ORIGINAL

Analysis of Reaction Rate in Propoxylation

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Propoxylation is useful for making materials of urethane foam and surfactants in industry. The reaction rate of the addition polymerization of propylene oxide (PO) was examined to find means for enhancing productivity. The reaction rate of propoxylation became maximum when PO concentration in the reaction mass was 33.3 wt %. This was confirmed theoretically using the reaction rate equation proposed by Ishii *et al.*

1 Introduction

Addition polymerization of PO with some initiator catalyzed by sodium isopropoxide was reported by Ishii *et al.* in 1959¹⁾.

They suggested that the reaction rate could be expressed as follows.

$$V_{po} = k_1 [\text{initiator}] [\text{PO}] [\text{catalyst}] \quad (1)$$

In 1963, the effects of catalyst concentration, reaction temperature, and molar ratio of the initiator to PO on the reaction rate of propoxylation were investigated²⁾. But the effect of PO concentration in reaction mass was not reported. In industrial propoxylation, it is popular that the PO dosing is continuous and changeable. Therefore, it is important to control dosing speed and concentration of PO in the reaction mass. The author proposed an equation concerning PO concentration in the reaction mass³⁾ previously. We investigated the effect of PO concentration to the reaction rate in this paper.

2 Experimental

2.1 Experimental device

Reaction Calorimeter RC-1³⁾ was used for this investigation. Its effective capacity and pressure durability was 1.5 L and 60 kgf/cm².

2.2 Measurement

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Molecular weight (Mn)

The number-average molecular weight (Mn) was calculated by Eq. (2).

$$Mn = 56100 \times F/V \quad (2)$$

F : functionality of the initiator

V : OH-value⁴⁾ (estimated by the method of acetylation with phthalic anhydride)

TU value

The TU (terminal unsaturation) value was measured by ¹H-MNR method⁵⁾ using a sampled polymer without treatment. ¹H-NMR spectra were recorded in deuterated chloroform (CDCl₃) and the concentration of the sampled polymer was about 5 wt/vol %. Typical ¹H-NMR spectra of a polymer obtained in this experiment on a VARIAN XL-300 (300 MHz) was shown in Fig.-1.

The TU value (meq/g) was calculated by Eq. (3).

$$\text{TU (meq/g)} = \frac{(I_2/2) + (I_3/3)}{(I_1/3)} \cdot \frac{(Mn-92)}{58} \cdot \frac{1000}{Mn} \quad (3)$$

58 : molecular weight of PO

92 : molecular weight of glycerol (initiator)

Mn : molecular weight of the sampled polymer

A signal due to methyl protons of PO was shifted 0.1~0.2 ppm upper to that of poly-

Fig.-1 Typical ^1H -NMR spectra of a polymer.

mers, so existence of non-reacted PO was not troublesome in estimating the TU values.

PO concentration in reaction mass

PO concentration in reaction mass was calculated by Eq. (4)³⁾.

$$\text{Log } C = 1.3238 \text{ Log } P + (1411.7/T) - 3.3148 \quad (4)$$

C : PO concentration (wt %) in reaction mass

P : Abs. pressure (kgf/cm^2)

T : Abs. temperature (K)

Eq. (4) was obtained by the analysis of the pressure/PO concentration curves shown in Fig.-2.

2.3 Materials

Polyether A (initiator, prepared by authors) was a glycerol/PO addition product, M_n of it was 628, and concentration of catalyst (potassium hydroxide) was 1.35 wt % (purity-accounted).

PO was a commercial grade produced by Showa Denko Co., Ltd.

Potassium hydroxide was a commercial grade produced by Asahi Glass Co., Ltd (48 % aqueous solution).

Glycerol was a commercial grade produced by Nippon Oils & Fats Co., LTD.

2.4 Method of Experiment

Polyether A was charged in RC-1, and controlled at certain level of temperature under reduced pressure with stirring. After

Fig.-2 The pressure/PO concentration curve at each temperature.

this treatment, dosing of PO was started under 0 kgf/cm^2 . And dosing of PO was continued until the end of experiment to keep certain level of PO concentration in the reaction mass. Sampling was carried out in every 1 h, and M_n of the sampled polymer was measured after stripping of PO under reduced pressure.

2.5 Evaluation

Reaction time required was defined as the time when M_n of the polymer reached to 3,000.

3 Results

The explanation of dosing pattern of PO and reaction time required (time for poly-

merization reached to 3,000 of *Mn*) are shown in Fig.-3.

TU values by analyzing samples synthesized at 120°C (*Mn* : 3,000) are shown in Fig.-4. It is cleared that the TU value is independent of PO concentration. The relations between reaction time required and PO concentration in reaction mass are also shown in Fig.-4. Each curve has the minimum point, which is located at about 33 wt % of PO concentration.

Exp. 1 Typical pattern of propoxylation in industry

Exp. 2 Special pattern experimented in this paper

PO 1,2 Dosing patterns of PO in Exp. 1,2

R.T. 1,2 Reaction time required in Exp. 1,2

Mn 1,2 *Mn* curve of polymer obtained in Exp. 1,2

Fig.-3 Dosing patterns of PO and reaction time required.

This means that reaction rate of propoxylation is maximum as PO concentration nears to 33 wt %. And this result could be expected mathematically as follows.

Now, we assume that *A* kg of initiator (*Mn* : *a*), *B* kg of catalyst (*Mn* : *b*) and *X* kg of PO (*Mn* : 58) are charged in reactor, then reaction velocity could be expressed.

$$V_{po} = k_2 \cdot \frac{(X/58)}{(A+B+X)} \cdot \frac{(A/a)}{(A+B+X)} \cdot \frac{(B/b)}{(A+B+X)} = K \cdot \frac{X}{(A+B+X)^3} \quad (5)$$

Fig.-4 Relation between PO concentration and the reaction time required and TU value.

Table-1 Comparison of reaction rate at each PO concentration.

No.	1	2	3	4	5
Polyether A (g)	200	200	200	200	200
PO (g)	800	200	100	50	10.5
PO (wt %)	80	50	33.3	20	5
Ratio of V_{po} *	0.22	0.84	1.00	0.86	0.35

* Standard : V_{po} value of No. 3

Table-2 Maximum pressure and temperature in runaway propoxylation⁶⁾.
(Phosphoric acid as chemical stopper)

Chemical stopper	Without dosing		With dosing	
Condition*	105°C × 28 wt %	120°C × 28 wt %	105°C × 28 wt %	120°C × 28 wt %
Abs. press. (kgf/cm ²)	10.8	14.2	7.4	11.7
Temperature (°C)	267*	281*	126	154

Condition* : temperature and PO conc. in reaction mass at starting time of runaway propoxylation
Temperature* : evaluated by RC-1 at Tr mode⁶⁾

Replacement with new constants, $K=k_2 \cdot (1/58) \cdot (A/a) \cdot (B/b)$ and $C=A+B$, yields

$$V_{po} = K \cdot \frac{X}{(C+X)^3} \quad (6)$$

V_{po} is maximum when $dV_{po}/dX=0$. The following shows a detail of the calculation.

$$\begin{aligned} \frac{dV_{po}}{dX} &= K \cdot \frac{(C+X)^3 - 3X(C+X)^2}{(C+X)^6} \\ &= K \cdot \frac{C-2X}{(C+X)^4} \quad (7) \end{aligned}$$

$$dV_{po}/dX=0 \rightarrow X=C/2$$

This means that maximum reaction rate is obtained when PO concentration in reaction mass is 33.3 wt % (a half quantity of initiator and catalyst). The V_{po} values calculated from equation (5) are shown in Table-1.

4 Discussion

Reaction rate can be accelerated by increase in reaction temperature or concentration of catalyst. In the former case, the TU value increases exponentially, and in the latter, the TU value increases a little by increase in catalyst concentration²⁾. Acceleration of reaction rate by the control of PO concentration (up to maximum, 33.3 wt %) needs no investment and increases little TU value. Since it has been confirmed⁶⁾ to be safe even when reaction runs away, to control PO concentration seems to be the best way to increase productivity.

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プロポキシレーションの反応速度解析

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プロポキシレーションはウレタンフォーム用の原料、界面活性剤などの工業的な製造手段として有用である。

われわれは生産性の向上を図ることを目的にプロピレンオキシド（以下、PO と略す）の逐次付加重合反応における反応速度の解析を実施した。

その結果、PO を連続的に投入する重合方法においては、反応液相中の PO 濃度を 33.3 wt % に保つとき最高の反応速度が得られることを実験によって実証し、かつ石井らの提唱した反応速度式から理論的に予測し得ることを明らかにした。

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