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### **N-Vinylpyrrolidone and Ethoxyethyl Methacrylate Copolymer: Synthesis, Characterization and Reactivity Ratios**

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# *N*-Vinylpyrrolidone and Ethoxyethyl Methacrylate Copolymer: Synthesis, Characterization and Reactivity Ratios

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Free radical copolymerization of *N*-vinyl-2-pyrrolidone with 2-ethoxyethyl methacrylates was carried out with 2,2'-azobisisobutyronitrile as an initiator in 1,4-dioxane. The resulting copolymer was characterized by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopic techniques. Thermal properties of copolymer were determined by DSC and TGA. The reactivity ratios of the monomers were computed by the Fineman-Rose (F-R), Kelen-Tudos (K-T) and extended Kelen-Tudos (EK-T) method at lower conversion, using the data obtained from both FTIR and elemental analysis studies; the results are in good agreement with each other. The average reactivity ratio, Alfrey-Price *Q* and *e* values were found to be  $r_1 = 0.769$ ,  $r_2 = 0.266$  and  $Q_1 = 0.0859$ ,  $e_1 = 0.4508$ , respectively for NVP/EOEMA copolymer. The distribution of monomer sequence along the copolymer chain was calculated using a statistical method based on obtained reactivity ratio. The number average molecular weight and polydispersity were determined by GPC.

**Keywords:** *N*-vinylpyrrolidone; ethoxyethyl methacrylate; reactivity ratio; comonomer sequence and distribution

## 1 Introduction

Copolymerization reactions are an excellent method for the preparation of macromolecules with specific chemical structures and for the control of properties such as solubility, polarity and hydrophilic/hydrophobic balances etc. (1, 2). The chemical structure of a copolymer depends not only on the two-monomer units forming the macromolecule, but also on how such units are distributed along macromolecular chains. This distribution is a direct consequence of each monomer's reactivity in the copolymer molecule (3). In the case of radical copolymerization, the reactivity of a free radical depends on the nature of the side groups linked to the radical carbon (4–6, 9). For this reason, it is possible to obtain highly functionalized copolymers, which are potentially useful materials with specific technological applications (4–8).

*N*-vinyl-2-pyrrolidone (NVP) monomer has been attracting much attention in these days and it has been widely investigated for applications in various fields (10–14). It is an interesting vinyl monomer used for the synthesis of functionalized copolymers with well-defined properties (4, 5, 7). NVP based

polymers are having very good biocompatibility, low toxicity, good film forming and adhesive characteristics (15). It is also frequently used as a comonomer in surface-active copolymer (16, 17) mainly because of its good amphiphilic character. NVP monomer contains highly polar amide group, which confirms to hydrophilic and polar property while the methylene and methane groups in the main and side chain confirms to hydrophobic property (18). The applications of NVP based polymer are found in plasma substitutes, in soluble drug carriers, and also in UV-curable bioadhesives (19, 20).

NVP has been copolymerized with various acrylic monomers to improve their properties. For example, NVP can be copolymerized with methacrylic acid (MAA) to introduce carboxyl groups that are useful for yielding a wide variety of products. NVP and acrylic based copolymers are extensively studied by many authors due to their versatile use in biomedical applications as membranes for ultra filtration/drug delivery, as soft contact lenses and as anticoagulant films (21). Senel et al. (22) reported a random copolymer of (*N*-Isopropylacrylamide-*co*-NVP) having thermo responsive properties. Solovskii et al. (23) and Bashir et al. (24) reported hydrogels based on (NVP-*co*-hydroxyethyl methacrylate) copolymer used in controlled drug delivery. The (glycidyl methacrylate-*co*-NVP) copolymer was tested for adhesive properties by Sundarajan et al. (15).

Considering the versatile use of NVP, we have attempted to synthesize a copolymer of NVP with 2-ethoxyethyl methacrylate (EOEMA). EOEMA has an ether functional group in

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addition to an ester group as compared to most of the vinyl acrylic monomers. These groups not only impart flexibility into the polymers, but also improve its processability and handling. Because of its soft and flexible nature, EOEMA based copolymers are widely used in contact lenses (25).

The present investigation describes the synthesis of the NVP/EOEMA copolymer by free radical polymerization and its characterization. Reactivity ratios were determined by F-R (26), K-T (27), and EK-T (28) methods using the data obtained by FTIR and elemental analysis. Structure of the obtained copolymer was characterized by FTIR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopic technique. 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 by elemental analysis. Thermal properties of the copolymer were studied by DSC and TGA. The average molecular weight and polydispersity were determined by GPC.

## 2 Experimental

NVP, EOEMA and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Aldrich Chemicals, Milwaukee, WI. Prior to use, NVP was distilled under reduced pressure and EOEMA was washed with dilute alkali followed by distilled water and dried over anhydrous sodium sulfate and stored below  $0^\circ\text{C}$ . AIBN was recrystallized from methanol and dried in a vacuum for 24 h. Other chemicals like solvents, 99% pure were used as received from Merck Chemicals, Mumbai, India.

Copolymerization of monomers was carried out in 1,4-dioxane at  $60^\circ\text{C}$  under nitrogen atmosphere. A known amount of EOEMA ( $M_1$ ), NVP ( $M_2$ ), 0.5% AIBN and 1,4-dioxane, as given in Table 1, were taken in a three-necked 100 mL round bottom flask placed in oil bath maintained at  $60^\circ\text{C}$ . The copolymerization was allowed to proceed to low conversion (less than 15%) under nitrogen atmosphere. Polymerization was stopped by cooling the reaction mixture to room temperature. The viscous copolymer product obtained was precipitated in diethyl ether/hexane mixture; and was reprecipitated using

1,4-dioxane in diethyl ether/hexane mixture to ensure complete removal of residual monomers. Copolymer samples were dried in vacuum at  $40^\circ\text{C}$  until constant weight.

### 2.1 Copolymer Characterization

Copolymers were characterized by recording proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$ -NMR) in deuterated chloroform as solvent by a Bruker AMX-400 spectrometer and  $^{13}\text{C}$ -NMR in DMSO as solvent by a Bruker AMX-400 spectrometer. Fourier transform infrared (FTIR) spectra in KBr pellets were recorded using a Shimadzu-1800S spectrometer. The mole fractions of the monomers in the copolymer were determined by elemental analysis.

### 2.2 Thermal Properties

Thermal behavior of the copolymer was analyzed by using a DSC-Mettler Calorimetric system under a stream of nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ . The corresponding glass transition temperature ( $T_g$ ) and melt temperature were estimated from the inflection point of the resulting line. Thermal degradability of the copolymer was studied by TGA using a Perkin-Elmer Thermal analyzer. TGA was carried out in a stream of nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## 3 Results and Discussion

### 3.1 Copolymers Characterization

NVP/EOEMA copolymers having different compositions were prepared according to the experimental details given in Table 1 using AIBN as initiator in 1,4-dioxane as a solvent under nitrogen atmosphere.

FTIR spectrum of the prepared copolymer is shown in Figure 1. Strong absorption peak at  $1727\text{ cm}^{-1}$  is due to the ester group of the EOEMA unit. The peak at  $1682\text{ cm}^{-1}$  is due to the  $\text{C}=\text{O}$  of NVP unit. Absorption at  $1386\text{ cm}^{-1}$  is due to  $\text{C}-\text{N}-\text{C}$  of the imide in the NVP unit.  $^1\text{H}$ -NMR spectrum of the copolymer is shown in Figure 2. The main chain methylene proton signals of both the NVP and

**Table 1.** Reaction conditions of NVP/EOEMA copolymer, FTIR and elemental analysis data

Sample name	Feed mole fraction of EOEMA ( $M_1$ )	% Conversion	N% by elemental analysis	Integral value		Mole fraction of EOEMA ( $m_1$ ) in copolymer by elemental analysis	Mole fraction of EOEMA ( $m_1$ ) in copolymer by FTIR
				Intensity of ester $\text{C}=\text{O}$ in EOEMA	Intensity of amide $\text{C}=\text{O}$ in NVP		
NVP-8	0.20	14.8	8.900	10.9	19.3	0.3643	0.3609
NVP-6	0.35	14.1	6.311	26.4	22.6	0.5492	0.5376
NVP-5	0.50	13.0	5.075	25.5	14.9	0.6375	0.6311
NVP-4	0.60	12.1	4.481	18.5	9.2	0.6799	0.6678
NVP-2	0.75	11.6	4.052	27.7	11.7	0.7106	0.7030

Solvent: 1,4-dioxane; temperature:  $60^\circ\text{C}$ , initiator AIBN: 0.05% based on the total weight of the monomers and solvent; monomer/solvent, 1/3 (W/V).

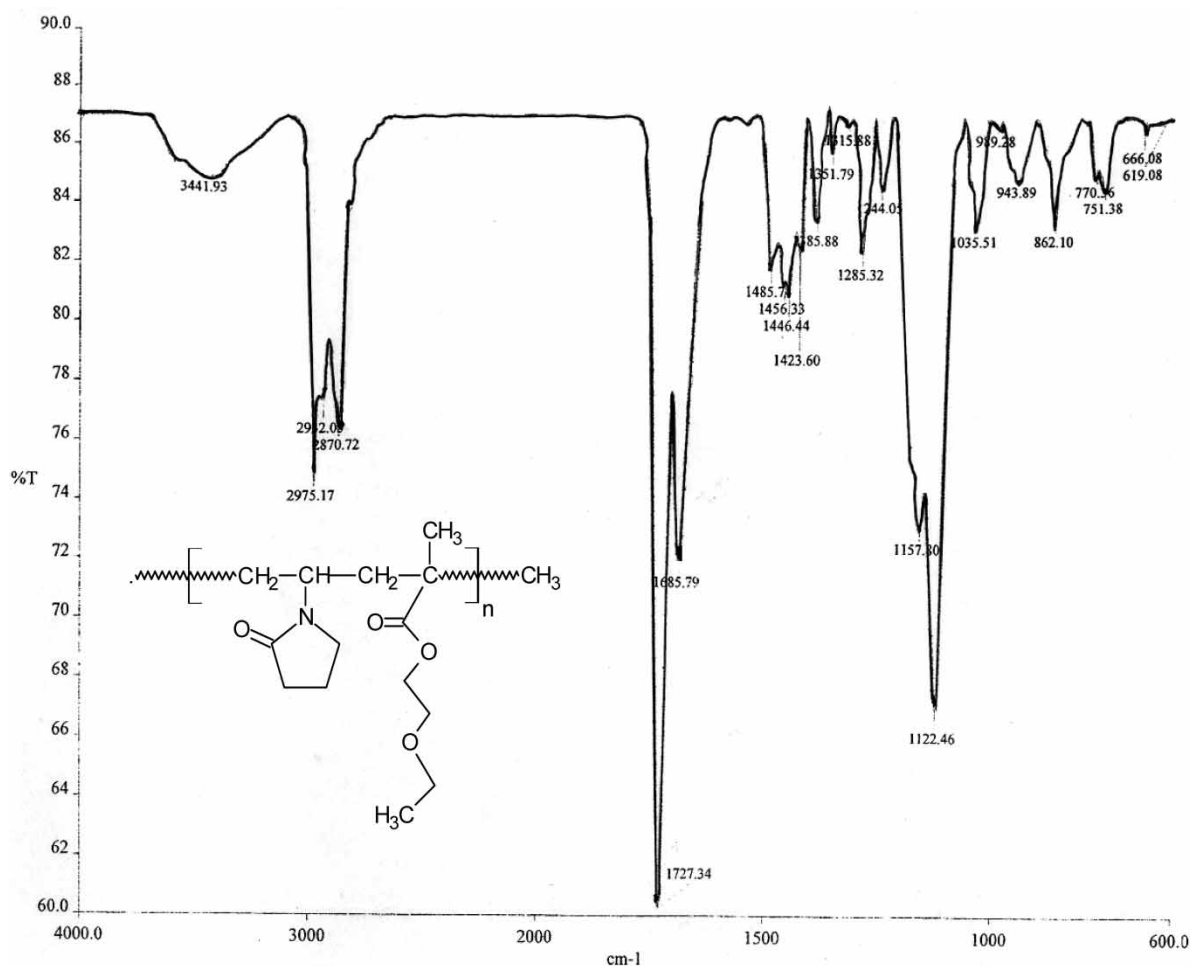


Fig. 1. FTIR spectra of NVP/EOEMA copolymer.

EOEMA unit resonate at  $\delta$  2.15–0.90 ppm, which overlap with a different type of compositional and configurational sequences. Similarly, the methyl ( $^7\text{CH}_3$  and  $^{11}\text{CH}_3$ ) protons of EOEMA signals at  $\delta$  0.85–1.35 ppm overlap with each other. The signals for three  $-\text{OCH}_2$  methylene ( $^8\text{CH}_2$ ,  $^9\text{CH}_2$ ,  $^{10}\text{CH}_2$ ) proton of EOEMA appeared at  $\delta$  3.4–3.7 ppm, whereas CH of NVP ( $^1\text{CH}$ ) appeared at  $\delta$  4.3 ppm. The ring methylene protons in NVP signals can be assigned at  $\delta$  3.2 ( $^3\text{CH}_2$ ),  $\delta$  2.2 ( $^5\text{CH}_2$ ),  $\delta$  1.9 and  $\delta$  2.1 ppm for ( $^4\text{CH}_2$  and  $^6\text{CH}_2$ ), respectively.

The  $\text{C}^{13}$ -NMR spectrum of NVP/EOEMA copolymer is shown in Figure 3. The carbonyl carbon ( $>\text{C}=\text{O}$ , i.e.,  $^3\text{C}$ ,  $^9\text{C}$ ) signals of both NVP and EOEMA units are appearing between  $\delta$  173.4–176.8 ppm. The spectral region around  $\delta$  70.0–17.0 ppm is quite complex and overlapping and are assigned to aliphatic carbon resonance in back bone and side chain of NVP/EOEMA copolymer. The side chain ring methylene carbon signal is assigned at  $\delta$  44.4 ( $^6\text{CH}_2$ ),  $\delta$  31.6 ( $^4\text{CH}_2$ ) and  $\delta$  17.8 ( $^5\text{CH}_2$ ) ppm. The signal for  $\text{OCH}_2$  of EOEMA comes between  $\delta$  63.8–67.1 and the methyl carbons of EOEMA ( $^8\text{CH}_3$ ,  $^{13}\text{CH}_3$ ) resonate at  $\delta$  14.8 ppm.

Average molecular weight of the copolymer was determined by gel permeation chromatography, average molecular weight found to be  $M_w = 1, 18,440$  and number average molecular weight was found to be  $M_n = 80, 674$ . The polydispersity was found to be 1.46.

### 3.2 Copolymer Composition

The composition of monomers in copolymer was determined by elemental analysis by N% which gives the % of NVP in the copolymer. Also, the composition of copolymers for a wide range of monomer feed can be determined by Fourier transform infrared spectroscopy (FTIR) through recorded analytical absorption bands for comonomers (29, 30). Pure poly *N*-vinyl pyrrolidone (PVP) has a characteristic, relatively broad, infrared band at  $1682\text{ cm}^{-1}$ . On the other hand, the carbonyl group band of EOEMA was observed at  $1727\text{ cm}^{-1}$  Figure 1 shows the FTIR spectral band of NVP/EOEMA copolymers. By calculating the absorbance of these peaks, we can determine the concentration of NVP and EOEMA in the copolymers. Absorbance peaks of carbonyl groups of NVP and EOEMA

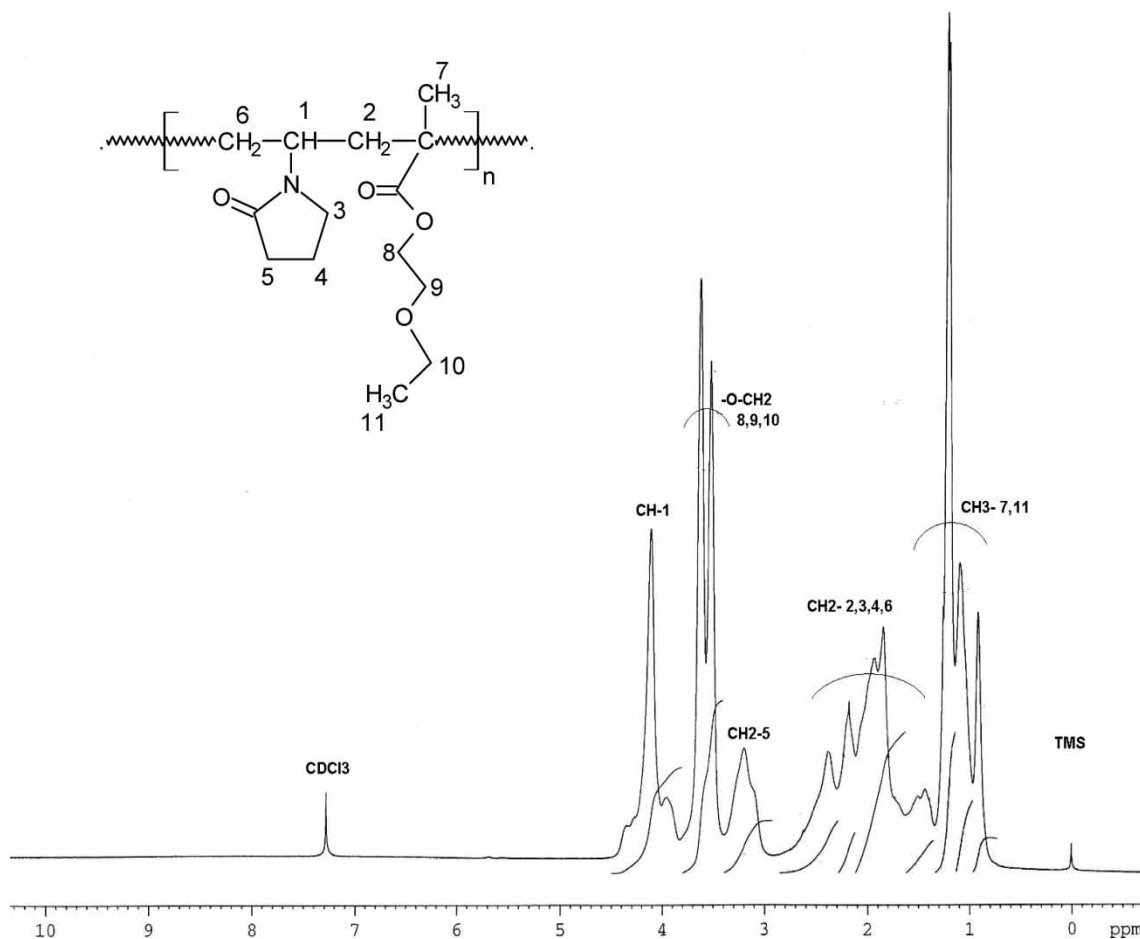


Fig. 2.  $^1\text{H}$ -NMR spectra of NVP/EOEMA copolymer.

in the copolymers are shown in Figure 4. It is evident that with an increase in EOEMA content, peak 1 increase correspondingly. Using the absorbance of carboxyl groups of EOEMA and NVP of all copolymers, the concentration of EOEMA and NVP in the copolymers was obtained. The compositions obtained by elemental analysis and by the FTIR method were compared and are listed in Table 1. The plot of the mole fraction of EOEMA ( $M_1$ ) in feed vs. that of the mole fraction of EOEMA ( $m_1$ ) in copolymer is shown in Figure 5(a). The azeotropic composition was found at 0.765 mole fraction of EOEMA in the feed. Below this mole fraction the copolymer is richer in EOEMA.

### 3.3 Monomer Reactivity Ratio

The comonomer composition sequence is one of the main factors that influence copolymer behavior and properties. Copolymer composition depends on the monomer feed composition and on the relative monomer reactivity. Therefore, it is very important to study the comonomer reactivity in these systems (31).

Copolymerization reactivity ratio of NVP and EOEMA were determined by the F-R, K-T, and EK-T methods using

the data obtained by both elemental analysis and FTIR spectroscopy. The equations used for F-R and K-T are:

$$G = Fr_1 - r_2 \quad (\text{F-R equation}) \quad (1)$$

$$\eta = (r_1 + r_2/\alpha)\xi - (r_2/\alpha) \quad (\text{K-T equation}) \quad (2)$$

where  $r_1$  and  $r_2$  are the reactivity ratios relating to the monomer EOEMA and NVP, respectively.  $G$  and  $F$  are F-R parameters.  $\eta$ ,  $\xi$ , and  $\alpha$  are K-T parameters. The plot of  $G$  vs.  $F$  will give a straight line with  $r_1$  as the slope and  $-r_2$  as the intercept (Figure 5 (b)).  $\eta$ ,  $\xi$ , and  $\alpha$  are mathematical functions of  $G$  and  $F$  as indicated and presented in Tables 2 and 3 for the K-T method. The K-T plot of  $\xi$  vs.  $\eta$  is shown in Figure 5(c) using FTIR and elemental analysis data.

The EK-T method, another linear least-square method, considers the drift of comonomer and copolymer composition with conversion. Therefore, it is suitable for the manipulation of our highly conventional data. The partial molar conversion of NVP is defined as:

$$\xi_{NVP} = \frac{W(\mu + x)}{\mu + y} \quad (3)$$

where  $W$  is the weight conversion of polymerization, and  $\mu$  is

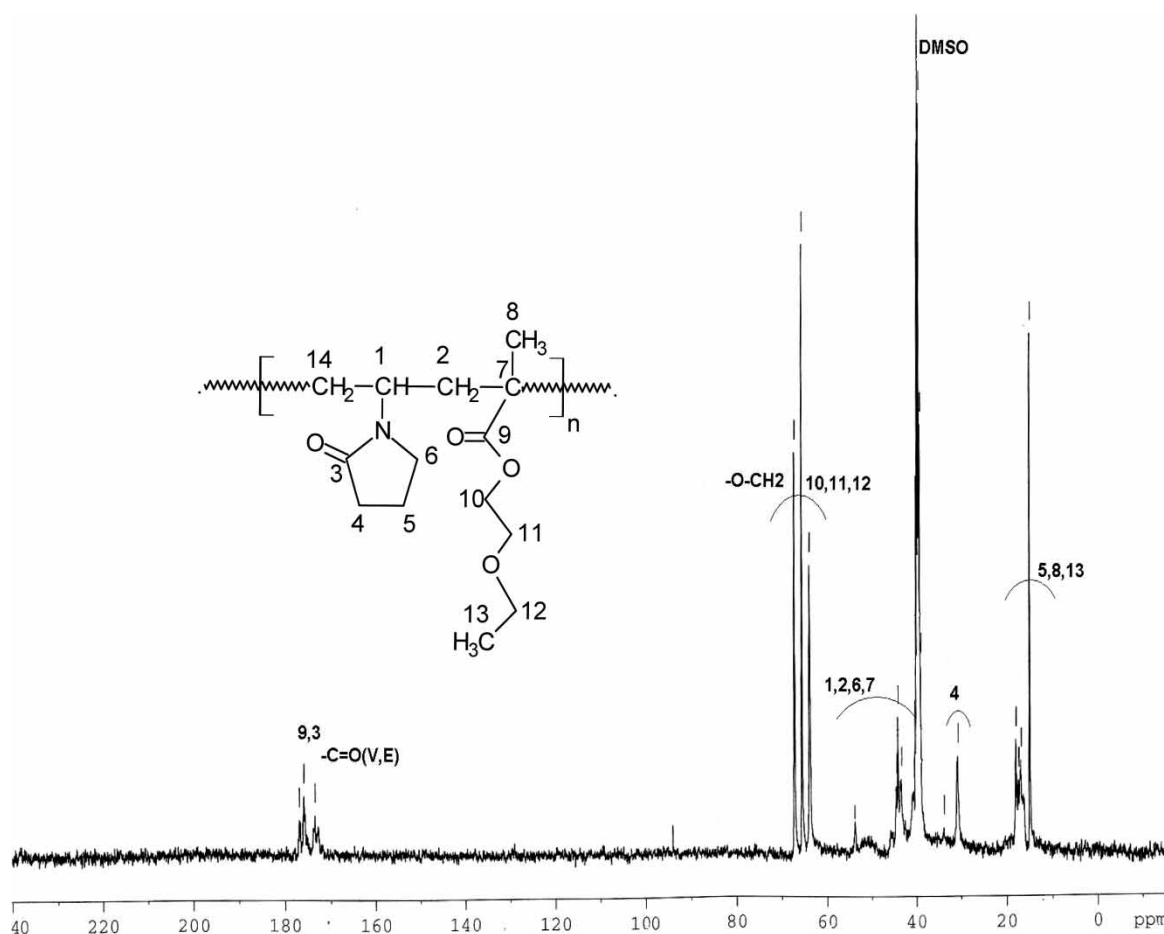


Fig. 3.  $^{13}\text{C}$ -NMR spectra of NVP/EOEMA copolymer.

the ratio of the molecular weight of NVP to that of EOEMA. The partial molar conversion of EOEMA is:

$$\xi_{EOEMA} = \xi_{NVP} \frac{y}{x} \quad (4)$$

then,

$$Z = \frac{\log(1 - \xi_{EOEMA})}{\log(1 - \xi_{NVP})} \quad (5)$$

where the value of  $\eta = G/(\alpha + F)$ ;  $\xi = (\alpha + F)$ ;  $G = (y - 1)/Z$ ;  $H = y/Z^2$  EK-T parameters are calculated from the above equations using Table 4 by elemental analysis and Table 5 by FTIR spectroscopy. The EK-T plot for copolymer samples is given in Figure 5(d). Table 6 shows the comparison of reactivity ratios of the monomers calculated from both elemental analysis and by FTIR spectroscopy, which are in good agreement with each other. It can be seen that the  $r_1$  value was greater than  $r_2$  because both  $r_1$  and  $r_2$  values are below one, these systems give an azeotropic polymerization at a particular composition of the monomers, which is calculated using average reactivity ratio obtained by elemental analysis by equation (6).

$$A_{\text{azeotrop}} = \frac{1 - r_2}{2 - r_1 - r_2} \quad (6)$$

At 0.765 mole fractions of EOEMA, the composition of EOEMA in feed and in the copolymer are the same. The higher  $r_1$  value of EOEMA confirms the higher reactivity of EOEMA towards the growing chain, regardless of whether the radical end was derived from EOEMA or NVP.

Alfrey-Price  $Q$  and  $e$  values of EOEMA and NVP were determined using average reactivity ratio obtained by elemental analysis by the following equations:

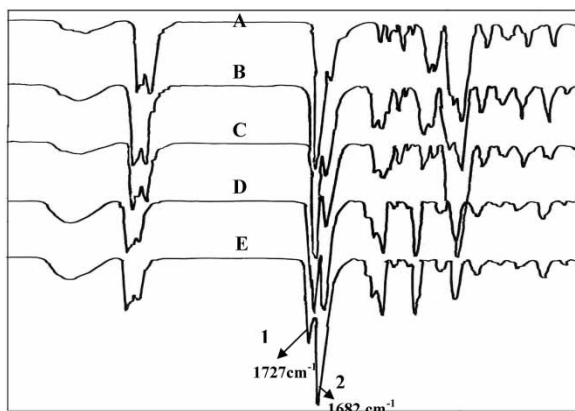
$$e_1 = e_2 + [(\ln r_1 r_2)]^{1/2} \quad (7)$$

$$Q_1 = (Q_2/r_2) \exp[e_2(e_1 - e_2)] \quad (8)$$

The values of  $Q_2 = 0.14$  and  $e_2 = -1.14$  are from the literature (32). The calculated  $Q$  and  $e$  parameters are found to be 0.0859 and 0.450, respectively for EOEMA. The positive values of  $Q$  and  $e$  obtained indicate electron acceptor character of EOEMA monomer. This type of monomer will easily undergo copolymerization with the electron donor monomers with a higher reactivity.

### 3.4 Copolymer Microstructure

Simona et al. (33) calculated the copolymer microstructure and sequence distribution of monomers in the formation of



**Fig. 4.** FTIR spectra of NVP/EOEMA copolymer prepared in various monomer feeds (NVP/EOEMA): (A) 25:75, (B) 40:60, (C) 50:50, (D) 65:35, (E) 80:20.

the copolymer. Here, we have attempted to calculate the sequence distribution of the resulting copolymer. The probability of finding the sequence of  $n$  EOEMA and  $n$  NVP units is calculated as follows (34):

$$N_{EOEMA(n)} = P_{11}^{n-1}(1 - P_{11}) \quad (9)$$

$$N_{NVP(n)} = P_{22}^{n-1}(1 - P_{22}) \quad (10)$$

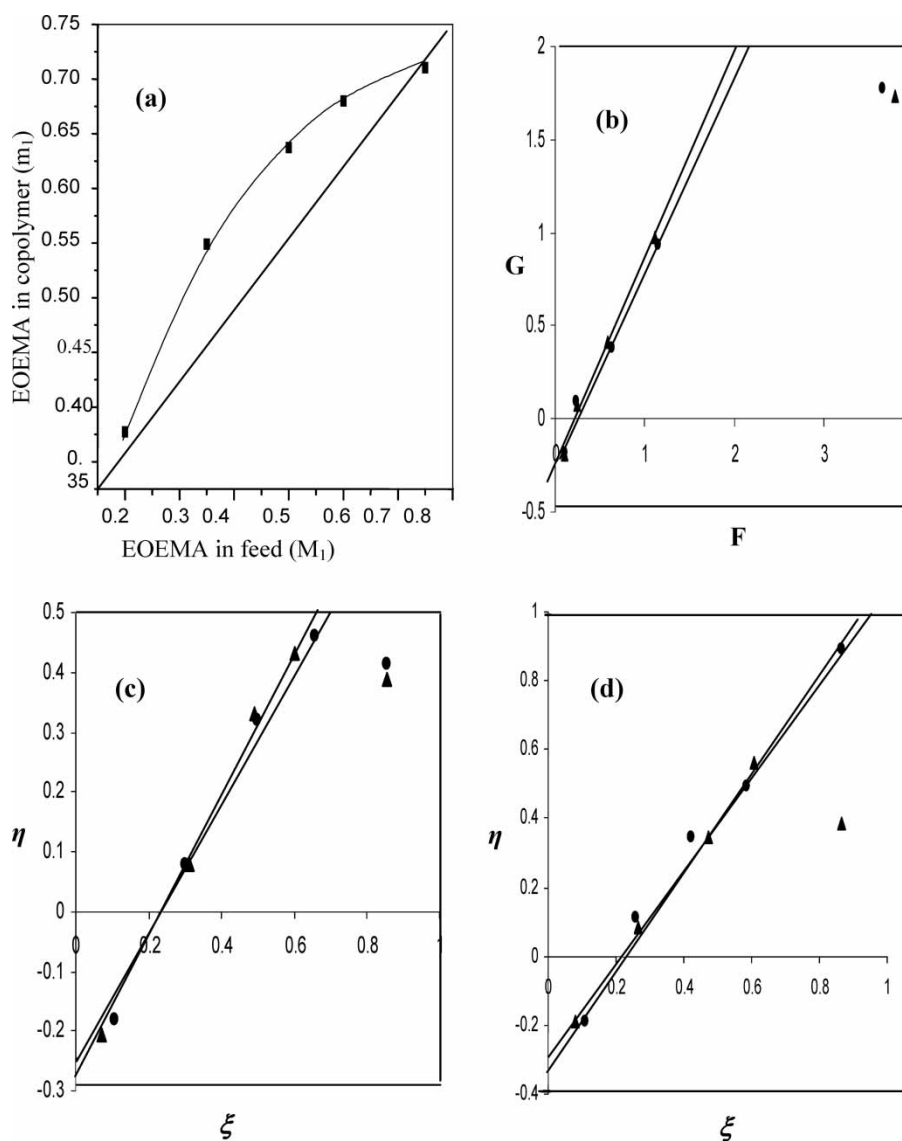
where  $P_{11}$  and  $P_{22}$  are the probability of an EOEMA (or NVP) unit to be followed by a EOEMA (or NVP) unit. These probabilities (Table 7) are calculated with the following equations:

$$P_{11} = r_1 R / r_1 R + r_1 \quad (11)$$

$$P_{22} = r_2 / R + r_2 \quad (12)$$

where  $R$  is the mole ratio of EOEMA to NVP in the feed.

The values of  $N_{EOEMA(n)}$  and  $N_{NVP(n)}$  shown in Figure 6, were calculated for the obtained copolymer at an equimolar



**Fig. 5.** FTIR (▲) and elemental analysis (●) data of (a) plot of mole fraction of EOEMA in feed ( $M_1$ ) vs. that of EOEMA in copolymer ( $m_1$ ); (b) F-R plot of  $G$  vs.  $F$ ; (c) K-T plot of  $\eta$  vs.  $\xi$ ; (d) EK-T plot of  $\eta$  vs.  $\xi$ .

**Table 2.** F-R and K-T parameter for NVP/EOEMA copolymer by elemental analysis

Sample no	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\eta = G/(\alpha + F)$	$\xi = F/(\alpha + F)$
NVP-8	0.2500	0.5731	-0.1862	0.1091	-0.2511	0.1472
NVP-6	0.5385	1.2183	0.0964	0.2380	0.1108	0.2735
NVP-5	1.0000	1.7586	0.4314	0.5686	0.3592	0.4735
NVP-4	1.6000	2.1240	0.8467	1.2053	0.4608	0.6559
NVP-2	3.0000	2.4554	1.7782	3.6653	0.4137	0.8528

$M_1$  = mole fraction of EOEMA in feed;  $M_2$  = mole fraction of NVP in feed;  $m_1$  = mole fraction of EOEMA in copolymer;  $m_2$  = mole fraction of NVP in copolymer;  $\alpha = (F_{\min} \cdot F_{\max})^{1/2} = 0.6323$ .

**Table 3.** F-R and K-T parameter for NVP/EOEMA copolymer by FTIR data

Sample no	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\eta = G/(\alpha + F)$	$\xi = F/(\alpha + F)$
NVP-8	0.2500	0.5647	-0.1927	0.1106	-0.2538	0.1457
NVP-6	0.5385	1.1626	0.0753	0.2494	0.0838	0.2779
NVP-5	1.0000	1.7107	0.4154	0.5846	0.3369	0.4746
NVP-4	1.6000	2.0100	0.8039	1.2736	0.4182	0.6626
NVP-2	3.0000	2.3670	1.7325	3.8022	0.3892	0.8543

$M_1$  = mole fraction of EOEMA in feed;  $M_2$  = mole fraction of NVP in feed;  $m_1$  = mole fraction of EOEMA in copolymer;  $m_2$  = mole fraction of NVP in copolymer;  $\alpha = (F_{\min} \cdot F_{\max})^{1/2} = 0.6560$ .

**Table 4.** EK-T parameter for EOEMA and NVP using elemental analysis

Sample name	$\xi_{VP}$	$\xi_{EOEMA}$	$Z$	$G$	$F$	$\xi$	$\eta$
NVP-8	0.1106	0.2534	2.4930	-0.1712	0.0922	0.1352	-0.2511
NVP-6	0.0944	0.2136	2.4255	0.0900	0.2070	0.2599	0.1130
NVP-5	0.8990	0.1581	1.8264	0.4153	0.5103	0.4112	0.3710
NVP-4	0.1132	0.1742	1.5936	0.7053	0.8362	0.5865	0.4947
NVP-2	0.1360	0.1113	0.8072	1.8032	3.7694	0.8647	1.2647

$\alpha = (F_{\min} \cdot F_{\max})^{1/2} = 0.5895$ .

**Table 5.** EK-T parameter for EOEMA and NVP using FTIR data

Sample name	$\xi_{VP}$	$\xi_{EOEMA}$	$Z$	$G$	$F$	$\xi$	$\eta$
NVP-8	0.1113	0.2514	2.4531	-0.1774	0.0938	0.1338	-0.2531
NVP-6	0.0938	0.2025	2.2974	0.0707	0.2203	0.2663	0.0854
NVP-5	0.0917	0.1569	1.7740	0.4006	0.5436	0.4724	0.3481
NVP-4	0.1027	0.1290	1.2747	0.7923	1.2370	0.6708	0.4296
NVP-2	0.1399	0.1104	0.7761	1.7614	3.9300	0.8662	0.5882

$\alpha = (F_{\min} \cdot F_{\max})^{1/2} = 0.6071$ .

**Table 6.** Monomer reactivity ratio for NVP/EOEMA copolymer

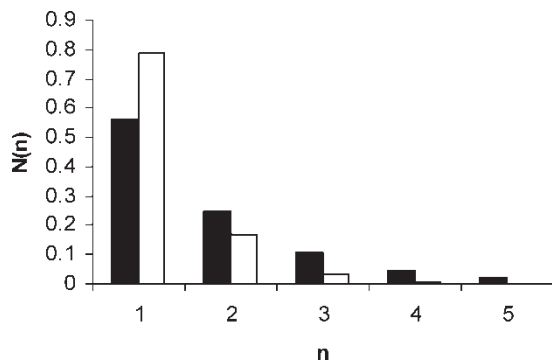
Method	By elemental analysis		By FTIR spectroscopy	
	$r_1$ (EOEMA)	$r_2$ (NVP)	$r_1$ (EOEMA)	$r_2$ (NVP)
F-R method	0.771	0.268	0.791	0.269
K-T method	0.774	0.258	0.769	0.253
EK-T method	0.760	0.272	0.764	0.276
Average	0.769	0.266	0.774	0.266

**Table 7.** Statistical data for the NVP/EOEMA copolymer

Sample	$P_{11}$	$P_{22}$	$\mu_{EOEMA}$	$\mu_{NVP}$
NVP-8	0.1612	0.5155	1.1922	2.064
NVP-6	0.2928	0.3306	1.4140	1.4939
NVP-5	0.4347	0.2101	1.7690	1.2660
NVP-4	0.5356	0.1506	1.8076	1.1773
NVP-2	0.6976	0.0814	3.3070	1.0886

$P_{11}$  the probability of EOEMA unit to be followed by a EOEMA unit,  $P_{22}$  the probability of a NVP unit to be followed by a NVP unit;  $\mu$  the mean sequence length.





**Fig. 6.** The probability of finding the sequence of  $n$  EOEMA unit (black columns) and  $n$  NVP units (white columns) at an equimolar feed.

feed. In our case, we observed that the NVP/EOEMA copolymer contains predominantly a sequence of EOEMA, which is in agreement with higher reactivity of EOEMA.

The mean sequence lengths  $\mu_{EOEMA}$  and  $\mu_{NVP}$  were also calculated using the following relations (35):

$$\mu_{EOEMA} = 1 + r_1(M_1/M_2) \quad (13)$$

$$\mu_{NVP} = 1 + r_2(M_2/M_1) \quad (14)$$

The value of  $\mu_{EOEMA}$  and  $\mu_{NVP}$  are presented in Table 7. The  $\mu_{EOEMA}$  values increases from 1.1922 to 3.3070 in the NVP/EOEMA copolymer with an increase of EOEMA concentration in the feed. Higher EOEMA content found in the synthesized copolymer correlated with the calculated  $r_1$  and

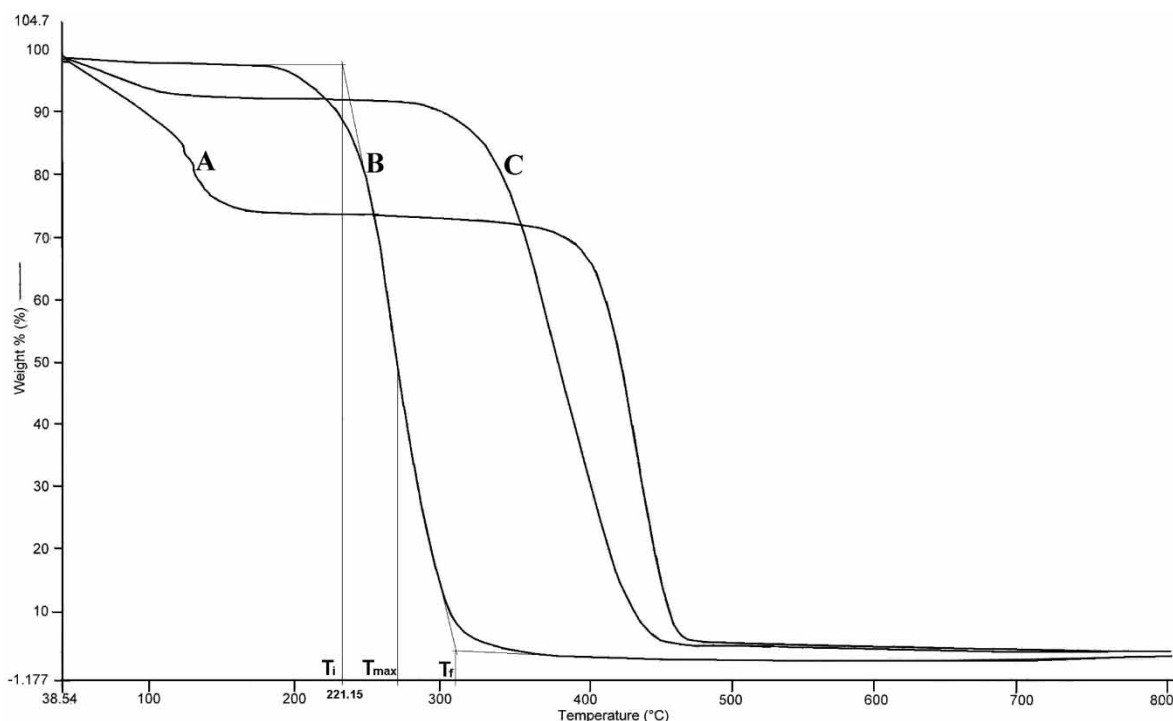
$r_2$  values indicates that the NVP/EOEMA composition is enriched with the EOEMA monomer.

### 3.5 Thermal Properties

#### 3.5.1 Thermal Property of the Copolymer was Studied by DSC and TGA

Homopolymer of poly NVP showed the glass transition temperature around  $148^\circ\text{C}$  (36) and poly EOEMA has very low glass transition temperature of  $T_g = -16^\circ\text{C}$  (37). Whereas the NVP/EOEMA copolymer showed improved  $T_g$  compared to the EOEMA homopolymer.

TGA was used to evaluate the thermal stability of the NVP/EOEMA copolymer as compared with the NVP homopolymer and EOEMA homopolymer. It was found that the NVP/EOEMA copolymer showed single step degradation, which is clearly distinguishable. This confirms that there is no homopolymer formation during the copolymer synthesis. With incorporation of a NVP content in copolymer, the initial decomposition temperature ( $T_i$ ), the temperature of maximum rate of weight loss ( $T_{max}$ ) and the final decomposition temperature ( $T_f$ ) of EOEMA were increased (Figure 7). The thermal stability data for copolymer and homopolymers are given in Table 8. Initial decomposition temperature  $T_i$  value for poly EOEMA and poly NVP are found to be  $221.15^\circ\text{C}$  and  $401.21^\circ\text{C}$ , respectively. Whereas, the NVP/EOEMA copolymer showed a decomposition temperature of  $333.95^\circ\text{C}$ , which is higher than that of poly EOEMA. Based on the results obtained, one can deduct that



**Fig. 7.** TGA Thermogram of (A) PolyNVP; (B) PolyEOEMA; (C) NVP/EOEMA copolymer.

**Table 8.** Thermal data obtained for copolymer by TGA

Polymer	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)
PolyEOEMA	221.15	271.20	310.13
PolyNVP	401.21	431.69	462.13
Copolymer NVP/EOEMA	333.95	388.45	437.95

the decomposition temperature of the copolymer increases with an increase in the content of the NVP component in the NVP/EOEMA copolymer.

### 3.6 Solubility

Solubility of copolymer samples were examined in different polar and non polar solvents. The NVP/EOEMA copolymers are completely soluble in most of the polar solvents like acetone, 1-4 dioxane, tetrahydrofuran, dimethylsulfoxide, dimethylformamide, dimethylacetamide, ethyl acetate, isobutyl acetate, and chloroform, and insoluble in non polar solvents like hexane, cyclohexane, carbon tetrachloride, diethyl ether and benzene.

We observed that, the increase in EOEMA content in the copolymer decreases its water solubility. NVP-8 is readily soluble in water, NVP-5 and NVP-6 are partially soluble whereas, NVP-2 and NVP-4 are totally insoluble in water. The NVP/EOEMA copolymer has an advantage of being soluble in most of the polar solvents. Hence, this study is helpful in designing NVP based copolymers to prepare pharmaceutical formulations in polar and nonpolar solvent mixtures.

## 4 Conclusions

Copolymers of NVP/EOEMA were prepared in 1,4-dioxane using AIBN as an initiator. The obtained copolymer shows excellent solubility in most of the polar solvents and water solubility variation due to acrylic content. The reactivity ratios were calculated using data obtained from FTIR and elemental analysis are in good agreement with each other. Calculated reactivity ratio and monomer sequence distribution indicates the copolymers formation with predominately random distribution of the monomer with a higher content of EOEMA units in the copolymer chain. The thermal property of poly EOEMA was found to be improved by copolymerizing with NVP.

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