Reactivity ratio determination and complete spectral assignment of 4-vinyl pyridine-ethyl acrylate copolymer by NMR spectroscopy

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4-Vinylpyridine-ethyl acrylate (V/E) copolymers of different compositions have been prepared by free radical bulk polymerization. The copolymer composition has been calculated from $^1$H-NMR spectra. The comonomer reactivity ratios of V/E copolymer have been calculated from linear Kelen-Tudos (KT) and non-linear error-in-variables method (EVM). The reactivity ratios obtained from KT and EVM are $r_V = 0.34 \pm 0.07$, $r_E = 0.23 \pm 0.07$ and $r_V = 0.36 \pm 0.08$, $r_E = 0.25 \pm 0.04$ respectively. The theoretical triads concentration has been determined from statistical model using terminal model reactivity ratios. The complete spectral assignment of these copolymers has been done with the help of distortionless enhancement by polarization transfer (DEPT) and two dimensional heteronuclear single quantum coherence (HSQC) spectra. The various type of $^1$H-$^1$H couplings in copolymer have been assigned with the help of 2D-total correlated spectroscopy (TOCSY).

High resolution NMR spectroscopy has been particularly effective in the determination of the intramolecular chain structure of the polymers. The information about the microstructure of the polymer is essential for clarifying the polymerization mechanism. The 2D-NMR spectroscopy has become an important technique for the determination of microstructure of copolymers. DEPT is used extensively for the analysis of the overlapping carbon resonances in $^1$C-NMR spectra. 4-Vinylpyridine polymers are industrially very important due to the presence of weakly basic nitrogen atom in the ring, they can be used in electrical field, polymer reagents, polymer supports in reaction catalysis such as oxidation-reduction reactions and in polyelectrolyte. The microstructure of 4-vinylpyridine-methyl acrylate copolymer is reported by Natonsohn et al. and by us but to the best of my knowledge, the reactivity ratios and microstructure of 4-vinyl pyridine-ethyl acrylate (V/E) copolymer has not been reported so far. In this paper, we report the reactivity ratios and microstructure of V/E copolymer, prepared by free radical bulk polymerization. The copolymer composition was calculated from $^1$H-NMR spectroscopy. The reactivity ratios were calculated using linear Kelen-Tudos (KT) method and non-linear least square error-in-variables method using RREVM program. The theoretical triads sequence distribution in terms of V- and E-units were calculated from statistical model using reactivity ratios obtained from RREVM program. The overlapped and complex $^1$H- and $^{13}$C[$^1$H]-NMR spectra of these copolymers have been assigned completely with the help of DEPT-135, DEPT-90, HSQC and TOCSY (low mixing time) experiments. The various resonance signals were found to be insensitive to compositional and configurational sequences. 2D TOCSY spectra of V/E copolymers show splitting in aliphatic and aromatic region which indicate their sensitivity toward various compositional and configurational sequences.

Materials and Methods

4-Vinylpyridine (Merck) and ethyl acrylate (GSC) monomers were first treated with NaOH and distilled water and then purified by vacuum distillation. A series of 4-vinylpyridine-ethyl acrylate (V/E) copolymers of different compositions was prepared by free radical bulk polymerization using benzoyl peroxide as an initiator (0.5% w/w) of monomers concentration) at 60°C. The details about polymerization time and monomer concentrations are given in Table 1. The per cent conversion was kept below 10 by precipitating the copolymers in petroleum ether. It is well known that if the per cent conversion is less than 10%, the formation of homopolymer is negligible so there is no need for removal of homopolymer. The copolymers were further purified by chloroform/petroleum ether system. NMR experiments were performed in CDCl$_3$ on a Bruker DPX-300 spectrometer at a frequency of 300.13 and 75.7 MHz for $^1$H and $^{13}$C[$^1$H]-NMR spectra, respectively. The details of recording of various 1D-NMR spectra i.e. $^1$H, $^{13}$C[$^1$H]-NMR,
Results and Discussion

Determination of copolymer composition and reactivity ratios

The copolymer composition was calculated from the relative intensity of \(-\text{OCH}_2\) protons of E-unit and \textit{ortho} protons (2, 6) of heterocyclic ring of V-unit using the following equation:

\[
F_E = \frac{I(-\text{OCH}_2)_E/2}{I(-\text{OCH}_2)_E/2 + I(2,6\text{protons of V})/2}
\]

where \(I(-\text{OCH}_2)_E\) and \(I(2,6\text{protons of V})\) are the relative areas under the resonance signal of \(-\text{OCH}_2\) protons of E-unit and 2, 6 protons of V-unit respectively. \(F_E\) is the mole fraction of E-unit in copolymers. Table 1 shows the comonomer mole fractions in feed and in V/E copolymer. The copolymer composition data were used to calculate the terminal model reactivity ratios using linear Kelen-Tudos method. The reactivity ratios obtained from Kelen-Tudos method are \(r_V = 0.34 \pm 0.07\), \(r_E = 0.23 \pm 0.07\). The reactivity ratios obtained from KT method along with feed in composition served as the initial estimate for the determination of reactivity ratios by non-linear error-in-variables method (EVM). The reactivity ratios obtained from EVM are \(r_V = 0.36 \pm 0.08\) and \(r_E = 0.25 \pm 0.04\).

\(^1\text{H}-\text{NMR studies}\)

The \(^1\text{H}-\text{NMR}\) spectrum of 4-vinylpyridine-ethyl acrylate (V/E) copolymer (\(F_E = 0.44\) mole fraction in copolymer) in CDCl\(_3\) at 24°C.
HOODA: SPECTRAL STUDY OF 4-VINYLPYRIDINE-ETHYL ACRYLATE COPOLYMER

725

The spectral region around δ 0.30-2.00 ppm is quite complex and can be assigned to aliphatic protons (-CH, -CH₂ and -CH₃) present in the copolymer. The resonance signal around δ 0.30-0.90 ppm is assigned to ²CH₁ protons of E-unit while the broad signal around δ 0.90-2.00 ppm is assigned to -CH and -CH₂ protons of V- and E-unit. The resonance signal around δ 3.49 ppm is assigned to -OCH₂ protons of E-unit. The heterocyclic protons appeared as a set of two multiplet, one centered around δ 6.25 ppm and another centered around δ 8.07 ppm. The multiplet centered around δ 6.25 ppm is assigned to 3,5 protons of heterocyclic ring while another around δ 8.07 ppm is assigned to 2,6 protons of heterocyclic ring. The complicated ¹H-NMR spectrum can be simplified with the help of DEPT and 2D-HSQC spectra.

13C/¹H-NMR studies

The ¹³C/¹H-NMR spectrum of V/E copolymer (Fₑ = 0.44 mole fraction in copolymer) along with assignment of various resonance signals is shown in Fig. 2. Various resonance signals in ¹³C/¹H-NMR spectrum of V/E copolymer have been assigned completely by comparing the spectrum of copolymer with those of homopolymers i.e. poly (4-vinyl pyridine)⁰ and poly (ethyl acrylate). The spectral region around δ 34.30-44.50 ppm is very complex and contain overlapping signals. This can be assigned to aliphatic carbons in the backbone i.e. -CH and -CH₂ group of V- and E-unit. The extent of overlapping of various carbon signals cannot be ascertained from ¹³C/¹H-NMR spectrum alone. The overlapped carbon regions can be resolved using DEPT-135 spectrum (Fig. 3). In this experiment, the methylene carbon appeared as a negative phase while methane carbon appeared as a positive phase, which is based upon the pulse sequence given in DEPT experiment⁴. On comparison with ¹³C/¹H-NMR spectra of homopolymers, the broad signal from δ 33.60-39.50 ppm is assigned to -CH₂ group of E-unit while the signal around δ 42.00-44.90 ppm is assigned to -CH₃ group of V-unit. The resonance signal around δ 39.50-42.00 ppm is assigned to -CH group of both V- and E-unit. The -CH region in V/E copolymer is confirmed by DEPT-90 spectrum also. The multiplet around δ 39.45-42.15 ppm is assigned to -CH group of both V- and E-unit. In HSQC spectrum as shown in Fig. 4, the
cross peak centered around $\delta$ 34.50-45.00 / 0.75-1.85 ppm is assigned to -CH and -CH$_2$ group of V- and E-unit respectively.

The resonance signal around $\delta$ 60.10 ppm is assigned to -OCH$_2$ group of E-unit. In DEPT-135 spectrum (Fig. 3), the inverse peak around $\delta$ 60.50 ppm also confirms the -OCH$_2$ region of E-unit. The cross peak centered around $\delta$ 3.45/ 59.50 ppm is assigned to -OCH$_2$ group in HSQC spectrum (Fig. 4). The resonance signal around $\delta$ 13.80 ppm is assigned to $^2$CH$_3$ group of side chain. In HSQC spectrum also the cross peak around $\delta$ 0.70/13.75 ppm is assigned to $^2$CH$_3$ group of side chain of E-unit. The heterocyclic carbons appeared as a set of three signals. The signal around $\delta$ 151.83 ppm is assigned to quaternary carbon (C-4) of V-unit while the signal around $\delta$ 149.74 and $\delta$ 122.49 ppm are assigned to C-2, C-6 and C-3, C-5 carbons of heterocyclic ring of V-unit respectively. In HSQC spectrum of V/E copolymer as shown in Fig. 4, the cross peaks around $\delta$ 149.50/7.98 and $\delta$ 122.50/6.25 ppm are assigned to C-2, C-6 and C-3, C-5 carbons of heterocyclic ring of V-unit. The presence of these single cross peaks confirm their insensitivity toward compositional and configurational sequences. The carbonyl carbon of E-unit appeared around $\delta$ 174.18 ppm.

None of the resonance signals in $^{13}$C-1H-NMR spectrum of V/E copolymer appeared as a multiplet, indicating their insensitivity to various compositional and configurational sequences. So the experimental concentration of various triad and tetrad sequences cannot be obtained by curve fitting of the resonance signals of V- and E-unit in the copolymer. But the theoretical concentration of triads can be obtained using terminal model reactivity ratios i.e. $r_V = 0.36$ and $r_E = 0.25$ and feed in composition in Harwood's program$^{15}$. Figure 5 (a, b) shows the plot of the normalized V- and E-centered triads concentration versus the mole fraction of 4-vinyl pyridine and ethyl acrylate monomers in feed, respectively. The increase in the concentration of V-unit in the copolymer increases the fraction of VVV triad while it decreases the fraction of EVE triad. The fraction of VVE triad...
HOODA: SPECTRAL STUDY OF 4-VINYLPYRIDINE-ETHYL ACRYLATE COPOLYMER

Fig. 4—2D- HSQC spectrum of V/E copolymer ($F_E = 0.44$ mole fraction in copolymer) in CDCl₃.

Fig. (5a,b)—The variation of V- and E-centered triad fractions versus the feed in mole fraction of V- and E-monomers respectively.
first increases with increase in the concentration of V-unit, passes through the maximum value and then starts decreasing. The maximum fraction of VVE triad is observed at 0.73 mole fraction of V-unit. Similar type of variation is observed for E-centered triad and maximum fraction of EEV triad is observed at 0.80 mole fraction of E-unit.

2D TOCSY studies

In order to understand the connectivity and confirm the various coupling in the copolymer chain, the TOCSY spectrum was recorded. The three bond coupling between the protons of directly coupled groups in V/E copolymers can be clearly seen in TOCSY spectrum (Fig. 6). The cross peak at δ 1.50/1.70 ppm (1) is due to the coupling between the protons of methylene group of V- and E-unit of the main chain. The cross peak around δ 1.65/2.20 ppm (2) is due to the coupling between -CH2 (E) and -CH(V) unit while the cross peak around δ 1.85/2.05 ppm (3) is assigned to the coupling of -CH of V-unit with -CH of another V-unit. The various geminal coupling between the protons of -CH2 (V), -CH2 (E), 2CH3 (E) and -OCH2 (E) are also possible which could not be distinguished due to the low value of the coupling constants. The coupling between the protons of -OCH2 (E) with 3CH3 (E) is also possible. It appeared as a set of three cross peaks as shown in Fig. 6 (a). On the basis of variation in intensity of these cross peaks with copolymer composition, the cross peaks around δ 3.82 / 1.08 (4), δ 3.61 / 0.97 (5) and δ 3.55 / 0.89 (6) ppm are assigned to the coupling of -OCH2 (E) in EEE, EEV and VEV triads with 3CH3 (E) protons respectively. The coupling within the heterocyclic protons ( 3H-1H and 3H-3H ) of V-unit is also possible [Fig. 6 (b)]. It appeared as a multiplet around δ 8.10-8.45/6.22-6.72 ppm. This multiplet may be assigned to the coupling of heterocyclic protons in different compositional sequences. The

<table>
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<td>9</td>
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assignment of various coupling in this region is carried out on the basis of variation in intensity of these signals with copolymer composition. The cross peak centered around $\delta$ 8.12 / 6.28 (7) ppm is assigned to the coupling of heterocyclic protons in VVV triad. The cross peak centered around $\delta$ 8.26 / 6.48 (8) ppm and $\delta$ 8.38 / 6.55 (9) ppm are assigned to the coupling in VVE and EVE triads respectively. These all possible couplings are shown in Table 2. Further four and five bond couplings are also possible in V/E copolymer which can be clearly seen in 80 ms TOCSY spectra. Due to these higher bond couplings TOCSY spectra at 80 ms is quite complex and overlapped.

The reactivity ratios of V/E copolymer calculated from KT and RREVM method are $r_V = 0.34 \pm 0.07$, $r_E = 0.23 \pm 0.07$ and $r_V = 0.36 \pm 0.08$, $r_E = 0.25 \pm 0.04$ respectively. The overlapped and complex proton and carbon -13 NMR spectra are well resolved with the help of DEPT-135 and 2D-HSQC spectra. The various types of couplings between different groups in V/E copolymer are assigned by TOCSY experiment.

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References