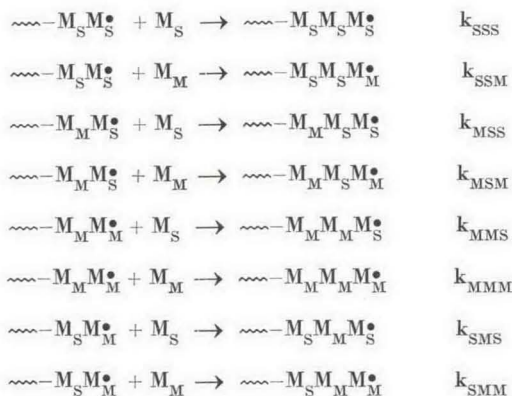


Considering that the reactivity of a growing chain in copolymerization might be influenced by the nature of the penultimate unit, eight possible propagation steps are recognized,



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

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

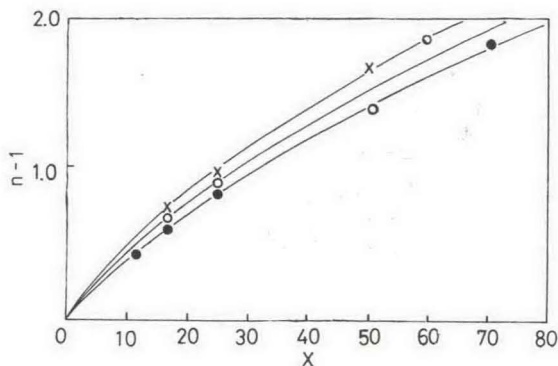


Fig. 1. Copolymer composition curves calculated from penultimate model. —x— 1 kg/cm²; —○— 2000 kg/cm²; —●— 4000 kg/cm²

in Table 1 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/cm².

Table 1. The monomer reactivity ratios calculated from penultimate model

| Pressure (kg/cm ²) | 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 ΔV^* is an activation volume.

Assuming that ΔV^* 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/cm² 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 cm³/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, ΔV_{SS}^* , has been known to be -11.5 cm³/mole from the data of NICHOLSON and NORRISH²⁾.

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

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