

## 펄스 레이저유도 중합 기법을 이용한 공중합 반응역학 모델의 규명

김 양 수\*† · K. F. O'Driscoll

캐나다 워털루대학교 화학공학과, \*인제대학교 화학공학과

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### Discrimination of the Copolymerization Kinetic Model Using a Pulsed Laser-induced Polymerization Technique

Yangsoo Kim\*† and K. F. O'Driscoll

Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

\*Dept. of Chemical Engineering, Inje University, 607 Obang-dong, Kimhae, Kyongnam 621-749, Korea

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**요 약:** 공중합 반응모델을 규명하기 위하여 pulsed UV-laser light source를 이용하여 얻어진 공중합체의 GPC chromatogram 분석을 수행함으로써 반응초기의 단량체 혼합물 구성에 따라 변화하는 공중합 반응의 총괄 성장반응 속도상수 ( $k_p$ )값을 결정하였다. 이때 공중합체 분자량 결정의 신뢰성을 높이기 위하여 GPC 분석은 UV/DRI 및 on-line viscometer를 multi-detector로 이용하였다. Butyl acrylate (BA)-methyl methacrylate (MMA) 공중합의 경우 공중합 조성의 관점에서는 terminal model을 잘 따르나  $k_p$ 에 대하여는 penultimate model에 의하여 공중합 성장반응이 설명되어졌으며, 대부분의 penultimate model을 따르는 공중합계에서와 마찬가지로 BA-MMA계에서도  $r_1 r_2 = s_1 s_2$ 의 관계가 성립되었다. 한편, Lewis acid로서 zinc chloride가 소량 첨가된 styrene (ST)-MMA 공중합계에 PLP 방법을 적용한 결과  $k_p$ 에 관하여 terminal model이 적용되었으며 이것은 동일한 공중합계에 Lewis acid를 첨가하지 않았을 경우와 전혀 다른 결과를 보여주었다. 공중합 반응의 성장반응 속도는 Lewis acid를 첨가함으로써 크게 증가되었다.

**ABSTRACT:** In an effort to discriminate the copolymerization kinetic model, the overall propagation rate constant ( $k_p$ ) depending upon the feed monomer composition was determined by analyzing the copolymer formed using a pulsed UV-laser light source. A reliability of the copolymer molecular weight estimation was improved by carrying out the combined analysis of UV/DRI and on-line viscometer as a multi-detector in the GPC analysis of the copolymer produced. The butyl acrylate (BA)-methyl methacrylate (MMA) copolymerization was characterized by the terminal model with respect to the copolymer composition, however, it conformed to the penultimate model regarding  $k_p$ . The relationship,  $r_1 r_2 = s_1 s_2$ , which is known to be held in the most copolymerization systems characterized by the penultimate propagation model, has been also proved in the BA-MMA copolymerization. The application of a PLP technique to the ST-MMA copolymerization in the presence of zinc chloride showed the terminal model different from the same copolymerization system in the absence of Lewis acid which is characterized by the penultimate model with respect to the overall propagation rate constant. It has been also shown that the addition of zinc chloride causes to increase the propagation rate remarkably.

**Keywords:** copolymerization model, terminal model, penultimate model, overall propagation rate constant, copolymer composition.

## INTRODUCTION

Most of the commercially important polymers are co- or ter-polymers composed of more than two components and they are mainly produced by the chain growth or step growth reaction mechanism. The properties of copolymer are depending upon its composition and thus the copolymer composition distribution is to be as narrow as possible in order to obtain a copolymer with desired properties. Therefore, a copolymerization reaction has to be controlled to produce a product of a desirable level of composition. And it is indispensable to have a well-defined reaction model for accomplishing the control objectives.

The reaction kinetics of free radical chain copolymerization is affected by the place and function of active center (i.e., free radical), and there are several reaction kinetic models proposed, which are terminal model, penultimate model, complex participation model, copolymerization with depropagation model, etc. The model discrimination between these reaction models is a prerequisite and important task for the reaction control purpose. Also how to efficiently and correctly carry out the model discrimination procedure has been an important research topic over several decades.<sup>1-4</sup>

The reliable parameter estimation of reactivity ratios involved in the free radical chain copolymerization reaction models is the first important step in the model discrimination procedure, and the efficient experimental design as well as a EVM (error in variables method)-type parameter estimation technique are necessary.<sup>5</sup> The next step is a determination of which experimental data are well fit to the reaction models. Copolymer composition,<sup>6</sup> sequence length distribution,<sup>6</sup> overall rate of copolymerization,<sup>7</sup> and overall propagation rate constant<sup>8</sup> depending upon the feed monomer composition are used to discrimi-

nate a reaction kinetic model between the models. However, Hill et al.<sup>6</sup> stated that the copolymer composition can only explain the experimental data in order to discriminate the reaction model. Also the experiments on the sequence length distribution and the overall rate of copolymerization could bring about severe measurement errors due to the complexity of experimental measurements.

Olaj et al.<sup>9</sup> developed a technique which utilizes a pulsed UV-laser light source to independently evaluate a propagation rate constant in the free radical chain polymerization. They showed that a propagation rate constant can be obtained from an analysis of the molecular weight distribution (MWD) by gel permeation chromatography (GPC) of the polymer produced by a pulsed laser-induced polymerization (PLP). It has been proved<sup>10</sup> that this PLP technique is characterized by the experimental simplicity and the reliability of rate data when compared with the conventional methods such as rotating sector<sup>11</sup> and spatially intermittent polymerization technique.<sup>12</sup> Davis et al.<sup>13,14</sup> applied this technique to a variety of copolymerization systems and carried out the model discrimination with success.

A determination of overall propagation rate constant in the free radical copolymerization by the PLP technique is highly relied on the correct measurement of the molecular weight of copolymer produced. In general, the copolymer molecular weight is determined by the weighted average procedure considering its composition and the equivalent homopolymer molecular weight of the corresponding component, which is estimated by the universal calibration method.

The universal calibration procedure requires the Mark-Houwink constants for the corresponding homopolymer, however, it has not been known the Mark-Houwink constants for many polymer systems (e.g., polybutylacrylate and polymethylacrylate etc.). Then the unknown Mark-Houwink

constants can be experimentally determined<sup>15,16</sup> and it gives rise to a large uncertainty in the copolymer molecular weight. It has been recently reported<sup>17</sup> that the utilization of multi-detector system as a GPC detector, which is a combination of on-line viscometer and a concentration detector (i.e., UV or DRI), attests an efficient and reliable molecular weight determination method by using a different molecular weight series of very narrow monodisperse polystyrene standard samples without relying on the universal calibration procedure.

In this study, butyl acrylate (BA)-methyl methacrylate (MMA) and styrene (ST)-MMA with Lewis acid (i.e.,  $\text{ZnCl}_2$ ) have been copolymerized using a pulsed UV-laser light source, and then the overall propagation rate constants varying with the copolymer feed composition were estimated for the purpose of copolymerization reaction model discrimination. A GPC was equipped with UV/DRI and on-line viscometer as a detector.

## EXPERIMENTAL

**Materials.** The monomers were purified from inhibitor by washing with aqueous sodium hydroxide, drying over calcium hydride, and finally distilling in an atmosphere of nitrogen under reduced pressure. The initiator, 2,2'-azobisisobutyronitrile (AIBN), was recrystallized from methanol solution, zinc chloride was dried blowing off hot nitrogen gas and then used without further purification, and other materials were used as supplied.

**Laser-induced Polymerizations.** The distilled monomers and initiator, if necessary together with  $\text{ZnCl}_2$ , were transferred to Pyrex ampoules (square cells:  $1 \times 1$  cm) and subsequently degassed and sealed. The reaction mixture was kept in liquid nitrogen until required. The PLP experimental set-up used in this study and the polymerization procedure were the same as the report

by Davis et al.<sup>10</sup> only except that the pulse repetition rate of the laser was controlled by four channel digital delay/pulse generator (Model DG535; Stanford Research Systems Inc.). The polymerization was carried out at 298 K.

**Analysis.** The copolymer composition was determined by considering the corresponding characteristic proton peak area by means of  $^1\text{H}$ -NMR. The chain length of copolymer formed between successive laser pulses were determined by using the combined analysis of dual GPC detector system. The on-line viscometer detector signal generates the data of  $[\eta]_i \cdot C_i$  and the differential refractive index (DRI) signal gives  $C_i$  data. Then the combination of these two detector signals for the polymer standards generates the viscosity calibration data. Also the hydrodynamic volume ( $[\eta]_i \cdot M_i$ ) calibration for the narrow disperse polystyrene standards enables an exact molecular weight determination of the copolymer without using the universal calibration method. The molecular weight ( $M_{\text{copolymer}}$ ) of the copolymer formed between successive laser pulses is then determined by following the above procedure, and thus it allows the estimation of the copolymer chain length ( $\nu_{\text{copolymer}}$ ) based on the weighted average procedure.

$$M_{\text{copolymer}} = \nu_1 \left[ (M_1)_0 + \frac{F_2}{F_1} (M_2)_0 \right]$$

$$\nu_{\text{copolymer}} = F_1 \cdot \nu_1 + F_2 \cdot \nu_2$$

Here  $F_i$ ,  $(M_i)_0$ , and  $\nu_i$  are the copolymer composition (i.e., the mole fraction of component  $i$  in the copolymer), the molecular weight of monomer  $i$ , and the equivalent chain length of homopolymer  $i$ , respectively.

Davis et al.<sup>10</sup> described how to determine the propagation rate constant using the PLP technique. And thus the monomer concentration

( $[M]$ ) from the total monomer conversion obtained by a gravimetric method, the dark time between successive laser pulses ( $t_f$ ), and  $\nu_{\text{copolymer}}$  are the necessary data. Then  $k_p$  for the copolymerization can be obtained by the following simple equation.

$$\nu_{\text{copolymer}} = k_p [M] t_f$$

## RESULTS AND DISCUSSION

**Characteristics of Terminal and Penultimate Model in the Propagation Kinetics of Copolymerization.** The copolymerization propagation rate constant ( $k_p$ ) and the copolymer composition ( $F_1$ ) are expressed by the following equations.<sup>18</sup>

$$k_p = \frac{r_1(f)f_1^2 + r_2(f)f_2^2 + 2f_1f_2}{\frac{r_1(f)f_1}{k_1(f)} + \frac{r_2(f)f_2}{k_2(f)}}$$

$$F_1 = \frac{r_1(f)f_1^2 + f_1f_2}{r_1(f)f_1^2 + r_2(f)f_2^2 + 2f_1f_2}$$

Here  $r_i$  is the reactivity ratio (i.e.,  $k_{ii}/k_{ij}$ ),  $f_i$  the mole fraction of component  $i$  in the feed monomer mixture, and  $k_i$  is the propagation rate constant. Also  $k_i(f)$  and  $r_i(f)$  represent that they are the composite function of  $f$ .

In the terminal model assuming that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain, it holds the following relationship.

$$k_i(f) = k_{ii}$$

$$r_i(f) = r_i$$

However, the penultimate model indicating that

the reactivity of the propagating species is affected by the next-to-last or penultimate monomer unit has the following complex functional relationship:

$$k_i(f) = k_{iii} \frac{r_{ii}f_i + f_i}{r_{ii}f_i + f_i/s_i} \quad (i \ \& \ j=1, 2; i \neq j)$$

$$r_i(f) = r_{ii} \frac{r_{ii}f_i + f_i}{r_{ii}f_i + f_i}$$

Here the monomer reactivity ratios,  $r_{ii}$  and  $r_{ji}$ , are defined as follows:

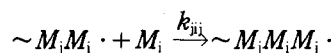
$$r_{ii} = k_{iii}/k_{ij} \quad (\equiv r_i)$$

$$r_{ji} = k_{jii}/k_{ji} \quad (\equiv r_i')$$

Also the radical reactivity ratio ( $s_i$ ) is characteristic of the penultimate model.

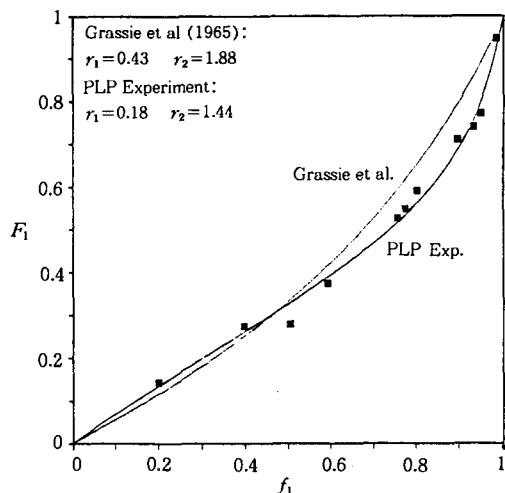
$$s_i = k_{jii}/k_{iii}$$

These reactivity ratios reveal that there are the following eight different propagating steps characterizing the penultimate kinetic model.



If  $s_1 = s_2 = 1$ ,  $r_1 = r_1'$  (i.e.,  $r_{11} = r_{21}$ ), and  $r_2 = r_2'$  (i.e.,  $r_{22} = r_{12}$ ), then the penultimate model is equivalent to the terminal model. Also if the copolymer composition measurements conform to the terminal model, then the relation,  $r_i = r_i'$ , holds.

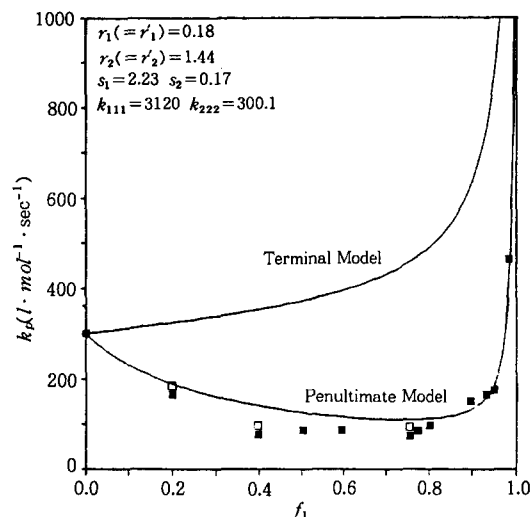
**Estimation of Reactivity Ratio for the Copolymerization of BA and MMA.** Fig. 1 shows the copolymer composition,  $F_1$  (i.e., the mole fraction of BA component in the copolymer) depending upon the feed composition,  $f_1$  (i.e., the mole fraction of BA in the BA(1)/MMA(2) mono-



**Figure 1.** Copolymer composition ( $F_1$ ) profile depending upon the feed monomer composition ( $f_1$ ) for the BA(1)-MMA(2) copolymerization. Symbols denote the experimental data points and the lines are the model predictions based on the terminal model.

mer mixture). The symbols are the experimental measurements for the copolymer produced by the PLP technique and the solid line represents the model prediction based on the terminal model. The reactivity ratios,  $r_1 (=0.18)$  and  $r_2 (=1.44)$ , have been determined by the EVM-type parameter estimation technique. Grassie et al.<sup>19</sup> reported  $r_1 = 0.43$  and  $r_2 = 1.88$  in the same copolymerization system, however, it shows that the terminal model prediction based on the reported reactivity ratio is comparable to that based on the reactivity ratio estimated in this study. Thus the copolymer composition depending upon the feed monomer composition in the copolymerization of BA and MMA is characterized by the terminal model.

**Propagation Kinetics for the Copolymerization of BA and MMA.** Fig. 2 shows the overall propagation rate constant ( $k_p$ ) of the copolymerization of BA and MMA depending upon the feed composition ( $f_1$ ). The symbols represent the experimental data obtained by the PLP technique and the two lines show the model



**Figure 2.** Overall propagation rate constant ( $k_p$ ) depending upon the feed monomer composition ( $f_1$ ) for the BA(1)-MMA(2) copolymerization. Symbols denote the experimental data points and the lines are the model predictions. Unfilled symbols indicate the experimental reproducibility.

predictions by the terminal and the penultimate model, respectively. In the penultimate model prediction,  $r_1 = r'_1$  and  $r_2 = r'_2$  have been assumed since the copolymer composition is characterized by the terminal model. And the homopropagation rate constant at 298 K for BA ( $k_{111}$ ) was determined from the Arrhenius-type rate constant equation reported by Heuts et al.<sup>20</sup> They obtained a highly reliable propagation rate constant data for BA using a PLP technique at very low temperatures ( $-40 \sim -10^\circ \text{C}$ ). The propagation rate constant at 298 K for MMA ( $k_{222}$ ) was taken from the data determined using a PLP technique by Davis et al.<sup>10</sup> The unknown radical reactivity ratios for the penultimate model prediction,  $s_1$  and  $s_2$ , were estimated using a standard optimal parameter estimation technique (Rosenbrock's direct search method<sup>21</sup> for the comparison of experimental data with the model predictions for  $k_p$ ). Fig. 2 clearly shows the the copolymerization of BA and MMA is characterized by the penultimate model

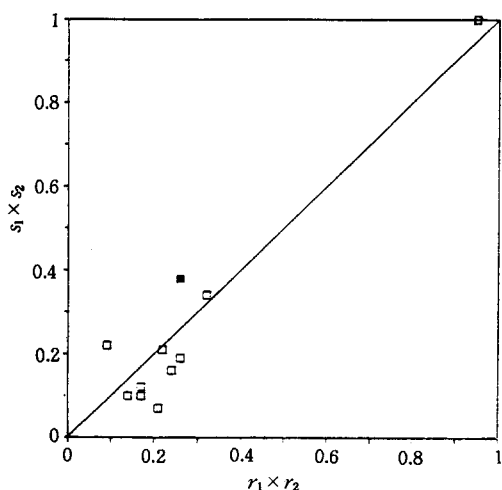
rather than the terminal model in the propagation step.

Fukuda<sup>18</sup> showed that many copolymerization systems characterized by the penultimate propagation model satisfies the following relationship between  $r_1$  and  $s_1$ .

$$r_1 r_2 = s_1 s_2$$

Fig. 3 shows that the copolymerization of BA and MMA (filled symbol) does also support that along with several other copolymer systems (un-filled symbols) known to be characterized by the penultimate model, of which the monomer reactivity ratios and the radical reactivity ratios are listed in Table 1 with the corresponding references.

**Propagation Kinetics for the Copolymerization of ST and MMA in the Presence of Lewis Acid.** It has been known<sup>22</sup> that the copolymerization of ST and MMA confirms to the terminal model with respect to composition, how-



**Figure 3.** Relationship of  $r_1 \times r_2$  vs.  $s_1 \times s_2$  in a variety of copolymerization systems characterized by the penultimate model. The filled symbol corresponds to the BA-MMA copolymerization and the others the copolymerization systems listed in Table 1. The solid diagonal line is  $r_1 \times r_2 = s_1 \times s_2$ .

**Table 1. Monomer Reactivity Ratio ( $r_i$ ) and Radical Reactivity Ratio ( $s_i$ ) for a Variety of Copolymerization Systems Characterized by the Penultimate Model**

$M_1$	$M_2$	$r_1$	$r_2$	$s_1$	$s_2$	$r_1 r_2$	$s_1 s_2$	Method	Ref.
BA	MMA	0.18	1.44	2.23	0.17	0.26	0.38	PLP	this study
ST	MMA	0.52	0.46	0.30	0.52	0.24	0.16	RS	18
ST	MMA	0.53	0.39	0.27	0.27	0.21	0.07	RS <sup>a</sup>	18
ST	EMA	0.62	0.35	0.46	0.45	0.22	0.21	PLP	25
ST	BMA	0.72	0.45	0.50	0.67	0.32	0.34	PLP	25
ST	LMA	0.57	0.45	0.59	0.33	0.26	0.19	PLP	18
ST	MA	0.73	0.19	0.94	0.11	0.14	0.10	PLP	14
ST	BA	0.95	0.18	0.90	0.11	0.17	0.10	PLP	14
pMOS	MMA	0.32	0.29	0.36	0.60	0.09	0.22	PLP	18
pCS	MA	1.21	0.14	0.35	0.35	0.17	0.12	RS	18
pMOS	ST	0.82	1.12	1.0	1.0	0.95	1.0	PLP	25

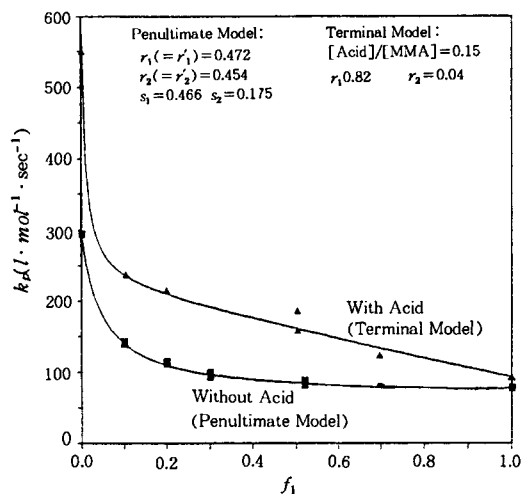
<sup>a</sup> In the presence of toluene.

EMA : ethyl methacrylate, BMA : butyl methacrylate, LMA : lauryl methacrylate, MA : methyl acrylate, pMOS : para-methoxy styrene, pCS : para-chloro styrene, RS : rotating sector method.

ever, it entirely fails to conform to that with respect to the overall propagation rate constant ( $k_p$ ). Davis et al.<sup>8</sup> obtained the same results for the ST-MMA copolymerization by using a PLP technique to measure  $k_p$ , and thus they claimed the penultimate model for the propagation step.

Hirai et al.<sup>23</sup> claimed the high alternating tendency for the ST-MMA copolymerization in the presence of zinc chloride ( $ZnCl_2$ ) as a Lewis acid and they postulated the complex formation reaction mechanism. Also the propagation rate for the homopolymerization of MMA in the presence of zinc chloride is known to be highly increased, in which the Lewis acid can enter into the complex formation with monomer causing a significant change in reactivity by perturbation in the electron density of the monomer.<sup>24</sup>

Fig. 4 shows the addition of Lewis acid increases the overall propagation rate constant for the ST-MMA copolymerization and also affects the propagation kinetics. The exact measurement of the overall propagation rate constant through the



**Figure 4.** Overall propagation rate constant ( $k_p$ ) depending upon the feed monomer composition ( $f_1$ ) for the ST(1)-MMA(2) copolymerization with and without Lewis acid. Symbols denote the experimental data points and the lines are the model predictions. Experimental results for the ST-MMA copolymerization without acid were taken from the report by Davis et al. (1989).<sup>8</sup>

PLP technique reveals that the transformation of propagation kinetics between two models is caused by the addition of Lewis acid. However, it needs to be further studied to obtain a supporting propagation kinetic mechanism involved in the complex formation for monomers and zinc chloride.

## CONCLUSION

The measurement of overall propagation rate constants for the BA-MMA copolymerization using a PLP technique showed that the propagation kinetics conforms to the penultimate model, while the copolymer composition is represented by the terminal model. The relationship,  $r_1 r_2 = s_1 s_2$ , which is known to be held in the most copolymerization systems characterized by the penultimate propagation model, has been also

proved in the BA-MMA copolymerization. The application of a PLP technique to the ST-MMA copolymerization in the presence of zinc chloride showed the terminal model different from the same copolymerization system in the absence of Lewis acid which is characterized by the penultimate model with respect to the overall propagation rate constant. It has been also shown that the addition of zinc chloride causes to increase the propagation rate remarkably.

The PLP technique is a highly reliable method for the discrimination of the copolymerization kinetic model through the exact estimation of the overall propagation rate constant. A reliability of the overall propagation rate constant measurement using a PLP technique in the copolymerization is further improved when the combined analysis of on-line viscometer and DRI is carried out in the GPC analysis of the copolymer produced.

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