

## High Pressure Copolymerization of Styrene with Maleic Anhydride

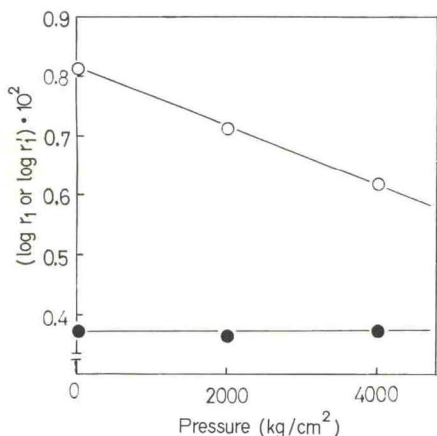


Fig. 2. Effect of pressure on the monomer reactivity ratios. —●—  $r_1$ ; —○—  $r_2$

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.

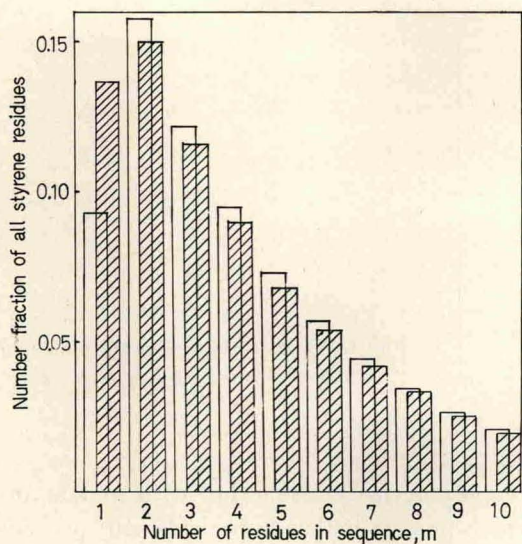


Fig. 3. Number distribution of styrene residues calculated from penultimate model,  $x = 150$ .  
 □ 1 kg/cm<sup>2</sup>; ▨ 4000 kg/cm<sup>2</sup>

## 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.

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