

The Kinetics and Mechanism of the Core-shell Styrene-butyl Acrylate Polymerisation

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Abstract: *The kinetics and mechanism for the synthesis of core-shell styrene-butyl acrylate was studied in this research using two methods: the first involved determining the number of polymers produced as a solid content with respect to time; the second consisted of determining the unreacted monomer concentration with respect to time with gas chromatography (GC). Based on the reaction rate equation obtained from the experiment, the equation for the reaction rate for each stage can be predicted. The order of styrene in the core-shell synthesis calculated from the experiment is supported by the estimation of the derived reaction mechanism. The order of the ammonium persulphate (APS) initiator and the order of the sodium lauryl sulphate (SLS) surfactant, obtained from the experiment, are not suitable for the estimated mechanism, which caused initiators and surfactants to play roles only in the first step of the reaction, at the time of core formation or during nucleation. The order of butyl acrylate in the styrene core grafting obtained from the experiment is supported by the result of the mechanism estimation that is thus derived.*

Keywords: core-shell, styrene-butyl acrylate, solid content, ammonium persulphate, sodium lauryl sulphate

1. INTRODUCTION

At present, the research concerning colour effects involves many interesting areas of study, including which colours may be produced by light reflection and the synthesis of emulsion polymers with core-shell morphology. Core-shell emulsion polymers have potential as a new material group for colour effects in applications such as coatings. This colour effect occurs because the monodispersed particles are arranged in an orderly manner in the face-centred cube crystal (fcc) and can reflect visible light.¹⁻⁴

A deep and detailed study on core-shell emulsion polymer synthesis does not exist today, and instead studies mainly involve the kinetics of core-shell polymers. A study on emulsion polymerisation kinetics, especially with core-shell polymers, is an interesting undertaking. Smith and Ewart⁶ presented a theory in their quantitative experiment, and the Harkins⁵ micellar theory is the basis of the theory for emulsion polymerisation kinetics. Smith and Ewart⁶ found

the connection equation of the number of particles or polymerisation rates as a function of surfactant and initiator concentrations.^{2,5,6}

The other theory for emulsion polymer reaction kinetics was presented by Fitch and Tsai¹⁰, based on the idea of self-nucleation from oligomer radicals constructed from the aqueous phase. The mechanism of this formation, as quantitatively determined by Fitch and Tsai¹⁰, not only explains the mechanism of nucleation in the emulsion polymer but also emphasises the importance of micelles and the absorption process and reactions in micelles. In general, a droplet monomer is believed to have no role in the emulsion polymerisation except as the source of monomers. Hansen and Ugelstad⁷ showed that there are three models for particle nucleation, namely micellar, homogeneous and droplet-initiated mechanisms.⁷⁻¹⁰

The other researchers such as Alexander and Napper¹¹, Harada *et al.*¹² and Barrett¹³ said that primary radicals are formed by the decomposition of initiators in the aqueous phase. If the initiators are ionic, then the radicals will be soluble in water, and they will seldom be absorbed directly into micelles or particles. If monomers are added to the aqueous phase, then monomer radicals are formed, which usually build into an oligomer that becomes the first step in the process of nucleating particles. The existence of an oligomer in the system has been analysed with gel permeation chromatography (GPC) by Fitch and Tsai¹⁰, Goodall *et al.*¹⁴ and Chen and Piirma¹⁵. The oligomers will be absorbed by micelles to form polymer particles and oligomers that may be soluble in water, damaged or unable to form nucleation particles.¹⁰⁻¹⁵

Ramos *et al.*¹⁶ conducted a study on styrene polymerisation kinetics using batch methods by comparing the influences of anionic and cationic polymerisation. The difference between anionic and cationic polymerisation was explained in terms of the particle coagulation, which is monitored by the cationic surfactant and the high rate of radical formation of cationic initiators. The polymerisation rate increases with increasing surfactant and initiator concentrations, both in the anionic and in the cationic polymerisations.¹⁶

This research is a follow-up study of previous polymer core-shell syntheses¹⁷ that uses a styrene monomer as the core and butyl acrylate monomer as the shell with the cross-linking agent glycidyl methacrylate (GMA). This research focuses on the study of the kinetics of polymerisation of the styrene core and butyl acrylate shell formation experimentally and estimates of the emulsion polymerisation mechanism of synthesis for the obtained core and shell. The determination of the polymerisation reaction kinetics of the styrene core and butyl acrylate shell is performed with two methods: the first involves measuring the number of emulsion polymers that are formed as the solid content, calculated

as a conversion percentage; and the second involves measuring the number of remaining styrene monomers with gas chromatography (GC).

2. EXPERIMENTAL

2.1 Materials

Styrene and butyl acrylate (Nippon Shokubai, Japan) were used as the monomers, sodium lauryl sulphate (SLS; Merck, Germany) as the surfactant, ammonium persulphate (APS; Merck) as the initiator and acrylic acid (Nippon Shokubai) as the stabiliser monomer. GMA (Merck) was used as the cross-linking monomer. KOH (Merck) was used as the pH neutraliser with demineralised water. Hydroquinone (Merck) was used as the reaction stopper in the determination of the solid contents, and isopropanol (Merck) was used to stop the reactions in the analysis with GC.

2.2 Experimental Procedure

The polymerisation technique used was the semicontinuous seeded emulsion polymerisation method, in which some water, styrene and SLS were initially charged into a reactor to form the seed, after which APS was added directly (shot). After the entire amount of APS was added, the remaining water, styrene and SLS (pre-emulsion) was conducted into a reactor containing the initial charge. Then, post polymerisation or ageing was conducted for 2 hours, and the second addition of APS was performed for the grafting process of butyl acrylate on the styrene core or butyl acrylate shell formation. Subsequently, the feeding of pre-emulsion butyl acrylate continued, and the ageing process was then conducted for an additional 2 hours.

For kinetic measurement of the core styrene, the concentration range of styrene was 15%–25%, that of SLS was 0.5–2.0 CMC (critical micelle concentration), and that of APS was 0.034%–0.140%; for kinetic measurements of the shell butyl acrylate shell, the range of concentrations of butyl acrylate was 9.9%–12.6%, that of SLS was 0.1–0.4 CMC, and that of APS was 0.01%–0.04%.

2.3 Determination of Solid Content over Time

To determine the solid content or the amount of styrene core emulsion polymer that formed, sampling was conducted every 15 minutes for 2 hours. About 2 g of the sample was added to 2 ppm of hydroquinone, and it was then weighed and dried in an oven at 105°C for 2 hours. The same procedure was carried out for the formation of the shell or the grafting of butyl acrylate onto the

styrene core. Initial monomer concentration varied, such that the theoretically obtained solid content value also varies, and this must be put in terms of conversion. Conversion is the experimental solid content value divided by the theoretical solid content value multiplied by 100%.

2.4 Determination of the Remaining Monomer Concentration with GC

To determine the amount of unreacted styrene monomer, GC was used. Sampling was performed every 15 minutes, where 1 g of emulsion polymer was added to 25 ml of isopropanol. Then, it was measured by GC. The sampling was performed for 2 hours. The same procedure was carried out for the formation of the butyl acrylate shell.

3. RESULTS AND DISCUSSION

3.1 The Reaction Order of Styrene

The rate of the emulsion polymerisation reaction for each reaction step, which consists of initiation, propagation and termination, has never been monitored experimentally because of the difficulty of the technique with respect to kinetic studies and the inability to directly measure the polymerisation rate for each step. The technique used here to describe the reaction rate in this research utilises two methods: the first is a gravimetric technique where the emulsion polymer formed is measured; the second is a concentration measurement of the unreacted monomer reactant using GC. The gravimetric measurements of the emulsion polymer with respect to time gives a $\log [\text{conversion/minute}]_0$ and the logarithm of initial styrene concentration is $\log [\text{styrene}]_0$ [Fig. 1(a)]. The measurement technique with GC, in which the concentration of the unreacted styrene is measured with respect to time, involves an initial rate logarithm curve that gives $\log [\text{styrene/minute}]_0$ to $\log [\text{styrene}]_0$ [Fig. 1(b)].

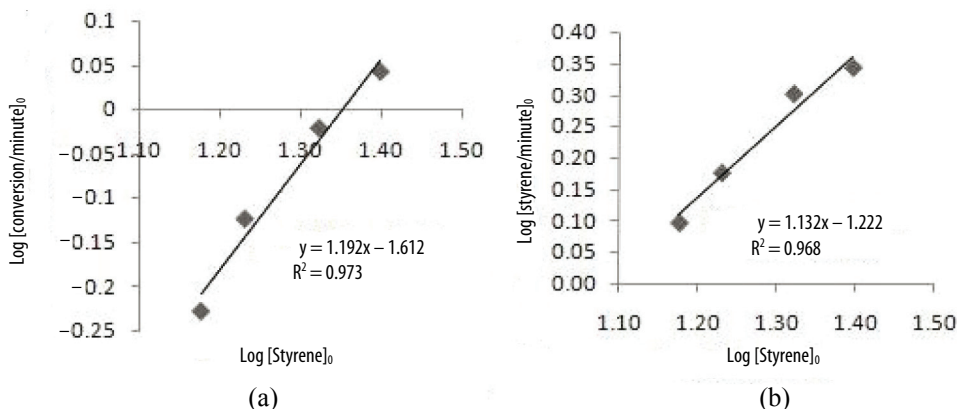


Figure 1: Log of the initial rate to log of the initial styrene concentration.

The styrene order obtained with the gravimetric method was 1.192, and the styrene order obtained with the GC method was 1.132. Results of the two methods did not show any significant difference. Therefore, the exponent obtained for the monomer concentration with reaction rate (R_p) was $R_p = [\text{styrene}]^{1.2}$. This order value was larger than in the theory proposed by Smith and Ewart⁶, in which it was quantitatively derived that the exponent obtained from the monomer is one. This is because the emulsion polymerisation process used in this research is the seeded semicontinuous method. In this method, the ability of a seed to grow is mainly influenced by the monomer concentration in the feeding step. With an increase in the monomer concentration, the reaction rate becomes larger than the rate proposed by the Smith and Ewart theory.⁶

3.2 The Reaction Order of SLS

The influence of surfactant concentration on the reaction rate is observed from the number of micelles formed. The bigger the SLS concentration, the more micelles formed. The micelles work to absorb the monomer radicals so that the polymerisation process may proceed. Nucleation generally occurs in micelles or micellar nucleations, where micelles will swell and then change into polymer particles. The formation of particles will stop if all the emulsifiers or surfactants have been absorbed by radicals, or if the absorption is influenced by the surfactant concentration or the number of micelles that exist in the solutions.

The SLS order obtained with the gravimetric method was 0.529 [Fig. 2(a)], and the SLS order obtained with the GC method was 0.510 [Fig. 2(b)]. The SLS order obtained from both methods was ≈ 0.52 . Therefore, the exponent obtained from the SLS concentration with the calculated reaction

rate was $R_p = [\text{SLS}]^{0.52}$. The SLS order obtained was lower than that found by the theory of Smith and Ewart⁶, which gave surfactant exponents ≈ 0.6 . The range of the SLS concentration has to be low in order to obtain particle sizes down to the range of 200–300 nm. Thus, by increasing the SLS concentration, the reaction rate is lower than that proposed by the Smith and Ewart⁶ theory.

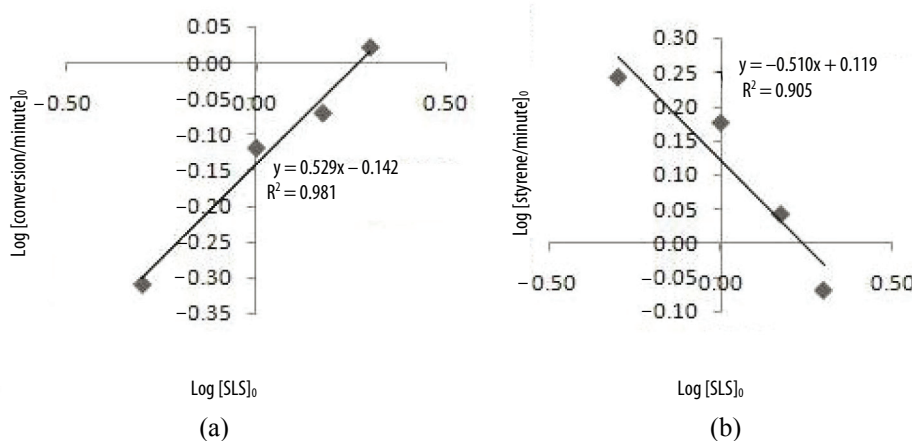


Figure 2: Log of the initial rate to log of the initial SLS concentration.

3.3 The Reaction Order of APS

The rate of initiator decomposition is equal to the rate of radical absorption into the micelles. Therefore, during the nucleation step in emulsion polymerisation, the initiator concentration influences the number of polymer particles formed. The impact of the initiator on the reaction rate is based on the ability of the initiator to produce free radicals. If the number of free radicals produced increases, then the collisions between radicals and monomers is larger, causing the polymer reaction to proceed at a faster rate.

The reaction order of APS obtained from the gravimetric method was 0.398 [Fig. 3(a)] and from the GC method it was 0.384 [Fig. 3(b)]. The exponent obtained for the APS concentration was $R_p = [\text{APS}]^{0.39}$. The results for this order were almost equal to the value proposed by Smith and Ewart⁶ of ≈ 0.4 . The reaction rate then increases along with an increase in the initiator concentration, even if the range of the initiator concentration is low in the experiment.

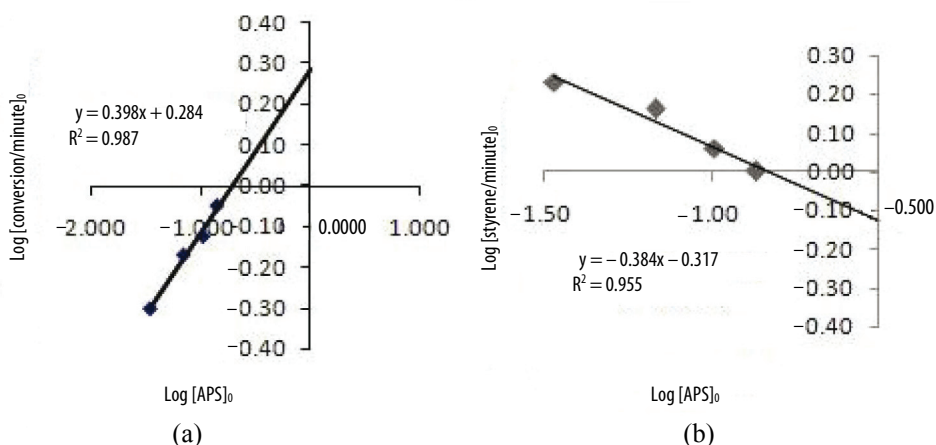


Figure 3: Log of the initial rate to log of the initial APS concentration.

The equation for the polymerisation reaction rate for the styrene core obtained in this research is as follows:

$$R_p = k[\text{styrene}]^{1.2}[\text{SLS}]^{0.52}[\text{APS}]^{0.39} \quad (1)$$

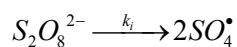
R_p is the polymerisation rate of the styrene core, and k is the rate reaction constant in the formation of the styrene core.

3.4 Mechanism of Reaction in the Formation of the Styrene Core

The order of the styrene monomer obtained in the experiment is $1.2 \approx 1$, therefore the reaction mechanism of styrene core formation can be estimated.

1. The initiation step. There are two steps during initiation, which consist of the following:

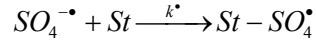
The formation of radicals from the ammonium sulfate initiator to sulfate radicals.



Rate of sulfate radical formation (R_i) is as follows:

$$R_i = k_i[S_2O_8^{2-}] \quad (2)$$

The chain initiation occurs, in which sulfate radicals collide with the styrene monomer (*St*).



Rate of chain initiation is as follows:

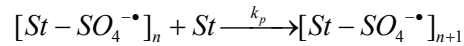
$$R_i = k^*[SO_4^{\cdot-}][St] \quad (3)$$

The formation of sulfate radicals in this initiation step is really fast, such that the rate of radical formation is the same as the rate of chain initiation. As a result, the equation of initiation rate becomes:

$$R_i = 2fk_i[S_2O_8^{2-}] \quad (4)$$

f shows the fraction of $SO_4^{\cdot-}$ free radicals, which is formed in the initiation step.

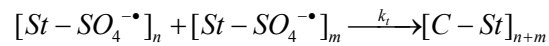
- The propagation step, or chain elongation, in which monomer radicals or oligomers collide with the styrene monomer are as follows:



The polymerisation rate in the propagation step is as follows:

$$R_p = -\frac{d[St]}{dt} = k_p[St][St - SO_4^{\cdot-}]_n \quad (5)$$

- The termination step, when free radicals collide with the other free radicals and as a result the styrene core forms:



Termination rate is as follows:

$$R_t = 2k_t[St - SO_4^{\bullet-}]^2 \quad (6)$$

The concentration of free radicals is considered constant during polymerisation because in each step of chain elongation, if a radical is attacked, other radicals will be formed. In that case, the entire series for chain propagation is not influenced by the total concentration of propagated radicals. Therefore, if the total concentration of the radicals is assumed to be in a steady state, the initiation rate of propagation for radicals is equal to the termination rate.

$$\frac{d[St - SO_4^{\bullet-}]}{dt} = R_i - R_t \quad (7)$$

In which R_i is the initiation rate, R_t is the termination rate and k_t is the termination constant; the steady state concentration of radicals obtained is as follows:

$$[St - SO_4^{\bullet-}] = \left(\frac{fk_i[S_2O_8^{2-}]}{k_t} \right)^{1/2} \quad (8)$$

$[S_2O_8^{2-}]$ is the initiator concentration by substituting equation (8) into equation (5) to produce the propagation rate as follows:

$$R_p = k_p \left(\frac{fk_i}{k_t} \right)^{1/2} [S_2O_8^{2-}]^{1/2} [St] \quad (9)$$

The order of St obtained from the experiment is supported by the estimated result for this mechanism.

The order of the $[S_2O_8^{2-}]$ or APS initiator obtained from the experimental value is not suitable for this mechanism. This is because the polymerisation method in this experiment used the seeded semicontinuous method, and the process of initiator addition was direct (shot). Thus, the function of the initiator is vital only during the initiation step. As in the case of the SLS surfactant, the dominant function of the surfactant is in establishing the initial charge, which will influence the formation of micelles, and thereby micellar nucleation will

proceed. In that case, both initiators and surfactants have functions in the reaction rates, but their functions are much more prevalent during the initial reaction or in the nucleation formation stage.

3.5 Reaction Kinetics of Butyl Acrylate Shell Grafting in Styrene Core

The kinetics of butyl acrylate grafting in the styrene core is determined by the order of butyl acrylate, which determines the order of the butyl acrylate monomer; it has a value of 1.924 according to the gravimetric method [Fig. 4(a)], and a value of 1.879 according to the GC method [Fig. 4(b)]. Therefore, the order of butyl acrylate grafting in the resulting styrene core is ≈ 2 .

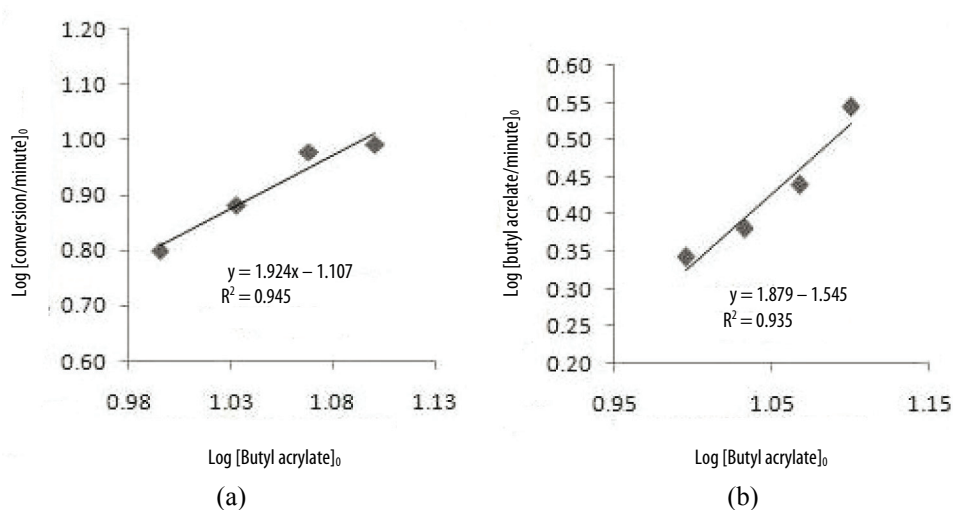


Figure 4: Log of the initial rate to log of the initial butyl acrylate concentration.

3.6 Grafting Mechanism of Butyl Acrylate Shell Formation

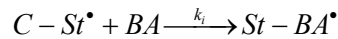
After the reaction kinetics driving the process of butyl acrylate grafting onto the styrene core is determined in the experiment, the emulsion polymerisation mechanism from the grafting process can be estimated, although it is very difficult to prove experimentally a mechanism that is estimated theoretically because the mechanism of emulsion polymerisation is complicated. No researcher up to this point has directly been able to experimentally prove the existence of a mechanism of emulsion polymerisation, especially monomer grafting onto a core with core-shell morphology.

The equation of the polymerisation reaction rate in the butyl acrylate grafting of the styrene core (R_g) is as follows:

$$R_g = k[\text{butylacrylate}]^{1.9}$$

The order of the butyl acrylate monomer (BA) is $1.9 \approx 2$; therefore, the reaction mechanism of the butyl acrylate grafting onto the styrene core can be estimated by considering how the styrene core radicals have formed in the initiation step.

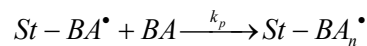
1. During the initiation step, the chain initiation is directly driven by the styrene core $[C - St^\bullet]$.



The rate of the chain initiation reaction is as follows:

$$R_i = k_i [C - St^\bullet] [BA] \quad (10)$$

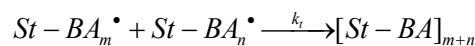
2. The propagation step, or chain elongation, in which a butyl acrylate-styrene oligomer reacts with BA :



The propagation rate is as follows:

$$R_p = k_p [St - BA_m^\bullet] [BA] \quad (11)$$

3. The termination step



The termination reaction rate is as follows:

$$R_t = k_t [St - BA^\bullet]^2 \quad (12)$$

At the initiation step, the chain initiation is directly driven by the styrene core, therefore the concentration of the styrene core radical can be assumed as follows:

$$[C - St^{\bullet}] = \frac{[BA]}{k_i} \quad (13)$$

By considering that the $[St - BA^{\bullet}]$ radical is assumed in a steady state and also the initiation rate for radicals is equal to the termination rate, the $[St - BA^{\bullet}]$ concentration may be determined as follows:

$$-\frac{d[St - BA^{\bullet}]}{dt} = k_i[St - BA^{\bullet}]^2 - k_i[C - St^{\bullet}][BA] = 0 \quad (14)$$

By substituting the concentration of $[C - St^{\bullet}]$ radical into equation (14), the concentration of the $[St - BA^{\bullet}]$ radical is as follows:

$$[St - BA^{\bullet}] = \frac{[BA]}{[k_i]^{1/2}} \quad (15)$$

The total rate is the same as the propagation rate; the following will occur:

$$\begin{aligned} R_p &= R_g = k_p[St - BA^{\bullet}][BA] \\ R_g &= \frac{k_p}{[k_i]^{1/2}}[BA]^2 \end{aligned} \quad (16)$$

Equation (16) is derived from the equation for the emulsion polymerisation rate for butyl acrylate grafting onto a styrene core. The order of BA in grafting onto the styrene core, which was obtained from the experiment, is supported by the estimated result of this mechanism. During the formation of the butyl acrylate shell, in this grafting reaction, the polymerisation step still exists; in other words, initiation, propagation and termination continue to occur. The main differences, compared with styrene core formation, are in the initiation step, in which the chain initiation is directly formed, and the radicals of the styrene core directly collide with the BA s.

4. CONCLUSION

The reaction kinetics for the synthesis of core-shell styrene-butyl acrylate using the semicontinuous seeded emulsion polymerisation method were studied using two methods: the first includes the determination of the number of

polymers produced as the solid content with respect to time; the second involves the determination of the unreacted monomer concentration with respect to time using GC. There is no difference between the results from the gravimetric method and those from the GC method. From the derived reaction rate law, the equation for the reaction rate can be estimated for each reaction step.

The styrene order for the core-shell synthesis obtained from this experiment is $1.2 \approx 1$, which is supported by the estimation of the derived reaction mechanism. The order of APS initiator and the order of SLS surfactant obtained from the present experimental values are not suitable for the estimated mechanism.

The order of butyl acrylate in the styrene core grafting process, obtained from this experiment is $1.9 \approx 2$. This value for the order of butyl acrylate is supported by the estimation of the mechanism that was derived.

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