CHAPTER 2

METHODOLOGY

2.1   SYNTHESIS

2.1.1   Polymerization and Copolymerization

Vinyl acetate (VAc) used was a commercial product from Kuraray Co. In polymerization of VAc, methanol was mainly used as a solvent. It works as a chain-transfer reagent, and the degree of polymerization can be controlled by its amount. As an initiator of polymerization, 2,2'-azobis(isobutyronitrile) (AIBN) was mainly used. Benzoyl peroxide (BPO) was also used for copolymerization with a functional monomer containing nitrogen because BPO does not contain nitrogen and therefore it is useful for the precise chemical determination of modified PVAL by elementary analysis.

Copolymers of VAc and functional monomers were synthesized using a 5L-glass reactor equipped with a stirrer, a thermometer, a reflux condenser and an apparatus supplying solution continuously, as shown in Figure 13. All the copolymerization reactions were carried out in homogeneous system at boiling temperatures of the system, $60°$ to $62℃$ under the atmosphere of nitrogen gas. In order to obtain copolymers having homogeneous composition of monomer ratio at higher conversions during copolymerization, the "feeding-comonomer method" was adopted where the supply of the more rapidly consumed comonomer was replenished:[1,2] the solution of comonomer was supplied continuously. The supply speed was regulated on the basis of the solid content analyzed occasionally and the balance amount was calculated using the monomer reactivity ratios, r_1 and r_2. An example of copolymerization is shown in Figure 14, which shows the relationship among
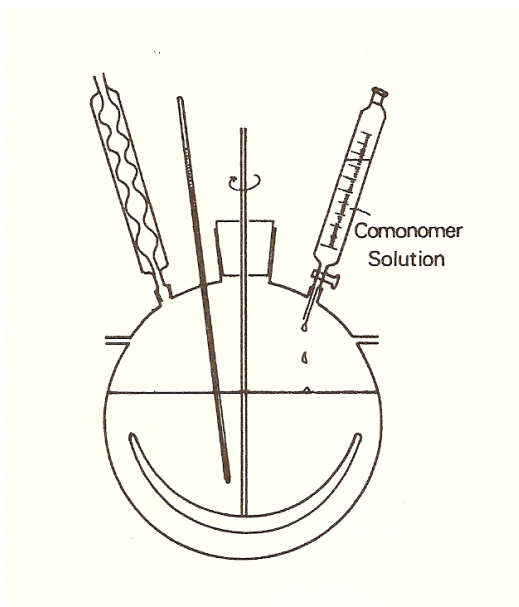
Figure 13 The reactor for copolymerization using "feeding-comonomer method".
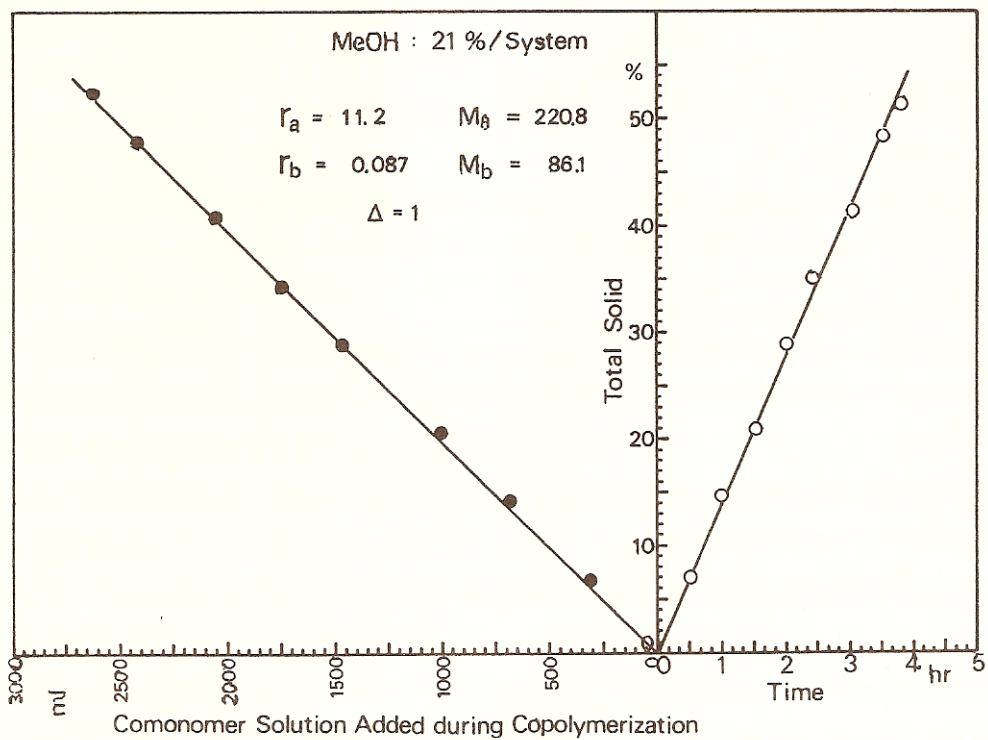
Figure 14 The relationship among copolymerization time, total solid and the amount of comonomer solution added in order to obtain a copolymer with homogeneous composition of monomer ratio at higher conversions.

copolymerization time, total solid and the amount of comonomer solution added.

The monomer reactivity ratios, r_1 and r_2, for the copolymerization of a functional monomer and VAc has been determined using the samples copolymerized at lower degrees of conversion of VAc under 5%.[3]

The copolymerization was finished by cooling the reactor and introducing air into it, and the residual VAc was distilled out by introducing methanol gas into the reactor under reduced pressure. The small amount of the modified PVAC was purified by reprecipitation of the methanol solution in water twice and analyzed using ^{1}H-NMR.

2.1.2 Equations for the "Feeding Comonomer Method"

2.1.2.1 Symbols

M_A, M_B Molecular weights of monomer A and B

$r_A,\ r_B$ Monomer reactivity ratios

$[A]\ [B]$ Mole amount of monomer A (More reactive monomer) and B in a reactor

Δ_A Mole fraction of monomer A in copolymer

$A,\ B$ Weight amount of monomer A and B in a reactor

A_0, B_0 Weight amount of monomer A and B in a reactor in the beginning

$[R]$ $[R] \equiv [A]/[B]$

$[f]$ $[f] \equiv d[A]/[B]$

R $R \equiv A/B = A_0/B_0$

f $f \equiv dA/dB$

k A Constant included in Mayo-Lewis equation

a Weight amount of monomer A fed

S_0 Weight amount of volatile component such as solvent in the beginning

$\alpha \cdot a$ Weight amount of solvent fed together with monomer A fed

β $\beta = 1$ when monomer A is volatile, otherwise $\beta = 0$

σ Weight fraction of solid content of system observed

C_B Conversion rate of monomer B

T Total charge weight in the beginning

G A constant defined by *Equation* (16)

2.1.2.2 Objective of Calculation

Input data: r_A, r_B Δ_A B_0 S_0 α β σ

Output data a C_B

2.1.2.3 Equations

1) Mayo-Lewis Equation

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} * \frac{r_A[A]+[B]}{[A]+r_B[B]} = \frac{[A]}{[B]} * \frac{r_A[A]/[B]+1}{[A]/[B]+r_B}$$ (1)

which can be simplified using $[R]$ and $[f]$ as follows:
$$[f] = k[R] \qquad (2)$$

where

$$k = \frac{r_A[A]/[B]+1}{[A]/[B]+r_B} = (r_A[R]+1)/([R]+r_B) \qquad (3)$$

2) Copolymer composition

Or
$$\Delta_A = [f]/([f]+1) \qquad\qquad [f] = \Delta_A/(1-\Delta_A) \qquad (4)$$

3) Weight amount

$$f = [f]M_A/M_B \qquad\qquad R = [R]M_A/M_B \qquad (5)$$

$$f = kR \qquad (6)$$

$$k = (r_A R + 1)/(R + r_B) \qquad (7)$$

4) Condition of constant ratio of monomers in system

$$R = A/B = A_0/B_0 \qquad (8)$$

5) Charge weight of monomer A in the beginning, A_0

$$A_0 = RB_0 = \frac{f}{k} \cdot B_0 = \frac{[f]M_A/M_B}{k} \cdot B_0 = \frac{M_A \cdot \Delta_A}{k \cdot M_B (1-\Delta_A)} \cdot B_0 \qquad (9)$$

$$R = \frac{M_A \cdot \Delta_A}{k \cdot M_B (1-\Delta_A)} \qquad (10)$$

6) Weight amount of monomers

From *Equation* (6)
$$\frac{A_0 + a - A}{B_0 - B} = k \cdot R \qquad (11)$$

$$A = A_0 - a/(k-1) \qquad (12)$$

$$B = A/R = B_0 - a/R(k-1) \qquad (13)$$

7) Relation between weight amount of monomer A fed, a, and solid content, σ.

$$\sigma = \frac{Copolymer + Non-volatiles}{Total\ Charge} = \frac{A_0 + a - \beta \cdot A + B_0 - B}{A_0 + a + B_0 + \alpha \cdot a} \qquad (14)$$

Using *Equations* (12) , (13) and the following T and G,

$$T = A_0 + B_0 + S \qquad (15)$$

$$G = (k - 1 + \beta + 1/R)/(k-1) \qquad (16)$$

$$a = \frac{T \cdot \sigma - A_0(1-\beta)}{G - \sigma(1+\alpha)} \qquad (17)$$

one obtains:

8) Conversion rate of monomer B

From *Equation* (14),
$$C_B \equiv (B_0 - B)/B_0 = \sigma \cdot T/B_0 + a/B_0 \cdot \{\sigma(1+\alpha) + \beta/(k-1) - 1\} - R(1-\beta) \qquad (18)$$

2.1.3　Alcoholysis and Preparation of Sample Products

　　Modified PVALs were obtained by alcoholysis of modified PVACs. The methanol solution of sodium hydroxide was added to the methanol solution of modified PVAC with stirring at 40℃. The addition of small amount of sodium hydroxide, 0.004 to 0.2 mole ratio to VAc units, was enough for alcoholysis for usual non-modified PVAC. On the other hand, more amount of sodium hydroxide was used in the cases of the modified PVACs containing the acidic group, -COOH, where alcoholysis occurred by sodium hydroxide exceeding the amount for neutralization . Modified PVALs having various degree of hydrolysis, DH, were obtained by controlling the amount of sodium hydroxide. Gelatinous PVAL generated by alcoholysis was ground, heated in the mixture of methanol, methyl acetate and small amount of water for removing residual sodium hydroxide, and dried. Some samples for analysis were washed in a Soxhlet's extractor with methanol and dried.

2.2　　CHARACTARIZATION AND STRUCTURAL ANALYSIS

2.2.1　General Characterization

　　General characterization of PVAL was based on the Japan industrial standard, JIS K6726-1977 or the method cited in the literature.[4]

Volatile Content　Approximately 5 g of sample is weighed into a standard weighing bottle and dried at 105 ± 2℃ until constant mass is obtained, then allowed to cool in a desiccator, and weighed again. The volatile content, R (%), is calculated by the formula,

$$R = 100 \times (s - w)/w$$

where s is mass of primary sample (g) and w is mass of dried sample (g).

Degree of Polymerization　Limiting viscosity number, $[\eta]$, was measured at 30℃ in water for non-modified PVAL and for modified PVALs with non-ionic groups. Aqueous solution of sodium chloride (1N) was used for modified PVALs with ionic groups. Viscosity-average degree of polymerization was calculated by using the equation presented by Sakurada.

$$Pv = ([\eta] \times 10^4/8.33)^{1.61,}.$$

Viscosity of aqueous solution　Viscosity of PVAL aqueous solution (4 wt%) was measured

using a Brookfield viscometer for samples giving clear solution as well as for samples showing opaque appearance. No viscosity data are shown for the samples generating insoluble gel in hot water and for the samples showing phase separation.

2.2.2　Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H-NMR spectra were obtained at 90MHz with Varian EM-390. For the measurement of ^{13}C-NMR, Varian HA-100 and Bruker SXP-4-100 were used at 25.144 and 22.63MHz, respectively. The latter is modified for pulse-Fourier transform spectrometer together with a Nicolet Model 1080-E computer while the former was interfaced with Varian DATA 620/I computer. As solvents and internal standard reagents, $CDCl_3$ and hexamethyldisiloxane were used for PVAC and modified PVACs, while D_2O and sodium trimethylsilylpropionate-d_6 were used for PVAL and modified PVALs.

2.2.3　Infrared (IR) Spectroscopy

IR spectra were obtained with IR-270 spectrometer from Shimadzu Corp. for the film samples of 10μ m thick.

2.2.4　Conductometric Titration

Conductometric titration was carried out using the CA-6A conductometer from Toa Electronics Ltd. for aqueous solution of modified PVALs. The sample of modified PVAL (3g) precisely weighed was dissolved in distilled water (100 ml) by heating. After cooling, N/2-sodium hydroxide aqueous solution (10 ml) was added and the solution was stored for 10 hours in a closed glass vessel. Standard N/10 sulfuric acid solution was used for the titration. From the titration amount between two crooked points observed in the data of conduction, the mole fraction of lactone generated between amido and hydroxyl groups as a side reaction was obtained. The value was corrected by the elimination of the effects of residual acetate group in the modified PVAL, which had been measured by ^{1}H-NMR or by

a chemical method, alkaline re-hydrolysis followed by acid titration.[5]

2. 3　NUMERICAL CALCULATIONS

　In order to analyze experimental results, numerical calculations have been carried out using BASIC. Typical calculations are as follows:

1) First-order Markoffian statistics: In analyzing sequence distribution of EVOH, calculation of "terpolymerization" has been performed considering the inversion addition of VAc monomer.

2) Conformational calculation:　Theoretical calculations have been performed for NMR vicinal coupling constants from interaction energies. Conformation of polymer chain has been calculated from the multiplication of matrices containing statistical weight factors.

3) Gel Network Formation:　Sol fraction and average polymerization degrees of sol part have been calculated as a function of crosslinking density based on the gel network formation theory presented by Flory,[6,7] Stockmayer,[8] Charlesby,[9] Scott[10] and others.

4) Swelling:　The equation presented by Flory[6] has been used for calculation.

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