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N-vinylpyrrolidone and 4-vinyl Benzylchloride Copolymers: Synthesis, Characterization and Reactivity Ratios

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The copolymers prepared in this study by free radical copolymerization of *N*-vinylpyrrolidone (M_2) with 4-vinylbenzylchloride (M_1) using 2,2′-azobisisobutyronotrile (AIBN) initiator in 1,4-dioxane solvent at 70°C were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. Polymer solubility was tested in both polar and nonpolar solvents. The thermal properties were studied by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). Copolymer compositions were established by H^1-NMR spectra, while reactivity ratios of the monomers were computed using the linearization methods viz., Fineman-Ross (FR) ($r_1 = 1.67$ and $r_2 = 0.67$), Kelen-Tudos (KT) ($r_1 = 1.77$ and $r_2 = 0.65$) and extended Kelen-Tudos (EK-T) ($r_1 = 1.72$ and $r_2 = 0.63$) methods at lower conversion. Furthermore, reactivity ratios in nonlinear error-in-variables method (RREVM) also compute the reactivity ratios ($r_1 = 1.76$ and $r_2 = 0.66$); these are found to be in good agreement with each other. The distribution of monomer sequence along the copolymer chain was calculated using a statistical method based on the calculated reactivity ratios.

Keywords: N-vinylpyrrolidone, 4-viny lbenzylchloride, reactivity ratios, copolymer composition

1. Introduction

4-Vinyl benzylchloride (VBC) consists of a benzylchloride group with a double bond that facilitates various chemical and polymerization reactions. For instance, benzyl group can undergo chemical reactions such as alkylation, amination, eterification, hydrolysis, sulfonation, sulfonium salt formation, thiol ester, thiol, thioether formation, etc. (1–5). Polymers of VBC can also undergo similar types of reactions. An indirect method of aminating vinylbenzyl polymer was described before by Hatch (6). The aminated resins were also prepared by the reaction of the copolymer of VBC and divinyl benzene (7). Polymers of VBC and their derivatives have been used as coatings, decolorization, filtration, flame retardants, etc. (8). *N*-vinylpyrrolidone (NVP) is another interesting vinyl monomer used in the synthesis of functionalized copolymers with specific properties (9–12). From the literature, it is realized that reactivity depends upon the comonomer as well as on the chemical nature of the side group (9–12). Thus, it is possible to obtain highly functionalized copolymers that are useful in technological applications (13–15).

Previously, no reports were published on the reactivity ratios and the sequence distribution of VBC. In continuation of our ongoing research on the synthesis and characterization of NVP-based copolymers (16), we report here the synthesis of poly(*N*-vinylpyrrolidone-*co*-4-vinyl benzyl chloride) copolymer (VBC-NVP). The polymers were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. Thermal properties were assessed by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). The composition of copolymers was determined by measuring peak intensities of the $-$CH group of NVP and $-$CH$_2$ group of VBC that are distinguishable through ^{1}H-NMR spectra. Reactivity ratios of the monomers were estimated by linear techniques viz., Fineman-Ross (F-R) (17), Kelen-Tudos (K-T) (18) and extended Kelen-Tudos (EK-T) (19) methods. These results were compared with the non-linear method of calculating reactivity ratios in error-variable model (RREVM) (20).The distribution of monomer sequence along the copolymer chain was also determined by the use of a statistical method based on the reactivity ratio obtained by the EK-T method.

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2. Experimental

2.1. *Materials*

NVP, VBC, poly(NVP) with $\bar{M}_w = 58{,}000$ and 2,2′-azobisisobutyronitrile (AIBN) were obtained from Aldrich Chemicals, Milwaukee, WI. NVP and VBC monomers were distilled under reduced pressure, dried over anhydrous sodium sulfate and stored below 0°C. AIBN was recrystallized twice from methanol and stored in a vacuum oven for about 24 h. Other solvents of 99% purity were used as received.

2.2. *Synthesis of copolymers*

Copolymerization was carried out in 1,4-dioxane solvent at 70°C under inert nitrogen atmosphere. Known amounts of VBC (M_1), NVP (M_2), 0.5% AIBN and 1,4 dioxane were taken in a three-necked 100 mL round bottom flask placed in an oil bath maintained at 70°C. Copolymerization was continued up to low conversion (less than 15%) and polymerization was ceased by rapid cooling of the reaction mixture to ambient temperature (30°C). The obtained solid was precipitated in diethyl ether/hexane mixture and reprecipitated using 1,4-dioxane in diethyl ether/hexane mixture to ensure complete removal of residual monomers. The samples were dried in vacuum at 40°C until attainment of constant weight.

2.3. *Solubility studies*

Solubility of the polymers was tested in various polar and non-polar organic solvents. To a 5 mL solvent in a standard test tube, about 5–10 mg of polymer was added and kept overnight. The solubility of the polymers was observed after 24 h.

2.4. *Copolymer characterization*

Copolymers were characterized by ^{1}H-NMR and ^{13}C-NMR techniques in deuterated chloroform/ dimethylsulfoxide using Bruker AV-300 Spectrometer (USIC, Karnatak University, Dharwad). FTIR spectra were recorded in KBr pellets using Shimadzu-1800S Spectrometer in the range of 400–4000 cm^{-1}. Thermal behavior of the copolymer was assessed by DSC-Mettler Calorimetric system (Sophisticated Test and Instrumentation Center, Cochin, India) under a stream of inert nitrogen gas at the heating rate of 10°C/min. The corresponding glass transition temperature (Tg) was 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 in a stream of inert nitrogen at the heating rate of 10°C/min.

3. Results and discussion

3.1. *Synthesis of polymers*

Five (VBC-NVP) copolymers with different compositions were prepared as per experimental details given in Table 1, using a AIBN initiator in 1,4-dioxane solvent under inert nitrogen atmosphere. The copolymers were found to soluble in acetone, 1,4-dioxane, tetrahydrofuran, dimethylsulfoxide, dimethyl formamide, dimethyl acetamide, ethyl acetate, isobutyl acetate, and chloroform but are insoluble in nonpolar solvents like n-hexane, cyclohexane, carbon tetrachloride, diethyl ether, benzene and hydroxyl-group containing solvents such as methanol and ethanol.

3.2. *Copolymer characterization*

FTIR spectrum of the copolymer (VBC-NVP-2) shown in Figure 1 as a strong aromatic-C–H stretching vibration of VBC observed at 3076 cm^{-1}; the peaks at 2954 and 2879 cm^{-1} are, respectivelyattributed to asymmetric and symmetric -C–H stretches, while the aromatic C=C stretching frequency gas occurred at 1561 cm^{-1}due to the VBC unit. The peak at 1682 cm^{-1} is due to C=O group of NVP unit and the one observed at 1386 cm^{-1} is due to C-N-C of the imide group corresponding to NVP unit.

The ^{1}H-NMR spectrum of the copolymer (VBC-NVP-1) shown in Figure 2, has the main chain methylene proton

Table 1. Reaction conditions of (VBC-NVP) copolymer

Sample code	*Feed mole fraction of VBC M_1*	*Wt% conversion*	*Integral value* I_{VBC}	I_{NVP}	*C*	*Copolymer composition of VBC m_1*
VBC-NVP-1	0.20	13.2	3.59	5.20	0.6903	0.2565
VBC-NVP-2	0.40	12.6	4.23	2.15	1.9674	0.4958
VBC-NVP-3	0.50	11.8	5.15	1.65	3.1212	0.6094
VBC-NVP-4	0.60	12.1	6.73	1.55	4.3419	0.6846
VBC-NVP-5	0.80	12.3	10.31	1.23	8.3821	0.8073

Solvent: 1,4-dioxane; temperature: 70°C, initiator AIBN: 0.5% based on the total weight of the monomers and solvent.

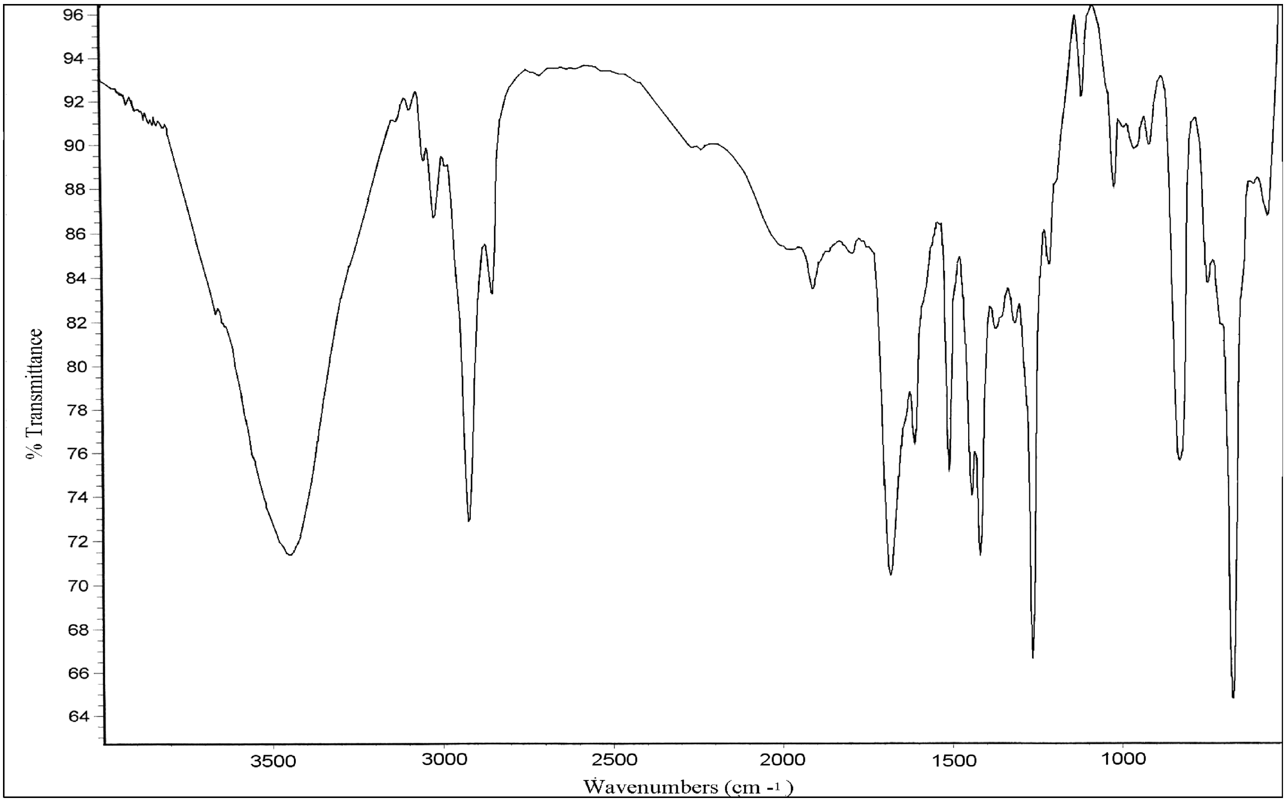

Fig. 1. FTIR spectra of (VBC-NVP-2) copolymer.

signals due to both NVP and VBC units that resonate at chemical shift (δ) of 2.42–1.61 ppm. The methine proton of NVP (—CH) appeared at $\delta = 3.54$ ppm. The ring methylene protons in NVP signals are assigned at $\delta = 2.4$ ($^3CH_2$), $\delta = 2.2$ ($^5CH_2$) and $\delta = 2.0$ ($^4CH_2$) ppm. Aromatic protons ($^8CH_2$ and $^9CH_2$) of VBC appear between δ of 7.40 and 6.41 ppm, while the methylene proton ($^{10}CH_2$) resonates at $\delta = 4.53$ ppm.

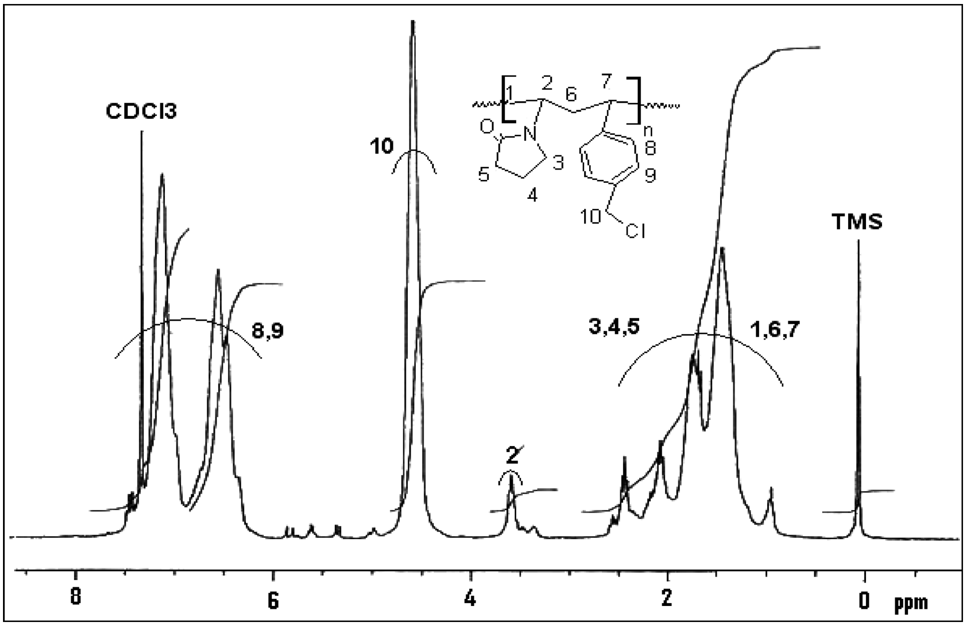

Fig. 2. ^{1}H- NMR spectra of (VBC-NVP-1) copolymer.

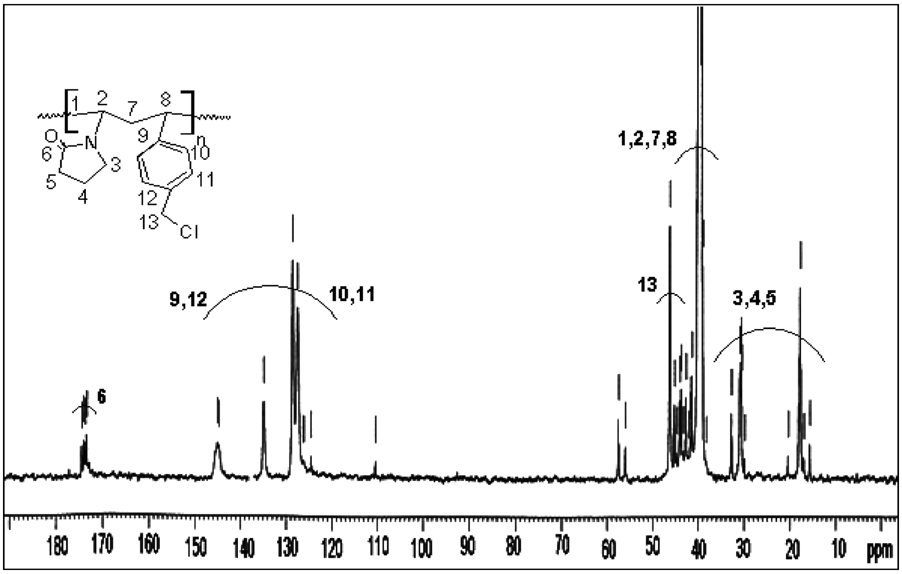

Fig. 3. ^{13}C- NMR Spectra of (VBC-NVP-2) copolymer.

The ^{13}C-NMR spectrum of the copolymer (VBC-NVP-2) is shown in Figure 3. Aromatic carbons of VBC (^{9}C,^{10}C,^{11}C,^{12}C) resonate between $\delta = 128.12$ and 146.23 ppm, while methylene carbon (Cl-^{13}CH$_2$) of VBC resonate at $\delta = 47.5$. The peaks in the range of $\delta = 17.5$–30.14 ppm are due to side chain methylene carbons (^{3}CH$_2$,^{3}CH$_2$,^{5}CH$_2$) of NVP. The peak at $\delta = 172.15$ is due to carbonyl carbon (^{6}C=O) of the NVP unit. The presence of carbonyl group of NVP and aromatic peaks of VBC confirms the formation of the copolymer.

3.3. *Thermal properties*

The *Tg* of the copolymers was determined by DSC. The *Tg* of poly(NVP) is found to be 148°C and that of poly(VBC) is 82°C, whereas the *Tg* of (VBC-NVP-3) copolymer is observed at 92°C. These results indicate that by copolymerizing NVP with VBC, there is an increase in *Tg* values of poly(VBC). Thermal stability of the homopolymers and copolymer of VBC and NVP was studied by TGA in the temperature range from 0°C to 800°C under inert nitrogen atmosphere. The TGA curves of poly(VBC), poly(NVP)

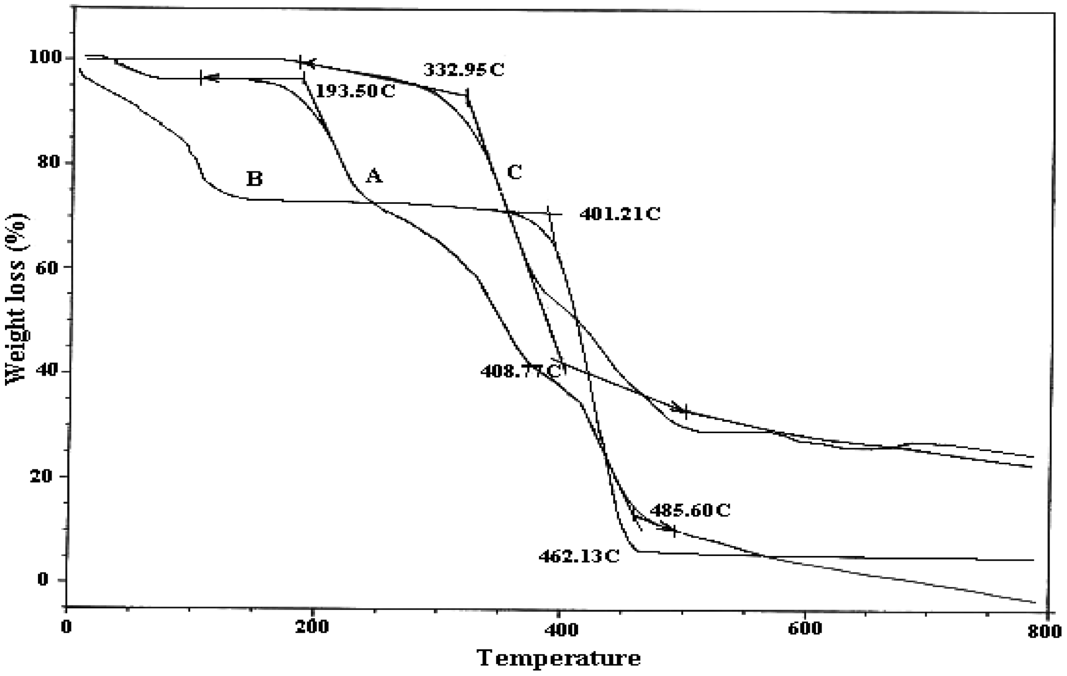

Fig. 4. TGA Thermograms of (A) Poly(VBC); (B) Poly(NVP); (C) (VBC-NVP-3) copolymer.

Table 2. Thermal data obtained for copolymer by TGA

		Temperature weight loss (°C)			
Polymers	*IDT*[a]	*30%*	*50%*	*70%*	*90%*
Poly(VBC)	193.50	268.32	352.25	428.14	480.26
Poly(NVP)	401.21	385.85	422.31	435.85	462.25
(VBC-NVP-3) Copolymer	332.95	368.74	425.82	495.56	—-

[a] IDT Initial decomposition temperature.

and of (VBC-NVP-3) shown in Figure 4 indicates that homopoymers and the copolymer has undergone a single step degradation. However, the initial decomposition of poly(VBC), poly(NVP) and (VBC-NVP-3) copolymers are 193.50°, 401.21° and 332.95°C, respectively. TGA results given in Table 2 indicate that the thermal stability of the poly(VBC) has increased by the incorporation of NVP in the copolymer.

3.4. *Copolymer composition*

^{1}H-NMR is a well established method to determine the copolymer composition. By measuring the intensities of the chemical shifts produced by the protons of monomeric units, mole fraction of the monomer (m_1) and comonomer (m_2) present in the copolymer can be determined (21, 22). Using the chemical shift values of ^{1}H-NMR, it is evident that the copolymer chain contains both the monomeric units indicating that –CH$_2$Cl (2H) proton of VBC unit of the copolymer and methine (1H) proton of the NVP units are well separated from each other. Their integral values were taken for the determination of mole fraction of monomer units present in the copolymer chain. Assuming m$_1$ as the mole fraction of VBC present in the copolymer and $m_2 = (1-m_1)$ that of the NVP unit, one can derive the equation using the integral values of one methine proton representing NVP monomer and two methylene protons (–CH$_2$Cl), representing VBC unit as:

$$C = \frac{\text{Integral value of CH}_2\text{ proton in VBC unit}}{\text{Integral value of methine proton}} \quad (1)$$

$$C = \frac{2m_1}{(1-m_1)} : m_1 = \frac{C}{2+C} \quad (2)$$

Table 1 shows the values of C and mole fractions of monomers in the feed and the copolymers. Kinetics aspects of the copolymerization were determined by plotting mole fractions of VBC in the feed (M_1) vs. that in the copolymer (m_1) (Fig. 5). The copolymer composition curve indicates that the composition, with respect to VBC, in the copolymer is always higher than the feed.

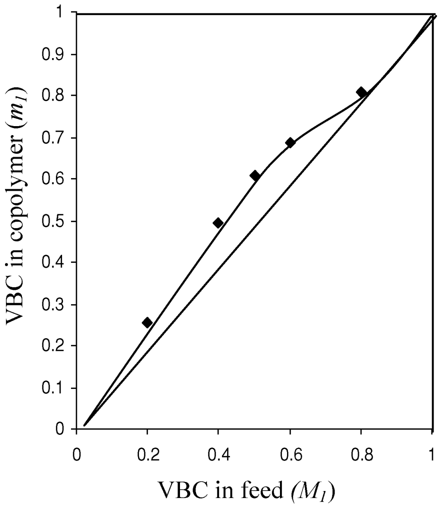

Fig. 5. ^{1}H-NMR data plot of mole fraction of VBC in feed (M_1) against VBC in copolymer (m_1).

3.5. *Monomer reactivity ratios*

The type of copolymer formed can be best understood from the values of reactivity ratios of the monomers. Copolymerization reactivity ratios of VBC and NVP were determined by F-R, K-T and EK-T methods using ^{1}H-NMR data. The obtained reactivity ratios from the linear methods were further confirmed by comparing with the nonlinear method using the RREVM. Table 3 shows the comparision of reactivity ratios of the monomers. It is seen that the r_1 is greater than r_2. Higher r_1 value of VBC further confirms the higher reactivity of VBC towards the growing chain regardless of whether the radical end was derived from VBC or NVP units. However, the copolymer sequence is random in nature due to the presence of more VBC units in the backbone.

Table 3. Monomer reactivity ratios for (VBC-NVP) copolymers

Method	r_1 *(VBC)*	r_2 *(NVP)*
F-R	1.67	0.67
K-T	1.77	0.65
EK-T	1.72	0.63
RREVM	1.76	0.66

Table 4. Structural data for the copolymers of VBC(1) with NVP(2)

	Composition[a] *(mole fraction)*		*Blockiness*[b] *(mole fraction)*		*Alternation*[b] *(mole fraction)*
Sample code	m_1	m_2	S_{1-1}	S_{2-2}	S_{1-2}
VBC-NVP-1	0.2565	0.7435	0.0720	0.5590	0.3690
VBC-NVP-2	0.4958	0.5042	0.2512	0.2596	0.4892
VBC-NVP-3	0.6094	0.3906	0.4967	0.2780	0.2252
VBC-NVP-4	0.6846	0.3154	0.4726	0.1035	0.4239
VBC-NVP-5	0.8073	0.1927	0.7226	0.1081	0.1693

[a] From NMR data.
[b] Statistically calculated using the reactivity ratios.

3.6. *Copolymer microstructure*

Statistical distribution of the dyad monomer sequence 1–1, 2–2 and 1–2 are calculated using the following relations (23):

$$S_{1-1} = m_1 - \frac{2m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \quad (3)$$

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

$$S_{1-2} = \frac{4m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \quad (5)$$

where r_1 and r_2 are the reactivity ratios obtained by the EK-T method for VBC and NVP, respectively; m_1 and m_2 are the mole fractions of VBC and NVP in the copolymer obtained from ^{1}H-NMR data. The mole fraction of 1–1, 2–2 and 1–2 sequences are shown by S_{1-1}, S_{2-2} and $S_{1-1,}$ respectively. These structural data given in Table 4, suggest that, the mole fractions of 1–1 sequences showed increasing trends with increasing mole fraction of VBC and the sequences of 2-2 decreases with the decreases in the NVP content. In order to understand the relationship between (VCB-NVP) copolymer compositions, we have determined the sequence distribution of the copolymer. The sequence length distribution is a statistical representation of the probability of monomer 2 to be attached to monomer 2. The distribution of sequence length was determined using the $r_1$and r_2 values along with the following equations (24), assuming that only the ultimate monomeric unit affects the rate constants of copolymerization, following the first order effect (Markov chain)

$$N_{VBC(n)} = P_{11}^{n-1}(1-P_{11}) \quad (6)$$

$$N_{NVP(n)} = P_{22}^{n-1}(1-P_{22}) \quad (7)$$

Here, $N_{VBC}(n)$ and $N_{NVP}(n)$ represents the probability of finding sequences of nVBC and nNVP monomers, respectively. P_{11} is the probability of monomer 1 (VBC) to be attached to monomer 1 and, P_{22} is the probability of monomer 2 (NVP) to be attached to monomer 2. Transition probabilities were calculated using Equations 8 and 9.

$$P_{11} = r_1x/r_1\,x + r_1 \quad (8)$$

$$P_{22} = r_2/x + r_2 \quad (9)$$

where x is the mole ratio of VBC to NVP in the feed. These data are given in Table 5. From the plot of $N_{VBC(n)}$ and $N_{NVP(n)}$ shown in Figure 6, we have calculated the copolymer at composition equimolar feed. In the present case, we found that (VBC-NVP) copolymer contains predominantly the sequence of VBC, which is in agreement with the higher reactivity of VBC.

M_1 and M_2 are feed mole fraction of VBC and NVP, P_{11} the probability of VBC unit to be followed by a VBC unit, P_{22} the probability of a NVP unit to be followed by a NVP unit; $x$is mean sequence length.

Table 5. Transition probability data for (VBC-NVP) copolymers

Sample Code	M_1	M_2	P_{11}	P_{22}
VBC-VP-1	0.20	0.80	0.1612	0.5155
VBC-VP-2	0.40	0.60	0.2928	0.3306
VBC-VP-3	0.50	0.50	0.4347	0.2101
VBC-VP-4	0.60	0.40	0.5356	0.1506
VBC-VP-5	0.80	0.20	0.6976	0.0814

4. Conclusions

The (VBC-NVP) copolymers of this study having different compositions were synthesized by free radical solution polymerization. Characterization of copolymers performed by FTIR, ^{1}H-NMR and ^{13}C-NMR techniques confirms the chemical structure. This copolymers showed good solubility in majority of polar solvents, but are insoluble in nonpolar solvents. The composition of copolymers was established by ^{1}H-NMR. Reactivity ratios of the monomers obtained by FR, KT, EK-T and RREVM methods agreed well. Reactivity ratios indicated that VBC is more reactive than NVP and the copolymer was of random nature showing the slight tendency to form small blocks. The monomer sequence distribution calculated from the statistical method indicated the formation of copolymer with predominantly random distribution of monomers and higher content of VBC units in the copolymer. DSC and TGA data indicated that *Tg* and thermal degradability of the VBC homopolymer was increased after copolymerizing with NVP.

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