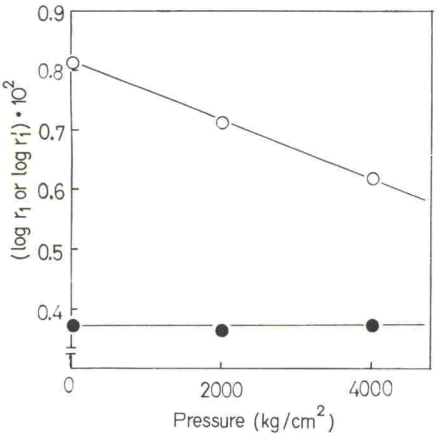

Fig. 2. Effect of pressure on the monomer reactivity ratios. $-\bullet-$ r_1; $-\circ-$ r_2

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, $\Delta V^* = -14.1$ cm^3/mole.

On the other hand, the following equation was derived from the preceding penultimate model equation by MILLER and NIELSEN[3].

$$P_{SSS} = r_1x/(r_1x + 1), \qquad P_{SSM} = 1/(r_1x + 1)$$

$$P_{MSS} = r'_1x/(1 + r'x), \qquad P_{MSM} = 1/(1 + r'x)$$

$$P_{MMM} = r_2/(x + r_2), \qquad P_{MMS} = x/(x + r_2)$$

$$P_{SMM} = r'_2/(x + r'_2), \qquad P_{SMS} = x/(x + r'_2)$$

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 Wn(m)

$$Wn(m) = P_{MSS}P_{SSM}P_{SSS}^{m-2} \qquad m \geqq 2 \qquad (7)$$

$$Wn(m) = P_{MSM} \qquad m = 1 \qquad (8)$$

At molar ratio (maleic anhydride/styrene), x = 150, pressure 1 and 4000 kg/cm^2, 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^2 increased as compared with the sequence distribution of copolymer obtained under atmosphere.

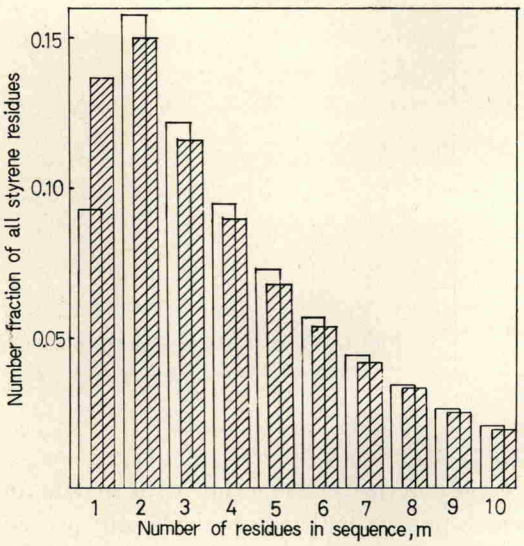

Fig. 3. Number distribution of styrene residues calculated from penultimate model, x = 150.
□ 1 kg/cm²; ▨ 4000 kg/cm²

2. *Analysis of IR spectra*

Ang and Harwood[4] 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^{-1} 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^{-1} 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^{-1} to that at 700 cm^{-1} for a given copolymer was used to calculate the fraction (f_{MSM}) of styrene unit centered in MSM triads in copolymers.

$$f_{MSM} = \frac{a - A_{759}/A_{700}}{a - c} \tag{9}$$

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.

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