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Thermodynamics of copolymerization of vinyl acetate and vinyl pivalate

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Abstract

Vinyl pivalate (VPi) and vinyl acetate (VAc) were copolymerized at low temperature using 2,2′-azobis(2,4-dimethylvaleronitrile) as an initiator. Copoly(VPi/VAc) was prepared in a broad range of chemical composition, from 0/10 to 10/0 of VPi/VAc molar feed ratio. A statistical treatment of the ^{1}H NMR peak intensities brought to the determination of the reactivity ratios of the comonomers. A thermodynamic study of the molecular dynamics simulation data led to the estimation of number-average sequence lengths of comonomers and Gibbs free energy change over VPi content. From this result, the retardation of copolymerization rate at about 5/5 composition was also explained. Enthalpies of –VAc–VPi*, –VPi–VAc*, and –VPi–VPi* formation were calculated as − 12.07, − 5.57, and − 18.33 kcal/mol, respectively.

Keywords: Vinyl pivalate; Vinyl acetate; Copolymerization

1. Introduction

Poly(vinyl alcohol) (PVA) is currently paid attention to for its various usabilities, ranging from textile to industrial and biomedical materials [1–7]. These usabilities of PVA are most ruled by the molecular weight and stereoregularity of PVA. Molecular weight of PVA can be enhanced to some extent by adopting low polymerization temperature and less amount of initiator during the polymerization of precursor [8–13]. Moreover, ultrahigh molecular weight PVA can be prepared by using special devices, such as photo-initiation polymerization [8–10].

Stereoregularity of PVA is a key characteristics that determines the field of application of PVA; chemical and physical properties of PVA can be differentiated by its stereoregularity. Previously, commercial PVAs, which were prepared by polymerization of vinyl acetate (VAc) and following saponification, had limited stereoregularity, to say, randomly distributed atactic configuration. VAc has been used in copolymerization with ethylene [18–22], methyl methacrylate [23], glycidyl methacrylate [24], and alkyl acrylate [25]. Copolymer of VAc and vinyl alcohol [26–29] also has been prepared by partial saponification of poly(vinyl acetate) (PVAc). Most famous among the copolymers of vinyl acetate is copoly(ethylene/VAc) which can be saponified to copoly(ethylene/vinyl alcohol) (EVA). EVA has been in focus for its singularity in packing material due to excellent oxygen barrier property. Recently, usability of EVA in various fields including biomedical application was inspected [30–32]. These researches were on the modification and improvement of PVA by changing the structural configuration. Many researchers tried to control the stereoregularity of PVA by adopting various vinyl ester monomers [8–17] and new polymerization methods [33–37]. But studies on varying molecular parameters of PVA have not been fully performed, not to mention the effects of stereoregularity on configuration of PVA.

Recently, our research group reported the copolymerization of vinyl pivalate (VPi) and VAc at low temperature by virtue of the introduction of low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), followed by in situ fibrillation [38–43]. By using this methodology, we can separate the grades of syndiotacticities of PVAs rather precisely. Copolymerization of VPi and VAc has several advantages over homopolymerization including lower cost and the grasp of effective stereoregularity control. However, prediction of characteristics of copoly(VPi/VAc) requires somewhat theoretical works, such as thermodynamic consideration.

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Thermodynamics of copolymerization is one of the fundamental elements for studying the effects of copolymerization parameters on copolymer properties. Up until now, it has not been easy work not because there are not effective models but because the known thermodynamic values are limited to some copolymer pairs. Recently, with the aids of molecular modeling methods, some thermodynamic parameters can be calculated and estimated on computer. These results can be applied to prediction of the characteristics of copolymerization process and product.

In the present work, copolymerization of VPi and VAc was performed at 30 °C using ADMVN. Molecular dynamics simulation of thermodynamic variables was performed to explain the decrease in copolymerization rate with increasing VAc content. Thermodynamic expansion of copolymerization of VPi and VAc was conducted over a wide range of monomer feed ratio. From the activation energy and enthalpy calculated, Gibbs free energy and number-average sequence lengths of successive VPi and VAc units were evaluated.

2. Thermodynamic expansion of copolymerization

2.1. Enthalpy of copolymerization

During the copolymerization of VAc (subscript 1) and VPi (subscript 2), there are four propagation reactions as below according to the terminal model. k_{ij} is the rate constant of addition of monomer j to the active radical i

$$-\mathrm{VAc}^* + \mathrm{VAc} \xrightarrow{k_{11}} -\mathrm{VAc}-\mathrm{VAc}^* \tag{1}$$

$$-\mathrm{VAc}^* + \mathrm{VPi} \xrightarrow{k_{12}} -\mathrm{VAc}-\mathrm{VPi}^* \tag{2}$$

$$-\mathrm{VPi}^* + \mathrm{VAc} \xrightarrow{k_{21}} -\mathrm{VPi}-\mathrm{VAc}^* \tag{3}$$

$$-\mathrm{VPi}^* + \mathrm{VPi} \xrightarrow{k_{22}} -\mathrm{VPi}-\mathrm{VPi}^* \tag{4}$$

Overall enthalpy of reaction can be expressed numerical average of the enthalpies of each reaction is as follows

$$\begin{aligned}\Delta H &= \frac{N_{11}}{N_0}H_{11} + \frac{N_{22}}{N_0}H_{22} + \frac{N_{12}}{N_0}H_{12} + \frac{N_{21}}{N_0}H_{21} \\ &= H_{11}X_1 + H_{22}X_2 \\ &\quad + X_1X_2[H_{12} + H_{21} - (H_{11} + H_{22})]\end{aligned} \tag{5}$$

where N_0 is total number of monomeric units; N_{ij} and H_{ij} are the number and enthalpy of diads of which monomer j follows the radical chain that has activated monomeric i units, respectively; $N_1 = N_{12} + N_{11}$, $N_2 = N_{12} + N_{22}$, $N_0 = N_1 + N_2$, $X_1 = N_1/N_0$, $X_2 = N_2/N_0$, and $N_{12} = N_0X_1X_2$. N_{12} and N_{21} can be assumed as same because of the equal possibilities of finding VAc–VPi and VPi–VAc diads in copolymer.

2.2. Randomness parameter and number averaged sequence length

Randomness parameter, ϕ, can be expressed statistically by the definition as follows [44]

$$\phi = \frac{P_{21}}{X_1} \tag{6}$$

where P_{ij} is the conditional probability that a monomeric i unit selected at random will be followed by a monomeric j unit. If the copolymer is completely random, this value converges to unity. Number averaged sequence lengths of monomer 1 and 2 are defined as follows [45]

$$W_{n1} = \frac{1}{P_{12}} = \frac{1}{1 - P_{11}} = \frac{1}{\phi X_2} \tag{8}$$

$$W_{n2} = \frac{1}{P_{21}} = \frac{1}{1 - P_{22}} = \frac{1}{\phi X_1} \tag{9}$$

2.3. Entropy of copolymerization

To evaluate the entropy of copolymerization, several factors must be considered together; to say, entropies due to propagation, chain configuration, and copolymerization randomness should be included as well as the residual entropy at 0 K by the glass state. Neglecting the residual and chain configurational entropies, entropy of copolymerization can be simplified as follows [46]

$$\begin{aligned}\Delta S &= -(S_{11}X_1 + S_{22}X_2 + \chi\phi X_1X_2) - R[(1 - \phi X_2) \\ &\qquad \times \ln(1 - \phi X_2) + \phi X_2 \ln \phi X_2] \\ &\cong -(S_{11}X_1 + S_{22}X_2) - R[(1 - \phi X_2)\ln(1 - \phi X_2) \\ &\qquad + \phi X_2 \ln \phi X_2]\end{aligned} \tag{10}$$

where χ is $(S_{12} + S_{21}) - (S_{11} + S_{22})$ and R is gas constant. χ can be set to zero for most case [47]. Therefore, Eq. (10) holds meaning in our radical copolymerization system.

2.4. Gibbs free energy of copolymerization

For open system, chemical potential must be considered for estimation of Gibbs free energy change, ΔG. In this paper, however, ΔG for closed system is assumed for convenience as follows

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

Eq. (11) can be expressed as Eq. (12) from Eqs. (5) and (10).

$$\begin{aligned}\Delta G &\cong H_{11}X_1 + H_{22}X_2 + X_1X_2\phi\Omega + T(S_{11}X_1 + S_{22}X_2) \\ &\qquad + RT[(1 - \phi X_2)\ln(1 - \phi X_2) + \phi X_2 \ln \phi X_2]\end{aligned} \tag{12}$$

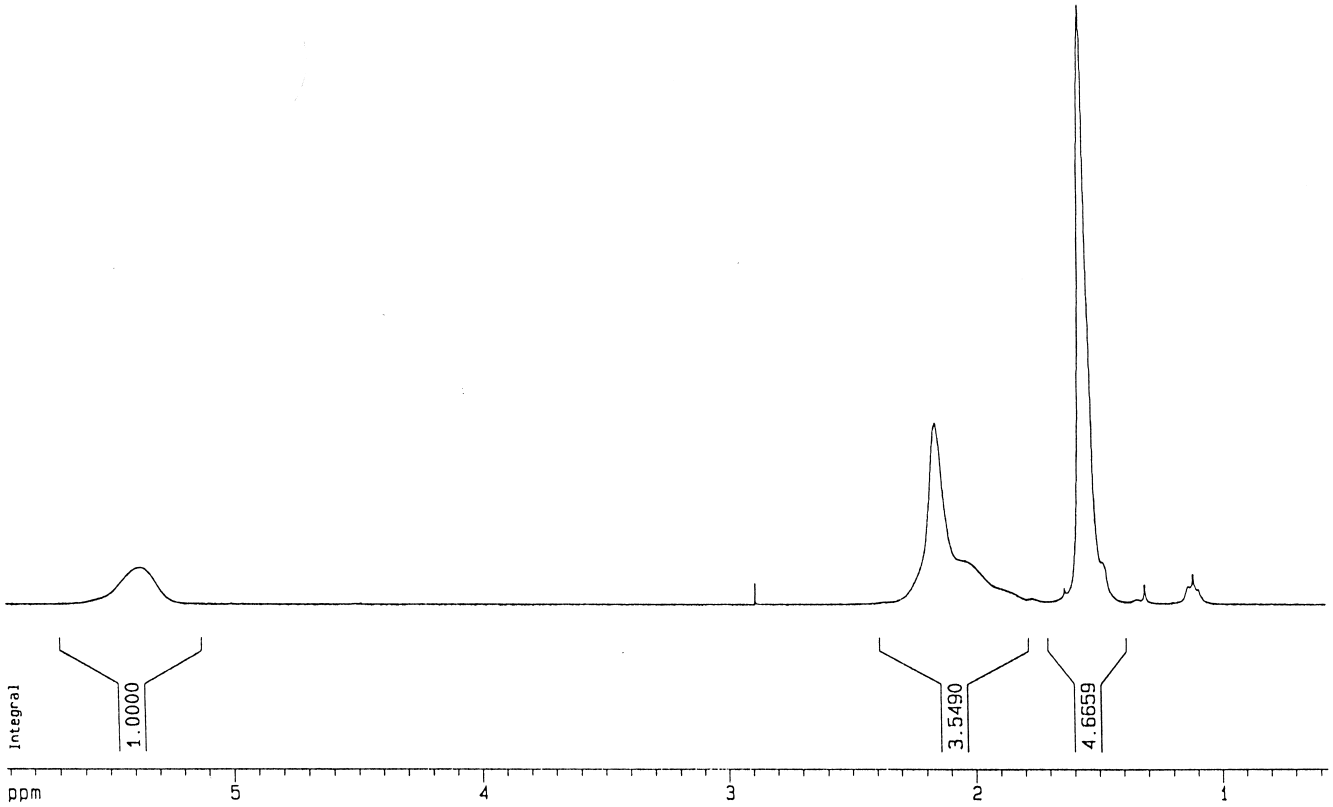

Fig. 1. ^{1}H NMR spectrum of copoly(VPi/VAc).

where

$$\Omega = \frac{1}{\phi}[H_{12} + H_{21} - (H_{11} + H_{22})].$$

3. Experimental

3.1. Materials

VPi and VAc were purchased from Shin-Etsu, washed successively with aqueous $NaHSO_3$ and water, dried over anhydrous $CaCl_2$, and redistilled under nitrogen at reduced pressure. ADMVN was purified after purchased from Wako Chemical by recrystallization from methanol. Other extra-pure reagents were used without further purification.

3.2. Homopolymerization and copolymerization

VPi and VAc mixture (100 ml) in different feed ratios was flushed with nitrogen at 10 °C for 3 h, ADMVN was added, and the mixture was stirred at 30 °C for predetermined time. Homopolymerization of VPi and VAc were also performed at the same polymerization condition. Unreacted monomer and catalyst were removed by distillation under vacuum. The resultant polymers were purified by reprecipitation: PVPi in acetone/water, copoly(VPi/VAc) in methanol/water, and PVAc in acetone/*n*-hexane, respectively.

3.3. Determination of copolymer composition

The copolymer compositions were determined using a Varian Sun Unity 300 MHz ^{1}H NMR spectrometer, with benzene-d_6 as the solvent, based on the resonance for the *tert*-butyl (pivaloyl) and methyl (acetyl) protons at 1.5 and 2.2 ppm, respectively, as shown in Fig. 1.

3.4. Molecular dynamics simulation

Activation energies were obtained using *Cerius*^{2} molecular dynamics simulation package with terminal model. Enthalpy was recalculated from the activation energy by Evans method [48].

4. Results and discussion

4.1. Copolymerization of VPi and VAc

It was expected that polymerization rate of copolymer would be changed gradually as increasing VAc, or VPi contents. Fig. 2 shows the copolymerization rates with the copolymer composition. There was no abrupt increase in

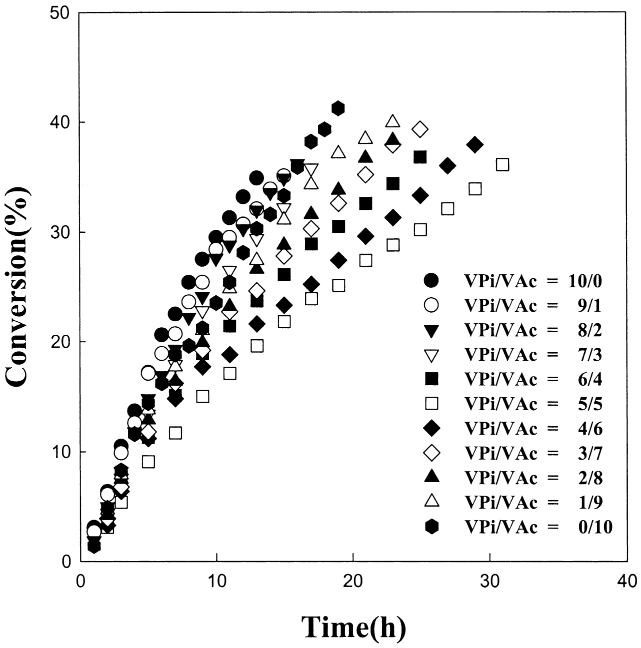

Fig. 2. Copolymerization rate for various VPi/VAc feed ratio at polymerization temperature of 30 °C with reaction time. (ADMVN concentration was fixed at 1×10^{-4} mol/mol of comonomer.)

copolymerization rates of VPi and VAc for all composition, which might be ascribed to the low reaction temperature. Copolymerization rate, however, was decreased with heterogeneity effect of relative monomer composition and minimized at about 5/5.

4.2. Molecular dynamics simulation

The activation energies of each reaction can be obtained from computer simulation. From the classical work of Evans et al. [48], the relation between the heat of polymerization and the activation energy defined such a quantitative form as follows

$$-\Delta E = \alpha \Delta H \qquad (0 < \alpha < 1) \tag{13}$$

The activation energies of each reaction were obtained by using molecular dynamics simulation package. Energy difference of PVAc arising from addition of one monomeric unit was obtained with terminal model. Joshi and Zwolinski [49] have reported polymerization enthalpy and entropy of VAc as −21.2 kcal/mol and -26.2×10^{-3} kcal/mol K, respectively. Constant α was calculated from simulated activation energy and reported enthalpy of VAc and applied for the others. Entropy of VPi has been assumed as that of VAc for convenience. Table 1 shows the activation energies and recalculated enthalpies of each propagation reactions. Reactive ratios were measured at conversions under 10%.

Enthalpy, entropy, and Gibbs free energy changes along the VPi molar content at 30 and 300 °C are shown in Fig. 3. Above ceiling temperature, where ΔG is zero, propagation cannot have the priority any more

Table 1
Activation energies and recalculated enthalpies of each reactions

	Activation energy (kcal/mol)	Enthalpy (kcal/mol)
$-\mathrm{VAc}^* + \mathrm{VAc}$	19.99	−21.20
$-\mathrm{VAc}^* + \mathrm{VPi}$	11.38	−12.07
$-\mathrm{VPi}^* + \mathrm{VAc}$	5.25	−5.57
$-\mathrm{VPi}^* + \mathrm{VPi}$	17.28	−18.33

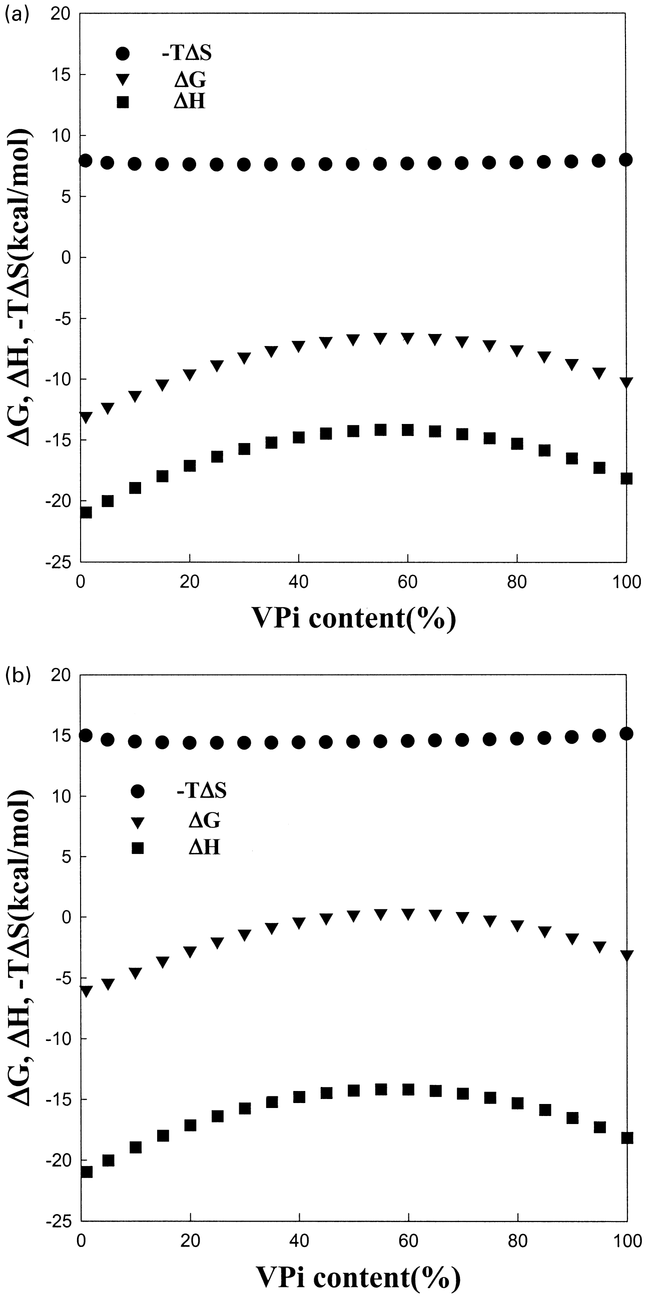

Fig. 3. Changes in thermodynamic variables of copolymerization of VPi and VAc along the VPi content at (a) 30 °C and (b) 300 °C.

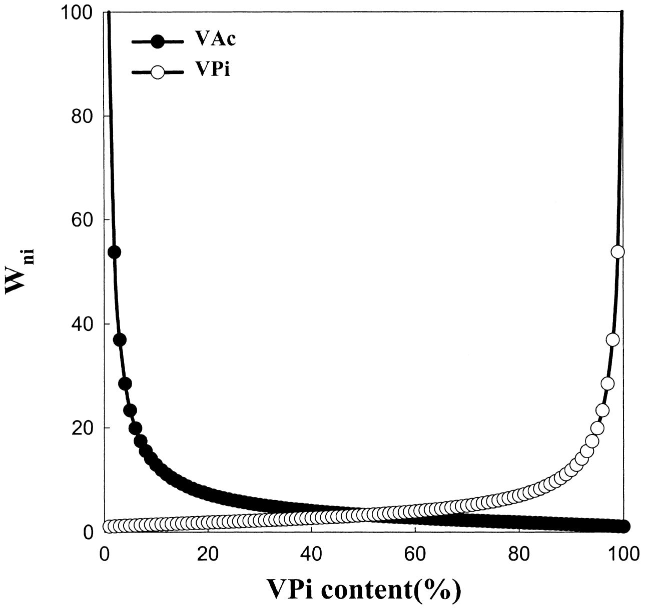

Fig. 4. Number averaged sequence lengths of VPi and VAc units with VPi content of copoly(VPi/VAc).

over the decomposition. In this study, copolymerization was performed at 30 °C, far below the ceiling temperature theoretically estimated about 300 °C. Therefore copolymerization of this study can be assumed to be stable. From Fig. 3(a), maximum ΔG value was observed when VPi molar content approached to 55%. This result implies that copolymerization rate comes to minimum value when the molar ratio of VPi/VAc is nearly unity, confirmed by experimental data shown in Fig. 2.

A previously reported [38], r_1, r_2, and product of these values, r_1r_2, of this study are larger than unity. It can be assumed, therefore, that ϕ of this study is always less than unity. ϕ has strong relationship with compositional randomness or blockiness. ϕ less than unity means self-propagation reactions will be favored over the alternation reactions. Number averaged sequence length is more realistic parameter of blockiness. Fig. 4 showed these values for various monomer compositions. From this result, blockiness of VPi and VAc can be compared directly. Number averaged sequence length of VPi increased with the increase of VPi content. When VPi molar content approaches to 50%, number averaged sequence length of VPi and VAc units come to the same value, 3.23. This result betrayed the assumption that copolymer chain has much longer VPi block at low conversion, which come to be shorter as the copolymerization proceeds due to the increase of relative amount of VAc in feed. This difference happens because thermodynamic theory considers the low conversion region only, where changes of mole ratio in feed can be neglected.

5. Conclusion

Thermodynamic parameters of copolymerization of VPi and VAc were determined by molecular simulation. These results show that the copolymerization of VPi and VAc is stable at 30 °C and most slowly progressed at about 50% of VPi content. Thermodynamic analysis of the copolymer also shows that the copolymer is composed of VPi and VAc short blocks when VPi content is of the value between 20 and 80%. If VPi content is lowered below 20%, there is a VAc block subdivided by an almost single VPi unit. There is a VPi block over 80% of VPi, with the same reason. In the near future, we will report on the relationship between copolymer composition and stereoregularity of resulting PVA.

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