit{ The metal ions were estimated spectrophotometrically.} \end{array}$ 

## CONCLUSION

The data of elemental analysis, FT-IR spectrum, <sup>1</sup>H NMR spectrum and UV–Visible spectrum supports the structure of HPEG-I terpolymeric resin. Among the electrolytes such as NaNO<sub>3</sub>, NaCl, NaClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, the NaNO<sub>3</sub> is more suitable electrolyte supporting to the ion exchange of metal ion under study by HPEG-I resin. Trivalent metal ion shows comparatively higher rates of metal uptake than divalent. This may be due to electrostatic assistance to ion exchange process. The effect of pH on a distribution ratio shows that the resin is more selective for Bi<sup>3+</sup> at lower pH (pH=4) but at higher pH pH=7 it is selective for Mg<sup>2+</sup>. Thus by varying pH, the resin HPEG-I can be employed for selective separation of Bi<sup>3+</sup> and Mg<sup>2+</sup> ions. The resin can be also selectively used for separation of Mg<sup>2+</sup> and Zn<sup>2+</sup>. At pH=4, the resin can be selectively used to exchange Mg<sup>2+</sup> but at pH=5, it can selectively exchange Zn<sup>2+</sup>. Distribution data shows that the resin HPEG-I can suitably use to separate Bi<sup>3+</sup> and Zn<sup>2+</sup> from the mixture. At pH=4, it conveniently exchange Bi<sup>3+</sup> where as at pH=5 to 7, it can selectively exchange Zn<sup>2+</sup>. Thus finally it can be concluded that the resin can be used as a selective ion exchange resin for the metal ions such as Bi<sup>3+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup>.

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## REFERENCES

[1] M V Tarase, W B Gurnule, A B Zade, E-J. Chem., 2009, 6 (3), 639-650.

[2] W B Gurnule, K A Nandekar, J R Dontulwar, *International Journal of Knowledge Engineering*, **2012**, **3** (1), 151-153.

[3] W B Gurnule, P K Rahangdale, L J Paliwal and R B Kharat, *Synth. React. Inorganic Metal. -Org. Chem.*, **2003**, **33** (7), 1187-1205.

[4] W B Gurnule, P K Rahangdale, L J Paliwal and R B Kharat, Progress in crystal growth and characterization of materials, 2002, 45, 155-160. [5] W B Gurnule, P K Rahangdale, L J Paliwal, R B Kharat, J. Appl. Polym. Sci., 2003, 89, 787-790.

[6] Gurnule W B, Rahangdale P K, Paliwal L J, Kharat R B, React & Funct polyms, 2003, 55, 255-265.

[7] W B Gurnule, P K Rahangdale, R B Kharat and L J Paliwal, Progress in crystal growth and characterization of materials, 2002, 45, 133-138.

[8] W B Gurnule, H D Juneja, and L J Paliwal, Ultra Science, 2001, 13(3), 333-339.

[9] W B Gurnule, H D Juneja and L J Paliwal, React & Funct polyms, 2002, 50(2), 95-100.

[10] V V Hiwase, A B Kalambe, K M Khedkar, S D Deosarkar, E-J. Chem., 2010, 7 (1), 287-294.

[11] S S Rahangdale, A B Zade, W B Gurnule, J. Appl. Polym. Sci., 2008, 108 (2), 747-756.

[12] H B Pancholi, M M Patel, High performance polymers, 1991, 3 (4), 257-262.

[13] A N Gupta, V V Hiwase, A B Kalambe, Der Pharma Chemica, 2012, 4(3), 1153-1159.

[14] A N Gupta, V V Hiwase, A B Kalambe, J. Chem. Pharma. Res., 2012, 4 (5), 2475-2482.

[15] D K Rath, P L Navak, S Lenka, J. Appl. Polym. Sci., 1994, 51, 1679-1682.

[16] W B Gurnule, S S Katkamwar, Der Pharma Lettre, 2012, 4 (5), 1360-1366.

[17] J R Patel, D H Sutaria, M N Patel, React. Polym, 1995, 25, 17-23.

[18] W B Gurnule, S S Katkamwar, J. Chem. Pharma. Res., 2012, 4 (4), 2193-2203.

[19] R Manavalan, M M Patel, Die. Angew. Makromol. Chem., 1983, 184, 717-723

[20] T K Pal, R B Kharat, Die. Angew. Makromol. Chem, 1989, 173, 55-68.

[21] D B Patel, W B Gurnule, A B Zade, Der Pharma Chemica, 2011, 3(3), 341-353.

[22] M Karunakaran, C T Vijayakumar, C Magesh, T Amudha, IJEST, 2011, 3(1), 162-176.

[23] D Urade, V Hiwase and A Kalambe, *Chem Sci Trans.* 2012, 1(3), 604-611.

[24] L D Field, S Sternell and J R Kalman, Org Struct from spectra, John Willey and Sons, New York, 1969, 2, 299.

[25] B L Hirani, S N Paliwal, J Choudhary, P R Choudhary, E-J. Chem., 2007, 4 (2), 265-271.

[26] D T Masram, K P Kriya, N S Bhave, Der Pharma Chemica, 2011, 3(3), 124-134.

[27] R S Azarudeen, M A Riswan Ahamed, D Jeyakumar, A R Burkanudeen, Iran Polym J, 2009, 18, 821-832.