피발산비닐과 아세트산비닐의 공중합에 관한 이론적 고찰

김한도, 김재필, 류원석*
서울대학교 재료공학부, *영남대학교 섬유패션학부

Theoretical Investigations on the Copolymerization of Vinyl Pivalate and Vinyl Acetate

Han Do Ghim, Jae Pil Kim, and Won Seok Lyoo*
Department of Materials Science and Engineering, Seoul National University, Seoul, Korea
School of Textiles, Yeungnam University, Kyongsan, Korea

1. Introduction

Thermodynamics of copolymerization is one of the fundamental elements for studying the effects of copolymerization parameters on the copolymer characteristics. 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, owing to the development 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. Poly(vinyl alcohol) (PVA) fiber is recognized as the best candidate because of its good machanical properties together with excellent resistance to alkalis[1,2]. PVA cannot be prepared by the direct polymerization due to tautomerism of vinyl alcohol monomer. Thus PVA is obtained by the saponification of poly(vinyl ester) like poly(vinyl acetate) (PVAc). In general, four polymerization methods of vinyl acetate (VAc) (bulk, solution, emulsion, and suspension) have been known.

In the present work, copolymerization of vinyl pivalate (VPi) and VAc was performed at 30 °C using 2,2′-azobis(2,4-dimethylvaleronitrile) (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. Experimental

2.1. 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.

2.2. Homopolymerization and copolymerization

100 ml of VPi and VAc mixture 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: poly(vinyl pivalate) in acetone/water, copoly(VPi/VAc) in methanol/water, and PVAc in acetone/n-hexane, respectively.

2.3. Acetylation of PVA

A mixture of 1 g of PVA, 2 ml of pyridine, 20 ml of acetic anhydride, and 20 ml of acetic acid was stirred in a three necked flasks at 100 °C for 24 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate PVAc. The PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

2.4. 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.

2.4. Molecular dynamics simulation

Activation energies were obtained using *Cerius*^{2} molecular dynamics simulation package with terminal model. Enthapy was recalculated from the activation energy by Evans method[3].

3. Results and Discussion

As reported in our previous study[4], polymerization rate of VAc is slower than that of VPi. Therefore, it was expected that polymerization rate of copolymer would be retarded by increasing VAc contents. Figure 1 shows the copolymerization rates with the copolymer composition. There was no abrupt increase in 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. Enthalpy, entropy, and gibbs free energy changes along the VPi molar content at 30 and 300 °C are shown in Figures 2 and 3. Above ceiling temperature, where ΔG is zero, propagation cannot have the priority any more 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 Figure 2, 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 Figure 1.

4. Reference

1) I, Sakurada, "Polyvinyl Alcohol Fibers" Marcel Dekker, New York, pp. 3-9, 361-389 (1985).
2) M. Masuda, "Polyvinyl Alcohol-Developments" John Wiley and Sons. New York, pp. 403-422, 711 (1991).
3) M. G. Evans, J. Gergely, and E. C. Seaman, *J. Polym. Sci.*, **3**, 866 (1948).
4) W. S. Lyoo, J. Blackwell, and H. D. Ghim, *Macromolecules*, **31**, 4253 (1998).
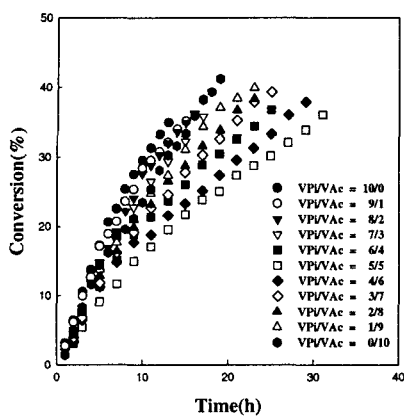
Figure 1. Copolymerization rate for various VPi/VAc feed ratio at polymerization temperature of 30 °C with reaction time. (ADMVN concentration was fixed at 1×10^{-4} mol/mol of comonomer).
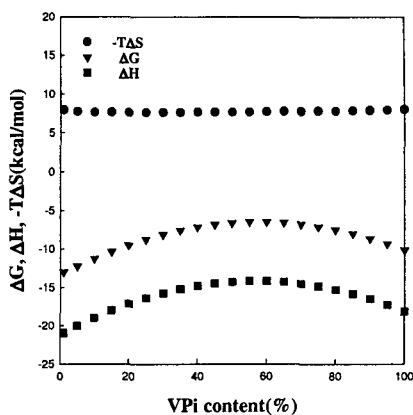
Figure 2. Changes in thermodynamic variables of copolymerization of VPi and VAc along the VPi content at 30 °C.
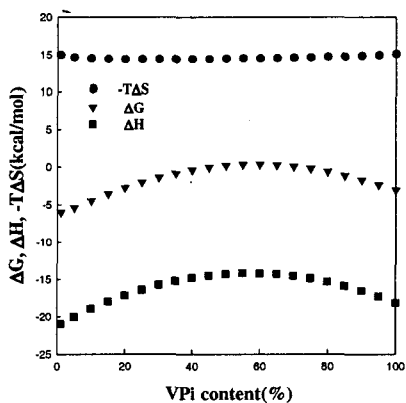
Figure 3. Changes in thermodynamic variables of copolymerization of VPi and VAc along the VPi content at 300 °C.