effectiveness factors. The relation of selectivity to the catalyst size is not so simple as was shown in the case of linear kinetics and a uniform pore model. It was found that from the experimental data and the structure of the catalyst the micro and macro pores model is most reasonable and the experimental data on selectivity coincides with the model by the consecutive reactions of Langmuir-Hinshelwood rate forms.

In general if the rate form is Langmuir type, the selectivity decreases more than it by the linear kinetics and this effect becomes more remarkable by the increase of adsorption constant.

Of course these experimental results might be illustrated by other models or reaction mechanisms. There remains yet some possibility because of the uncertainty on the experimental accuracy. Progress in the study on catalytic processes will analyze them more definitely.

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Nomenclature

A	= reactant
B	= intermediate
C	= product
D	= diffusion coefficient, suffix eA , eB and K refers to A , B and micro pore, respectively.
E	= E_1/E_2 , defined by Eqs. (6) and (7)
E'	= E'_1/E'_2 , defined by Eq. (24)

K_A	= the equilibrium constant of adsorption of acetylene [atm ⁻¹]
k	= k_1 and k_2 ; the rate constants of the first, and second step reactions: k^0 refers to the apparent rate constant, and k' refers to the rate constant in micro pore
l	= the length of the porous matter
L	= the radius of the micro particles
m, m'	= modulus defined by Eqs. (7) and (24), respectively
p	= partial pressure, suffix o means the value outside the particle
p_A	= partial pressure of acetylene
p_E	= partial pressure of ethylene
p_{H_2}	= partial pressure of hydrogen
R	= the radius of the catalyst particle
r_1, r_2	= catalytic reaction rate of the first and second reaction
r	= radial distance in a catalyst particle
S	= selectivity, S^0 refers to it by $p_{B0}=0$
S_p, S_m	= selectivity in the reactor of piston flow type and of complete mixing type
s	= k_1/k_2 , s' is equal to k'_1/k'_2
X	= conversion of A

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THE EFFECT OF MICRO-MIXING ON THE HOMOGENEOUS POLYMERIZATION OF STYRENE IN A CONTINUOUS FLOW REACTOR*

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Homogeneous polymerization of styrene was carried out in a continuous stirred tank reactor, and it was made clear that special attention should be paid to the segregation of reaction mixture in the reactor for the reactor design of polymerization. Both the effect of micro-mixing on the volume efficiency of reactor and on the properties of polymer and the type of impeller to bring the reaction field homogeneous were discussed.

Introduction

For the fluid mixing which takes place in a continuous

flow reactor, two different mechanisms must be considered. The one is macro-mixing resulting from the residence time distribution of fluid elements in the reactor and the other is micro-mixing caused by the mass exchange between the fluid elements in the reactor.

Danckwerts²⁾ and Zwietering¹²⁾ introduced the concept

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a) reactor vessel

b) impeller

1 pre-mixer	5 side inlet of dextrin
2 capillary	6 thermocouple or thermometer
3 inlet of reactor	7 paddle impeller
4 outlet of reactor	8 ribbon spiral impeller

Fig. 1 Experimental apparatus

of the intensity of segregation for the micro-mixing and made theoretical discussions on the characteristics of the continuous flow reactor. The effect of micro-mixing, i. e. coalescence and redispersion of the dispersed droplets on the heterogeneous reaction has been discussed by several investigators^{1,3,9,10} and the importance of this effect in the analysis of the reactor has been pointed out experimentally^{6-8,11}. In the homogeneous reaction, the rate of mass exchange between fluid elements seems to be very high and thus the effect of mass exchange on the reactor performance has been ignored. However, it may be deduced that the micro-mixing becomes one of the important factors for the continuous reactor performance, when the fast reaction and the reaction in the field of higher viscosity are considered. For the polymerization reaction which took place in the reaction field of relatively lower viscosity, the validity of the assumption of the perfect micro-mixing was confirmed in the previous paper⁴. In this paper, the effect of micro-mixing on both the conversion of polymerization and the average degree of polymerization will be discussed for the case that the polymerization proceeds in the viscous reaction field.

Experimental Apparatus and Procedure

Polymerization of styrene in toluene using α, α' -azobisisobutyronitril (ABIN) as initiator was performed in a continuous stirred tank reactor. The materials used were purified by the same way as in the previous paper⁴.

Polymerization reactions were carried out in the stirred tank reactor shown in Fig. 1 which was a cylindrical glass vessel equipped with the impeller made of stainless steel. Two types of impellers, paddle and spiral shown in Fig. 1b were used.

Styrene monomer and ABIN dissolved in toluene were fed separately, from their reservoirs into the premixer with small volume at the desired constant flow rates, and then the mixture was introduced into the bottom of the reactor. The pressure of the reservoirs were kept constant with deoxygenized nitrogen to assure constant flow rate. The reaction mixture was removed from the reactor by overflow through the exit pipe placed at the side wall of the reactor. Reaction mixture was sampled out of the effluent stream. The conversion of styrene and the average degree of polymerization were measured by the same method as used in the previous paper⁴. The concentrations of monomer and ABIN in the premixer were adjusted to 6.90 g-moles/liter and 0.0342 g-moles/liter, respectively. The reaction was allowed to proceed in nitrogen atmosphere and at 80.0°C.

In any run, the temperature difference between the reaction mixture at the reactor wall and the center of the reactor was less than 2°C. The impeller speed was varied in the range from 180 to 250 r.p.m. for the paddle impeller and from 80 to 150 r.p.m. for the ribbon spiral impeller.

Prior to the experiments of reaction, the measurement of residence time distribution was carried out with the use of dextrin solution as the viscous liquid and sodium chloride aqueous solution as the tracer. The concentration of sodium chloride was measured by titration method.

Experimental Results and Discussion

Macro-mixing of the reactor

To identify the characteristics of micro-mixing of the reactor used, step response method was used. Fig. 2 shows the experimental results of $1-F(t)$. In these experiments, the viscosity of the mixture of the dextrin solution and sodium chloride solution was 35 poise and the mean residence time was 120 min. The points shown by symbols $\circ$ and $\times$ represent the experimental results on the paddle and ribbon spiral impellers, respectively. The experimental results fall in a straight line with slope -1 through the origin and, therefore, it can be said that the mixture in the reactor is in a perfectly macro-mixed state, i. e. statistically perfect mixing state. Since the value of viscosity, 35 poise approximately corresponded to the one of the reaction mixture at the conversion of 0.75 and further the reaction mixture of the polymerization was ascertained to

show Newtonian fluid behavior approximately, the reaction mixture might be viewed as a perfectly macro-mixed state when the reactor was operated at the condition of mean residence time more than 120 min and of viscosity less than 35 poise.

Conversion of styrene and average degree of polymerization

Let the case be considered that the polymerization reaction proceeds at a steady state in the continuous flow reactor in which the reaction mixture is in a perfectly macro-mixed state.

The conversion of styrene and the average degree of polymerization may be estimated from the values computed for the ultimate two cases of degree of micro-mixing, no micro-mixing and perfect micro-mixing, using the rate equations for elementary reactions developed in the previous paper⁴⁾.

1) Case of no micro-mixing reactor :

In this case, the conversion of styrene $f_{M,N}$ is given as follows,

$$f_{M,N} = \int_0^\infty f_{M,B} \exp(-t/\theta) d(t/\theta) \quad (1)$$

where, θ represents the mean residence time and $f_{M,B}$ denotes the conversion of styrene obtained at the reaction time, t by batch operation under the same reaction conditions as the flow operation. The curve b in Fig. 3 shows the value of $f_{M,N}$ calculated by the Eq.(1) with the value of $f_{M,B}$ shown by the curve a in Fig. 3.

Fig. 2 Validity of the assumption of perfectly macro-mixed reactor

key	Type	Impeller	speed
○	Batch	Paddle	150 r.p.m.
●	Batch	(Ample)	0
△	Flow	Paddle	180
▲	Flow	Paddle	250
×	Flow	Spiral	80~150
curve a; Batch			
curve b; No micro-mixing (flow)			
curve c; Ideal mixing (flow)			

Fig. 3 Conversion of styrene

The quantities of dead polymer containing P units $n_{P,N}$ obtained by this type of reactor is given by the following equation.

$$n_{P,N} = \int_0^\infty n_{P,B} \exp(-t/\theta) d(t/\theta) \quad (2)$$

where, the value $n_{P,B}$ denotes the quantities of dead polymer containing P units obtained by the batch operation at the reaction time t under the same reaction conditions as those of the flow operation. The viscosity average degree of polymerization of polymer obtained by the batch operation $\bar{P}_{\mu,B}$ and the one obtained by the continuous flow operation $\bar{P}_{\mu,N}$ are given by the following Eqs.(3) and (4) respectively.

$$\bar{P}_{\mu,B}^\alpha = \frac{\sum_{P=2}^\infty P^{1+\alpha} n_{P,B}}{\sum_{P=2}^\infty P n_{P,B}} \quad (3)$$

$$\bar{P}_{\mu,N}^\alpha = \frac{\sum_{P=2}^\infty P^{1+\alpha} n_{P,N}}{\sum_{P=2}^\infty P n_{P,N}} \quad (4)$$

where, α is the power number of Mark-Howinks' equation. From Eqs.(2), (3) and (4), $\bar{P}_{\mu,N}$ is obtained by the following equation.

$$\bar{P}_{\mu,N}^\alpha = \int_0^\infty \bar{P}_{\mu,B}^\alpha f_{M,B} \exp(-t/\theta) d(t/\theta) / f_{M,N} \quad (5)$$

The symbol, ○ in Fig. 4 shows the experimental values obtained by the batch operation and the curve a is the smoothed value connecting the observed values. The value $\bar{P}_{\mu,N}$ calculated by Eq.(5) with the smoothed curve a is shown in Fig. 4 as the curve b .

2) Case of perfect micro-mixing reactor, i. e. ideally mixed reactor :

Since the concentrations of monomer and the others are uniform throughout the perfect micro-mixing reactor*, the conversion of monomer is expressed as the following equation with the mass balance.

$$1 - f_{M,P} = \frac{1}{1 + (\gamma\delta)^{1/2} (df_{M,B}/dt)_i (1 - f_{K,P})^{1/2} \theta} \quad (6)$$

where,

$$(df_{M,B}/dt)_i = (k_p^2 \phi / k_t)^{1/2} (2 k_d C_{K,i})^{1/2} \quad (7)$$

and k_p , k_t and k_d represent the reaction rate constants of propagation, termination and initiator decomposition, respectively. The values ϕ and $f_{K,P}$ are initiator efficiency and conversion of initiator, respectively. As mentioned in the previous paper^{4,5)}, the value of $(\gamma\delta)$

key	Type	Impeller	speed
○	Batch	Paddle	150r.p.m.
△	Flow	Paddle	180
▲	Flow	Paddle	250
×	Flow	Spiral	80~150

curve a; Batch
 curve b; No micro-mixing (flow)
 curve c; Ideal mixing (flow)

Fig. 4 Viscosity average degree of polymerization

obtained by the batch reactor can be determined apparently by the polymer weight fraction in the reaction mixture, independently of the reaction conditions, i. e. initial concentrations of monomer and initiator and the reaction temperature, and thus it may be also used in the flow operation. The curve *c* in Fig. 3 was calculated by Eq.(6) using the data in the previous paper⁴⁾.

The average degree of polymerization can be obtained as follows,

$$\bar{P}_{\mu, N} / \bar{P}_{\mu, i} = (\gamma\delta)^{1/2} (1 - f_{M, P}) / \varepsilon (1 - f_{K, P})^{1/2} \quad (8)$$

where, ε represents the ratio of initiator efficiency at conversion $f_{M, P}$ to the one at $f_{M, P}=0$ and is also determined only by the polymer weight fraction in the reaction mixture⁴⁾. The curve *c* in Fig. 4 was calculated by Eq.(8) with the values $(\gamma\delta)$, ε , $f_{M, P}$ and $f_{K, P}$.

Generally, in the isothermal operation of the reaction with the reaction order higher than unity, the conversion obtained by the perfectly macro-mixed reactor is lower than that obtained by the plug flow reactor or batch operation, and the conversion obtained decreases with the increase in the degree of micro-mixing. The reaction rate of styrene polymerization initiated by ABIN can be described as being of first order in styrene and a half order in ABIN. In the range of lower conversion where auto-acceleration effect may be neglected, the conversion obtained by batch operation is the highest. The conversion given by the curve *b* should be higher than the one of the curve *c*, theoretically. With the increase in the extent of the polymerization reaction, the auto-acceleration effect becomes appreciable and can not be neglected. In the plug flow reactor or batch operation, this effect gradually appears with the increase in the extent of reaction. While, in an ideally mixed reactor, the feed stream is dispersed immediately in the

circumstance where the auto-acceleration effect is remarkable, and thus the apparent reaction rate coefficient of polymerization markedly increases throughout the reactor. Therefore, the conversion obtained by an ideally mixed reactor increases steeply with the increase in the value θ or f_M beyond the conversion of 0.4 and approaches to the value given by the curve *a* in the range of higher conversion under the operating condition of this experiment. While, the conversion obtained by a no micro-mixing reactor is less sensitive for the auto-acceleration effect and the conversion given by the curve *b* becomes lower than the curve *c* in the range where the auto-acceleration effect can not be neglected.

For the average degree of polymerization, the curve *c* computed on the assumption of an ideally mixed reactor is the highest in the range of higher conversion, because the average degree of polymerization is more sensitive for the auto-acceleration effect than the conversion⁴⁾.

The experimental results of flow system are shown in Figs. 3 and 4. The points shown by the symbols Δ and $\blacktriangle$ show the results obtained with the paddle impeller at the stirrer speed 180 and 250r.p.m., respectively. In comparatively low conversion, the experimental results agree with the value which are calculated on the assumption of the perfectly micro-mixed reactor. As the mean residence time and the conversion of styrene increase, the experimental results deviate from the curve *c* and approach to the curve *b*. The points shown by the symbols $\times$ in Fig. 3 and 4 indicate the experimental results obtained by the reactor with the ribbon spiral impeller and fall in the curve *c* approximately.

Let us consider the reason why the experimental values do not fall in the curve *c* calculated on the assumption of an ideally mixed state. For the polymerization reaction, there are several special characters caused by the complexity of reaction mechanisms and remarkable increase in the viscosity of reaction mixture with the increase in the extent of the reaction. The polymerization reaction seems to be independent of stirrer speed since, as clearly seen from Fig. 3, the results obtained by ample tube with the diameter 3mm agree well with

* It is generally accepted that the auto-acceleration effect expressed by the term δ in Eq.(6) originates from the diffusion controlled termination reaction. In this case, it is doubtful that a state of perfect mixing in molecular scale exists in principle. The state of perfect micro-mixing defined in this paper denotes a state that the concentrations of several substances are uniform throughout the reactor over the distance equal to the scale of radical segregation caused by the diffusion controlled termination.

those obtained by the batch reactor maintaining the paddle impeller speed 150 r.p.m.. Though some errors may be associated with the determination of conversion, these errors seem to be comparatively small and are not sufficient to explain the deviation of experimental results from the curve *c*.

Let us consider the behavior of the inflowing stream in the reactor with the paddle impeller. Under the operating condition of this work, the viscosity of the reaction mixture became comparatively high in the range of higher conversion. The feed stream coming into the reactor from the bottom was transported upwards in the direction of the paddle impeller in the state segregated from the surrounding reaction mixture and was broken up into many comparatively coarse streaks by the shearing force near the impeller. The coarse streaks circulated throughout the reactor with the discharged flow from the impeller and was transformed into finer streaks gradually. Finally, a crowd of these streaks was carried out of the reactor. It was clarified by the tracer response that the reactor could be treated as a perfectly macro-mixed reactor and this fact may be caused by the higher circulating rate, i.e. that a circulating time of the discharged flow is short enough compared with the mean residence time. While, the fact, ascertained by the inspection of reaction mixture, that the mixture consisted of a great number of fine streaks, shows perhaps that the rate of mass exchange between the streaks was comparatively low. The deviations of experimental results in Figs. 3 and 4 from curve *c* is perhaps owing to the lower rate of mass exchange between the streaks.

When the paddle impeller was used, the critical conversion at which experimental point began to deviate from the curve *c* increased with the increase in the impeller speed.

It is easily seen in the case of constant viscosity that the reaction mixture in the reactor having larger mean residence time should be essentially more homogeneous because the greater degree of micro-mixing might be achieved. In the polymerization reactions, however, the increase in the mean residence time leads to the increase in the viscosity of the reaction field. Therefore, assuming the greater effect of viscosity than that of mean residence time on the degree of micro-mixing, it is clearly understood that the degree of micro-mixing decreases with the increase in the mean residence time as is observed in the experiments.

The experimental results obtained by the ribbon spiral impeller fall in the curve *c*. The shearing force in the reactor with a paddle impeller is especially strong near the impeller, while in the reactor with a ribbon spiral impeller, convectional circulation and shearing force are distributed uniformly all over the reactor. It is considered that these uniformly distributed circulation flow and shearing force bring on a great advance in the rate of mass exchange between the streaks.

To Conclude

The polymerization of styrene was carried out in a continuous stirred tank reactor. The experimental re-

sults obtained by the reactor with the paddle impeller did not agree with the value calculated on the assumption of the ideal mixing. The fact mentioned above was explained by the cause that the rate of mass exchange between fluid elements was comparatively low and the content in the reactor was not in the state of the ideal mixing.

It was shown that the effect of micro-mixing on both the volume efficiency of a reactor and the properties of polymer produced was too great to be ignored when auto-acceleration effect was polymerization was not negligible, and the type of impeller to bring the reaction field to an ideally mixed state was discussed.

The mechanisms of micro-mixing and the scale of segregation must be made clear for the research of mixing performance in future.

Nomenclature

C_K	= concentration of initiator	[g-moles/liter]
$F(t)$	= response to a step tracer input	[—]
f_K	= conversion of initiator	[—]
f_M	= conversion of monomer	[—]
k_p	= rate constant of propagation reaction	[liter/g-moles·sec]
k_d	= rate constant of initiator decomposition reaction	[1/sec]
k_t	= rate constant of termination reaction	[liter/g-moles·sec]
P	= degree of polymerization	[—]
P_n	= viscosity average degree of polymerization	[—]
t	= time	[sec, min]
α	= Mark-Houwink power number	[—]
γ	= ratio of density of reaction mixture to the one in feed state	[—]
δ	= $(k_p^2\phi/k_t)/(k_p^2\phi/k_t)_i$	[—]
ε	= ϕ/ϕ_i	[—]
ϕ	= initiator efficiency	[—]
θ	= mean residence time	[sec, min]

Subscript

i	= state of initial or feed
B	= batch operation
N	= no micro-mixing state
P	= perfect micro-mixing state

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