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## High Pressure Copolymerization of Styrene with Maleic Anhydride

By GOICHI ENOMOTO \*), YOSHIKI OGO \*\*), and TATSUYA IMOTO \*\*)

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### SUMMARY:

The radical copolymerization of styrene with maleic anhydride was investigated in an acetone solution at 40°C under high pressure up to 4000 kg/cm<sup>2</sup>. Effects of pressure on the monomer reactivity ratio considering the influence of the penultimate monomer unit were studied from kinetic data and IR spectra. It has been found that the radical copolymerization rate increases with pressure, especially concerning the reaction of maleic anhydride with a polymer chain possessing a maleic anhydride unit preceding the active styrene chain end.

### ZUSAMMENFASSUNG:

Die radikalische Copolymerisation von Styrol mit Maleinsäureanhydrid wurde in Aceton als Lösungsmittel bei 40°C unter Drücken bis zu 4000 kg/cm<sup>2</sup> untersucht. Der Effekt des Druckes auf das Reaktivitätsverhältnis der Monomeren wurde unter Berücksichtigung des Einflusses der vorletzten Monomereinheit auf Grund kinetischer Daten und der IR-Spektren untersucht. Es wurde gefunden, daß die Geschwindigkeit der radikalischen Copolymerisation mit dem Druck ansteigt, besonders bei der Reaktion zwischen Maleinsäureanhydrid mit einer Polymerkette, die vor dem aktiven Styrol-Kettenende eine Maleinsäureanhydrideinheit besitzt.

### Introduction

Radical copolymerization under high pressures has been studied by several groups of workers in recent years and the great majority of works on high pressure copolymerization have dealt with the effect of the pressure on the monomer reactivity ratio in the copolymerization system. Quantitative treatments of radical copolymerizations have generally assumed that the reactivity of a growing free radical is determined solely by its terminal monomer unit.

However it is necessary to consider that the reactivity of a growing chain in copolymerization is influenced by the nature of the penultimate monomer unit in some copolymerization systems. In an effort to determine the effect of penultimate monomer unit (penultimate effect) on copolymerization, copolymerization of styrene (S) with maleic anhydride

(M) was studied under high pressure in the present investigation since BARB<sup>1)</sup> had recognized the fact that this copolymerization system indicate the existence of penultimate effect.

### Experimental

*Styrene* was washed with 10% sodium thiosulfate solution, 10% sodium hydroxide solution and water. After drying over calcium chloride the liquid was distd. under reduced pressure (bp<sub>30</sub> 54°C).

*Maleic anhydride* was recrystallized twice from chloroform solution and dried at reduced pressure (bp 56–57°C).

*Acetone* was treated with potassium dichromate for several hrs and distd. (bp 56–57°C).

*Methanol* was distd. by the usual method.

A 54% freshly purified monomer mixture containing a given amount of acetone as solvent was filled into a glass sliding tube and then the tube was put in an autoclave at 40°C and pressurized. The pressure of the reaction system was measured by strain pressure gauge directly connected to autoclave. After appropriate time, the pressure was reduced and product removed.

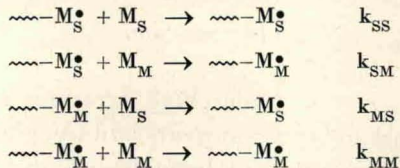
The copolymer mixture thus obtained was precipitated into a large amount of methanol as a precipitant, dried completely at room temp. and reduced pressure.

The compositions of the copolymers were calculated from the CH analysis. The IR spectra were measured at room temp. using uniform membrane of obtained copolymer.

### Results and Discussion

#### 1. Analysis of kinetic data

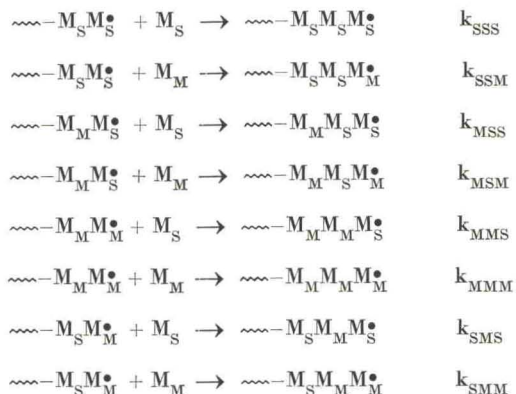
In the copolymerization process, there are four possible ways in which a monomer can add:



where  $\sim\sim\sim\text{-M}_S^\bullet$  and  $\sim\sim\sim\text{-M}_M^\bullet$  represents chains ending in the  $M_S$  and  $M_M$  monomer unit respectively, and where the parameters,  $r_1 = k_{SS}/k_{SM}$  and  $r_2 = k_{MM}/k_{MS}$  are defined as monomer reactivity ratios.

A copolymer composition equation which derives from the foregoing four propagating step in copolymerization cannot satisfactorily represent the experimental results in case of copolymerization with styrene and maleic anhydride system. In view of the above fact, BARB<sup>1)</sup> mentioned that a study of molecular models on copolymerization suggested the penultimate monomer unit might also be importance.

Considering that the reactivity of a growing chain in copolymerization might be influenced by the nature of the penultimate unit, eight possible propagation steps are recognized,



$$\frac{d[\text{M}_S]}{d[\text{M}_M]} = \frac{1 + [r'_1 x(r_1 x + 1)] / (r'_1 x + 1)}{1 + r'_2/x[(r_2 + x)/(r'_2 + x)]} = n \quad (1)$$

where

$$x = [\text{M}_S]/[\text{M}_M]$$

$$r_1 = k_{SSS}/k_{SSM}, \quad r'_1 = k_{MSS}/k_{MSM}$$

$$r_2 = k_{MMM}/k_{MMS}, \quad r'_2 = k_{SMM}/k_{SMS}$$

Eq. (1) was simplified as follows because the reactivity of anhydride radical to maleic anhydride is zero,  $k_{MMS} = k_{SMM} = 0$ .

$$n - 1 = r'_1 x(1 + rx)/(1 + r'_1 x) \quad (2)$$

Fig. 1 shows the copolymer composition calculated from Eq. (2) at various pressures and the solid curves based on the  $r_1, r_2$  values listed

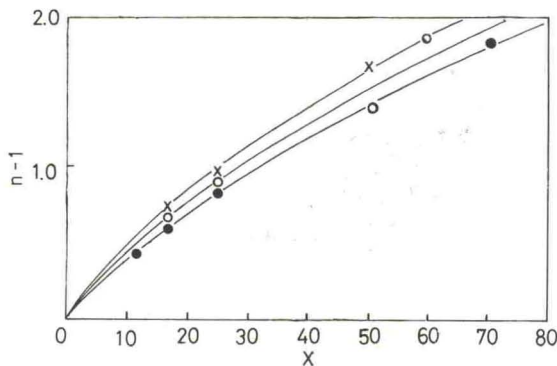


Fig. 1. Copolymer composition curves calculated from penultimate model. —x— 1 kg/cm<sup>2</sup>; —○— 2000 kg/cm<sup>2</sup>; —●— 4000 kg/cm<sup>2</sup>

in Table I were the best fit for the experimental data. The ratio  $r'_1/r_1$  which means the degree of penultimate effect decreased from 2.8 to 1.7 on increasing the pressure from 1 to 4000 kg/cm<sup>2</sup>.

Table I. The monomer reactivity ratios calculated from penultimate model

Pressure (kg/cm <sup>2</sup> )	$r_1$	$r'_1$	$r'_1/r_1$
1	0.023	0.065	2.8
2000	0.022	0.055	2.5
4000	0.023	0.042	1.7

The effect of pressure on the rate of chemical reactions can be related to the volume change from reactants to the transition state with VAN'T HOFF's equation.

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \quad (3)$$

where  $\Delta V^*$  is an activation volume.

Assuming that  $\Delta V^*$  does not vary with the pressure, Eq. (3) lead to

$$\ln \frac{(k)_P}{(k)_1} = -\frac{\Delta V^*}{RT} (P - 1) \approx -\frac{\Delta V^*}{RT} \quad (4)$$

where  $(k)_P$  and  $(k)_1$  are the rate constants at  $P$  kg/cm<sup>2</sup> and atmosphere, respectively.

By substituting  $r_1 = k_{SSS}/k_{SSM}$  and  $r'_1 = k_{MSS}/k_{MSM}$  into Eq. (4), the following equations are obtained.

$$\left(\frac{\partial \ln r_1}{\partial P}\right)_T = \left[\frac{\partial \ln (k_{SSS}/k_{SSM})}{\partial P}\right]_T = -\frac{(\Delta V_{SSS}^* - \Delta V_{SSM}^*)}{RT} \quad (5)$$

$$\left(\frac{\partial \ln r'_1}{\partial P}\right)_T = \left[\frac{\partial \ln (k_{MSS}/k_{MSM})}{\partial P}\right]_T = -\frac{(\Delta V_{MSS}^* - \Delta V_{MSM}^*)}{RT} \quad (6)$$

According to Eq. (5) and (6) we can expect an difference of the activation volume on the copolymerization reactions. As shown Fig. 2, a plot of  $\log r_1$  or  $r'_1$  against pressure were linear,  $\Delta V_{MSS}^* - \Delta V_{MSM}^*$  was calculated 2.6 cm<sup>3</sup>/mole. The constancy of the reactivity ratios with pressure leads to  $\Delta V_{SSS}^* = \Delta V_{SSM}^*$ .

Since the activation volume of the propagation reactions of styrene,  $\Delta V_{SS}^*$ , has been known to be -11.5 cm<sup>3</sup>/mole from the data of NICHOLSON and NORRISH<sup>2</sup>).

$$\Delta V_{SSS}^* = \Delta V_{MSS}^* = -11.5 \text{ cm}^3/\text{mole}$$

$$\Delta V_{MSM}^* = \Delta V_{MSS}^* - 2.6 = -14.1 \text{ cm}^3/\text{mole}$$

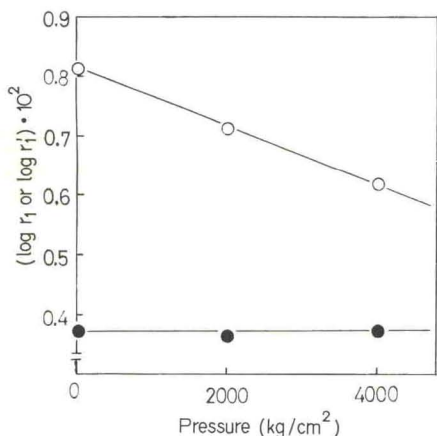


Fig. 2. Effect of pressure on the monomer reactivity ratios. —●—  $r_1$ ; —○—  $r_2$

These facts indicate that the copolymerization reaction with maleic anhydride and polymer chain which possess maleic anhydride unit preceding the active styrene chain end especially increase with pressure,  $\Delta V^* = -14.1 \text{ cm}^3/\text{mole}$ .

On the other hand, the following equation was derived from the preceding penultimate model equation by MILLER and NIELSEN<sup>3</sup>).

$$\begin{aligned} P_{SSS} &= r_1 x / (r_1 x + 1), & P_{SSM} &= 1 / (r_1 x + 1) \\ P_{MSS} &= r_1' x / (1 + r_1' x), & P_{MSM} &= 1 / (1 + r_1' x) \\ P_{MMM} &= r_2 / (x + r_2), & P_{MMS} &= x / (x + r_2) \\ P_{SMM} &= r_2' / (x + r_2'), & P_{SMS} &= x / (x + r_2') \end{aligned}$$

where  $P_{MSM}$  is the instantaneous probability of adding monomer of type M to a growing chain ending in M-S.

The probability of occurrence among all the sequences of type M of a sequence exactly  $m$  units long is  $W_n(m)$

$$W_n(m) = P_{MSS} P_{SSM} P_{SSS}^{m-2} \quad m \geq 2 \quad (7)$$

$$W_n(m) = P_{MSM} \quad m = 1 \quad (8)$$

At molar ratio (maleic anhydride/styrene),  $x = 150$ , pressure 1 and 4000 kg/cm<sup>2</sup>, sequence distribution of copolymer was calculated from Eq. (7) and (8) as shown Fig. 3. When the effect of unit other than terminal on the reactivity of a growing chain with adding monomer is considered ( $m = 1$ ), the sequence distribution of copolymer obtained under 4000 kg/cm<sup>2</sup> increased as compared with the sequence distribution of copolymer obtained under atmosphere.

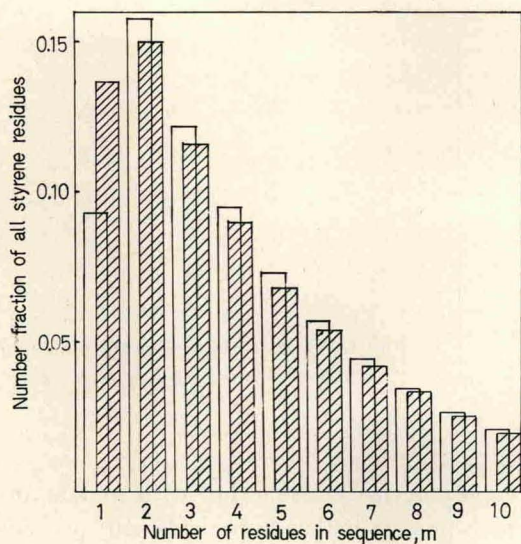


Fig. 3. Number distribution of styrene residues calculated from penultimate model,  $x = 150$ .  
 □ 1 kg/cm<sup>2</sup>; ▨ 4000 kg/cm<sup>2</sup>

## 2. Analysis of IR spectra

ANG and HARWOOD<sup>4)</sup> investigated the infrared spectra of styrene-maleic anhydride copolymers. On the basis of these data obtained, the authors mentioned that the phenyl absorption at 700 cm<sup>-1</sup> was found to be independent of sequential environment and this absorption proved useful in determining copolymer compositions. In contrast, the phenyl absorption at 759 cm<sup>-1</sup> proved to be sensitive to sequential environment and use was made of this feature to measure sequence distribution in the copolymers.

The ratio ( $A_{759}/A_{700}$ ) of the absorbance at 759 cm<sup>-1</sup> to that at 700 cm<sup>-1</sup> for a given copolymer was used to calculate the fraction ( $f_{\text{MSM}}$ ) of styrene unit centered in MSM triads in copolymers.

$$f_{\text{MSM}} = \frac{a - A_{759}/A_{700}}{a - c} \quad (9)$$

The Eq. (9) can be written by the following Eq. (10), where  $a = 0.725$ , the  $A_{759}/A_{700}$  value observed for polystyrene and where  $c = 0.110$ , the  $A_{759}/A_{700}$  value observed for alternating copolymers.

$$f_{\text{MSM}} = [0.725 - (A_{759}/A_{700})]/0.615 \quad (10)$$

Fig. 4 shows the dependence of the  $\log f_{\text{MSM}}$  on the reaction pressure. Evidently, the value of  $f_{\text{MSM}}$  increased on pressure. These facts suggest that a high pressure favored the formation of M-S-M type copolymer.

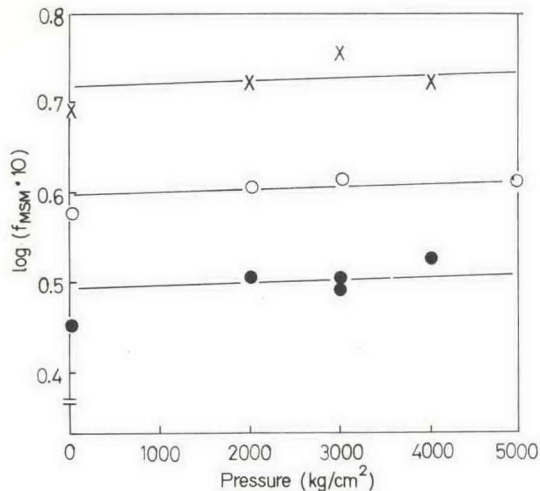


Fig. 4. Effect of pressure on  $f_{\text{MSM}}$   
 -●- x = 43.1; -○-  
 x = 25.3; -x- x = 12.6

It may be concluded from the results of these investigations that the copolymerization reaction with maleic anhydride and polymer chain which possess maleic anhydride unit preceding the active styrene chain end especially increase with pressure, namely penultimate effect disappears with pressure.

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