

에틸렌과 α -올레핀의 기상 공중합 반응성비의 결정에 관한 이론적 연구

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Determination of Reactivity Ratios in Gas Phase Copolymerization of Ethylene/ α -Olefin

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요약 : 에틸렌과 α -올레핀의 기상 공중합용 촉매의 반응성비를 결정하기 위해, 기존의 공중합체의 조성을 이용하는 방법과는 달리, 압력변화와 공중합체의 중량과 같은 실험데이터를 사용하는 새로운 방법을 제시하였다. 계산되는 반응성비는 공중합체의 중량에 크게 의존하였으나 공중합체의 중량 대신 단량체의 조성을 측정하거나 중합반응을 높은 전환율에 이르기까지 지속시킬 경우 그 실험오차가 크게 개선될 것으로 예측되었다.

Abstract : A modified method is proposed for determination of the reactivity ratios of catalysts for gas phase copolymerization of ethylene and α -olefin. Experimental data such as pressure variation and copolymer weight are used instead of the copolymer compositions. Calculated values of the reactivity ratios depended strongly on the copolymer weight. However, the experimental error is expected to be reduced by measuring monomer compositions rather than copolymer weight, or by progressing the polymerization reaction to high conversions.

INTRODUCTION

Copolymerization of ethylene/ α -olefin becomes more important from industrial view point due to the increase in market share of linear low density polyethylene and ethylene-propylene rubbers. The properties of copolymers depend largely upon their composition, which are controlled principally

by the selection of appropriate catalysts. The performance of copolymerization catalysts can be evaluated by the reactivity ratios as well as their polymerization activity. The conventional methods for determination of the reactivity ratios require tedious measurement of the copolymer compositions.

In this study, we propose theoretically a modi-

fied method to obtain the reactivity ratios of gas phase copolymerization of ethylene/ α -olefin by measurements of pressure variation and copolymer weight, which is easier and more accurate than those of copolymer composition. This proposed method will be applied to the copolymerization of ethylene and propylene with Stauffer catalyst in near future.

DESCRIPTION OF THE METHOD

Reactivity ratios of copolymerization have been characterized conventionally by a number of methods.^{1,2,3} These methods require many sets of experimental data of copolymer compositions as a function of fractional concentration of monomers in the reaction medium to obtain reliable reactivity ratios. In addition, it is assumed that the composition of monomers should remain constant throughout the experiment. This cannot be achieved in a batch type reactor system especially when the reactivity ratios are quite different from each other. To avoid this problem, a semicontinuous reactor can be employed, in which monomers are kept flowing continuously into the reactor at a certain ratio. Large amount of monomers is needed to have a reaction medium of constant monomer composition.

The most difficult problem in determination of reactivity ratio lies in the fact that the composition of the copolymers should be measured, which has most frequently resorted to instruments such as IR or ¹³C-NMR. The former instrument can be easily accessible, however, the analysis could result in significant experimental error especially for crystalline polymers. The latter instrument should be operated at a high temperature to dissolve copolymers of poor solubility, and is not often available due to its excessive price. Of course, ¹³C-NMR has been used for the precise determination of reactivity ratios for ethylene/ α -olefin copolymerization.⁴⁻⁷ From these view points, a modified method for the determination of the reactivity ratios is proposed without measurement of the copoly-

mer compositions.

Experimental reactor system usually consists of a mixing chamber and a reactor. Gaseous monomers are mixed in a certain proportion in the mixing chamber at an elevated temperature to avoid from condensation problem, and allowed to flow into the reactor to start the copolymerization reaction. Let's consider ethylene/propylene gas phase copolymerization system as an example.

Propylene is introduced into the mixing chamber to a pressure of P_p , followed by addition of ethylene to a total pressure of P_t . Number of moles of propylene and ethylene can be found using the equations of state developed for P-V-T relationships of nonideal gases, and Benedict-Webb-Rubin equation⁸ can be used for this purpose.

Values of parameters for the Benedict-Webb-Rubin equation, such as B_o , A_o , C_o and so on, are given in a number of references.⁹ With P_p and volume of the mixing chamber, quantity of propylene added initially can be obtained by computing the density of propylene with the B-W-R equation(1). To calculate the number of moles of ethylene, the B-W-R equation can still be used employing a mixing rule as in equation(2)

$$P = RT\rho + (B_oRT - A_o - C_o/T)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + c\rho^3(1 + \gamma\rho^2)(e^{-\alpha a^2}) \quad (1)$$

$$\begin{aligned} \text{Mixing Rule : } B_o &= \sum_i X_i B_{oi} & b &= (\sum_i X_i B_{oi}^{1/3})^3 \\ A_o &= (\sum_i X_i A_{oi}^{1/2})^2 & a &= (\sum_i X_i a_i^{1/3})^3 \\ C_o &= (\sum_i X_i C_{oi}^{1/2})^2 & c &= (\sum_i X_i c_i^{1/3})^3 \\ \alpha &= (\sum_i X_i \alpha_i^{1/3})^3 & \gamma &= (\sum_i X_i \gamma_i^{1/3})^3 \end{aligned} \quad (2)$$

If a guessed value for number of moles of ethylene is taken, then mole fraction, X_i , and density, ρ , are given from the number of moles of propylene previously calculated. Values of parameters in the B-W-R equation for each monomer along with mole fraction, X_i , and density, ρ , are substituted in equation(1), and pressure, P , can be obtained.

Until P converges sufficiently to P_t , the proce-

cedure is repeated with a new guessed value for number of moles of ethylene to obtain the quantities of ethylene and propylene in the mixing chamber.

Now the valve connecting the mixing chamber to the reactor is fully opened. The pressure of the mixing chamber is equal to that of reactor at all times, which decreases as the polymerization goes on. It can be assumed that mole fraction of each monomer in the mixing chamber is identical to that in the reactor throughout the polymerization. This is because the degree of disorder, hence the partial molar entropy of each monomer in the two vessels is almost same with each other. That is why the present method is confined to a gas phase copolymerization, and the experimental system should be safe from any condensation.

At the end of polymerization, the final pressure, P_f is recorded, and the unreacted monomers are evacuated from the reactor to stop the reaction. Weight of the copolymer produced, W , is carefully measured.

Now let's take a guessed value for mole fraction of propylene, X_p , in the gas phase at the end of polymerization.

The mole fraction of propylene in the mixing chamber is also X_p as discussed above. The densities of the unreacted monomers in the mixing chamber and the reactor can be computed using the B-W-R equation with P_f and X_p . Then quantity of unreacted monomers in the reactor and the mixing chamber is obtained from the densities of unreacted monomers and the volumes of the two vessels. Therefore from the number of moles of ethylene and propylene introduced initially into the system, and from the quantities of the unreacted monomers, the weight of copolymer produced as well as its composition can be known as :

$$\text{Copolymer weight calculated} = (n_{P_o} - n_P) M_P + (n_{E_o} - n_E) M_E \quad (3)$$

$$\text{Copolymer composition} = \frac{(n_{E_o} - n_E) M_E}{(n_{P_o} - n_P) M_P + (n_{E_o} - n_E) M_E} \quad (4)$$

where n_{P_o} , n_P , n_{E_o} and n_E are initial and final number of moles of propylene and ethylene respectively. M_P and M_E are respective molecular weight of propylene and ethylene.

This procedure is reiterated taking a new guessed value of X_p unless the copolymer weight calculated is well close to that measured experimentally.

Conversion of the polymerization can be given as :

$$x = \frac{(n_{P_o} - n_P) + (n_{E_o} - n_E)}{n_{P_o} + n_{E_o}} \quad (5)$$

The determination of reactivity ratios is now considered. In this case, monomer composition has been changed, and the copolymerization equation is not valid any more. Skeist's equation¹⁰ (6) has been integrated by Meyer et al.¹¹

$$\ln(1-x) = \int_{f_{1o}}^{f_1} \frac{1}{F_1 - f_1} df_1 \quad (6)$$

to obtain equation(7), in which f_1 and F_1 correspond to monomer and copolymer compositions respectively.

$$1-x = \left[\frac{f_1}{f_{1o}} \right]^\alpha \left[\frac{1-f_1}{1-f_{1o}} \right]^\beta \left[\frac{f_{1o}-\delta}{f_1-\delta} \right]^\gamma \quad (7)$$

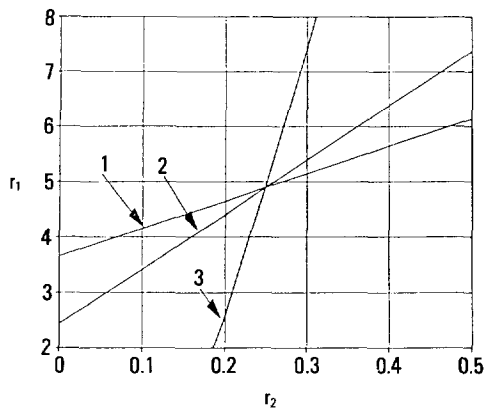
where $\alpha = \frac{r_2}{(1-r_2)}$, $\beta = \frac{r_1}{(1-r_1)}$, $\gamma = \frac{(1-r_1r_2)}{(1-r_1)(1-r_2)}$ and $\delta = \frac{(1-r_2)}{(2-r_1-r_2)}$ are functions only of reactivity ratios r_1 and r_2 .

$$\text{As } f_{1o} \left[= \frac{n_{E_o}}{n_{P_o} + n_{E_o}} \right], \quad f_1 \left[= \frac{n_E}{n_P + n_E} \right] \text{ and con-}$$

version x are given previously, a plot of r_1 as a function of r_2 can be drawn using equation(7). This is a nonlinear equation, nevertheless, the absence of multiple zeros makes simple numerical root finding techniques such as Bisection or Regula falsi be applicable for this purpose.

Fig. 1 shows an example of the plot between r_1 and r_2 . Reactivity ratios r_1 and r_2 can be determi-

Determination of Reactivity Ratios



Simulation Data	1	2	3
$P_p^{(atm)}$	3.0	4.0	5.0
$P_t^{(atm)}$	6.0	6.0	6.0
$P_r^{(atm)}$	4.3	4.3	2.4
$W^{(g)}$	4.5	4.8	28.1

Fig. 1. A plot of r_1 as a function of r_2 obtained from corresponding simulation data.

ned from the intersection of the lines constructed with corresponding simulation data.

APPLICABILITY OF THE METHOD

Temperature and pressure of the copolymerization system can be measured very accurately, while weight of the copolymer could be a source of experimental error. If experimental data resulted in some scatterness of the intersections in Fig. 1, it would indicate the significance of experimental error or violation of assumptions introduced in the present method.

Fig. 2 shows the copolymer weight as a function of r_1 for r_2 to lie within 5% and 10% error range around 0.25. It is to be noted that the weight of copolymer decreases as r_1 becomes larger and larger compared with r_2 . This is because the copolymer is getting more enriched in ethylene unit rather than propylene unit, and because more propylene molecules remain unreacted in the monomer

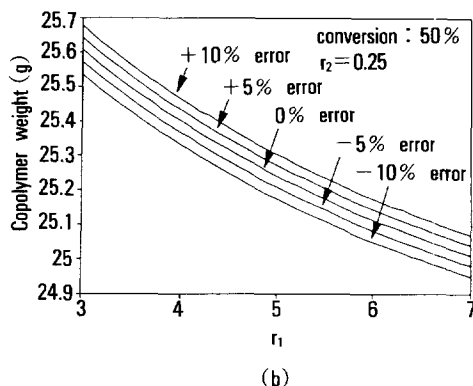
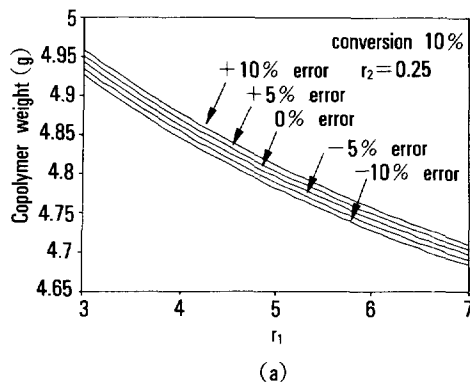


Fig. 2. Copolymer weight as a function of r_1 at $r_2 = 0.25 \pm 5\%$ and 10% error range.

phase, as r_1 overwhelms r_2 . Fig. 2-a indicates that accuracy of measurement of the copolymer weight is an important influential factor for the applicability of the present method. However, Fig. 2-b shows r_1 and r_2 become less sensitive to the copolymer weight as the conversion increases. The situation is also expected to be better when comonomer has higher molecular weight than propylene as in linear low density polyethylene.

Mole fraction of ethylene and propylene can be determined directly by measuring the compositions of reaction medium instead of the copolymer weight using gas chromatography if available. From the mole fraction of two monomers, the number of moles of unreacted monomers and the conversion are obtained to plot r_1 as a function of r_2 using equation (7).

Fig. 3 demonstrates monomer composition(mole

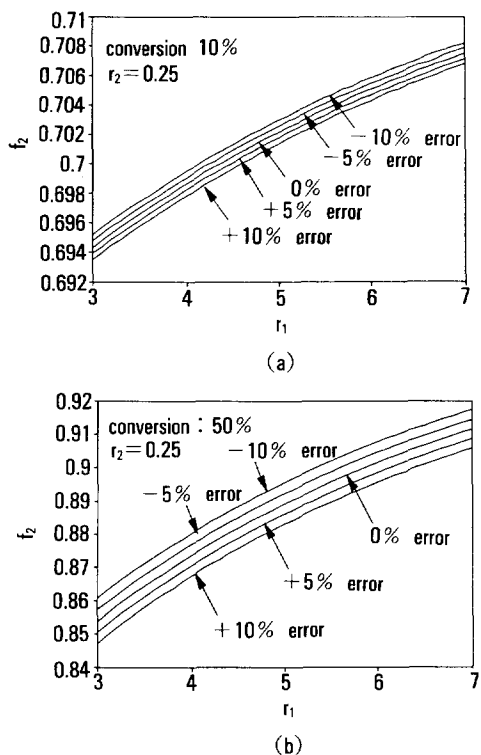


Fig. 3. Mole fraction of propylene as a function of r_1 at $r_2=0.25 \pm 5\%$ and 10% error range.

fraction of propylene) at a conversion of 10 and 50 % as a function of r_1 so that r_2 lies within 5 and 10% error range around 0.25.

Mole fraction of ethylene and propylene being needed rather than their absolute concentration, gas chromatography can give sufficiently accurate data by observing the ratio of the chromatographic peaks.

When the reactivity of catalyst toward different monomers changes with polymerization time, the composition of monomers and pressure variation should be measured continually. Reactivity ratios as a function of polymerization time can be found from the intersection of lines corresponding to the two neighboring sets of experimental data.

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