Available online at www.sciencedirect.com
ScienceDirect
Polymer 47 (2006) 7827—7834
polymer
www.elsevier.com/locate/polymer

# $^{1}$H NMR and $^{13}$C NMR investigations of sequence distribution and tacticity in poly(vinyl alcohol-*co*-vinyl levulinate)

Yanmei Wang [a,*,1], Hirokuni Ono [a,*], Atsushi Ikeda [a], Naruhito Hori [a], Akio Takemura [a], Tatsuhiko Yamada [b], Toshihide Tsukatani [c]

[a] *Department of Biomaterials, Graduate School of Life and Agricultural Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan*
[b] *Forestry and Forest Products Research Institute, Box 16, Tsukuba, Ibaraki-ken 305-8687, Japan*
[c] *Nicca Chemical Co. Ltd., 4-23-1 Bunkyo, Fukui, Fukui-ken 918-0000, Japan*

Received 20 February 2006; received in revised form 12 August 2006; accepted 20 August 2006
Available online 18 September 2006

## Abstract

The microstructure of poly(vinyl alcohol-*co*-vinyl levulinate) (VOH—VLA copolymer) was studied by $^{1}$H NMR and $^{13}$C NMR techniques. The sequence distributions could be obtained from the six methine triads observed in the 500-MHz $^{1}$H NMR spectra of the copolymers: the three methylene dyads and the three carbonyl triads observed in 125.6-MHz $^{13}$C NMR spectra of the copolymers. The reaction activity order of different tacticity hydroxyl in PVA was found to be rr > mr > mm by investigating VOH-centered methine tacticity triads. The vinyl levulinate content (VLC), the number-average sequence length, dyad—triad relation and triad—triad relation ($R$) were calculated from methine triads, methylene dyads and carbonyl triads in $^{1}$H NMR and $^{13}$C NMR spectra successfully, and they were in good agreement with each other. The consistency of the dyad—triad and triad—triad relations shows that head to head or tail to tail fragments are hardly present in VOH—VLA copolymer.

*Keywords:* Poly(vinyl alcohol-*co*-vinyl levulinate); Sequence distribution; Tacticity

## 1. Introduction

It has been well established that, in general, the sequence distribution of co-monomers has a large influence on the chemical and physical properties of copolymers and may exert an important influence on the practical uses of the polymer. The importance of the sequence distributions of vinyl alcohol and vinyl acetate units in vinyl alcohol—vinyl acetate (VOH—VA) copolymers with respect to the surface activity has been recognized for a long time [1]. Classical methods such as calorimetry [2,3], infra-red spectroscopy [4], and iodine color absorption [5] have been used to give some qualitative indication of the sequence distribution of the VOH—VA copolymers. However, $^{1}$H NMR and $^{13}$C NMR spectroscopies can provide quantitative information on the monomer distribution and nature of linkages in copolymers. Previously, several papers have demonstrated the usefulness of high-resolution $^{1}$H NMR and/or $^{13}$C NMR methods in determining composition, sequence distribution, and tacticity of ethylene—vinyl alcohol (E—VOH) copolymers [6—9], ethylene—vinyl acetate (E—VA) copolymers [10—12], VOH—VA copolymers [13—20], vinyl alcohol—vinyl propionate (VOH—VP) copolymer [21], vinyl alcohol—crotonic acid copolymer [22] and vinyl chloride—vinyl acetate (VC—VA) copolymers [23].

Concentrating on the microstructural analysis of VOH—VA copolymers, researchers have obtained compositional sequence distribution from $^{1}$H NMR data of the compositional VOH-centered methine triads and VA-centered methine triads

---

* Corresponding authors. Tel.: +81 3 5841 5267; fax: +81 3 5684 0299.
*E-mail addresses:* aiwym2002@yahoo.co.jp (Y. Wang), ahono@mail.ecc.u-tokyo.ac.jp (H. Ono).

[1] Present address: Henkel Research Center of Advanced Technology Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan.

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.08.046

[14,15], $^{13}$C NMR data of the compositional methylene dyads [13,16–19], and $^{13}$C NMR data of the configurational carbonyl triads [14,15]. It was found that anomalous linkage such as head to head or tail to tail fragments was hardly present in VOH–VA copolymer by investigation of the triad–dyad and triad–triad relations [14].

Because no work has been done on the synthesis of VOH–VLA copolymer so far, it is certain that its microstructure has not been studied. As is well known, two-dimensional NMR method is widely used to investigate the sequence distribution and tacticity in vinyl polymers such as poly(vinyl chloride) [24,25], poly(vinyl alcohol) [26–29], poly(vinyl acetate) [30], poly(vinyl butyral) [31], poly(vinyl amine) [32], ethylene–vinyl alcohol copolymer [8] and ethylene–vinyl acetate copolymer [33]; however, the microstructure analysis of VOH–VA copolymer via $^{1}$H and $^{13}$C NMR methods has been investigated systematically by many researches, therefore, we can obtain the information on the sequence distribution and tacticity of VOH–VLA copolymer from $^{1}$H and $^{13}$C NMR spectra by comparison with that of VOH–VA copolymer because these two kinds of copolymer hold the similarity in structure; in essence, both of them belong to the partial substituted polyvinyl ester.

This paper is focused on firstly the investigation of the sequence distribution and tacticity via six methine compositional triads observed in the $^{1}$H NMR spectra of VOH–VLA copolymers: three methylene compositional dyads and three carbonyl configurational triads observed in $^{13}$C NMR spectra; secondly the reaction activity of hydroxyl in PVA via VOH-centered methine tacticity triad which has not been reported in the above mentioned copolymers so far to the best of our knowledge; thirdly the vinyl levulinate content (VLC), number-average sequence length, the dyad–triad and triad–triad relations obtained from the two NMR methods. By investigating the consistency of the dyad–triad and triad–triad relations, the information about the anomalous linkage of the copolymer will be acquired.

## 2. Experimental

### 2.1. Materials

VOH–VLA copolymers with various VLC, prepared from homogenous acylation of PVA (nominal average molecular weight: 89 000–98 000, nominal degree of hydrolysis: 99%) with levulinic acid (LA) in *N*,*N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) solvent system, using *N*,*N*-dicyclohexylcarbodiimide (DCC) as a condensation agent and 4-pyrrolidinopyridine (PP) as a catalyst at room temperature under nitrogen atmosphere according to our previous report [34] were used.

### 2.2. NMR measurements

The 500 MHz $^{1}$H NMR spectra were recorded on a JEOL JNM-A500 FT-NMR spectrometer (Japan Electric Co., Ltd.) at 70 °C. Sample concentration was approximately 5% (w/v) in perdeuterated dimethyl sulfoxide (DMSO-$d_6$, Isotec), tetramethylsilane (TMS) as the internal standard, 3-mm tubes were used at 500 MHz, the spectra width amounted to 10 000 Hz, the acquisition time was 1.6 s; a pulse delay of 2 s and a pulse width of 11 us were chosen, 16 transients were accumulated after four dummies.

The 125.6 MHz $^{13}$C NMR spectra were recorded on JEOL JNM-A500 FT-NMR spectrometer (Japanese Electric Co., Ltd.) at 20 °C, DMSO-$d_6$ and perdeuterated methanol (MeOH-$d_4$, Isotec) was used as solvent for the samples in the $^{13}$C NMR experiment for any purpose. The signals of solvents were chosen as internal locking peaks. The sample concentration was 10% (w/v); 5-mm tubes were employed. The free-induction decays of 15 000–20 000 times was obtained by using a pulse width of 7 us, an acquisition time of 0.54 s, and a pulse delay time of 2.0 s basically according to the report of Ovenall [35]. The digital resolution amounted to 1.85 Hz/point, corresponding to a spectra width of 30 303 Hz.

The sequence distributions were determined by comparing the relative intensities of the protons or carbons involved. In performing quantitative NMR measurements via compositional or configurational sequence distributions, one must take into account differences in nuclear Overhauser effects (NOE) and spin–lattice relaxation times ($T_1$). No NOE or $T_1$ value has been determined, but one additional $^{13}$C NMR experiment was performed on two VOH–VLA copolymers with VLC 0.24 and 0.58 with a much longer pulse delay (5 s) and gated decoupling technique to remove NOE. The results were identical with those obtained via $^{13}$C NMR with the standard methods. Therefore, we assumed that no differential spin–lattice relaxation times are present for different stereoisomeric (mm, mr, and rr) triad, compositional methine triad and methylene dyad sequences in the $^{1}$H NMR and $^{13}$C NMR. Within this limit relative peak areas are proportional to the number of proton and carbon atoms involved.

Therefore, the methine compositional triad sequence distributions of VOH–VLA copolymers were determined by comparing the relative intensities of the protons in $^{1}$H NMR spectra. The methylene compositional dyad sequence distributions of VOH–VLA copolymers were determined by comparing relative intensities of carbons involved in $^{13}$C NMR spectra. Carbonyl compositional triad sequence distributions were determined from the relative intensities of three carboxylic carbon signals by formulated equations.

In the following section, the two kinds of monads are denoted by (VOH) and (VLA), while the three kinds of methylene dyad sequences are given by (VOH,VOH), (VOH,VLA) and (VLA,VLA). A similar notation is used for the six kinds of methine triads, which are due to CH(VOH) and CH(VLA) triads, CH(VOH) triads include (VOH,VOH,VOH), (VOH, VOH,VLA) and (VLA,VOH,VLA); CH(VLA) triads include (VOH,VLA,VOH), (VLA,VLA,VOH) and (VLA,VLA,VLA). The three carbonyl triad sequences are (VOH,VLA,VOH), (VLA,VLA,VOH) and (VLA,VLA,VLA), which are same as those of CH(VLA) triad in essence.

## 3. Results and discussion

### 3.1. $^1$H NMR spectra of VOH–VLA copolymers

Fig. 1 shows the $^1$H NMR spectra of VOH–VLA copolymer with VLC of 0.24 recorded in DMSO-$d_6$ at 70 °C. Based on the assignments of VOH–VA [14] and VOH–VLA copolymers in our previous paper [34], we can straightforwardly assign all signals. The complete assignment of $^1$H NMR is given in Table 1 and will be discussed in detail.

#### 3.1.1. Methylene and methyl resonances

The methylene proton resonance of backbone centered at 1.44, 1.58 and 1.80 ppm are rather broad in Fig. 1, due to a combination of spin–spin coupling and configurational splitting but they can be easily assigned to three kinds of methylene dyads (VOH,VOH), (VOH,VLA), (VLA,VLA) on the basis of $^1$H NMR assignment of VOH–VA copolymer [13–20]. Quantitative information about the methylene dyads, however, is more easily obtained from an analysis of the $^{13}$C NMR methylene dyad data; this will be discussed later.

We have known from our previous report [34] that the signals at 2.43 and 2.69 ppm are due to the two methylene proton resonances of levulinate group. The signal at 2.10 ppm is due to the methyl proton resonance of levulinate group. Vinyl levulinate content (VLC) was calculated from the signal area intensity ratio between the protons due to levulinate groups and those due to the polymer backbone.

We have known that VLC is calculated by the following equation

$$\mathrm{VLC} = I_{\mathrm{CH_2(e)}}/I_{\mathrm{CH_2(a+a')}} \tag{1}$$

where $I_{\mathrm{CH_2(e)}}$ represents the peak integral value of the methylene proton resonance of levulinate at 2.69 ppm, $I_{\mathrm{CH_2(a+a')}}$ represents the peak integral value of methylene dyad proton resonance of backbone.

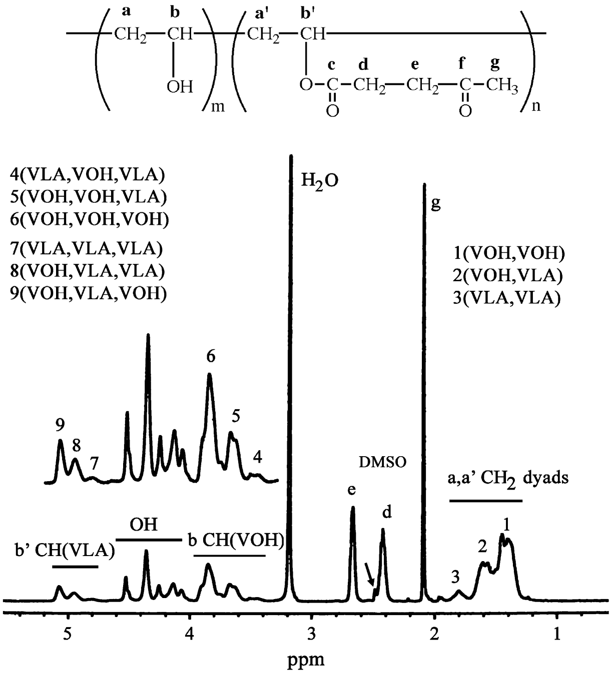

Fig. 1. $^1$H NMR spectra (500 MHz) of VOH–VLA copolymer (VLC = 0.24) recorded in DMSO-$d_6$ at 70 °C.

Table 1
$^1$H NMR spectra assignments of VOH–VLA copolymer (TMS as internal standard)

| Chemical shift, ppm | Protons | Dyads or triads |
|---|---|---|
| 1.42, 1.46 | Methylene | (VOH,VOH) |
| 1.57, 1.61 | Methylene | (VOH,VLA) |
| 1.80 | Methylene | (VLA,VLA) |
| 1.95 | Methyl (residual acetate) | |
| 2.10 | Methyl (g) | |
| 2.43 | Methylene (d) | |
| 2.49 | DMSO | |
| 2.69 | Methylene (e) | |
| 3.19 | $H_2O$ | |
| 3.47 | Methine | (VLA,VOH,VLA) |
| 3.65 | Methine | (VOH,VOH,VLA) |
| 3.76 | Methine | mm(VOH,VOH,VOH) |
| 3.85 | Methine | mr(VOH,VOH,VOH) |
| 3.90 | Methine | rr(VOH,VOH,VOH) |
| 4.81 | Methine | (VLA,VLA,VLA) |
| 4.96 | Methine | (VOH,VLA,VLA) |
| 5.08 | Methine | (VOH,VLA,VOH) |
| 4.07, 4.14, 4.26, 4.36, 4.52 | Hydroxyl | OH |

Table 2 summarizes VLC values calculated from Eq. (1), those from methine triads in $^1$H NMR and methylene dyads in $^{13}$C NMR are described later. VLC values obtained from elemental analysis are also given in Table 2 for comparison. They were in good agreement with each other.

#### 3.1.2. Methine resonances

*3.1.2.1. Methine compositional triads.* As shown in Fig. 1, the methine proton signals are observed as two fields separated by hydroxyl signals, which are assigned to the two kinds of methine protons adjacent to the levulinate groups and hydroxyls with increasing field strength based on the assignments of VOH–VA copolymer [13–15]. They are due to the methine triads (VOH,VLA,VOH), (VOH,VLA,VLA) and (VLA,VLA,VLA) of CH(VLA), and methine triads (VOH,VOH,VOH), (VOH,VOH,VLA) and (VLA,VOH,VLA) of CH(VOH) with increasing field strength.

Table 2
Comparison of VLC values obtained from Eq. (1), methine triads, methylene dyads and elemental analysis

| Sample no. | VLC | | | |
|---|---|---|---|---|
| | Formula (1) ($^1$H NMR) | CH triads ($^1$H NMR) | $CH_2$ dyads ($^{13}$C NMR) | Elemental analysis |
| 1 | 0.14 | 0.15 | 0.14 | 0.12 |
| 2 | 0.24 | 0.24 | 0.24 | 0.28 |
| 3 | 0.58 | 0.57 | 0.57 | 0.55 |
| 4 | 0.69 | 0.69 | 0.70 | 0.65 |
| 5 | 0.91 | 0.91 | 0.90 | 0.95 |

When the same notation is adopted for each integral value as described in Eq. (1), the molar fractions of the six methine compositional dyads may be expressed as follows:

$$\begin{aligned}&[\mathrm{OOO}]/[\mathrm{OOL}]/[\mathrm{LOL}]/[\mathrm{OLO}]/[\mathrm{OLL}]/[\mathrm{LLL}]\\ &\quad = I(\mathrm{VOH,VOH,VOH})/I(\mathrm{VOH,VOH,VLA})\\ &\qquad /I(\mathrm{VLA,VOH,VLA})/I(\mathrm{VOH,VLA,VOH})\\ &\qquad /I(\mathrm{VOH,VLA,VLA})/I(\mathrm{VLA,VLA,VLA}) \qquad (2)\end{aligned}$$

where the molar fractions of the six methine triads are expressed as the corresponding abbreviation in square bracket.

The six methine triad molar fractions of VOH–VLA copolymers with different VLC are listed in Table 3; the three carbonyl triad molar fractions, which will be discussed later in $^{13}$C NMR, are also given in Table 3 for comparison. The six methine triad molar fractions of VOH–VLA copolymers as a function of VLC are shown in Fig. 2. As shown in Table 3, the molar fractions of carbonyl triads are in good agreement with those of CH(VLA) triads.

Based on the methine triad analysis of VOH–VA copolymer [14], the VLC can be also calculated from methine triads using Eq. (3). In addition, the information about the number-average sequence length of vinyl levulinate unit (LLA) and number-average sequence length of vinyl alcohol unit (LOH) can be acquired from Eqs. (4) and (5), respectively.

$$\begin{aligned}\mathrm{VLC} &= \mathrm{ICH(VLA)}/\{\mathrm{ICH(VLA)}+\mathrm{ICH(VOH)}\}\\ \mathrm{ICH(VLA)} &= I(\mathrm{VOH,VLA,VOH})+I(\mathrm{VOH,VLA,VLA})\\ &\quad + I(\mathrm{VLA,VLA,VLA})\\ &= [\mathrm{OLO}]+[\mathrm{OLL}]+[\mathrm{LLL}]\\[6pt] \mathrm{ICH(VOH)} &= I(\mathrm{VOH,VOH,VO})+I(\mathrm{VOH,VOH,VLA})\\ &\quad + (\mathrm{VLA,VOH,VLA})\\ &= [\mathrm{OOO}]+[\mathrm{OOL}]+[\mathrm{LOL}] \qquad (3)\end{aligned}$$

$$\begin{aligned}\mathrm{LLA} &= \mathrm{ICH(VLA)}/I(\mathrm{VOH,VLA,VOH})\\ &\quad + 1/2I(\mathrm{VOH,VLA,VLA})\\ &= \{[\mathrm{OLO}]+[\mathrm{OLL}]+[\mathrm{LLL}]\}/\{[\mathrm{OLO}]+1/2[\mathrm{OLL}]\} \qquad (4)\end{aligned}$$

$$\begin{aligned}\mathrm{LOH} &= \mathrm{ICH(VOH)}/I(\mathrm{VLA,VOH,VLA})\\ &\quad + 1/2I(\mathrm{VOH,VOH,VLA})\\ &= \{[\mathrm{OOO}]+[\mathrm{OOL}]+[\mathrm{LOL}]\}/\{[\mathrm{LOL}]+1/2[\mathrm{OOL}]\} \qquad (5)\end{aligned}$$

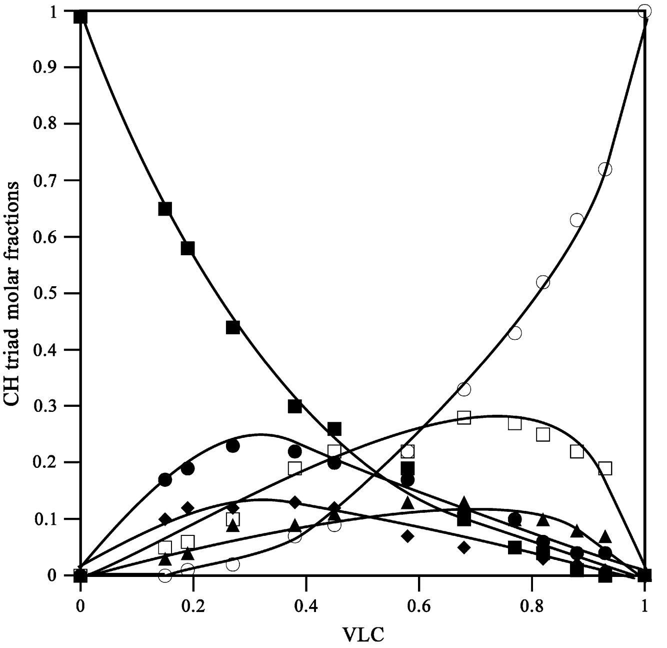

Fig. 2. CH triad molar fractions of VOH–VLA copolymers as a function of VLC (■) [OOO]; (●) [OOL]; (▲) [LOL]; (◆) [OLO]; (□) [OLL]; (○) [LLL].

VLC values calculated from methine triads (Eq. (3)) are in good agreement with those obtained from Eq. (1), elemental analysis and methylene dyad data of $^{13}$C NMR are described later (see Table 2).

The values of LLA, LOH acquired from methine triad and those from methylene dyad and carbonyl triad described later are summarized in Table 4. The values of sequence length LLA and LOH calculated from methine triads in $^{1}$H NMR are also in good agreement with those from methylene dyads and carbonyl triads in $^{13}$C NMR described later.

*3.1.2.2. The tacticity triads of (VOH,VOH,VOH) methine triad.* As shown in Fig. 1, in the CH(VOH) triads region, (VOH, VOH,VOH) methine triad centered at 3.85 ppm can be seen to be split in three subpeaks, which can be assigned to the three tacticity-induced rr, mr and mm (VOH,VOH,VOH) methine triads with increasing the field strength based on the analysis of ethylene–vinyl alcohol by $^{1}$H NMR [7], the detailed assignment is shown in Table 1.

Table 3
The methine triad and carbonyl triad molar fractions of VOH–VLA copolymers with different VLC

| Sample no. | VLC | CH(VOH) triads | | | CH(VLA) triads | | | C=O triads | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | [OOO] | [OOL] | [LOL] | [OLO] | [OLL] | [LLL] | [OLO] | [OLL] | [LLL] |
| 1 | 0.15 | 0.67 (0.79)[a] | 0.15 (0.18) | 0.03 (0.03) | 0.10 (0.67)[b] | 0.05 (0.33) | 0 (0) | 0.66 | 0.34 | 0 |
| 2 | 0.24 | 0.48 (0.63) | 0.23 (0.30) | 0.05 (0.07) | 0.12 (0.50) | 0.10 (0.42) | 0.02 (0.08) | 0.51 | 0.42 | 0.07 |
| 3 | 0.58 | 0.13 (0.30) | 0.19 (0.44) | 0.11 (0.26) | 0.08 (0.14) | 0.27 (0.47) | 0.22 (0.39) | 0.14 | 0.49 | 0.37 |
| 4 | 0.69 | 0.07 (0.23) | 0.08 (0.26) | 0.16 (0.51) | 0.05 (0.07) | 0.28 (0.41) | 0.36 (0.52) | 0.06 | 0.45 | 0.49 |
| 5 | 0.91 | 0 (0) | 0.022 (0.22) | 0.078 (0.78) | 0.01 (0.01) | 0.17 (0.19) | 0.73 (0.80) | 0 | 0.22 | 0.78 |

[a] The values in the bracket express the molar ratio of every methine triad based on that of the whole CH(VOH) triads.

[b] The values in the bracket express the molar ratio of every methine triad based on that of the whole CH(VLA) triads.

Table 4
The number-average sequence length of VOH–VLA copolymers with different VLC

| Sample no. | VLC | LLA | | | LOH | |
|---|---|---|---|---|---|---|
| | | CH(VLA) triads | $CH_2$ dyads | C=O triads | CH(VOH) triads | $CH_2$ dyads |
| 1 | 0.15 | 1.20 | 1.33 | 1.20 | 8.10 | 8.19 |
| 2 | 0.24 | 1.41 | 1.50 | 1.39 | 4.61 | 4.75 |
| 3 | 0.58 | 2.66 | 2.71 | 2.59 | 2.10 | 2.05 |
| 4 | 0.69 | 3.64 | 3.68 | 3.51 | 1.55 | 1.58 |
| 5 | 0.91 | 9.52 | 10.0 | 9.09 | 1.11 | 1.13 |

We can acquire the information about the reaction activity of different tacticity hydroxyl in PVA by investigating the tacticity triads of (VOH,VOH,VOH) methine triad. Fig. 3 shows the expanded $^1$H NMR spectra of VOH–VLA copolymer with three VLC at methine and hydroxyl regions recorded at 70 °C in DMSO-$d_6$. The intensities of rr and mr decrease compared to that of mm in (VOH,VOH,VOH) methine triad with increasing VLC (see Table 5); this indicates that the reaction activity order of different tacticity hydroxyl was rr > mr > mm when the esterification of PVA with LA occurred. The order is opposite to that of steric hindrance of the three kinds of tacticity triads. That is, the hydroxyls of (VOH,VOH,VOH) methine tacticity triads with smaller steric hindrance, rr and mr, are easier to be substituted by levulinate than that of mm with bigger steric hindrance at the esterification of PVA.

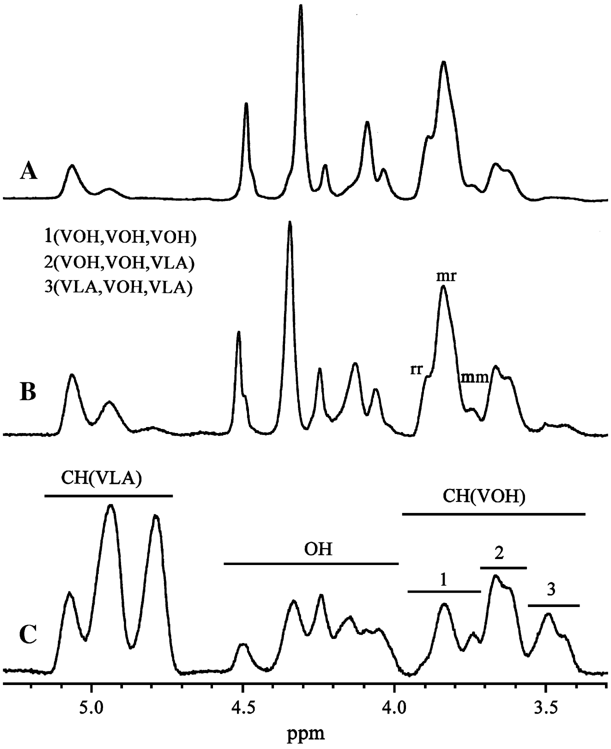

Fig. 3. Expanded 500-MHz $^1$H NMR spectra of VOH–VLA copolymer with different VLC recorded at 70 °C in DMSO-$d_6$, only the methine and hydroxyl resonances shown. (A) VLC = 0.15; (B) VLC = 0.24; (C) VLC = 0.58.

Table 5
The height ratio of signal in the tacticity triads of (VOH,VOH,VOH) methine triad

| Configurational triads | P(VOH–VLA15)[a] | P(VOH–VLA24) | P(VOH–VLA58) |
|---|---|---|---|
| rr | 0.284(0)[b] | 0.260(−0.024) | 0.167(−0.117) |
| mr | 0.621(0) | 0.615(−0.006) | 0.517(−0.104) |
| mm | 0.095(0) | 0.125(+0.03) | 0.316(+0.22) |

[a] P(VOH–VLA) expresses VOH–VLA copolymer, the values after VLA express VLC of the copolymer.

[b] The values in the bracket express the change of signal height ratio compared with that of VOH–VLA copolymer with VLC of 0.15.

## 3.2. $^{13}$C NMR of VOH–VLA copolymers

### 3.2.1. Methylene dyads of VOH–VLA copolymer

Fig. 4 shows the partial $^{13}$C NMR spectrum of VOH–VLA copolymer with VLC of 0.24 at methyl, methylene and methine regions recorded in MeOH-$d_4$. In order to avoid the interference of the signals at 39.5 ppm due to residual DMSO by those of methylene carbon at 39.1 ppm, MeOH-$d_4$ was used as a solvent for quantitative measurement. The signals at 27.8 ppm (d) and at 28.3 ppm (g) are attributable to methylene carbon having carboxyl group and methyl carbon in levulinate group, respectively. Two distinct multiplet signals and a multiplet signal overlapped with the sharp signal of methylene carbon having carbonyl group in levulinate (e) are observed in the methylene region of the copolymer backbone from 37.6 ppm to 46.4 ppm. These three signals can be assigned to the three compositional dyads of (VOH,VOH), (VOH,VLA) and

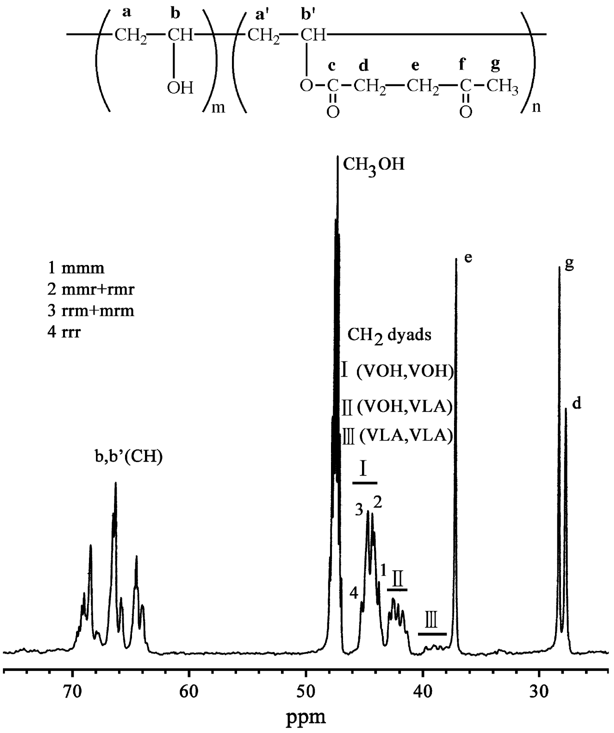

Fig. 4. $^{13}$C NMR (125.6-MHz) spectrum of VOH–VLA copolymer (VLC = 0.24) recorded in MeOH-$d_4$, only methine, methylene and methyl signals shown.

(VLA,VLA) with increasing field strength based on the microstructure analysis of the similar copolymers such as VOH−VA [13–20] and VOH−VP [21]. Each of these three methylene dyads shows additional configurational splittings. For the (VOH,VOH) dyad region, these splittings are assigned in terms of tetrads. They have been assigned as rrr, rrm + mrm, mmr + rmr, and mmm from low to high field according to the similar absorption peaks in PVA [36,37].

In our previous paper [34], the VLC and number-average sequence length (LLA and LOH) were determined from the three methylene triads by the following equations:

$$\mathrm{VLC} = [\mathrm{L}] = [\mathrm{LL}] + [\mathrm{OL}]/2 \tag{6}$$

$$[\mathrm{O}] = [\mathrm{OO}] + [\mathrm{OL}]/2 \tag{7}$$

$$\mathrm{LLA} = 2[\mathrm{L}]/[\mathrm{OL}] \tag{8}$$

$$\mathrm{LOH} = 2[\mathrm{O}]/[\mathrm{OL}] \tag{9}$$

where [L], [O] represent the molar fractions of monads (VLA) and (VOH), respectively. Similarly [OO], [OL] and [LL] express the molar fractions of methylene dyads (VOH,VOH), (VOH,VLA) and (VLA,VLA), respectively.

The VLC values calculated by Eq. (6) are in good agreement with those by Eq. (1), Eq. (3) from methine triads and elemental analysis (see Table 2). The values of LLA and LOH obtained from $^{13}$C NMR methylene dyads by Eqs. (8) and (9) are also in good agreement with those from $^{1}$H NMR methine triads by Eqs. (4) and (5) and from $^{13}$C NMR carbonyl triads which will be described later (see Table 4).

The methylene triad molar fraction of VOH−VLA copolymers as a function of VLC is shown in Fig. 5.

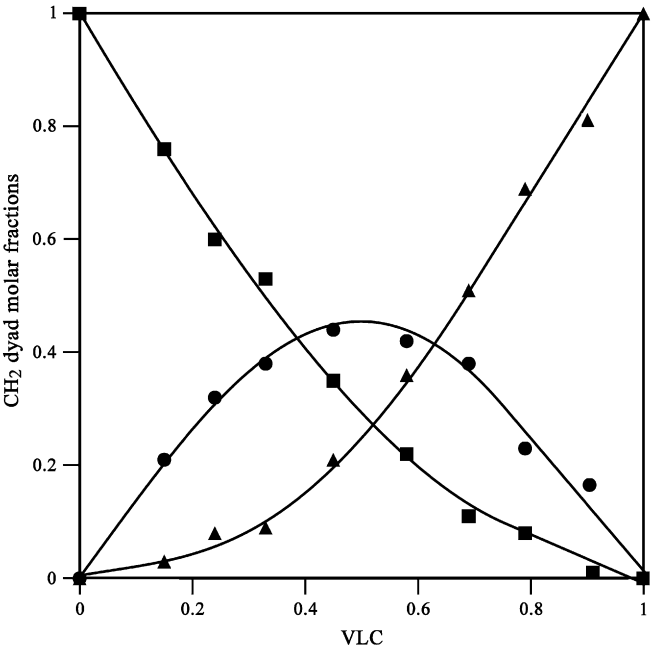

Fig. 5. Methylene triad molar fractions of VOH−VLA copolymers as a function of VLC (■) [OO]; (●) [OL]; (▲) [LL].

A block character ($\eta$) is expressed as:

$$\eta = [\mathrm{OL}]/2[\mathrm{O}][\mathrm{L}] \tag{10}$$

$\eta$ is a measure of departure from random character [38]. It takes $0 \leq \eta < 1$ for blockier distributions, $\eta = 1$ for completely random cases, and $1 < \eta \leq 2$ for alternate-like cases.

In our previous report [34], the methylene dyad analysis indicated that the block character of the copolymer was 0.92, it is very close to 1, therefore, VOH−VLA copolymers are categorized as random polymer, which means PVA is randomly substituted with levulinate when esterification takes place.

### 3.2.2. Carbonyl triads of VOH−VLA copolymer

Fig. 6 shows $^{13}$C NMR spectra of two VOH−VLA copolymers in DMSO-$d_6$, only carboxylic carbon and carbonyl carbon signals are shown. Since more than three carboxylic carbon splittings are observed in the $^{13}$C NMR spectra of VOH−VLA copolymer with higher VLC in MeOH-$d_4$, it is difficult to assign them. In addition, VOH−VLA copolymer with VLC less than 0.1 cannot dissolve in methanol, therefore, MeOH-$d_4$ was not used as the solvent for analyzing carbonyl triads of this copolymer.

As shown in Fig. 6, three carboxylic carbon signals centered at 172.0 ppm are observed. In order to prove whether the carboxylic carbon signals in the $^{13}$C NMR spectra contain compositional as well as configurational information, we synthesized a copolymer with VLC of 0.05. The $^{1}$H NMR spectrum of this low VLC copolymer displays only one peak at 5.08 ppm due to (VOH,VLA,VOH) methine triad and no upfield absorption at 4.96 ppm due to (VOH,VLA,VLA) and 4.81 ppm due to (VLA,VLA,VLA) in CH(VLA) triad fields (see Fig. 7), which leads to the conclusion that only isolated VLA units are present in the copolymer.

As shown in Fig. 6A, the $^{13}$C NMR spectrum of this low VLC copolymer also shows three carboxylic carbon signals with an intensity ratio of approximately 0.29, 0.48 and 0.23 from low to high field, in reasonable agreement with the data obtained from the three hydroxyl signal intensity ratio of $^{1}$H NMR spectrum of pure PVA from high to low field:

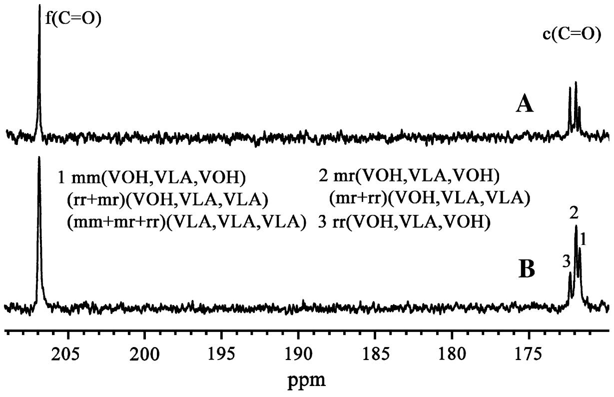

Fig. 6. Partial $^{13}$C NMR spectra of VOH−VLA copolymers in DMSO-$d_6$: VLC = 0.05 (A); VLC = 0.24 (B), only carboxylic carbon and carbonyl carbon shown.

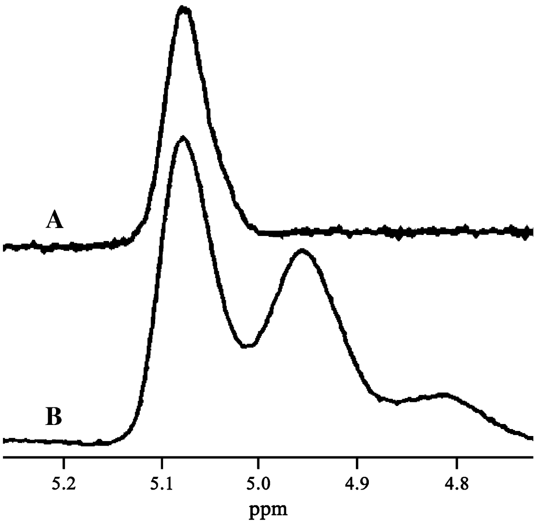

Fig. 7. $^1$H NMR spectra of VOH–VLA copolymers in DMSO-$d_6$: VLC = 0.05 (A); VLC = 0.24 (B), only CH(VLA) triads shown.

rr = 0.30, mr = 0.49 and mm = 0.21, the three hydroxyl signals of pure PVA from high field to low field are assigned to the syndiotactic (s), heterotactic (h), and isotactic (i) triads of PVA, respectively [36,39,40]. The $^1$H NMR spectrum of hydroxyl proton signals of pure PVA in DMSO-$d_6$ is shown in Fig. 8. This indicates that the three carboxylic carbon signals as shown in Fig. 6 are due to configurational splitting of isolated VLA unit rather than compositional splitting.

The carboxylic carbon signals in the $^{13}$C NMR spectra of VOH–VLA copolymers can be corrected for configurational splittings to infer the 'true' compositional triads from the spectra. Assuming that carboxylic carbon absorption in pure poly(vinyl levulinate), i.e. PVA fully substituted by LA, is not resolved by configurational splitting in DMSO-$d_6$ and resonates at upfield position in the $^{13}$C NMR spectrum and any hydroxyl in a racemic (r) position with respect to an levulinate side group leads to a down field shift on the basis of carbonyl triad analysis of VOH–VA copolymer [14,15], a set of equations for the carboxylic carbon region is given as follows:

$$\begin{aligned} I(\mathrm{h}) &= (\mathrm{mm}+\mathrm{mr}+\mathrm{rr})[\mathrm{LLL}] + (\mathrm{mm}+0.5\mathrm{mr})[\mathrm{OLL}] \\ &\quad +(\mathrm{mm})[\mathrm{OLO}] \\ I(\mathrm{c}) &= (\mathrm{rr}+0.5\mathrm{mr})[\mathrm{OLL}] + (\mathrm{mr})[\mathrm{OLO}] \\ I(\mathrm{l}) &= (\mathrm{rr})[\mathrm{OLO}] \end{aligned} \tag{11}$$

where $I$(h), $I$(c), and $I$(l) represent the measured integral values of the carboxylic carbon resonance in the $^{13}$C NMR spectra at high, central and low fields, respectively. The values of parameter mm, mr and rr are 0.21, 0.49 and 0.30, respectively. Then the molar fractions of three carbonyl compositional triads can be obtained from these three equations, the values are shown in Table 3. The molar fractions of carbonyl triads are in good agreement with those of CH(VLA) triads.

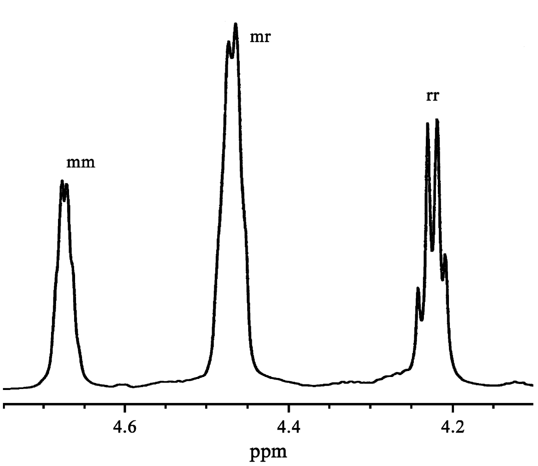

Fig. 8. $^1$H NMR spectrum of pure PVA in DMSO-$d_6$, only hydroxyl signals shown.

Using the molar fractions of carbonyl compositional triads, the number-average sequence length of vinyl levulinate (LLA) can be also obtained from Eq. (12). The values of LLA obtained from carbonyl triads of $^{13}$C NMR are in good agreement with those obtained from methylene dyads of $^{13}$C NMR and methine triads of $^1$H NMR (see Table 4).

$$\mathrm{LLA} = \{[\mathrm{LLL}]+[\mathrm{OLL}]+[\mathrm{OLO}]\}/\{[\mathrm{OLO}]+1/2[\mathrm{OLL}]\} \tag{12}$$

### 3.2.3. $^{13}$C methine resonance

As shown in Fig. 4, $^{13}$C methine carbon resonance is too complicated to unravel because of the sensitivity of the methine carbons to both configurational and compositional sequences, and the severe overlap of vinyl alcohol and vinyl levulinated centered compositional triads. The detailed $^{13}$C methine carbon microstructure information of the related vinyl alcohol–vinyl acetate copolymer has not been known yet so far [14]. We will apply 2D NMR method to investigate the detailed sequence distribution and tacticity of $^{13}$C methine resonance in our next work.

### 3.3. Comparison of $^1$H NMR and $^{13}$C NMR

The methine triad, methylene dyad and carbonyl triad sequence distributions of the copolymers were obtained from $^1$H NMR and $^{13}$C NMR spectra successfully. The values of VLC obtained from methine triads and methylene dyads are in good agreement with those from Eq. (1) and elemental analysis. The values of the number-average sequence length of vinyl alcohol unit (LOH) and vinyl levulinate unit (LLA) calculated from $^1$H NMR methine triads, $^{13}$C NMR methylene dyads and $^{13}$C NMR carbonyl triads are also in good agreement with each other.

In addition, the dyad–triad relation and triad–triad relation ($R$) can be obtained, where the $R$ value is defined as follows based on the microstructure analysis of VOH–VA copolymer [14,15].

$$\begin{aligned} R_{\mathrm{VLA}} &= [\mathrm{LL}]/[\mathrm{OL}] = \{[\mathrm{LLL}]+1/2[\mathrm{OLL}]\}/\{[\mathrm{OLL}]+2[\mathrm{OLO}]\} \\ R_{\mathrm{VOH}} &= [\mathrm{OO}]/[\mathrm{OL}] = \{[\mathrm{OOO}]+1/2[\mathrm{OOL}]\}/\{[\mathrm{OOL}]+2[\mathrm{LOL}]\} \end{aligned} \tag{13}$$

Table 6
The dyad–triad and triad–triad relation ($R$) values of VOH–VLA copolymers

| Sample no. | VLC | $R_{VLA}$ | | | $R_{VOH}$ | |
|---|---|---|---|---|---|---|
| | | $CH_2$ dyads ($^{13}C$ NMR) | C=O triads ($^{13}C$ NMR) | CH(VLA) triads ($^1H$ NMR) | $CH_2$ dyads ($^{13}C$ NMR) | CH(VOH) triads ($^1H$ NMR) |
| 1 | 0.15 | 0.14 | 0.10 | 0.10 | 3.62 | 3.55 |
| 2 | 0.24 | 0.23 | 0.19 | 0.21 | 1.88 | 2.13 |
| 3 | 0.58 | 0.85 | 0.80 | 0.83 | 0.52 | 0.55 |
| 4 | 0.69 | 1.34 | 1.25 | 1.32 | 0.29 | 0.28 |
| 5 | 0.91 | 4.50 | 4.05 | 4.29 | 0.056 | 0.063 |

The $R$ values obtained by dyads and triads data are also in good agreement with each other (see Table 6). That is, the dyad–triad relationship between the $^{13}C$ NMR methylene dyads and the $^1H$ NMR methine triads is fulfilled, the dyad–triad relationship in the $^{13}C$ NMR spectra between the methylene dyad and carbonyl triad is fulfilled, and the triad–triad relationship between the $^{13}C$ NMR carbonyl triad and the $^1H$ NMR vinyl levulinate-centered methine triad CH(VLA) is fulfilled.

The consistency of these dyad–triad and triad–triad relations shows that head to head or tail to tail fragments are hardly present in these systems according to the report of Van der Velden and Beulen on the sequence distributions in VOH–VA copolymers [14]. This result is in agreement with that of previous work, where it was shown that the head to head fragment in free radically polymerized poly(vinyl acetate) for preparation of PVA amounts to 1–2% [41].

## 4. Conclusions

The methine triad, the methylene dyad and the carbonyl triad sequence distributions of VOH–VLA copolymers were obtained from $^1H$ NMR and $^{13}C$ NMR spectra successfully. The vinyl levulinate content, the number-average sequence length and dyad–triad relation ($R$) were also calculated from methine triads, methylene dyads and carbonyl triads in $^1H$ NMR and $^{13}C$ NMR spectra successfully, and they are in good agreement with each other.

The reactive order of different tacticity hydroxyl in PVA was rr > mr > mm when the esterification of PVA with LA occurred.

The consistency of the dyad–triad and triad–triad relations shows that head to head or tail to tail fragments are hardly present in VOH–VLA copolymer.

## Acknowledgements

The authors are grateful to Dr. K. Hurihata for the helpful discussion on NMR measurements.

## References

[1] Shiraishi M, Toyoshim K. Br Polym J 1973;5:419–32.
[2] Tubbs RK. J Polym Sci Part A1 1966;4:623.
[3] Scholtens BJR, Bijsterbosch BH. J Polym Sci Polym Phys Ed 1979; 17:1771.
[4] Nagai E, Sagane N. Kobunshi Kagaku 1955;12:195.
[5] Hayashi S, Nakano C, Motoyama T. Kobunshi Kagaku 1963;20:303.
[6] Moritani T, Iwasaki H. Macromolecules 1978;11(6):1251–9.
[7] Ketels H, Beulen J, Van der Velden G. Macromolecules 1988;21: 2032–7.
[8] Bruch MD. Macromolecules 1988;21:2707–13.
[9] Amiya S, Iwasaki H, Fujiwara Y. Nippon Kagaku Kaishi 1977;11: 1698–701.
[10] Wu TK. J Polym Sci Part A2 1970;8:167–72.
[11] Wu TK, Ovenall DW, Reddy GS. J Polym Sci Polym Phys Ed 1974; 12:901–11.
[12] Wu TK. J Polym Sci Polym Phys Ed 1976;14:343–52.
[13] Moritani T, Fujiwara Y. Macromolecules 1977;10(3):532–5.
[14] Van der Velden G, Beulen J. Macromolecules 1982;15:1071–5.
[15] Toppet S, Lemstra PJ, Van der Velden G. Polymer 1983;24: 507–12.
[16] Bugada DC, Rudin A. Polymer 1984;25:1759–66.
[17] Isasi JR, Cesteros LC, Katine I. Macromolecules 1994;27:2200–5.
[18] Garnaik B, Thombre SM. J Appl Polym Sci 1999;72:123–33.
[19] Budhlall BM, Landfester K, Nagy D, David Sudol E, Dimonie VL, Sagl D, et al. Macromol Symp 2000;155:63–84.
[20] Amiya S. Progress in Pacific polymer science 3. In: Proceedings of the Pacific polymer conference 3rd. Berlin: Springer; 1994. p. 367–79.
[21] Sánchez-Chaves M, Arranz F, Montes M. Polymer 1988;29:2243–8.
[22] Amiya S, Uetsuki M. Macromolecules 1982;15(1):166–70.
[23] Okada T, Hashimoto K, Ikushige T. J Polym Sci Polym Chem Ed 1981; 19:1821–34.
[24] Mirau PA, Bovey FA. Macromolecules 1986;19(1):210–5.
[25] Crowther MW, Szeverenyi NM, Levy GC. Macromolecules 1986; 19(5):1333–6.
[26] Gippert GP, Brown LR. Polym Bull 1984;11(6):582–92.
[27] Hikichi K, Yasuda M. Polym J 1987;19(9):1003–12.
[28] Hikichi K. Progress in Pacific polymer science 2. In: Proceedings of the Pacific polymer conference 2nd; 1992. p. 167–74.
[29] Brar AS, Kumar R, Yadav A, Kaur M. Polymer Preprints 2001; 42(1):43–4.
[30] Dutta K, Mukherjee M, Brar AS. J Polym Sci Part A Polym Chem 1999;37(5):551–6.
[31] Bruch MD, Bonesteel JK. Macromolecules 1986;19:1622–7.
[32] Chang C, Muccio DD, St Pierre T. Macromolecules 1985;18(11): 2334–7.
[33] Beshah K. Macromolecules 1992;25:5597–600.
[34] Wang YM, Ono H, Ikeda A, Hori N, Takemura A, Yamada T, Tsukatani T. Polymer 2005;46:9793–802.
[35] Ovenall DW. Macromolecules 1984;17:1458–64.
[36] Wu TK, Ovenall DW. Macromolecules 1973;6:582–4.
[37] Wu TK, Sheer ML. Macromolecules 1977;10:529–31.
[38] Ito K, Yamashita Y. J Polym Sci Part A 1965;3:2165–87.
[39] DeMember JR, Hass HC, MacDonald RL. Polym Lett 1972;10: 385–9.
[40] Moritani T, Kuruma I, Shibatani K, Fujiwara Y. Macromolecules 1972; 5:577–80.
[41] Finch CA. Polyvinyl alcohol properties and applications. New York: Wiley; 1973. p. 225 [chapter 10].