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N,N-dicyclohexylcarbodiimide assisted synthesis and characterization of poly(vinyl alcohol-*co*-vinyl levulinate)

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Abstract

Poly(vinyl alcohol-*co*-vinyl levulinate) was synthesized by *N,N*-dicyclohexylcarbodiimide assisted esterification of poly(vinyl alcohol) with free levulinic acid using 4-pyrrolidino pyridine as a catalyst in *N,N*-dimethyl acetamide/lithium chloride solvent system in order to optimize the reaction condition. The vinyl levulinate content in the copolymer was attained up to 0.95. The ^{13}C NMR dyad compositional analysis indicated the block character of the copolymer was 0.92, suggesting almost random poly(vinyl alcohol-*co*-vinyl levulinate) was formed. Glass transition temperature dependence on vinyl levulinate content of the copolymers fitted better into Gordon–Taylor equation as compared with Fox equation and the glass transition temperature of poly(vinyl levulinate) was given as 2.3 °C by the least regression method.
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Keywords: Poly(vinyl alcohol-*co*-vinyl levulinate); Dyad compositional analysis; Glass transition temperature

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1. Introduction

Levulinic acid (LA) is a major product of controlled degradation of hexoses by acids and has been obtained from wood because its cellulose can be converted to glucose usually by heating with dilute acid [1]. Recently, a cost effective method for preparing LA in high yield from biomass has been developed [2]. We have also reported that LA can be obtained in solvolysis process using glycols and cyclic-carbonates [3,4]. LA, therefore, has potential of being a kind of renewable chemical because it is produced from renewable cellulose containing plants.

Probably from the reason above, LA and its derivatives have been tried to use in the preparation of polymers such as rubbers [5,6], copolymers [7,8], polyamides [9–12], and epoxy resins [13–15].

Recently, application of LA in biodegradable polymers have attracted great attention probably because LA is accepted as a less toxic compound. It is a base of flavor ingredients as alkyl levulinates used for many products and of calcium levulinate, a hydrated calcium salt of levulinic acid, which has been used as a calcium supplement orally or intravenously [16]. LA has been introduced into cellulose and chitosan, natural polysaccharides, as cellulose levulinate [17,18] and *N*-carboxybutyl chitosan, respectively [19,20].

As for the synthesis of bacterial polyesters LA has been used as an organic acid cosubstrate for the production of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) from glucose [21] and xylose [22] in order to increase 3-hydroxyvalerate content. However, poly(vinyl alcohol), one of biodegradable synthetic polymer [23–25], incorporating with LA has received little attention up to now. Therefore, we are interested in synthesizing poly(vinyl alcohol-*co*-vinyl levulinate) (VA–VL copolymer) by the esterification of PVA with LA because this copolymer is considered to be environmentally benign.

PVA is recognized as one of the few vinyl polymers soluble in water and often functionalized by the esterification of its hydroxyl groups with appropriate reagents to alter its properties. The esterified product leads to vinyl

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alcohol-vinyl ester copolymers with a known structure which can be used in wide range of applications such as a biodegradable material [26] and a support for sustained delivery of water-soluble bioactive compounds [27]. The product can be crosslinked by the reaction of its residual hydroxyl groups with multi-functional reagents [28].

The homogeneous esterification of PVA has been typically conducted in dimethyl sulfoxide [28–30], and 1-methyl-2-pyrrolidone [31], but recently Tosh et al. have reported that *N,N*-dimethyl acetamide (DMAc)/lithium chloride (LiCl) solvent system was an appropriate solvent for PVA to prepare poly(vinyl acetate), in which maximum solubility of PVA was 6.7% without any gel formation but only the crystalline structure of PVA was changed without any degradation or cross-linking during dissolution [32,33]. In these esterifications acid anhydride or acid chloride have been usually used. The limitation, however, is that levulinic anhydride and chloride cannot be commercially available.

Carlotti et al. [34] reported that PVA with various degree of grafting was obtained by using free lactic acid and glycolic acid in water medium although water is believed to be disadvantageous solvent for esterification. Their method, however, provided no levulinic ester in our previous investigation.

Meanwhile, *N,N*-dicyclohexylcarbodiimide (DCC), especially combining pyridine derivatives as catalysts, has been known as a condensation agent in esterification of carboxylic acid [35–38] with alcohols at room temperature. The application of DCC has also made it possible to synthesize telechelic oligoesters [39] and polyester [40,41] at room temperature. Hassner et al. [42] reported that only a few of the 4-substituted pyridines could be used as a acylation catalyst and the most effective catalysts were found to be 4-pyrrolidino pyridine (PP) and 1,1,3,3-tetramethyl-4-(4-pyridyl) guanidine.

In DCC/PP system DCC can convert free carboxylic acid to anhydride with changing into *N,N*-dicyclohexylurea (DCU) which is easily removed from reaction system and PP catalyst can transform the anhydride to activated acyl pyridinium species [35,37,42] which react readily with alcoholic hydroxyl groups to yield not only target esters but also the reusable acid and catalyst for subsequent cycles. The removed DCU has been known to be regenerated to DCC by the application of heat [43].

We, therefore, applied DCC/PP system in DMAc/LiCl solvent to the homogeneous esterification of PVA with free LA. This kind of application has been made in the esteterification of cellulose [43–45] but not yet in that of PVA to the best of our knowledge.

This research is focused on investigating firstly the optimal condition for preparing VA–VL copolymers with various vinyl levulinate content (VLC), by varying the addition level of DCC, PP, PVA concentration and reaction temperature, secondly compositionally sequence of VA–VL copolymer by ^{13}C NMR, and thirdly the glass transition temperature (T_g) dependence on VLC in the copolymer.

2. Experimental

2.1. Materials

Polyvinyl alcohol (Aldrich Chemical Co. Ltd., nominal average molecular weight; 89,000–98,000, nominal degree of hydrolysis; 99%) was purchased and used as received. Extra-pure grade reagents in accordance with Japanese Industrial Standard were used through the experiments. DMAc was stored for more than 1 week over potassium hydroxide prior to use. LiCl was dried at 100–105 °C overnight and stored in a desiccator until used. All the other reagents were used as received.

2.2. Synthesis of VA–VL copolymer

The transparent DMAc/LiCl solvent system was prepared by dissolving 1.1 g (0.026 mol) of LiCl in 110 ml (1.19 mol) of DMAc at 70–80 °C in a three-necked 200 ml round-bottom flask equipped with a magnetic stirrer, a thermometer, a nitrogen inlet and a drying tube. The concentration of LiCl in the solvent system was maintained at 1% (wt./vol.) through the experiments according to the report of Tosh et al. [32]. The solvent system was cooled to room temperature and 1.1 g (25 mmol equivalent to OH group) of PVA was added and followed by stirring until clear with heating again to 70–80 °C. The PVA solution was cooled to room temperature. Esterification of PVA was conducted in situ by adding 5.1 g (25 mmol) of DCC, 0.3 7 g (2.5 mmol) of PP and 3.63 g (31.3 mmol; 0.25 mol excess to OH mol of PVA) of LA in sequence for 24 h at room temperature under nitrogen atmosphere, to lead to a turbid reaction mixture.

2.3. Purification of VA–VL copolymer

Transparent reaction solution was obtained by the filtration of precipitated DCU from the resultant, which was confirmed by ^{1}H NMR. The solution was poured into diisobutyl ketone (DIBK) to remove DMAc, LiCl, PP and most of unreacted LA, resulting precipitation of crude VA–VL copolymer. The collected crude copolymer precipitant was dissolved into methanol and then reprecipitated with DIBK to obtain purified VA–VL copolymer. In some cases the reprecipitation procedure was repeated several times. The extracted copolymer was dried in a vacuum oven at 30–35 °C for more than 24 h.

Methanol did not dissolve the PVA used but dissolved the VA–VL copolymer prepared in this experiment well. Thus, unreacted PVA is considered to be removed by the filtration of the methanol solution.

2.4. NMR measurement

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 FT NMR spectrometer (Japan electric Co., Ltd) at 20 °C at a frequency of 500 and 125.6 MHz, respectively. Deuterized dimethyl sulfoxide (DMSO-d_6) or methyl alcohol (MeOH-d_4) was used for any purpose. In order to determine the VA–VL compositional dyad sequence distribution of the copolymer, signal intensities of methylene carbons in the polymer chain were measured with using gated decoupling technique in ^{13}C NMR. The free-induction decays of more than 10,000 times was obtained with using a pulse width of 7 μs, an acquisition time of 0.54 s, and a pulse delay time of 2.0 s basically according to the report of Overnall [46]. Head-to-head bonding fashion in original PVA was ignored on the assignment of ^{1}H and ^{13}C NMR spectra since no consideration has been made for this bonding fashion in almost all NMR studies on poly(vinyl alcohol-acetate). All the measurements for signal intensity were triplicate and the values were averaged.

2.5. Elemental analysis

Elemental analysis of VA–VL copolymers were performed by a Perkin–Elmer 240 model CHN elemental analyzer (Perkin–Elmer, Japan) and their VLC was calculated. Samples were dried over phosphorus pentoxide in a desiccator under vacuum pressure at room temperature for 48 h prior to analysis.

2.6. Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of VA–VL copolymers with various VLC was determined by a Perkin–Elmer DSC-7 (Perkin–Elmer, Japan) previously calibrated with indium. Temperature scans were conducted from −150 to 150 °C at a heating rate of 20 °C/min under helium atmosphere. The samples with ca. 10 mg were sealed into aluminum pans and submitted to two heating processes. In the first heating, the temperature was raised from room temperature to 150 °C to avoid thermal history. Afterwards, the sample was quickly cooled to −150 °C with liquid nitrogen, and then re-heated up to 150 °C for second run. T_g was taken at the mid-point of the transition range during the second run.

3. Results and discussion

3.1. Determination of VLC

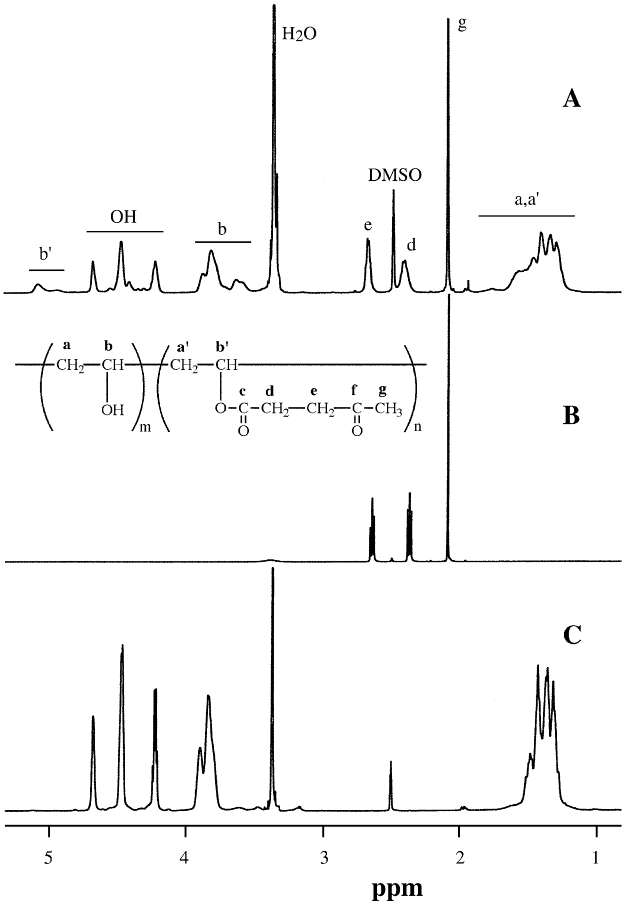

Fig. 1. ^{1}H NMR spectra of VA–VL copolymer (A); LA (B); PVA (C) in DMSO-d_6.

Fig. 1 shows the ^{1}H NMR spectra of a sample of VA–VL copolymer, LA and PVA together with the assignment of signals in the copolymer. The copolymer provides not only the signals due to the feature of the original PVA backbone structure [47–49] but also the signals due to levulinate group. The signals at 2.10 ppm and a set of 2.43 and 2.69 ppm in the spectrum of the copolymer are attributable to the methyl and two methylene protons of levulinate unit [50], respectively. The broad multiplet signal at the region from 1.2 to 1.9 ppm is due to methylene protons in the copolymer backbone. The multiplet signals centered at 3.76 ppm and at 5.02 ppm are assignable to two kinds of methine protons bearing hydroxyl groups and the levulinate units in the backbone, respectively [47–49].

These findings clearly demonstrate that VA–VL copolymer was successfully formed by the homogeneous esterification.

VLC may be calculated from the signal area intensity ratio between the protons due to levulinate groups and those due to the polymer backbone.

When each integral value will be expressed by putting I in front of the corresponding signal, e.g. $I_{CH_2}(d)$ and $I_{CH_2}(a+a')$ which are the integral values of $CH_2(d)$ proton signal and of the $CH_2(a)$ and $CH_2(a')$ signals, VLC may be calculated by the following equations:

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

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

$$\mathrm{VLC} = \frac{2I_{\mathrm{CH_3}}(g)}{3I_{\mathrm{CH_2}}(a + a')} \tag{1c}$$

where a, a', d, e and g are signals designated in Fig. 1.

Eq. (1b) was adopted because the signal of $\mathrm{CH_2}(e)$ is not overlapped with that of residual DMSO and gives fairly large integral value.

Table 1 summarizes VLC values calculated from ^{1}H NMR using the Eq. (1b), those from ^{13}C NMR data described later and those from elemental analysis for several VA–VL copolymers with different LA charge ratio. The values calculated from both ^{1}H and ^{13}C NMR are in good agreement with those from elemental analysis. We applied ^{1}H NMR calculation for the measurement of VLC because it is less time-consuming than two other methods.

3.2. Synthesis of VA–VL copolymer with high VLC

3.2.1. Reaction temperature

Fig. 2 shows VLC as a function of reaction temperature when esterification condition was fixed as follows: Reaction time; 24 h, LiCl/DMAc concentration; 1% (wt./vol.), PVA concentration based on the LiCl/DMAc solvent; 1% (w/v), the molar ratio of DCC to LA; 0.8, the molar ratio of LA and PP to PVA hydroxyl equivalent; 1.25 and 0.1, respectively.

VLC tends to decrease linearly with increasing temperature up to 60 °C. The amount of precipitate was found to decrease with increasing reaction temperature. ^{1}H NMR spectra of the DCU precipitate obtained at more than 40 °C exhibited some foreign signals probably due to *N*-acylurea which is produced by a side-reaction of carboxylic acids. The formation of unreactive *N*-acylurea is known to hamper the esterification as reported by Moore and Stupp [40]. The shortage of cooling system in our laboratory made low temperature experiments impossible, we adopted a reaction temperature of 25 °C for further esterification.

3.2.2. Reaction time

VLC dependence on the reaction time was examined in the same condition as described in the temperature examination above except for the addition level of PP catalyst. Fig. 3 shows VLC as a function of reaction time. VLC increases with increasing reaction time up to 24 h, and then level off at each PP addition level. The reaction period of 24 h, therefore, seems to be efficient for the esterification from the viewpoint of time-saving.

Table 1
Comparison of VLC values obtained from NMR and elemental analysis

^{1}H NMR	^{13}C NMR	Elemental analysis
0.14	0.15	0.12
0.24	0.24	0.28
0.58	0.57	0.55
0.69	0.70	0.65
0.91	0.90	0.95

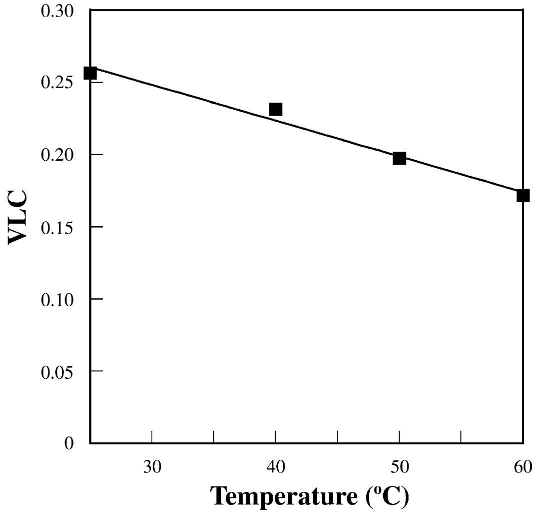

Fig. 2. VLC as a function of reaction temperature.

3.2.3. DCC charge ratio

Fig. 4 shows VLC as a function of the charge amount of DCC based on LA with maintaining PP molar ratio at 0.1. VLC curve levels off from DCC charge ratio around 0.8. Because DCC charge ratio of 0.8 seems to be efficient enough for the reaction, this charge ratio was maintained for further esterification.

3.2.4. PP catalyst charge ratio

Fig. 5 shows VLC as a function of the charge molar ratio of PP at different PVA concentration. VLC increases with increasing PVA concentration. VLC increases until the addition level of PP up to 0.2 and then levels off at each PVA concentration. The charge ratio of PP more than 0.2

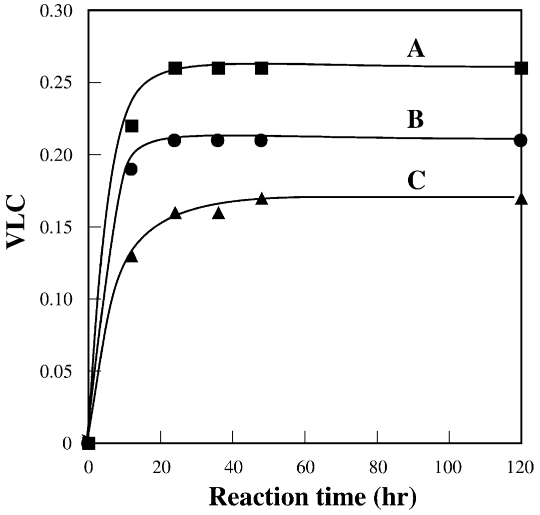

Fig. 3. VLC as a function of reaction time at different PP molar ratio based on PVA: 0.1 (A), 0.05 (B), 0.03 (C). Reaction temperature; 25 °C, LiCl/DMAc concentration; 1% (wt./vol.), PVA concentration based on the LiCl/DMAc solvent; 1% (w/v), the molar ratio of DCC to LA; 0.8, the molar ratio of LA to PVA hydroxyl equivalent; 1.25.

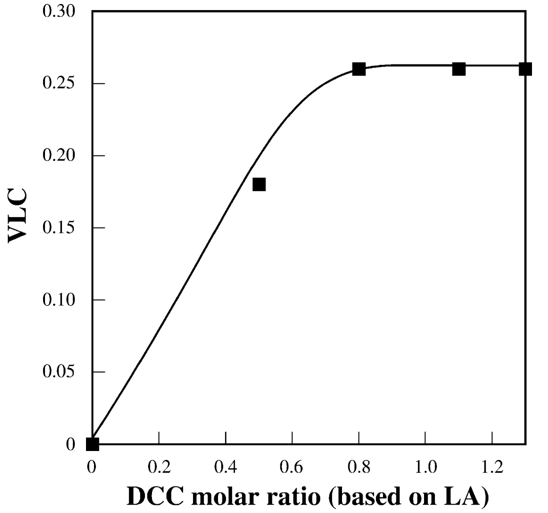

Fig. 4. VLC as a function of the charge amount of DCC based on LA. Reaction condition: reaction temperature; 25 °C, reaction time; 24 h, LiCl/DMAc con.; 1% (w/v), PVA con.; 1% (w/v), the molar ratio of LA and PP to PVA; 1.25 and 0.1, respectively.

would be effective to obtain VA–VL copolymers with high VLC from the feature of these curves.

3.2.5. LA charge ratio

Fig. 6 shows VLC as a function of the charge molar ratio of LA based on PVA at four PVA concentration levels. As LA addition level increases until 2.0, VLC generally increases and then decreases when PVA concentration exceeds 3%. PVA concentration of 5% provided unexpectedly low VLC at high LA addition levels. It was observed that PVA concentration more than 3% at high LA addition levels gave a large amount of PVA precipitate at the beginning of the reaction and then the precipitate re-dissolved as the reaction proceeded. The period of re-dissolving was prolonged as PVA and LA concentrations increased. Moreover, PVA concentration of 5% gave more viscous reaction system than that of 3%. These might be responsible for providing low VLC in the system of 5% PVA concentration. The retardation of re-dissolving suggests that longer reaction time than 24 h is required when high PVA concentration and high LA addition level are adopted in order to obtain VA–VL copolymers with high VLC. Actually the copolymers with higher VLC than original ones are obtained when the reaction time prolongs to 48 h as shown in Fig. 6(E). However, the problem that high PVA concentration gives high viscosity system uneasy to treat still remains. Note that VLC of 0.95 was achieved at LA molar ratio of 2.0 and PVA concentration of 3% for 48 h. We can tailor-make the copolymers with various VLC up to 0.95 so far by changing formulations we examined.

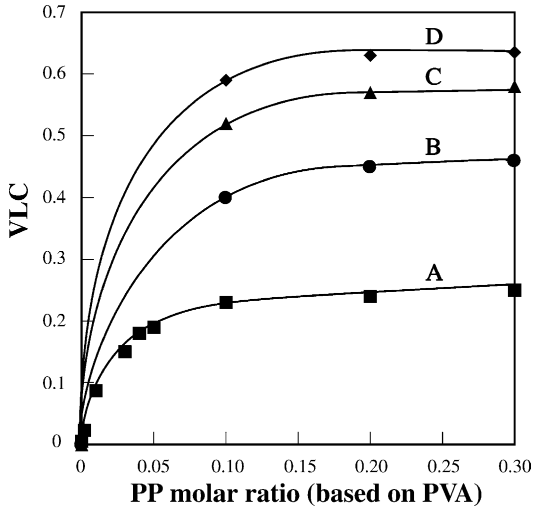

Fig. 5. VLC as a function of the charge molar ratio of PP at different PVA concentration (w/v): 1% (A), 2% (B), 3% (C), 5% (D). Reaction condition: Reaction temperature; 25 °C, reaction time; 24 h, LiCl/DMAc con.; 1% (w/v), the molar ratio of DCC to LA; 0.8, LA molar ratio based on PVA; 1.25.

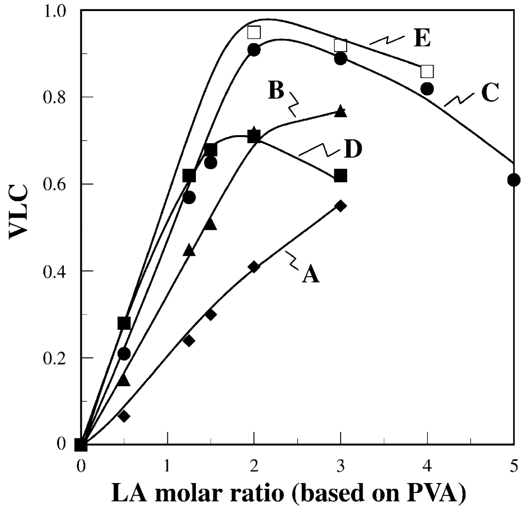

Fig. 6. VLC as a function of the charge molar ratio of LA at different PVA concentration (w/v): 1% (A), 2% (B), 3% (C), 5% (D), 3% for 48 h (E). Reation condition: LiCl/DMAc con.;1% (w/v), PP molar ratio to PVA; 0.2, DCC/LA molar ratio; 0.8, reaction temp.;25 °C, reaction time; 24 h (A)–(D), 48 h (E).

3.3. VLC and dyad sequence analysis of VA–VL copolymers by ^{13}C NMR

Fig. 7 shows the ^{13}C NMR spectra of VA–VL copolymer with VLC of 0.56, LA and PVA in DMSO-d_6. The copolymer clearly gives signals due to carboxylic carbon at 173.0 ppm, to carbonyl carbon at 208.3 ppm, to a set of two methylene carbons at 27.8 and 37.3 ppm and to methyl carbon at 28.3 ppm in levulinate group together with those due to methine carbons at around 66.5 ppm and methylene carbons at around 43.0 ppm in PVA backbone of various sequences. Upon reaction with PVA the signals at 174.6 and 208.9 ppm due to LA shift to 173.0 and 208.3 ppm, respectively.

Fig. 8 shows the enlarged partial spectra of VA–VL copolymers with three VLC at methyl and methylene region

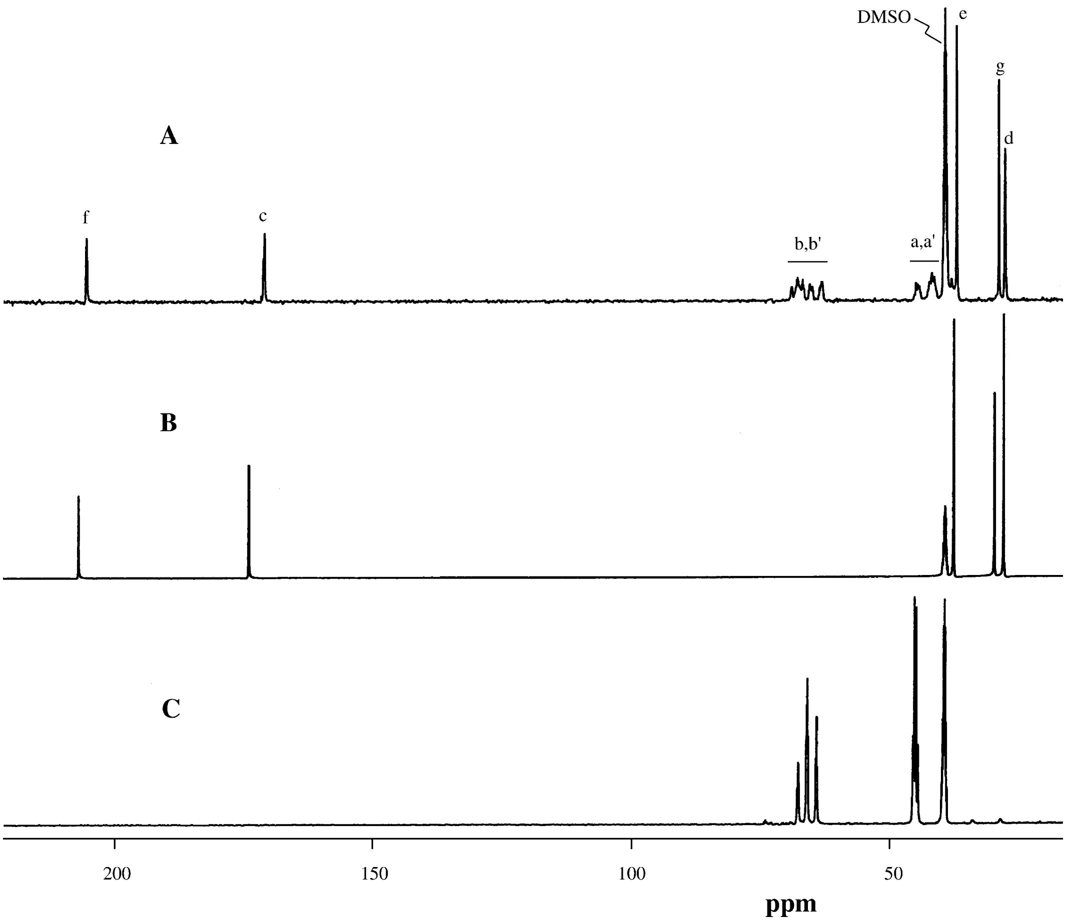

Fig. 7. ^{13}C NMR spectra of VA–VL copolymers with VLC of 0.56 (A), LA (B) and PVA (C) in DMSO-d_6.

in MeOH-d_4. In order to avoid the interference of the signals at 39.5 ppm due to residual DMSO with 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 to 46.5 ppm. As VLC increases the signal centered at 44.5 ppm decreases, the signal centered at 42.1 ppm increases until VLC reaches 0.56 and then decreases. At the same time the signal centered at 39.1 ppm overlapped with levulinate methylene signal at 37.3 ppm increases. PVA only gave a multiplet signal at 44.5 ppm in a spectrum using DMSO-d_6 as shown in Fig. 7. These three signals, therefore, can be assignable to the three compositional dyads of (VA,VA), (VA,VL) and (VL,VL) in order of decreasing frequency, where VA, and VL denote vinyl alcohol unit and vinyl levulinate unit, respectively. The chemical shift dependence on the degree of esterification is very much similar to those of vinyl alcohol–vinyl acetate copolymers [47,48,51–55] and vinyl alcohol–vinyl propionate copolymers [56].

As Overnall reported T_1 of methylene carbon of 10% acetylated poly(vinyl alcohol) is 0.17–0.18 s [46], a pulse delay time of 2.0 s (ca 10 times longer than the T_1) was applied to ^{13}C NMR measurements of VA–VL copolymers. The integral areas of three compositional dyads and two methylene carbons at 37.3 and 27.8 ppm were measured on the assumption that the Overhauser effect enhances equally among these signals [57].

When the same notation is used to each integral value as that described in ^{1}H NMR, a molar ratio of the three compositional dyads may be expressed as follows:

$$[\mathrm{VA,VA}]/[\mathrm{VA,VL}]/[\mathrm{VL,VL}] = I(\mathrm{VA,VA})/\mathrm{I}(\mathrm{VA,VL})/\mathrm{I}(\mathrm{VL,VL}) \quad (2)$$

where the molar fractions of the three dyads are expressed as the corresponding abbreviation in square bracket.

The signal of (VL,VL), however, overlaps with the methylene carbon signal of CH$_2$(*e*) as shown in Fig. 8. The appropriate *I*(VL,VL) may be obtained by taking $I_{\mathrm{CH}_2}(d)$ from the total integral value of *I*(VL,VL) and $I_{\mathrm{CH}_2}(e)$. The corrected *I*(VL,VL) value is then,

$$I(\mathrm{VL,VL}) = \{I(\mathrm{VL,VL}) + I_{\mathrm{CH}_2}(e)\} - I_{\mathrm{CH}_2}(d) \quad (3)$$

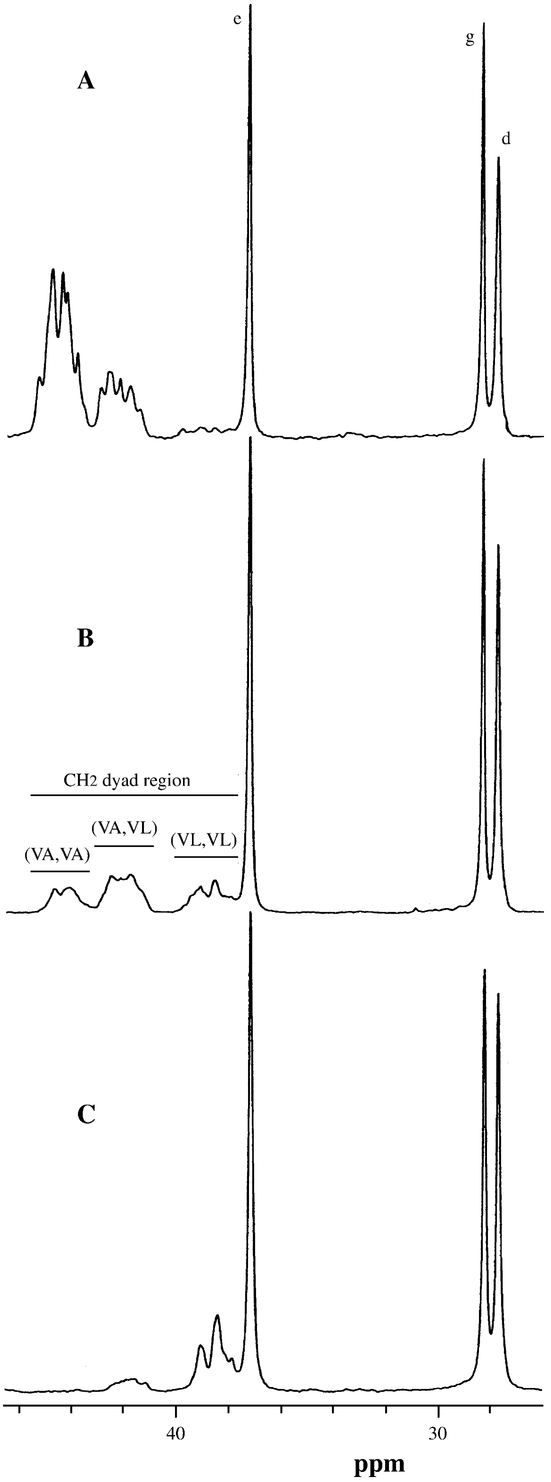

Fig. 8. Enlarged partial ^{13}C NMR spectra of VA–VL copolymers at methyl and methylene region in MeOH-d_4: VLC = 0.2 (A), VLC = 0.56 (B), VLC = 0.91 (C).

By using Eq. (2) and (3) a quantitative description of sequential distribution and randomness in VA–VL copolymer may be made [47,52,55].

Molar ratios of VA units and VL units are given as the following equations:

$$[\mathrm{VA}] = [\mathrm{VA,VA}] + [\mathrm{VA,VL}]/2 \tag{4}$$

$$[\mathrm{VL}] = [\mathrm{VL,VL}] + [\mathrm{VA,VL}]/2 \tag{5}$$

where the molar fractions of vinyl alcohol and vinyl levulinate are expressed as the corresponding abbreviation in square bracket.

VLC will be then,

$$\mathrm{VLC} = [\mathrm{VL}]/\{[\mathrm{VA}] + [\mathrm{VL}]\} \tag{6}$$

A number average sequence length of vinyl alcohol units (LOH) and that of vinyl levulinate units (LLA) are also given as:

$$\mathrm{LOH} = 2[\mathrm{VA}]/[\mathrm{VA,VL}] \tag{7}$$

$$\mathrm{LLA} = 2[\mathrm{VL}]/[\mathrm{VA,VL}] \tag{8}$$

A block character (η) is expressed as:

$$\eta = [\mathrm{VA,VL}]/2[\mathrm{VA}][\mathrm{VL}] \tag{9}$$

The VLC values calculated by Eq. (6) are in good agreement with those from ^{1}H NMR (Table 1).

The dependences of number average sequence length of LOH and that of LLA on VLC are shown in Fig. 9. Reciprocal relation between LOH and LLA is observed and two curves expectedly cross at VLC of 0.5, where LOH and LLA are almost 2.2. This implies that [VA,VA], [VA,VL] and [VL,VL] are almost 28, 46 and 28 in 100 dyads, respectively.

The diagram of [VA,VL] dyads proportion as a function of VA molar fraction is shown in Fig. 10.

When η for a copolymer falls between 0 and 1, the polymer shows characteristic of block structure. When η is in the range from 1 to 2, the co-monomer tends to alternative in the polymer structure. Block character of $\eta = 1$ means random copolymers.

In order to measure the block character of the copolymers it is convenient to linearize Eq. (9) as follows:

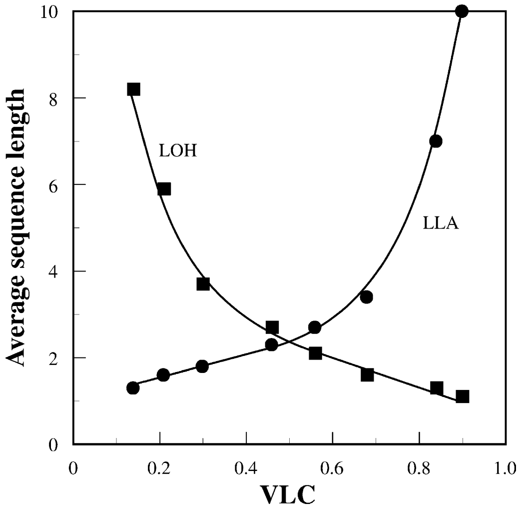

Fig. 9. Dependences of average sequence length on VLC.

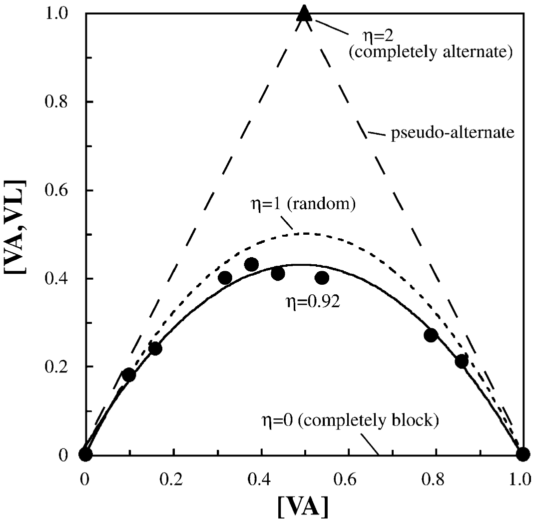

Fig. 10. Diagram of [VA,VL] dyads proportion as a function of VA molar fraction.

$$[\mathrm{VA,VL}]/2 = \eta[\mathrm{VA}][\mathrm{VL}] \tag{10}$$

Then η value may be obtained as a slope of the linear function.

By using the least regression method η value and the multiple correlation coefficient (R^2) were calculated as 0.92 and 0.996, respectively. This finding clearly indicates that VA–VL copolymers are almost compositionally random.

3.4. Thermal analysis

Table 2 lists the measured T_g values of VA–VL copolymers with different VLC. The weight fraction of vinyl alcohol (W_A) and that of vinyl levulinate (W_B) may be converted from VLC value of the copolymer as follows:

$$W_A = 44(1-\mathrm{VLC})/(44+98\ \mathrm{VLC}) \tag{11}$$

$$W_B = 1-W_A = 142\ \mathrm{VLC}/(44+98\ \mathrm{VLC}) \tag{12}$$

where 44 and 142 represent the molecular weight of VA and VL, and 98 is the weight difference between them. W_B is also exhibited in Table 2.

Table 2
T_g dependence on the molar fraction and weight fraction of vinyl levulinate unit

VLC	W_B (%)	T_g (°C)
0	0	70.0[a]
0.13	32.5	52.1
0.20	44.7	44.4
0.28	55.7	35.9
0.40	68.3	28.8
0.57	81.1	16.9
0.71	88.8	12.4
0.87	95.6	6.1
0.91	97.0	5.2

[a] T_g of PVA.

T_g of VA–VL copolymer was greatly affected by the amount of introducing LA to PVA. T_g of poly(vinyl levulinate), i.e. PVA fully substituted by LA, was evaluated by using Gordon–Taylor equation expressed as [58]:

$$T_g = (T_{gA}W_A + KT_{gB}W_B)/(W_A + KW_B) \tag{13}$$

where T_{gA} and T_{gB} represent the glass transition temperature of PVA and poly(vinyl levulinate), and K is the constant for each polymer unit, related to the specific volume of each polymer unit at its T_g.

For fitting the data Eq. (13) can be transformed into linear function as follows:

$$T_g = (1/K)(T_{gA}-T_g)W_A/W_B + T_{gB} \tag{14}$$

The values of $1/K$ and T_{gB}, therefore, can be given by the slope and the intercept of the linear plot of T_g vs. $(T_{gA}-T_g)W_A/W_B$ as shown in Fig. 11. The least regression method provides significant linear fitting with $R^2=0.996$. The slope and the intercept values provides $K=0.76$ and $T_{gB}=2.3$ °C, respectively. The standard deviation of T_{gB} was 1.2. On the other hand, a group of T_{gB} values calculated by Fox equation [59] in the copolymers with different VLC gave higher average of T_{gB} (5.3 °C) with wider standard deviation (6.3) than those by Gordon–Taylor equation. Fig. 12 depicts T_g of VA–VL copolymers obtained from experiments and predicted from Gordon–Taylor equation. The experimental data fits the Gordon–Taylor equation very well.

4. Conclusions

1. Homogeneous estrification of PVA with LA by using DCC as a condensation agent and PP as a catalyst in DMAc/LiCl solvent system was investigated in order to obtain (vinyl alcohol–vinyl levulinate) copolymers with high VLC. The effective reaction temperature was found to be 25 °C. VA–VL copolymers with VLC up to 0.95

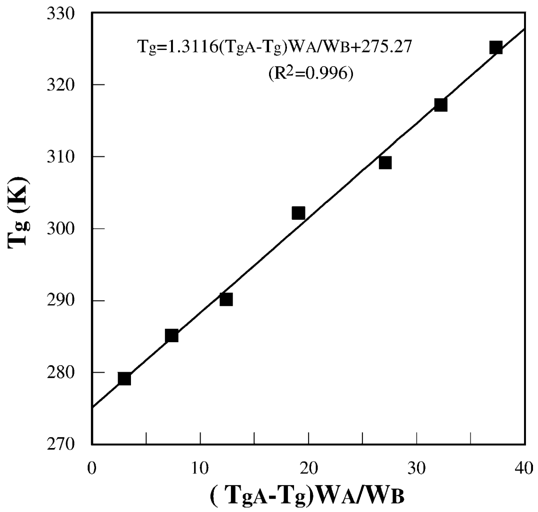

Fig. 11. T_g vs. $(T_{gA}-T_g)W_A/W_B$ for VA–VL copolymers.

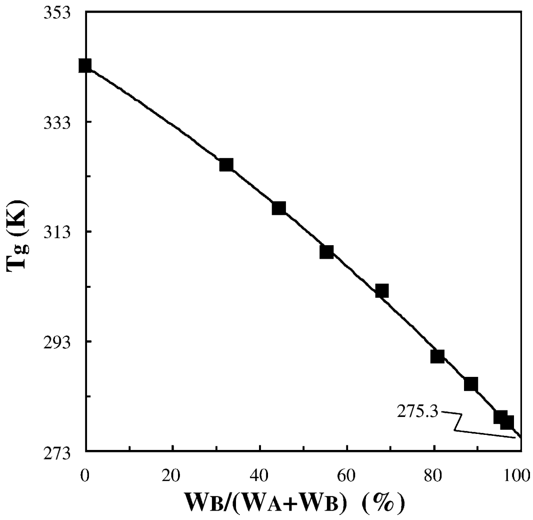

Fig. 12. T_g of VA–VL copolymers. Full squares express experimental data and line shows the theoretical curve from Gordon–Taylor equation ($K=0.76$).

could be tailor-made according to the formulation investigated. VLC of 0.95 was attained at the following conditions: Reaction time; 48 h, PVA concentration in LiCl/DMAc (1% wt./vol.); 3%, DCC molar ratio to LA; 0.8, the molar ratio of LA and PP to PVA hydroxyl equivalent; 2 and 0.2, respectively.

2. The dyad compositional analysis of the copolymers was conducted by ^{13}C NMR. The block character (η) evaluated by the least regression method was obtained as 0.92 with the multiple correlation coefficient of 0.996. Because η is very close to one VA–VL copolymers are compositionally random, i.e. PVA is randomly substituted with LA.
3. T_g dependence on VLC was examined by the application of Gordon–Taylor and Fox equations. The experimental data fitted Gordon–Taylor equation better than Fox equation. T_g value of poly(vinyl levulinate) was calculated as 2.3 °C (275.3 K).

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