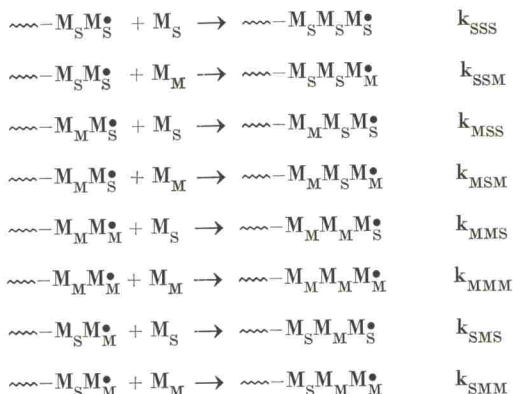


Considering that the reactivity of a growing chain in copolymerization might be influenced by the nature of the penultimate unit, eight possible propagation steps are recognized,



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

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

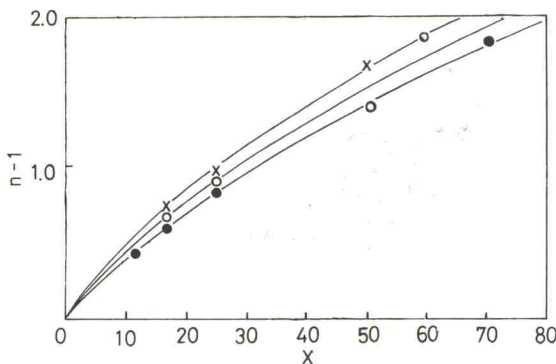


Fig. 1. Copolymer composition curves calculated from penultimate model. —x— 1 kg/cm²; —o— 2000 kg/cm²; —•— 4000 kg/cm²

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/cm².

Table I. 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⁾.

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

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