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,

$$\sim\sim-M_SM_S^\bullet + M_S \rightarrow \sim\sim-M_SM_SM_S^\bullet \qquad k_{SSS}$$

$$\sim\sim-M_SM_S^\bullet + M_M \rightarrow \sim\sim-M_SM_SM_M^\bullet \qquad k_{SSM}$$

$$\sim\sim-M_MM_S^\bullet + M_S \rightarrow \sim\sim-M_MM_SM_S^\bullet \qquad k_{MSS}$$

$$\sim\sim-M_MM_S^\bullet + M_M \rightarrow \sim\sim-M_MM_SM_M^\bullet \qquad k_{MSM}$$

$$\sim\sim-M_MM_M^\bullet + M_S \rightarrow \sim\sim-M_MM_MM_S^\bullet \qquad k_{MMS}$$

$$\sim\sim-M_MM_M^\bullet + M_M \rightarrow \sim\sim-M_MM_MM_M^\bullet \qquad k_{MMM}$$

$$\sim\sim-M_SM_M^\bullet + M_S \rightarrow \sim\sim-M_SM_MM_S^\bullet \qquad k_{SMS}$$

$$\sim\sim-M_SM_M^\bullet + M_M \rightarrow \sim\sim-M_SM_MM_M^\bullet \qquad k_{SMM}$$

$$\frac{d[M_S]}{d[M_M]} = \frac{1 + [r_1'x(r_1x + 1)]/(r_1'x + 1)}{1 + r_2'/x[(r_2 + x)/(r_2' + x)]} = n \qquad (1)$$

where

$$x = [M_S]/[M_M]$$

$$r_1 = k_{SSS}/k_{SSM}, \qquad r_1' = k_{MSS}/k_{MSM}$$

$$r_2 = k_{MMM}/k_{MMS}, \qquad r_2' = k_{SMM}/k_{SMS}$$

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

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

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

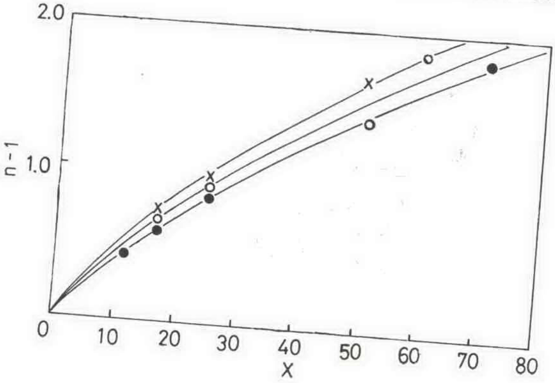

Fig. 1. Copolymer composition curves calculated from penultimate model. –×– 1 kg/cm²; –○– 2000 kg/cm²; –●– 4000 kg/cm²

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/cm^2.

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.

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

where ΔV^* is an activation volume.

Assuming that ΔV^* does not vary with the pressure, Eq. (3) lead to

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

where $(k)_P$ and $(k)_1$ are the rate constants at P kg/cm^2 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.

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

$$\left(\frac{\partial \ln r_1'}{\partial P}\right)_T = \left[\frac{\partial \ln (k_{MSS}/k_{MSM})}{\partial P}\right]_T = -\frac{(\Delta V^*_{MSS} - \Delta V^*_{MSM})}{RT} \tag{6}$$

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^3/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 cm^3/mole from the data of NICHOLSON and NORRISH[2)].

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

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