

Esterification of Styrene-Maleic Anhydride Copolymer by Mixed Alcohols

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Synopsis

A copolymer (MW = 1800) of styrene (St) and maleic anhydride (MAN) was esterified with an excess amount of an alcohol mixture, and then the relation between the esterification rates of the individual alcohols and the contents of the esters in the esterific copolymer was examined. At first, the rate constant of an individual esterification was obtained for four different alcohols (*n*-butanol, *i*-butanol, *i*-amylalcohol, and benzylalcohol) in a noncatalyst system. Then, the mixed esterification of *n*-butanol and *i*-amylalcohol was carried out; from the analysis of the ester contents, the following equation was obtained:

$$[P_1]/[P_2] = k_1[B_1]_0/k_2[B_2]_0.$$

From this result, it was concluded that, in esterification with alcohols involving *n* species, the content of the individual ester can be expressed by the following equation:

$$[P_j] / \sum_{i=1}^n [P_i] = k_j[B_j]_0 / \sum_{i=1}^n k_i[B_i]_0$$

where [P] = concentration of esters in the copolymer, [B]₀ = initial concentration of alcohols, and *k* = rate constant of esterification (*i, j* = 1, 2, . . . , *n*).

INTRODUCTION

We selected styrene-maleic anhydride copolymers as a model for esterification because this polymer keeps its maleic anhydride group with its high functionality and reacts independently, the phenyl and maleic anhydride groups being in a line alternatively.

The reaction of the copolymer of St-MAN and alcohol is expressed by eq. (1).¹ The individual ester thus formed is difficult to change into the double ester without a catalyst.² It was considered that the copolymer of the mixed-ester type was formed by using a mixed-alcohols system according to eq. (2). (See following page for eqs. (1) and (2).) Therefore, the mixed alcohols were allowed to react with the maleic anhydrous groups of the copolymer. We examined several alcohols to determine whether or not the composition of the introduced esters had any additivity related to the alterations in the feed composition and to determine the relation between the formation rates of the individual esters

obtained by the reaction of the above alcohols and the concentration rates of the alcohols.

EXPERIMENTAL

Copolymers of St-MAn. St-MAn copolymers were polymerized in benzene, with α, α' -azobisisobutylnitrile used as initiator, according to the method of a previous report.³

The composition of the copolymer was determined by potentiometric titration⁴ with sodium methylate. The rate of the maleic anhydride group was 0.48. The acid anhydride groups were considered to be present as single units.

Esterification Reaction. The esterifications were carried out with the reaction mixtures shown in Table I, under an atmosphere of nitrogen and in

TABLE I
Esterification Condition (Primary Alcohol)^a

Alcohol	Polymer concentration, moles of anhydride units/l.	Alcohol concentration, moles/l.	Moles of anhydride units/alcohol
<i>n</i> -Butanol	0.350	1.73	0.20
<i>i</i> -Butanol	0.360	1.79	0.20
<i>i</i> -Amyl alcohol	0.360	1.79	0.20
Benzyl alcohol	0.350	1.76	0.20

^a Methyl-ethyl ketone solution system (80.0°C).

a four-necked flask maintained at $80.0 \pm 0.3^\circ\text{C}$. The flask was equipped with a mercury-sealed Hershberg stirrer, a thermometer, a coil-type condenser, and a capillary for taking up samples. Approximately 40-ml samples of polymer solution were taken out of the flask at certain intervals, diluted with acetone as required, reprecipitated with 10 times as much petroleum ether as the solution, again reprecipitated from acetone solution with petroleum ether, and finally dried under reduced pressure.

Esterification with Mixed Alcohols. With the same apparatus and method mentioned above, the mixed esterification with *n*-butanol and *i*-amyl alcohol was carried out both in a solution system and in a nonsolvent system under the conditions shown in Tables II and III.

Measurement of Esterification Rate. The rate of disappearance of maleic anhydride groups was measured by infrared absorption spectroscopy.⁵ The analytical curve (Fig. 1) was depicted by measuring a tetrahydrofuran solution in which the copolymers of styrene with maleic anhydride and the completely individual esterified copolymers of *n*-butyl were mixed properly. The quantity of the ester groups was fixed on the straight line shown in Figure 1. Equation (3) shows the relation between the concentration of the maleic anhydride groups C_m (moles/l.) and the absorptivity D of each absorption band:

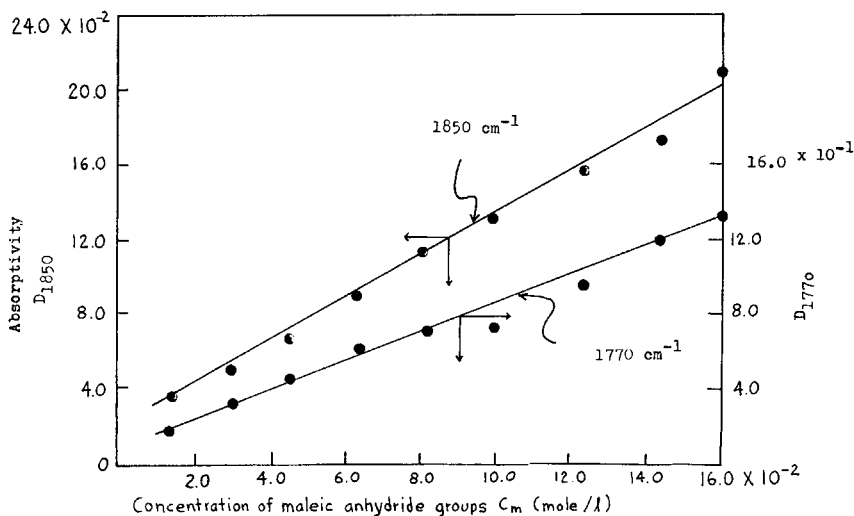


Fig. 1. Analytical curve for the determination of esterification values (IR spectrum).

TABLE II
Mixed Esterification Conditions (MEK Solution System)^a

Polymer concentration, moles of anhydride units/l.	0.360	0.360	0.358
Mixed alcohols	<i>n</i> -Butanol, moles of anhydride units/l.	0.60	0.88
	<i>i</i> -Amyl alcohol, moles of anhydride units/l.	1.17	0.89
Ratio of mixed alcohols	0.51	1.0	2.0

^a Polymer concentration/mixed alcohol concentration = 0.20; reaction temperature: 80.0°C.

TABLE III
Mixed Esterification Condition (Nonsolvent System)^a

Polymer concentration, moles of anhydride units/l.	0.027	0.027	0.027
Mixed alcohols	<i>n</i> -Butanol, moles of anhydride units/l.	0.31	0.45
	<i>i</i> -Amyl alcohol, moles of anhydride units/l.	0.60	0.45
Ratio of mixed alcohols	0.50	1.0	2.0

^a Polymer concentration/mixed alcohol concentration = 0.030; reaction temperature 80.0°C.

$$C_m = (D_{1850} - 1.90 \times 10^{-2})/1.10 = (D_{1770} - 7.20 \times 10^{-2})/8.30. \quad (3)$$

Equation (4) shows the relation between the esterification rate E (mole-%) and the concentration of maleic anhydride groups (moles/g) in the polymer:

$$E = (100 - 20.2C_m/C)/[(0.074C_m/C) + 1] \quad (4)$$

where C is the concentration of the sample solution (g/ml).

Separation and Quantitative Analysis of the Alkoxy Group. The copolymer ester was reacted with hydroiodic acid in phenol at 150°C, to convert the alcohol moieties of ester units into alkyl iodides, and was absorbed in *n*-heptane at -78°C. After these treatments, the quantity of each alkoxy group in the mixed esterification was quantitatively determined by gas chromatography.⁶

RESULTS AND DISCUSSION

The Rate of Individual Esterification

If the esterification between a maleic anhydride group in the polymer and an alcohol is the usual second-order reaction, the rate equation can be described as follows:

$$d[P]/dt = k([A]_0 - [P])([B]_0 - [P]) \quad (5)$$

where $[P]$ = ester group concentrations in the polymers, $[A]_0$ initial concentrations of maleic anhydride groups, $[B]_0$ initial concentration of alcohol, and k = the rate constant of the reaction.

If the alcohol is present in large excess and if the variation in the concentration can be ignored, eq. (6) is obtained:

$$d[P]/dt = k([A]_0 - [P]) \cdot [B]_0 \quad (6)$$

Equation (7) was obtained by integrating eq. (5) with respect to time:

$$\ln(100 - \theta E)/(100 - E) = k \cdot t([B]_0 - [A]_0) \quad (7)$$

where E is the esterification value, $\theta = [A]_0/[B]_0$.

Figure 2 shows a diagram in which the reaction time t and $\log(100 - E)$ are plotted. From Figure 2, it can be confirmed that eq. (7) is valid. The rate constant of each esterification reaction was obtained from the calculation of the slope of each plot in Figure 2; the constants are shown in Table IV. In reactions involving primary alcohols, the rate of individual

TABLE IV
Rate Constants of Certain Alcohols*

Reactants	Rate constant of reaction, hr ⁻¹
<i>n</i> -Butanol	1.18 × 10 ⁻²
<i>i</i> -Butanol	1.18 × 10 ⁻²
<i>i</i> -Amylalcohol	0.68 × 10 ⁻²
Benzylalcohol	0.29 × 10 ⁻²

* MEK solution system.

esterification decreased as the carbon chain became longer; this seems to be due to steric hindrance. In the case of primary alcohols with the same

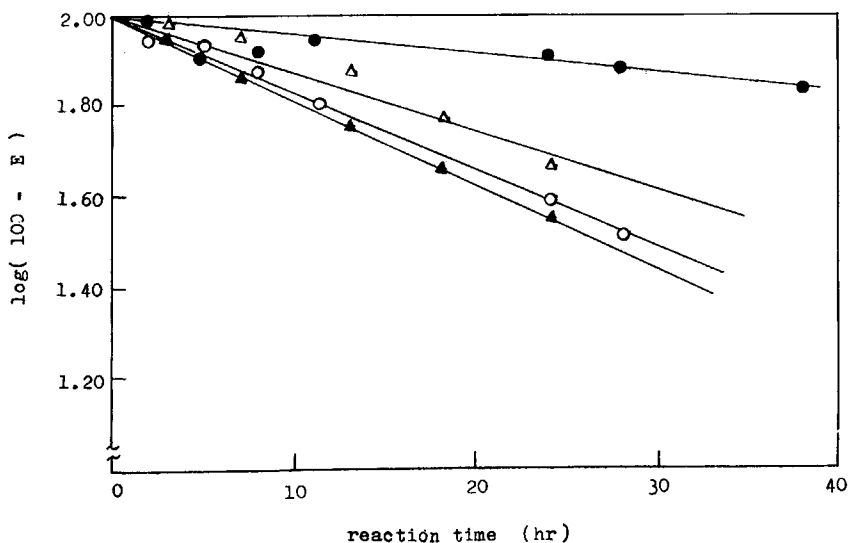


Fig. 2. Relation between reaction time and $\log(100 - E)$: (O) *n*-butanol; (▲) *i*-butanol; (Δ) *i*-amylalcohol; (●) benzylalcohol.

carbon number, the esterification rate was considered to be smaller in alcohols with branches than in those without branches. The difference between the two was, however, not very great in this experiment.

According to the report by Siegel,¹ in a nonsolvent system the individual esterification reaction of a styrene-maleic anhydride copolymer with primary alcohol occurs easily. In this experiment, the esterification reaction was carried out for 5 hr at 80°C; the individual esterification value thus obtained was about 80%. On the other hand, in reactions conducted in MEK, the reaction rate was very slow. This seemed to be largely due to solvation, which hindered the alkoxy group from attacking.

Equation of the Dualistic System

If the esterification reactions of styrene-maleic anhydride copolymer with two kinds of alcohols are independent, the reaction rates can be shown as follows:

$$d[P_1]/dt = k_1([A]_0 - [P])([B_1]_0 - [P]) \quad (8)$$

$$d[P_2]/dt = k_2([A]_0 - [P])([B_2]_0 - [P]). \quad (9)$$

Equation (10) is obtained by calculating the ratio of eq. (8) to eq. (9) and by ignoring the variation in alcohol concentration:

$$d[P_1]/d[P_2] = k_1/k_2([B_1]_0/[B_2]_0). \quad (10)$$

The integration of this equation results in eq. (11):

$$[P_1]/[P_2] = k_1/k_2([B_1]_0/[B_2]_0). \quad (11)$$

The relation between $[P_1]/[P_2]$ and $[B_1]_0/[B_2]_0$ in the combination of alcohols is shown the linear slopes (k_1/k_2) in Table V.

TABLE V
Combination of Alcohols and Ratio of Reaction Rates^a

Alcohol 1	Alcohol 2	k_1/k_2
<i>n</i> -Butanol	<i>i</i> -Amyl alcohol	1.7
<i>n</i> -Butanol	Benzyl alcohol	4.0
<i>n</i> -Butanol	<i>i</i> -Butanol	1.0
<i>i</i> -Butanol	<i>i</i> -Amyl alcohol	1.7
<i>i</i> -Butanol	Benzyl alcohol	4.0
<i>i</i> -Amyl alcohol	Benzyl alcohol	2.3

^a MEK solution system.

Comparison with Measured Figures

The relation between the ratio of the alkoxy groups introduced to polymers and the reaction time is shown in Figures 3 and 4 in Tables VI and VII for the sake of comparison. Figure 3 shows that if the ratio of

TABLE VI
Ratio of Alkoxy Groups^a

Initial concentration of <i>n</i> -butanol/initial concentration of <i>i</i> -amyl alcohol	Concentration of <i>n</i> -butyl individual ester/ concentration of <i>i</i> -amyl individual ester				
	3 hr ^b	7 hr	12 hr	18 hr	24 hr
0.51	0.67	0.81	0.80	—	1.1
1.0	1.20	1.4	1.6	1.7	2.4
2.0	—	3.0	2.8	3.2	3.3

^a MEK solution system.

^b Reaction time.

TABLE VII
Ratio of Alkoxy Groups (Nonsolvent System)

Initial concentration of <i>n</i> -butanol/initial concentration of <i>i</i> -amyl alcohol	Concentration of <i>n</i> -butyl single ester concentration of <i>i</i> -amyl single ester			
	5 hr ^a	6 hr	7 hr	8 hr
0.50	—	1.0	1.1	1.0
1.0	1.3	2.1	2.1	2.7
2.0	4.2	4.3	4.0	4.0

^a Reaction time.

feed alcohols is constant, the ratio of alcohols introduced is constant even when the reaction time varies from 5 to 20 hr. Figure 4 shows the same results as Figure 3 so long as the reaction time is within 5 to 8 hr. These facts show that both esterifications proceed independently within the above

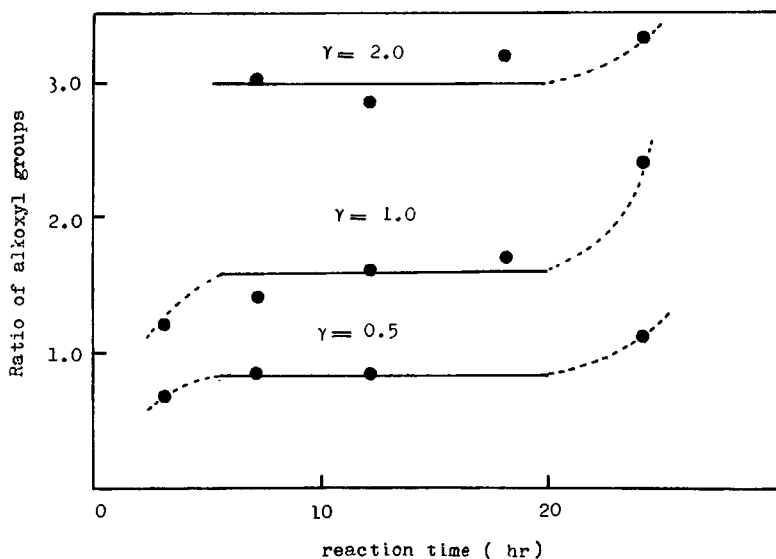


Fig. 3. Relation between ratio of alkoxy groups and reaction time (solvent system)

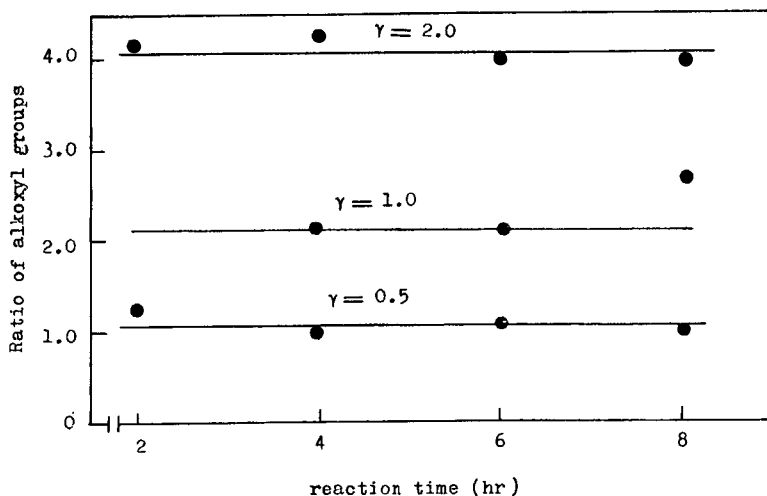


Fig. 4. Relation between ratio of alkoxy groups and reaction time (nonsolvent system)

time. In Figure 3, the line deviates from a straight line at the beginning and at the end of the reaction time. As to the latter case, it seemed to be due to the condition where alcohols were no longer excessive. Therefore, it was considered that a constant value was obtained if excess alcohols was maintained. In the range of the straight line, there was a constant relation between the reaction time and the ratio of alkoxy groups introduced; this relation is depicted in Figure 5. A solution system, however, shows the linear part in Figure 3. Therefore, this relation may be described as follows:

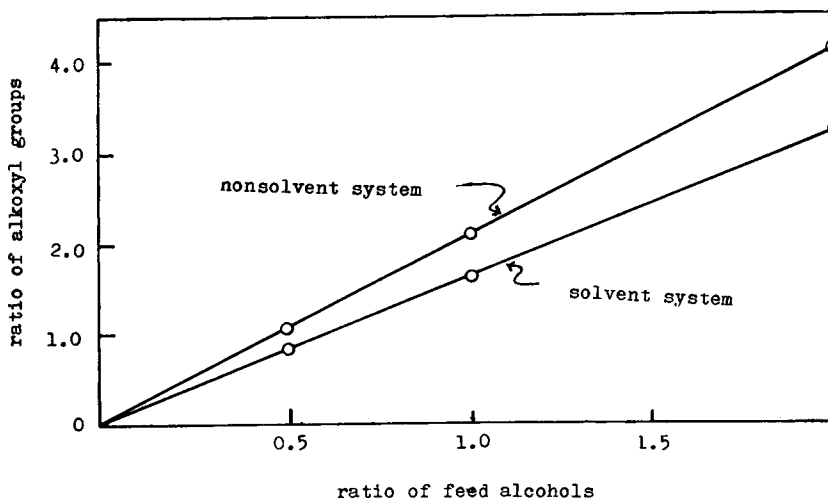


Fig. 5. Relation between ratio of alkoxy groups and ratio of feed alcohols.

$$[P_1]/[P_2] = k[B_1]_0/[B_2]_0. \quad (12)$$

When eq. (11) is compared with eq. (12), eq. (11) is found to be similar, with the exception of k and k_1/k_2 . Table VIII compares the k_1/k_2 values of

TABLE VIII
Comparison of K with k_1/k_2

K^a		k_1/k_2^b
(Solvent system)	(Nonsolvent system)	
1.6	2.0	1.7

^a K : Calculated using the experimental results.

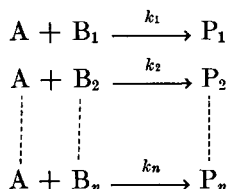
^b k_1/k_2 : Value indicated in Table V.

n-butanol and *i*-amylalcohol in Table V with the slopes of these lines in Figure 5; the comparison indicates that the values are very close in the solution system.

In the nonsolvent system, both K and k_1/k_2 deviate a little; in consideration of the solvent effects in the solvent system, this may be due to the use of the same reaction rate obtained in the model measurement. On the other hand, in the solution system it may be considered, on the basis of results obtained, that k ($= 2.0$) shows the esterification rate ratio in the nonsolvent system. When two kinds of alcohol were allowed to react, the ratios of the alkoxy groups introduced into the polymers are as is shown in eq. (11). Therefore, if the ratios of the feed alcohols and the reaction rates are determined, the ester composition can be controlled.

Computation Equation for a Multicomponent System

If this reaction was carried out in systems with more than two components, it was seen that each reaction proceeded independently, as has previously been mentioned. Therefore, this reaction may be described as follows:



The rates of each reaction are shown by the following equation:

$$d[\text{P}_j]/dt = k_j([\text{A}]_0 - [\text{P}])([\text{B}_j]_0 - [\text{P}]) \quad (j = 1, 2, \dots, n) \quad (13)$$

where $[\text{P}]$ = concentration of all the alkoxy groups in the polymer, $[\text{P}_j]$ = concentration of the j alkoxy group; $[\text{B}_j]$ = initial concentration of the j alcohol; $[\text{A}]_0$ = initial concentration of anhydrous rings.

The concentration changes of all the alkoxy groups are shown in eq. (14). If the concentration changes of each alcohol can be ignored, eq. (15) is derived from the ratios of both sides of eq. (13) and (14):

$$d[\text{P}]/dt = \sum_{i=1}^n k_i([\text{A}]_0 - [\text{P}])([\text{B}_i]_0 - [\text{P}]) \quad i = 1, 2, \dots, n \quad (14)$$

$$d[\text{P}_j]/d[\text{P}] = d[\text{P}_j] / \sum_{i=1}^n d[\text{P}_i] = k_j[\text{B}_j]_0 / \sum_{i=1}^n k_i[\text{B}_i]_0 \quad i, j = 1, 2, \dots, n. \quad (15)$$

As the right side of eq. (15) is constant, it can be integrated into eq. (16):

$$[\text{P}_j] / \sum_{i=1}^n [\text{P}_i] = k_j[\text{B}_j]_0 / \sum_{i=1}^n k_i[\text{B}_i]_0. \quad (16)$$

The left side of eq. (16) shows the molar fraction of the j alkoxy group. Therefore, when $k_j[\text{B}_j]_0 / \sum_{i=1}^n k_i[\text{B}_i]_0$ is shown on the axis of the abscissas and $f_m \left(= [\text{P}_j] / \sum_{i=1}^n [\text{P}_i] \right)$ is shown on the axis of the ordinates, a straight line of slope 1 is depicted.

Correspondence with Experimental Values

In an attempt to find the correspondence with experimental values, let n be 2 in eq. (16). In n -butanol (B_1) and i -amylalcohol (B_2) systems, the relation between the molar fraction of the n -butyl ester and $k_1[\text{B}_1]_0 / (k_1[\text{B}_1]_0 + k_2[\text{B}_2]_0)$ is as is depicted in Figures 6 and 7. In the solution system, each plot exists on a straight line with a slope of 1. In the non-solvent system, when a value of 1.7 for k_2/k_1 was used for the solution sys-

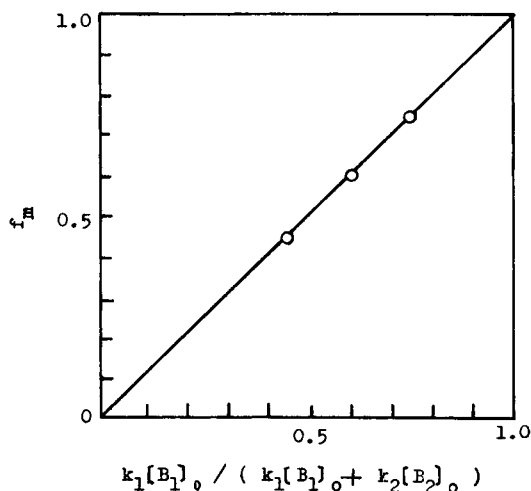


Fig. 6. Relation between molar fraction of *n*-butyl ester and $k_1[B_1]_0/(k_1[B_1]_0 + k_2[B_2]_0)$ (solvent system); f_m = the molar fraction of *n*-butoxy group; (O) $K = 1.6$.

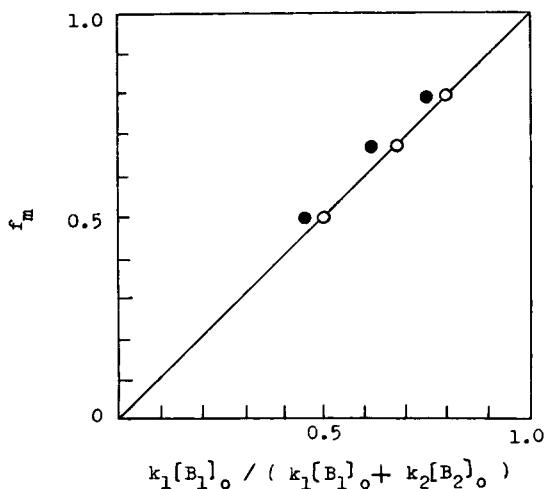


Fig. 7. Relation between molar fraction of *n*-butyl ester and $k_1[B_1]_0/(k_1[B_1]_0 + k_2[B_2]_0)$ (nonsolvent system); f_m = the molar fraction of *n*-butoxy group; (●) $k_1/k_2 = 1.7$, (O) $K = 2.0$.

tem, each plot slipped off the straight line with slope = 1. If the k value was 2.0, as in Table VIII, each plot followed this straight line. Therefore, in each case, the relation of eq. (16) was valid. If the assumption mentioned above was valid in the system of *n*-component alcohols, it was as is shown in eq. (16).

CONCLUSIONS

In the esterification reaction between a two-component system of a primary alcohol and the styrene-maleic anhydride copolymer, chosen as

model, the molar fraction of the j alkoxy group introduced into this copolymer was written as follows:

$$[P_j] / \sum_{i=1}^n [P_i] = k_j [B_j]_0 / \sum_{i=1}^n k_i [B_i]_0. \quad (16)$$

Therefore it was proved that, regardless of the presence of solvent, the composition of an esterified substance could be freely controlled by determining both the esterification rate and the initial concentrations of each constituent of the alcohol mixtures; it was also obvious that the additivity of these constituents was valid. It might be necessary also to consider the effects of the relationship between the solvent and the ionization of the carboxylic acid group. From this experiment, it was concluded that these effects were not very large within the same system.

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