American Journal of Polymer Science 2014, 4(1): 16-23
DOI: 10.5923/j.ajps.20140401.03

Reactivity Ratios of N-Vinylpyrrolidone - Acrylic Acid Copolymer

P Hemalatha[1,*], M K Veeraiah[1], S Prasanna Kumar[2], Netkal M Madegowda[3], M Manju[4]

[1]Department of Chemistry, Sri Siddhartha Institute of Technology, Tumkur
[2]Clov Chem, India Private Limited, Harohalli, Bangalore
[3]Department of Chemistry, Western Illinois University, Macomb, IL, USA
[4]Department of Chemistry, Sri Krishna Institute of Technology, Bangalore

Abstract Copolymers of N-vinylpyrrolidone (NVP) and Acrylic acid (AA) were prepared by using hydrogen peroxide as initiator and water as solvent at 45℃ under nitrogen atmosphere at different compositions. The copolymers were characterized by FTIR, H^1NMR and C^{13}NMR. The copolymer reactivity ratio was computed by the Fineman- Rose(F-R) and Kelen Tudos(K-T) method at lower conversion, using the data obtained by Acid - Value studies. The Copolymer microstructure and Sequence distribution of monomers in the copolymer was calculated by statistical method.

Keywords N-vinylpyrrolidone, Acrylic acid, FTIR, H^1NMR, C^{13}NMR, Reactivity ratios, Sequence distribution

1. Introduction

Copolymerization is one of the important techniques adopted in effecting systematic changes in the properties of the commercially important polymers. The chemical structure of copolymer depends not only on the monomer units forming the macromolecule but also how such units are distributed along macromolecular chains. This distribution is a direct consequence of each monomer's reactivity in the copolymer molecule [1]. Reactivity ratios are the most important parameters for composition equation of copolymers and they offer information about the reactivity of monomer pairs. However, the copolymer composition is important in evaluating its own utility. The copolymer composition and its distribution are dependent on their reactivity ratios, which can be evaluated either by employing linear and nonlinear methods or by using other copolymer composition equations [2-4].

Many polymers with reactive functional groups are now being synthesized, tested and used not only for their macromolecular properties, but also for the properties of functional group. These groups provide an approach to a subsequent modification of the polymer for specific end application [5].

N-vinylpyrrolidone (NVP) has been widely investigated for applications in various Fields, [6-10] as these are known to exhibit good biocompatibility due to their hydrophilic nature and low cytotoxicity [11-13]. 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 [14-18].

S. Sundararajan et al. synthesized the copolymer of Glycidal Methacrylate and N- vinylpyrrolidone and the reactivity ratio was determined [19]. It indicates that Glycidal Methacrylate is more reactive and the copolymer formed is random in nature. S. Vijay Kumar et al. studied the reactivity ratio of N-Vinylpyrrolidone and Ethoxy ethyl methacrylate. They found out the reactivity ratio of the copolymer and the distribution of the monomer sequence along the copolymer chain was also calculated [20]. A.S. Brar et al. synthesized the copolymer of N-Vinylpyrrolidone – Methylmethacrylate by free radical bulk polymerization and they determined the reactivity ratio [21]. Dilek Solpan et al. synthesized copolymer N-Vinyl Pyrrolidone – Methylmethacrylate and they studied the swelling property of these hydrogels [22]. Mitesh.B.Patel et al. synthesized the copolymer of N-Vinylpyrrolidone – 2, 4 – Dichlorophenyl methacrylate and they determined that the reactivity ratio of both the monomers is less than unity [23]. They have also determined the Azeotropic composition of the copolymer. Nicolas Gatica et al. synthesized the copolymer of N-Vinylpyrrolidone – Vinyltrimethylsilane and N-Vinylpyrrolidone – Vinyltrimethoxysilane and reported that the copolymers formed are random [24].

In the present work a copolymer of NVP with acrylic acid (AA) is synthesized. The prepared copolymer is characterized by FTIR, H^1-NMR and C^{13} NMR. Reactivity ratios of monomer are calculated using Fineman- Rose (F-R) [25] and Kelen - Tudos(K-T) [26] methods at lower conversion, using the data obtained from Acid Value studies.

---

* Corresponding author:
phlssit@gmail.com (P Hemalatha)

Distribution of the monomer sequences along the copolymer chain is determined by the statistical methods based on the reactivity ratio obtained by K-T method.

2. Experimental

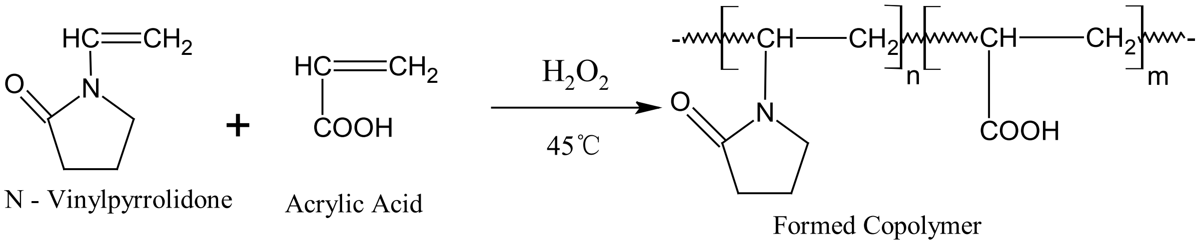
2.1. Materials

N-Vinylpyrrolidone (Sigma-Aldrich), Acrylic acid (SD Fine Chemicals) are washed with Fuller's Earth and is kept for a night to settle. Hydrogen peroxide (Spectro Chem) 30% and other solvents are of AR Grade which are of 99% purity. They are used as received from SD Fine Chemicals, Mumbai, India.

2.2. Synthesis of Copolymer

As both the monomers are soluble in water, the copolymerization is carried out in presence of water. Known amounts of monomer NVP, AA and water are taken in a three necked 100ml round bottom flask. When the mixture is heated up to 45℃, 0.5% hydrogen peroxide is added and heated for 3 hours in nitrogen atmosphere with continuous stirring. At this juncture the process is stopped and the reaction is allowed to cool down to the room temperature. The high viscous reaction mixture is poured into the Petri dish and evaporated in vacuum.

2.3. Structure of Copolymer



2.4. Copolymer Characterization

Copolymers are characterized by FTIR spectra using Shimadzu-1800S spectrometer on KBr pellets in the range of 400-4000cm^{-1}. The H^1-NMR and C^{13}-NMR (Brucker AMX-400, at Indian Institute of Science, Bangalore) spectra of copolymers are recorded in methanol as solvent and Tetramethylsilane (TMS) as an internal standard.

3. Results and Discussion

Different homo and copolymers were obtained by the free radical solution polymerization technique. The copolymer with different compositions of NVP –AA is prepared using hydrogen peroxide as initiator in the presence of water as solvent under nitrogen atmosphere at 45℃. The data on the composition of the feed and copolymers are given in Table-1 and Figures 1&2. Figure 1&2 show the copolymerization behavior of monomer as a function of their reactivity ratios and monomer feed ratios.

Table 1. Monomer and Copolymer composition

Sample No	Monomer feed		Monomer in polymer	
	NVP(M1)	AA(M2)	NVP(m1)	AA(m2)
0	0	20	-	-
1	0.1	0.9	0.4975	0.5025
2	0.2	0.8	0.6888	0.3112
3	0.4	0.6	0.7643	0.2357
4	0.6	0.4	0.8619	0.1381
5	0.8	0.2	0.9219	0.0781
6	0.9	0.1	0.9576	0.0424
7	20	0	-	-

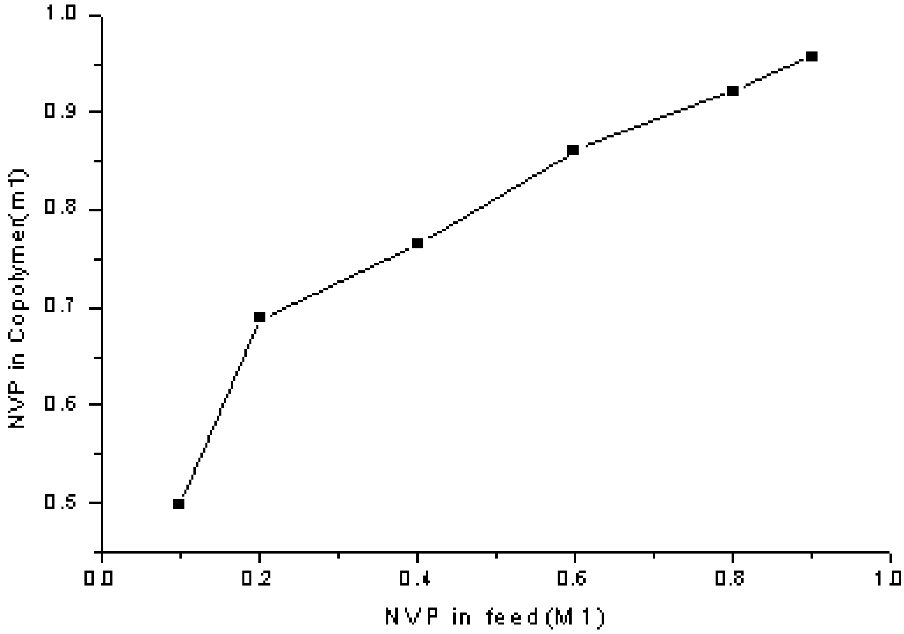


Figure 1. For NVP monomer

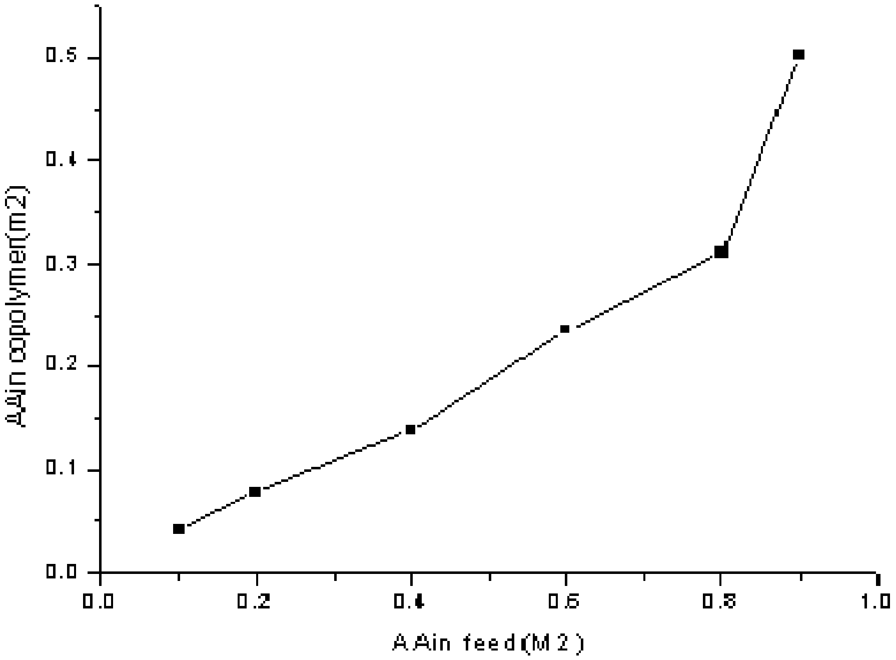


Figure 2. For AA Monomer

3.1. Characterization of Polymers

3.1.1. Solubility Studies

Solubility of the homo and copolymer is tested in various polar and non polar organic solvents. They are soluble in solvents like tetrahydrofuran, dimethyl sulfoximide, dimethyl formamide, dimethyl acetamide, isopropylalcohol and methanol. But they are insoluble in ethylacetae, chloroform, 1,4-dioxane, chlorobenzene, toluene, n-hexane, n-heptane, cyclohexane, carbontetrachloride, diethyl ether and benzene.

3.1.2. Fourier Transform Infrared (FTIR) Spectral Studies

The structures of all the copolymer are confirmed by FTIR spectra as shown in Figure – 3

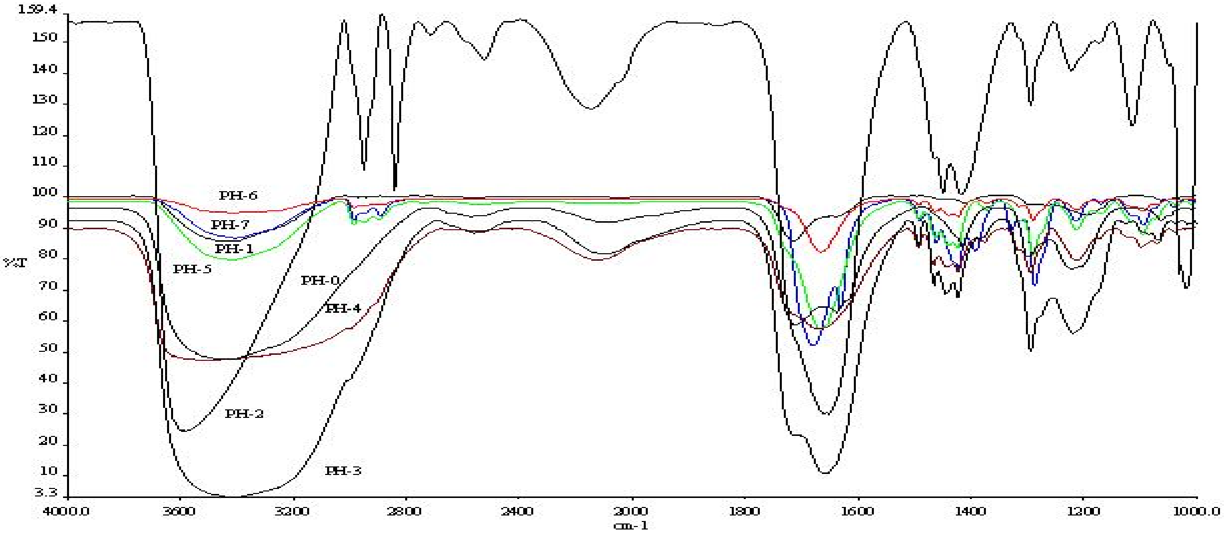


Figure 3. FTIR spectra of Copolymer

Only important peaks are assigned. A strong absorption band observed in the region 1680 cm^{-1} to 1724 cm^{-1} is due to the –C = O of NVP and carboxylic acid of AA. The peak at 1440 cm^{-1} is due to OC-OH stretching vibration. The peak at 3440cm^{-1} is due to –OH bond of AA. The peak at 1330 cm^{-1}is due to-C-N- stretching in lactam.

3.1.3. Nuclear Magnetic Resonance Spectroscopy (H^1- NMR) :

H^1- NMR spectrum of copolymer is as shown in Figure – 4

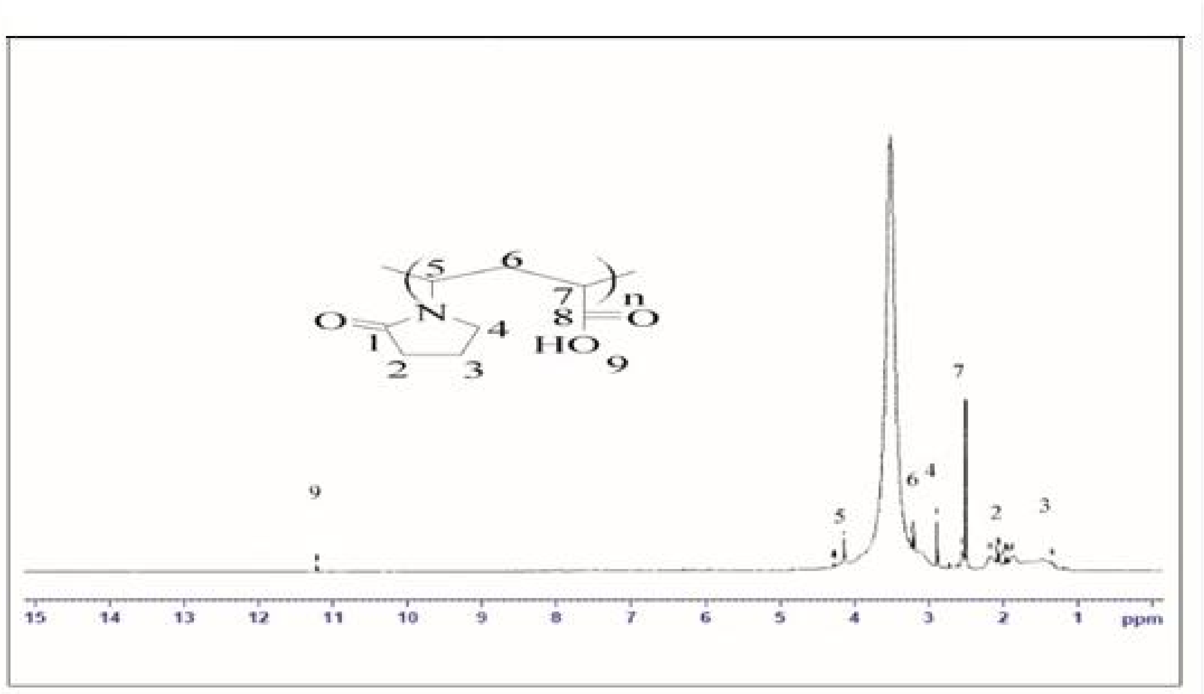


Figure 4. H^1 NMR spectra of the Copolymer

The main chain methylene proton of both NVP and AA units resonate at δ 4.2, 3.5 and 2.5 ppm. The –CH group of NVP appears at δ 4.8 ppm. The ring methylene proton in NVP are assigned at δ =2.2, δ = 1.5 and δ = 2.8 ppm respectively. The proton present in carboxylic group of AA resonates at δ = 11.2 ppm.

3.1.4. Nuclear Magnetic Resonance Spectroscopy (C^{13}– NMR) :

The structure of copolymer is also confirmed by C^{13}– NMR spectrum which is shown in Figure – 5.

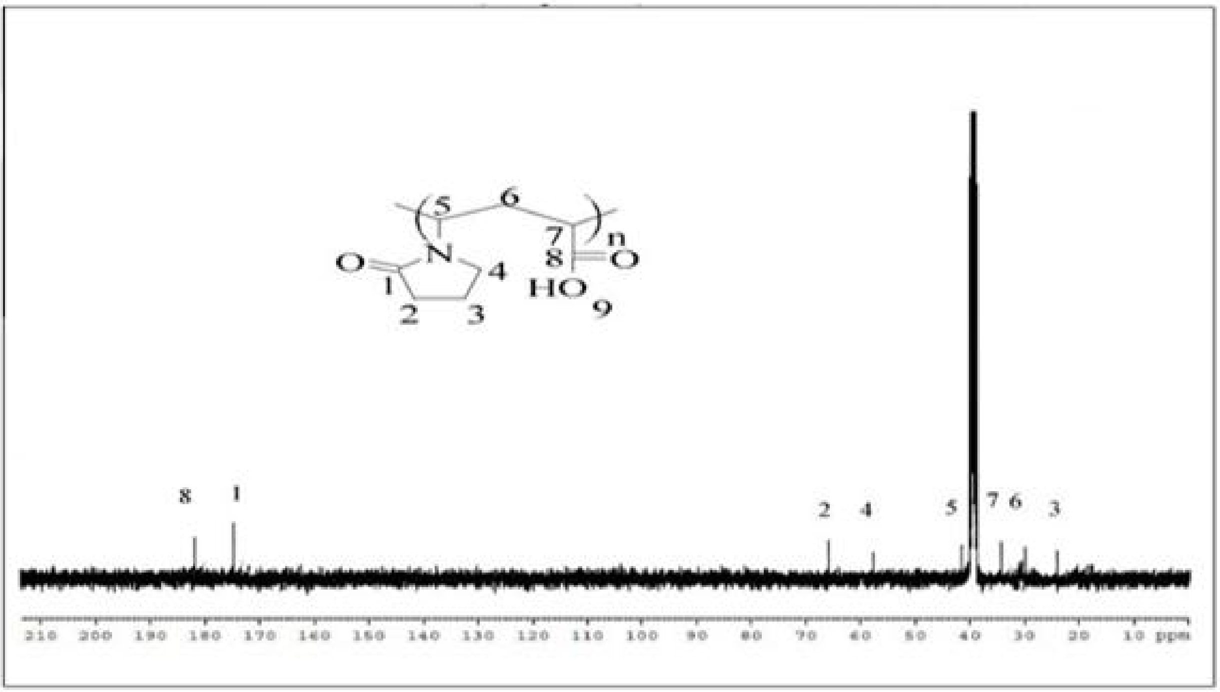


Figure 5. C^{13} NMR of Copolymer

The carbonyl carbon (- C=0) signals of both NVP and AA appear between δ 177 to 181 ppm. The carbon atoms present in the parent chain appear at δ = 42, 30 and 35 ppm region. The side chain ring methylene carbon signals are assigned at δ = 68, δ =25 and δ = 58 ppm respectively.

3.2. Copolymer Composition and Monomer Reactivity Ratio

Reactivity ratios of NVP and AA were determined by F- R and K-T methods using the data obtained by Acid Value method. The values are given in Table - 2. The equations used for F-R and K-T are

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

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

Where r_1 and r_2 are the reactivity ratios relating to the monomer NVP and AA respectively. G and F are F-R parameters, ŋ ξ and α are K-T parameters. The plot of G vs. F as shown in Fig-6 gave a straight line with r_1 as slope and- r_2 as the intercept. ŋ, ξ and α are mathematical functions of G and F as indicated and presented in Table-2 for the K-T method. The K-T plot of ξ vs. ŋ is shown in Fig-7 using Acid value data.

Table 2. F-R and K- T parameter for NVP /AA copolymer by Acid value method

Sample No	x=M1/M2	y=m1/m2	G=x(y-1)/y	F=x2/Y	ŋ =G/(α+F)	ξ =F/(α+F)
1	0.1111	0.9902	-0.0011	0.0125	-0.0049	0.0557
2	0.2500	2.2129	0.1370	0.0282	0.5717	0.1178
3	0.6667	3.2426	0.4611	0.1371	1.3229	0.3933
4	1.5000	6.2399	1.2596	0.3606	2.2020	0.6303
5	4.0000	11.8021	3.6611	1.3557	2.3361	0.8651
6	9.0000	22.5854	8.6015	3.5864	2.2648	0.9443

Table 3. Monomer reactivity ratios for NVP/AA Copolymer by F-R and K-T methods

Method	r_1	r_2	r_1r_2
F-R Method	2.381	0.179	0.425
K-T Method	2.533	0.180	0.455
Average	2.457	0.179	0.440

In the present case of the copolymer, the product $r_1r_2 < 1$ indicating that the type of copolymer is random.

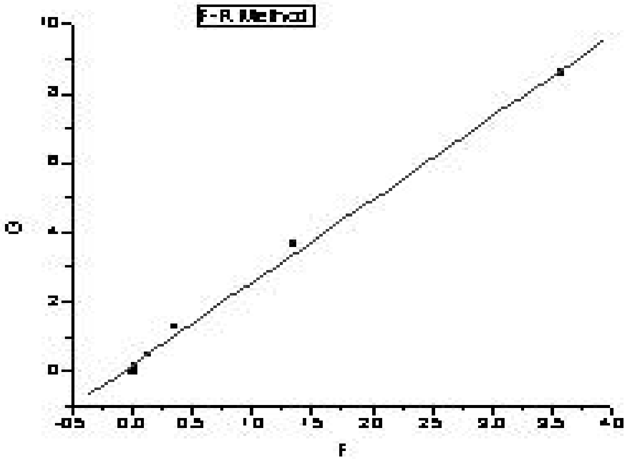


Figure 6. Plot for F-R Method

3.3. Copolymer Microstructure

3.3.1. Probability of Finding a Monomer

Simona et al. calculated the copolymer microstructure and sequence distribution of monomer in the formation of the copolymer. Here, we have attempted to calculate the sequence distribution of the resulting copolymer. The probability of finding the sequence of n NVP and n AA units is calculated as follows.

$$N_{NVP(n)} = P_{11}^{n-1}(1-p_{11}) \tag{3}$$

$$N_{AA(n)} = P_{22}^{n-1}(1-p_{11}) \tag{4}$$

Where P11 and P22 are the probability of an NVP (or AA) unit to be followed by a NVP (or AA) unit. These probabilities Table-(3) are calculated with the following equations and tabulated in Table - 4.

$$P_{11} = r_1R/r_1R+r_1 \tag{5}$$

$$P_{22} = r_2/R+r_2 \tag{6}$$

Where R is the mole ratio of NVP to AA in the feed.

In our case we observed that the NVP/AA copolymer contains predominantly a sequence of NVP. As the concentration in the feed increases the sequence length P_{11} is also increasing considerably, which is in agreement with higher reactivity of NVP.

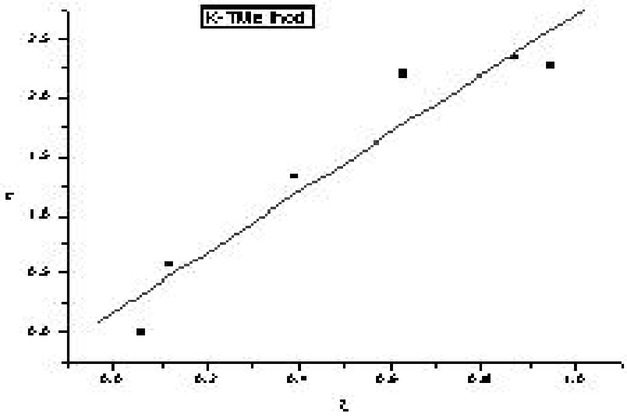


Figure 7. Plot for K- T Method

Table 4. Probability values of finding the monomer

Sample Name	Monomer feed		monomer in polymer		P_{11}	P_{22}
	NVP(M1)	AA(M2)	NVP(m1)	AA(m2)		
1	0.1	0.9	0.4975	0.5025	0.1000	0.6171
2	0.2	0.8	0.6888	0.3112	0.2000	0.4173
3	0.4	0.6	0.7643	0.2357	0.4000	0.2117
4	0.6	0.4	0.8619	0.1381	0.6000	0.1066
5	0.8	0.2	0.9219	0.0781	0.8000	0.0428
6	0.9	0.1	0.9576	0.0424	0.9000	0.0195

Table 5. Mean sequence lengths of monomers in copolymer

Sample Name	Monomer feed		monomer in polymer		µNVP	µAA
	NVP(M1)	AA(M2)	NVP(m1)	AA(m2)		
1	0.1	0.9	0.4975	0.5025	0.2720	2.6119
2	0.2	0.8	0.6888	0.3112	0.6130	1.7164
3	0.4	0.6	0.7643	0.2357	0.6330	1.2686
4	0.6	0.4	0.8619	0.1381	3.6750	1.1194
5	0.8	0.2	0.9219	0.0781	9.8000	1.0447
6	0.9	0.1	0.9576	0.0424	22.050	1.0199

Table 6. Structural Data for the copolymer

Sample name	**Monomer feed**		**Monomer in the copolymer**		**S_{1-1}**	**S_{2-2}**	**S_{1-2}**
	NVP(M_1)	**AA(M_2)**	**NVP(m_1)**	**AA(m_2)**			
1	0.1	0.9	0.4975	0.5025	0.1670	0.202	0.6011
2	0.2	0.8	0.6888	0.3112	0.4397	0.0621	0.4982
3	0.4	0.6	0.7643	0.2357	0.5611	0.0325	0.4065
4	0.6	0.4	0.8619	0.1381	0.7337	0.0099	0.2564
5	0.8	0.2	0.9219	0.0781	0.8468	0.003	0.1503
6	0.9	0.1	0.9576	0.0424	0.9161	0.0009	0.0831

3.3.2. Mean Sequence Length

The mean sequence lengths μNVP and μAA are calculated using the following equation.

$$\mu NVP = 1+ r_1(M_1/M_2) \qquad (7)$$

$$\mu AA = 1+ r_2(M_2/M_1) \qquad (8)$$

The value of μNVP and μAA are presented in Table - 5.

The μNVP values increase from 0.2720 to 22.050 in the copolymer NVP/AA with an increase of NVP concentration in the feed. Higher NVP content found in the synthesized copolymer correlated with the calculated r_1 and r_2 values indicates that the NVP/AA composition is enriched with the NVP monomer.

3.3.3. Statistical Distribution of Monomer

Statistical distribution of the monomer sequence 1-1, 2-2 and 1-2 are calculated using the following relations

$$S_{1-1} = m_1 - 2m_1m_2/\ 1+ [(2m_1-1)^2 + 4r_1r_2m_1m_2]^{1/2} \qquad (9)$$

$$S_{2-2} = m_2 - 2m_1m_2/\ 1+ [(2m_1-1)^2 + 4r_1r_2m_1m_2]^{1/2} \qquad (10)$$

$$S_{1-2} = 4m_1m_2/\ 1+ [(2m_1-1)^2 + 4r_1r_2m_1m_2]^{1/2} \qquad (11)$$

Where r_1 and r_2 are the reactivity ratios, m_1 (NVP) and m_2 (AA) are mole fractions in the copolymer. The mole fractions of 1-1, 2-2 and 1-2 sequences are shown by $S_{1-1,}$ S_{2-2} and S_{1-2} respectively. Structural data are given in Table 6.

The mole fraction of 1-1 sequence increases as the mole fraction of NVP increases, indicating a higher and higher incorporation of NVP in the copolymer. The sequence length of AA linking to AA S_{2-2} is very less, indicates that there is possibility of AA forming homopolymer but it is very less. The values of S_{1-2} indicate that there is incorporation of AA in the copolymer but the extent is less.

4. Conclusions

Copolymer of N-Vinyl Pyrrolidone and Acrylic acid is synthesized by free radical solution polymerization technique. The formed copolymer is soluble in most of the polar solvents and insoluble in non polar solvents. The copolymer is characterized by FTIR, H^1-NMR and C^{13} NMR. The reactivity ratio of NVP (r_1) is greater than that of AA (r_2) and the product r_1r_2 is less than one. This shows that the monomers are distributed in the copolymer chain in random fashion. The statistical data calculated - Probability of finding the monomer and Mean frequency length indicate that the copolymer is rich in NVP. This is confirmed by determining the sequence distribution of monomers by statistical method.

ACKNOWLEDGMENTS

I thank faculty of SSIT for their support in conducting the experiments.

REFERENCES

[1] H.F Mark, N.M. Bikales. C.G.Overberger and G.Menges, 1986, Encyclopedia of Polymer Science and Engineering, Wiley Interscience, New York.

[2] Miller, A.; Szafko, J.; Turska, E. 1977, Reactivity ratios for acrylonitrile–vinyl chloroacetate copolymerization systems, Journal of Polymer Science, 15(1), 51–63.

[3] Bajaj, P.; Sen, K.; Hajir, Bahrama, 1996, S. Solution polymerization of acrylonitrile with vinyl acids in dimethylformamide, Journal of Applied Polymer Science, 59(10), 1539–1550.

[4] Soykan, C., Coskun M., and Ahmedzade, M. 2000, Synthesis and characterization of phenacyl methacrylate – acrylonitrile copolymers and determination of monomer reactivity ratios, Polymer International, 49(6), 479–484.

[5] Vogl.O.; Albertsso, A.C.; Janovic,.Z. 1985, New Developments in Speciality Polymers, Polymeric Stabilizers, Polymer. 26(9), 1288-1296.

[6] Radic, D.; Gargallo, L. 1997, Synthesis, Reactivity Ratios, and Solution Behavior of Vinylpyrrolidone-co-Monoalkyl Itaconate and Vinylpyrrolidone-co-Dialkyl Itaconate Copolymers, Macromolecules, 30 (4), 817–825.

[7] Queroz, D.; Vargas, R.R.; Higa, O. Z.; Ribeiro R.R.; Vitolo, M. 2002,Lactam–amide graft copolymers as novel support for enzyme immobilization, Journal of Applied Polymer Science, 84(4), 767–777.

[8] Bajpai, S.K.; Sonkusley, J.2002, Hydrogels for oral drug delivery of peptides: Synthesis and characterization , Journal of Applied Polymer Science, 83(8), 1717–1729

[9] Beitz, T.; Kotz, J.; Wolf, G.; Lleinpeter, E.; Fribery, S.E.2001,

Poly(N-vinyl-2-pyrrolidone) and 1-Octyl-2-pyrrolidinone Modified Ionic micro emulsions, Journal of Colloid and Interface Science, 240(2), 581–589.

[10] Basri, M.; Harun, A.; Ahmad, M.B.; Razak, C.A.N; .Salleh, A.B. 2001, Immobilization of lipase on poly (N-vinyl-2-pyrrolidone-co-styrene) hydrogel, Journal of Applied Polymer Science, 82(6), 1404–1409.

[11] Vijaysekaran, S.; Chirila, T.V.; Hong, Y.; Tahija, S.G.; Dalton, P.D.; Constable, I.J.; McAllister. 1996, Poly(I-vinyl-2-pyrrolidinone) hydrogels as vitreous substitutes: Histopathological evaluation in the animal eye, Journal of Biomaterials Science,7(8), 685-696.

[12] Ranucci, H.; Spagnoli, G.; Sartore, L.; Bignottie F.; Ferruti, P. Synthesis and molecular weight characterization of end-functionalized N-vinyl-2-pyrrolidone oligomers, Macromolecular Chemistry and Physics, 196(3), 763–774.

[13] Lee, H. Y.; Yu, S.A.; Jeong K.H.; Kim, Y. 2007, Poly(vinyl pyrrolidone) conjugated lipid system for the hydrophobic drug delivery, Macromolecular Research, 15(6), 547-552.

[14] Otagiri, M.; Imai, T.; Koinuma, H.; Matsumoro, U. 1989, Spectroscopic study of the interaction of coumarin anticoagulant drugs with polyvinylpyrrolidone, Journal of Pharmaceutical and Biomedical Analysis, 7(8), 929–935.

[15] Mumper, R.J.; .Dugauid, J.G.; Anwer, K.; Barron, M.K.; Nitta, H.; Rolland, A.P. 1996, Polyvinyl Derivatives as Novel Interactive Polymers for Controlled Gene Delivery to Muscle, Pharmaceutical Research, 13(5), 701-709.

[16] Reddy, B.S.S.; Arshady R.; George, M. 1985, Copolymerization of N-vinyl-2-pyrrolidone with 2,4,5-trichlorophenyl acrylate and with 2-hydroxyethyl methacrylate: Reactivity ratios and molecular weights, European Polymer Journal, 21(6), 511–515.

[17] Morariu, S.; Hulubei, C. 2006, Radical Copolymerization of Functional N-Substituted Maleimides with N-Vinyl-2-Pyrrolidone, High Performance Polymers, 18, 185-198.

[18] Bauduin, G, ; Boutevin, B.; Belbachir, M.; Meghabar, R. 1995, Determination of Reactivity Ratios in Radical Copolymerization: A Comparison of Methods for a Methacrylate/N-Vinylpyrrolidone System, Macromolecules, 28(6), 1750-1753.

[19] Soundarajan, S.; Reddy, B.S.R. 1991, Glycidyl methacrylate and N-vinyl-2-pyrrolidone copolymers: Synthesis, characterization, and reactivity ratios, Journal of Applied Polymer Science, 43(2), 251-258.

[20] Vijay Kumar, S.; Musturappa, T.E.; Prasannakumar, S.;Mahadevan, K.M.; Sheregara, B.S. 2007, N - Vinylpyrrolidone and Ethoxyethyl Methacrylate Copolymer: Synthesis, Characterization and Reactivity Ratios, Journal of Macromolecular Science, Part A, 44(11), 1161-1169.

[21] Brar, A.S.;.Rajeev Kumar. 2002, Investigation of microstructure of the N-vinyl-2-pyrrolidone/methyl methacrylate copolymers by NMR spectroscopy, Journal of Applied Polymer Science, 85(6), 1328-1336.

[22] Dilek Solpan; Zeynep Kolge; Murat Torun. 2005, Preparation and Characterization of Poly(N - Vinylpyrrolidone - co - Methacrylic Acid) Hydrogels, Journal of Macromolecular Science, Part A, 42(6), 705-721.

[23] Mitesh.B.Patel; Dharmesh.A.Patel; Arabinda Ray and Rajni.M.Patel, 2003, Microbial screening of copolymers of 2,4-dichlorophenyl methacrylate with N-vinylpyrrolidone: synthesis and characterization, Polymer International, 52(3), 367-372.

[24] Nicolas Gatica; Fernando R. Diaz; Ligia Gargallo; Deodato Radic. 1998, Vinyltrimethylsilane-co-N-vinyl-2-pyrrolidone and vinyltrimethoxysilane-co-N-vinyl-2-pyrrolidone copolymers Synthesis and reactivity ratios, Polymer Bulletin, 40(6), 707-713.

[25] Kelen, T.; Tudos, F. 1975, Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method, Journal of Macromolecular Science: Part A - Chemistry, 9(1), 1-27.

[26] Kelen, T.; Tudos, F.; Foldes ,B. T.; Turcsanyi, B. 1976, Analysis of Linear Methods for Determining Copolymerization Reactivity Ratios. III. Linear Graphic Method for Evaluating Data Obtained at High Conversion Levels, Journal of Macromolecular Science: Part A - Chemistry , 10(8), 1513-1540.