CASE 3

Optimization of Polymerization Reactions

Abstract: In this research we applied quality engineering principles to a synthetic plastics reaction known as a polymerization reaction, regarded as one of the slowest of all polymerization reactions, and a reaction with a wide molecular mass distribution, to enhance productivity and obtain a polymerized substance with a narrow molecular mass distribution.

1. Introduction

In manufacturing processes for chemical products, quality and cost depend strongly on a synthetic reaction condition. The reaction handled in this research, a synthetic reaction of resin called a *polymerization reaction*, is one of the slowest of all such reactions and has a wide molecular weight distribution. Although we had tried many times to improve productivity and molecular weight distribution, no significant achievement was obtained. In general cases of polymerization reaction, for a complete product we have conventionally measured its molecular weight distribution and analyzed the average molecular weight calculated. The objective of this study was to accomplish an unachieved goal by applying quality engineering to this polymerization reaction. Regarding the application of quality engineering to a chemical reaction, there is one case of doubling productivity by using a dynamic operating window for an organic synthesis reaction. However, the case contains some problems in reproducibility, such as having both peaks and V-shapes in a factor effect plot of the SN ratio.

To solve these problems, we have taken advantage of the ratio of the rate of main reaction β_1 and that of side reaction β_2: β_1/β_2. By doing this we obtained fairly good reproducibility. In our research, in reference to an organic synthesis reaction, we applied quality engineering to a polymerization reaction by improving a method of handling a polymerization degree distribution and calculating reaction speed β and the SN ratio.

2. Experimental Procedure

Objective

Since, in general, a polymer substance consists of various types of molecular weight, it has a particular molecular weight. A polymer in this experiment is an intermediate material used as a raw material in the following process. In this case, its molecular weight should be neither too large nor too small. Therefore, using the quality engineering method, we attempted to enhance productivity and obtain a polymerized substance with a narrow molecular weight. To enhance productivity, a high reaction speed and a stable reaction are both essential.

To obtain a polymerized substance with a narrow molecular weight distribution, the constitution of the resulting molecular weight should be high. Therefore, by classifying an ingredient not reaching a certain molecular weight M_n as an *underreacted substance*, one ranging from M_n to M_m as a *target substance*, and one exceeding M_m as an *overreacted substance*, we proceeded with our analysis.

Experimental Device

We heated material Y, solvent, and catalyst in a 1-L flask. After a certain time, we added material X to the flask continuously. Next came the reaction of X and Y. When the addition of X was complete, dehydration occurred and polymerization took place.

Table 1
Control factors and levels for the first L_{18} orthogonal array (%)

		Level		
Column	Control Factor	1	2	3
1	None	—	—	—
2	A: amount of material X	96	100	106
3	B: amount of agent 1	33	100	300
4	C: amount of agent 2	85	100	115
5	D: reaction speed	90	100	110
6	E: maturation time	0	33	100
7	F: material supply time	0	33	100
8	G: continuously supplied material: X or Y	X	X	Y

Table 2
Control factors and levels for the second L_{18} orthogonal array (%)

		Level		
Column	Control Factor	1	2	3
1	C: amount of agent 2	100	115	—
2	A: amount of material X	92	96	100
3	B: amount of agent 1	100	300	500
4	H: agent type	1	2	3
5	I: supply method of material	1	2	3
6	J: supply method of agent 1	1	2	3
7	F: material supply time	33	100	150
8	K: material type of Y	1	2	3

Table 3
Change in constitution of yields at each reaction time (%)

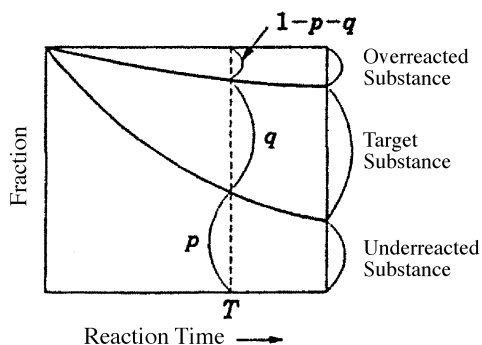|	Reaction Time				
	0.3	1	2	3	4
Underreacted substance	97.1	30.9	20.7	19.1	12.3
Target substance	2.9	62.0	72.2	63.6	61.1
Overreacted substance	0	7.1	7.1	17.3	26.7
Total	100	100	100	100	100

Figure 1
Dynamic operating window method

Layout of Orthogonal Array

In the first experiment, we selected seven control factors and allocated them to an L_{18} orthogonal array with a larger interval of level. Table 1 shows the factor and levels. After analyzing the experimental result of the first L_{18} experiment, we designed and conducted the second L_{18} experiment (Table 2).

Data Gathering for Analysis

We sampled the polymerizing solution in each of runs 1 to 18 allocated in the L_{18} orthogonal array at a certain interval. Then, using gel permeation chromatography (GPC), we gauged the constitution of a material and polymers.

As a specific example, Table 3 shows a change in the constitution at each reaction time in run 2 in the first L_{18} orthogonal array. The data for a molec-
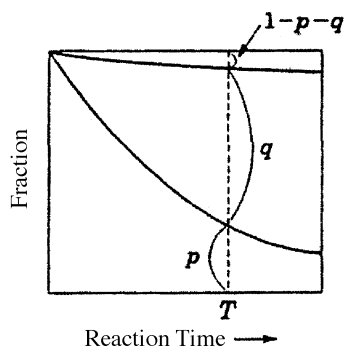

Figure 2
Reaction regarded as ideal

ular mass and its distribution were computed as converted values of the standard polystyrene molecular mass.

3. Analysis by Dynamic Operating Window Method

Generic Function

Since a chemical reaction is an impact phenomenon between molecules, by setting the constitution of underreacted substances in a yielded substance to p, we defined the following equation as a generic function on the basis that reaction speed is proportional to density of material:

$$p = e^{-\beta T}$$

Taking the reciprocal of both sides and logarithmizing, we have

$$\ln(1/p) = \beta T$$

Setting $Y = \ln(1/p)$, we obtain the following zero-point proportional equation:

$$Y = \beta T$$

Now β is a coefficient of the reaction speed.

Concept of Operating Window

If we categorize a yield as underreacted, target, and overreacted based on the molecular mass, as a chemical reaction progresses, the constitution of the target substance rises (Figure 1).

Setting the constitution of an underreacted substance at the point of reaction time T to p and that of an overreacted substance to q, we can express that of an overreacted substance by $1 - p - q$. Since an ideal reaction is regarded as one with a faster reaction speed and higher constitution then a target substance (Figure 2), we should lower the constitution of an underreacted substance immediately and maintain that of an overreacted substance as low as possible.

Then, taking into account the following two reaction stages, we estimated a reaction speed for each stage β.

R_1: a material (molecular mass M_1, monomer) and polymers (molecular mass $M_2 - M_{n-1}$,

polymer, that is, a dimer consisting of two combined molecules) convert into target substances (molecular mass $M_n - M_{m-1}$) and overreacted substances (molecular mass more than M_m):

material + polymer (M_2) + ···
   + polymer (M_{n-1}) (M_n + ··· + M_{m-1}) + M_m ···

We define the reaction speed at this stage as β_1.

R_2: A material (molecular mass M_1, monomer), polymers (molecular mass $M_2 - M_{n-1}$, polymer, that is, a dimer consisting of two combined molecules), and target substances (molecular mass $M_n - M_{m-1}$, monomer) convert into overreacted substances (molecular mass more than M_m):

material + polymer (M_2) + ···
   + polymer (M_{n-1}) + (M_n + ··· + M_{m-1}) M_m ···

We define the reaction speed at this stage as β_2.

A reaction speed in each stage is not a theoretical rate of a simple chemical reaction per se, however, but a rate in which the underreacted substances described above convert into a yield. The reason that we deal with the reaction in this manner is to prepare a mechanism of additivity. As a result, since R_1 indicates a yielding rate of target and overreacted substances and R_2 represents that of an overreacted substance, our final objective is to obtain an optimal configuration to maximize the difference between two rates, R_1 and R_2.

Now for R_1 and R_2 we calculate the constitution of an underreacted substance at the point of time T_i, p_i and $p_i + q_i$, and compute rates of reaction β_{1i} and β_{2i}.

$$R_1: \quad p_i = e^{-\beta_{1i}/T_i} \qquad \ln \frac{1}{p_i} = \beta_{1i} T_i$$

$$R_2: \quad p_i + q_i = e^{-\beta_{2i} T_i} \qquad \ln \frac{1}{p_i + q_i} = \beta_{2i} T_i$$

In this case, the reaction speed to yield a target substance β_1 should be larger and the reaction speed to yield an overreacted substance β_2 should be smaller.

$$\beta_{1i} = \frac{Y_{1i}}{T_i} = \frac{1}{T_i} \ln \frac{1}{p_i}$$

$$\beta_{2i} = \frac{Y_{2i}}{T_i} = \frac{1}{T_i} \ln \frac{1}{p_i + q_i}$$

Using these equations, we can calculate β_{1i} and β_{2i} for each of K measurement points. Now, since we need to maximize a reaction speed of yielding a target substance, β_{1i} and to minimize that for an overreacted substance, β_{2i}, by computing β_{1i} as a larger-the-better SN ratio η_1 and β_{2i} as a smaller-the-better SN ratio η_2, we find factors to maximize $\eta_1 + \eta_2 = \eta$. This is a dynamic operating window method.

$$\eta_1 = -10 \log \left[\frac{1}{K} \left(\frac{1}{\beta_{11}^2} + \cdots + \frac{1}{\beta_{1K}^2} \right) \right]$$

$$\eta_2 = -10 \log \left[\frac{1}{K} (\beta_{21}^2 + \cdots + \beta_{2K}^2) \right]$$

When a reaction speed is stable throughout a total reaction, we can analyze the reaction with only one β at a single observation point in a more efficient manner. If we use a single observation point, the calculation is

$$\eta = \eta_1 + \eta_2$$

$$= -10 \log \frac{1}{\beta_1^2} - 10 \log \beta_2^2 = 10 \log \frac{\beta_1^2}{\beta_2^2}$$

As sensitivity S, we consider β_1 regarding productivity:

$$S = 10 \log \beta_1^2$$

Example of Analysis

We now show the calculations for the experimental data for run 2 in the first L_{18} orthogonal array. The observation points of β_1 and β_2 can differ. Then, setting the observation points so as to estimate β_1 and β_2 most accurately at T_1 and T_2, respectively, we compute β_1 and β_2 from each single point.

Decreasing speed of an underreacted substance:

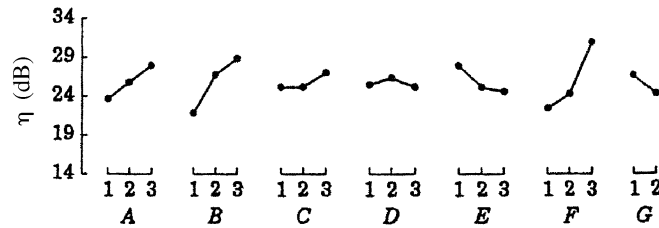$$\beta_1 = \frac{1}{T_1} \ln \frac{1}{p_1} = \frac{1}{1} \ln \frac{1}{0.309} = 1.1757$$

Figure 3
Factor effect plot of the SN ratio in the first L_{18} experiment

Yielding speed of an overreacted substance:

$$\beta_2 = \frac{1}{T_2} \ln \frac{1}{p_2 + q_2} = \frac{1}{4} \ln \frac{1}{0.123 + 0.611} = 0.0776$$

SN ratio:

$$\eta = 10 \log \frac{\beta_1^2}{\beta_2^2} = 10 \log \frac{(1.1757)^2}{(0.0776)^2} = 23.6105 \text{ dB}$$

Sensitivity:

$$S = 10 \log \beta_1^2 = 10 \log (1.1757)^2 = 1.4059 \text{ dB}$$

4. Result of the First L_{18} Experiment

Figures 3 and 4 show the factor effect plots of the SN ratio, η, and sensitivity, S, in the first L_{18} experiment. In addition, Table 4 shows the optimal levels for the SN ratio and sensitivity. By prioritizing sensitivity for factors whose optimal SN ratio and sensitivity are different, we determine factor levels in the second L_{18} experiment.
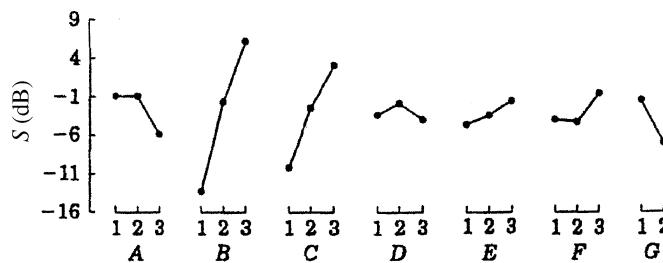
5. Result of the Second L_{18} Experiment

Considering the result of the first L_{18} experiment, we determined factors and levels for the second L_{18} experiment as follows. We have the following control factors:

    E: We fixed its levels to zero at E_1 by focusing on productivity because the maturation time is zero under the optimal configuration.

    D: We fixed its levels to D_2 by selecting the current level because of its small factor effect.

    G: We fixed its levels to G_1 because *X* has turned out to be a good choice in terms of continuously supplied material.

For other factors, *A*, *B*, *C*, and *F*, in order to delve further into optimal levels, we changed each level. On the other hand, as new control factors, we deliberately selected *H*, *I*, *J*, and *K*. As for factor *C*, although we had tested as technically wide a range as possible in the first L_{18} experiment, we included it once again to associate it with the result in the first L_{18} experiment because the first column emptied in the layout of the second experiment.

Figure 4
Factor effect plot of sensitivity in the first L_{18} experiment

Table 4

Optimal configuration in the first L_{18} experiment[a]

	Factor						
	A	**B**	**C**	**D**	**E**	**F**	**G**
SN ratio	3	3	(3)	(2)	1	3	(1)
Sensitivity	1	3	3	(2)	(3)	(3)	1

[a] Parentheses indicate small-effect level.

Figures 5 and 6 summarize the factor effect plots of the SN ratio, η, and sensitivity, S, in the second L_{18} experiment. According to each result for the SN ratio and sensitivity, we determined the optimal levels as shown in Table 5.

6. Results of Confirmatory Experiment

According to the first and second L_{18} experiments, we obtained less rugged results for the factor effects of the SN ratio and sensitivity. The implied high additivity of the SN ratio is based on reaction speed. Then we conducted a confirmatory experiment under each optimal configuration of the first and second L_{18} experiments. Tables 6 and 7 show the results of the first and second L_{18} confirmatory experiments, respectively.

For the first L_{18} experiment, we conducted a confirmatory experiment under the optimal configuration for each SN ratio and sensitivity value. The result of the first L_{18} experiment reveals that whereas we obtained fairly good reproducibility in

gain for the SN ratio, there was a small gap in gain for the sensitivity. Under the optimal configuration for sensitivity, we can confirm that the gain improved by 5.0 dB, the reaction speed almost doubled, and the reaction time approximately halved. Because sensitivity $S = 10 \log\beta_1^2$,

$$\text{Gain} = 10 \log \beta_{1\text{optimal}}^2 - 10 \log \beta_{1\text{current}}^2$$

$$= 10 \log \frac{\beta_{1\text{optimal}}^2}{\beta_{1\text{current}}^2}$$

On the other hand, since the gain is 5.0 dB, that is, the real (nondecimal) number is 3.1,

$$\frac{\beta_{1\text{optimal}}^2}{\beta_{1\text{current}}^2} = 3.1$$

$$\frac{\beta_{1\text{optimal}}}{\beta_{1\text{current}}} = 1.8$$

For the second L_{18} experiment, we conducted a confirmatory experiment under the optimal configuration determined by both the SN ratio and sensitivity. As a result of the second L_{18} confirmatory experiment, the gain in actual sensitivity is increased to 9.2 dB from that of the first L_{18} experiment. This is equivalent to a 2.9-fold improvement in reaction speed (i.e., the reaction speed is reduced by two-thirds).

On the other hand, if we compare two molecular mass distributions of polymerized substances under the current configuration (8720 dB) and the optimal configuration (8840 dB) by adjusting the average molecular mass to the target value, we can obtain almost the same result. That is, we cannot determine a way to narrow down the range of molecular mass distribution in this research.
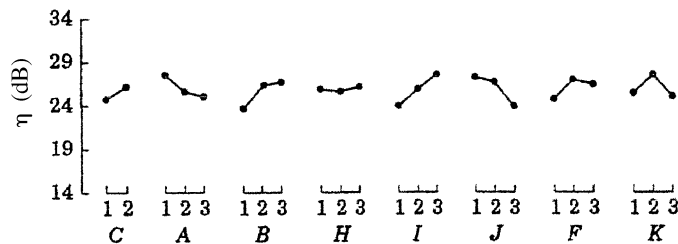

Figure 5
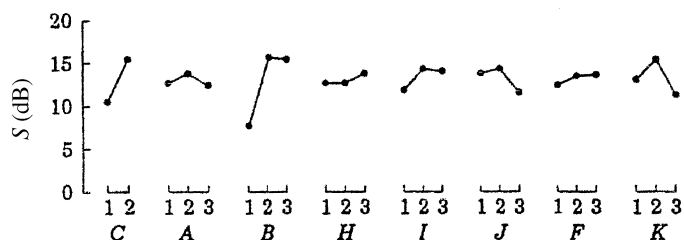Factor effect plot of the SN ratio in the second L_{18} experiment

Figure 6
Factor effect plot of the sensitivity in the second L_{18} experiment

7. Conclusions

Experimental Achievements

The productivity improved dramatically because the reaction speed doubled under the optimal configuration compared to that under the current configuration. It was difficult to improve the molecular mass distribution; consequently, although the reaction speed was enhanced, the molecular mass distribution was not. However, improving the productivity threefold while retaining the same level of current quality (molecular mass distribution) was regarded as a major achievement.

Future Reearch

Since the reaction speed was increased despite little improvement in molecular mass distribution, our research can be regarded as a significant success from a company-wide standpoint. However, judging from the definition of SN ratio used, we expected

that the molecular mass distribution would also be improved. We explain considerations of improvement in molecular mass distribution as follows.

In the L_{18} experiments and their confirmatory experiments, the reaction speed β for estimation of the SN ratio is calculated by the data measured at the initial stage of reaction. Looking at the experimental data, we find that in the latter half of the experiment, the reaction saturates and deviates considerably downward from $Y = \beta T$ (particularly β_1), as shown in Figure 7. This is because a reverse or termination reaction occurred in the polymerization reaction. If we measure and compare molecular mass distributions in the initial stage of reaction, where such reactions are very minimal, we can observe improvement not only in the SN ratio but also in molecular mass distribution. Then the measurement point of molecular mass distribution in the confirmatory experiment is considered too late.

However, since the initial stage of reaction has small molecular masses as a whole, we need to

Table 5
Optimal configuration in the second L_{18} experiment[a]

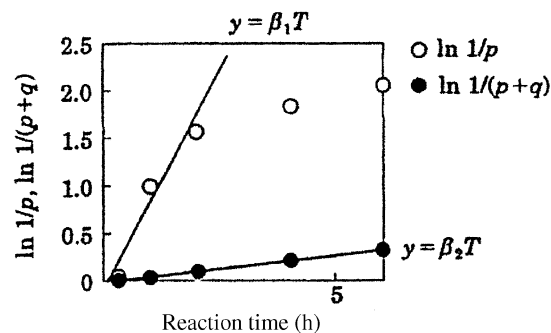|	Factor							
	C	**A**	**B**	**H**	**I**	**J**	**F**	**K**
SN ratio	2	1	3	(3)	3	1	2	2
Sensitivity	2	(2)	2,3	(3)	2,3	1,2	(2)	2
Optimal level	2	1	3	3	3	1	2	2

[a] Parentheses indicate small effect level.

Figure 7
Example of lapse of reaction time

Table 6
Results of the first L_{18} confirmatory experiment

Configuration	Factors							SN Ratio		Sensitivity	
								Estimation	Confirmation	Estimation	Confirmation
Optimal η	A_3	B_3	C_3	D_3	E_1	F_3	G_1	38.7	34.8	10.8	9.9
Current	A_2	B_2	C_2	D_2	E_3	F_3	G_1	30.6	28.1	3.0	7.2
Gain								8.1	6.7	7.5	2.7
Optimal S	A_1	B_3	C_3	D_2	E_3	F_3	G_1	30.4	29.6	16.3	12.2
Current	A_2	B_2	C_2	D_2	E_3	F_3	G_1	30.6	28.1	3.0	7.2
Gain								−0.2	1.5	13.3	5.0

Table 7
Results of the second L_{18} confirmatory experiment

Configuration	Factors							SN Ratio		Sensitivity	
								Estimation	Confirmation	Estimation	Confirmation
Optimal η	C_2	A_1	B_3	H_3	I_3	J_1	F_2	K_2	33.1	35.5	19.2	16.4
Current	C_1	A_3	B_1	H_2	I_1	J_1	F_2	K_2	23.0	28.1	5.8	7.2
Gain									10.1	7.4	13.4	9.2

continue the polymerization reaction until the average molecular mass attains the target. Our confirmatory experiment demonstrates that after doing so, the molecular mass distribution is no longer improvable. Therefore, to improve molecular mass distribution, research on design of experiments and analytical methods, including consideration of a reverse reaction and consideration of a termination reaction, should be tackled in the future.

Achievement through Use of Quality Engineering

Experiments in production technology beginning at the beaker level in a laboratory using conventional development processes require a considerable amount of time. By evaluating a polymerization reaction with an SN ratio reflecting a generic function in a chemical reaction, we can improve reproducibility in factor effects and enhance productivity threefold, thereby obtaining a significant achievement in a short period of time.

References

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