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Product Relation of Copolymerization Reactivity Ratios

Akira Yamada[a]; Masaya Yanagita[a]
[a] Institute of Physical and Chemical Research, Yamato-Cho, Saitama, Japan

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LETTER TO THE EDITOR

Product Relation of Copolymerization Reactivity Ratios

The copolymerization reactivity ratios designated as $r_i = k_{ii}/k_{ij}$ are characteristic of thermodynamic conditions, such as temperature, pressure, and concentration, in which the temperature dependence has been demonstrated by kinetic procedures [1-4]. It is noted that in radical copolymerization the simple product of the reactivity ratios, e.g., $r_1 r_2$, generally tends to move toward unity with increasing temperature [2] and that for ionic copolymerization it is usually close to unity [5]. Such an inclination, however, involves some ambiguity in evaluating all the reported data [6] concerning the polymerization conditions.

In a stricter sense, we here provide the product relation of the copolymerization reactivity ratios, namely,

$$r_1 r_2{}^{\beta} = \alpha \quad \text{or} \quad (k_{11}/k_{12})(k_{22}/k_{21})^{\beta} = \alpha \tag{1}$$

where α and β are the thermodynamic parameters that will be defined in the following description.

In terms of transition state theory, the reactivity ratios can be expressed by

$$r_1 = \exp\,[(\Delta S^{\ddagger}_{11} - \Delta S^{\ddagger}_{12})/R]\ \exp\,[-(\Delta H^{\ddagger}_{11} - \Delta H^{\ddagger}_{12})/RT] \tag{2a}$$

and

$$r_2 = \exp\,[(\Delta S^{\ddagger}_{22} - \Delta S^{\ddagger}_{21})/R]\ \exp\,[-(\Delta H^{\ddagger}_{22} - \Delta H^{\ddagger}_{21})/RT] \tag{2b}$$

Then Eq. (1) will be replaced by

$$r_1 r_2{}^{\beta} = \exp\left[\frac{(\Delta S^{\ddagger}_{11} - \Delta S^{\ddagger}_{12}) + \beta(\Delta S^{\ddagger}_{22} - \Delta S^{\ddagger}_{21})}{R}\right] \exp\left[-\frac{(\Delta H^{\ddagger}_{11} - \Delta H^{\ddagger}_{12}) + \beta(\Delta H^{\ddagger}_{22} - \Delta H^{\ddagger}_{21})}{RT}\right] \tag{3}$$

When a copolymerization system examined with varying temperature exhibits this product relation, the right side of Eq. (3) should hold the definite value independent of the temperature, where that condition is given by

$$(\Delta H^{\ddagger}_{11} - \Delta H^{\ddagger}_{12}) + \beta(\Delta H^{\ddagger}_{22} - \Delta H^{\ddagger}_{21}) = 0 \tag{4}$$

Therefore, the parameters β and α, can be defined as

$$\beta = -(\Delta H^{\ddagger}_{11} - \Delta H^{\ddagger}_{12})/(\Delta H^{\ddagger}_{22} - \Delta H^{\ddagger}_{21}) \tag{5}$$

$$\alpha = \exp\left\{[(\Delta S^{\ddagger}_{11} - \Delta S^{\ddagger}_{12}) + \beta(\Delta S^{\ddagger}_{22} - \Delta S^{\ddagger}_{21})]/R\right\} \tag{6}$$

The parameter β is designated as the ratio of enthalpy differences between each successive propagation and α is predominantly made up of entropy terms forming the function of β. Equation (6) seems to be realized in some copolymerization systems (see Table 2), i.e., the α values observed tend to increase with increasing and decreasing β-value for Groups RI and CI, respectively (cf. Group PI in Table 3).

The product relation would be also interpreted by the Q-e scheme due to Alfrey and Price [7], as follows:

$$r_1 r_2^{\beta} = [Q_1/Q_2]^{1-\beta} \exp\left\{-(e_1^2 - (1+\beta)e_1 e_2 + \beta e_2^2)\right\} \tag{7}$$

and furthermore by the copolymerization factors, q and ϵ, proposed by Schwan and Price [8], as

$$r_1 r_2^{\beta} = \exp[(1-\beta)(q_2 - q_1)/RT]$$

$$\exp[-7.23 \times 10^{20}(\epsilon_1 - \epsilon_2)(\epsilon_1 - \beta\epsilon_2)/RT] \tag{8}$$

Although Eqs. (7) and (8) are also derived as the function of β, each right-hand side of the equations can not hold constant because of the four variable parameters, Q, e, q, and ϵ, with temperature, i.e., especially in Eq. (8) the necessary conditions to hold the α value definite are $(q_2 - q_1)/T$ = const and $(\epsilon_1 - \epsilon_2)(\epsilon_1 - \beta\epsilon_2)/T$ = const. Thus the product relation has been disproved by the Q-e scheme.

The parameters α and β are readily evaluated on a logarithmic plot according to Eq. (1) as an intercept and a slope, respectively, as shown schematically in Fig. 1.

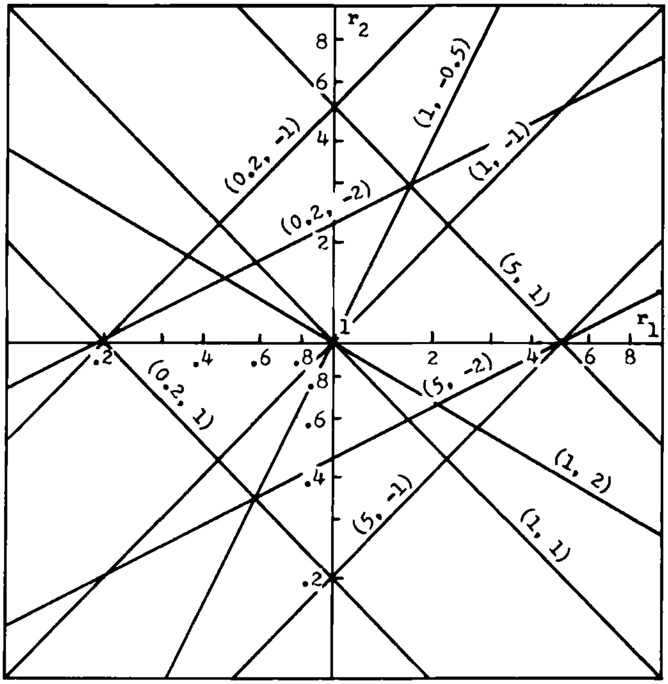

Fig. 1. Product relation expressed schematically on logarithmic diagram against various sets of α, β values.

In Table 1 some idealized conditions are expressed in thermodynamic terms according to Eqs. (5) and (6).

The α and β values calculated from the literature data [6] in which temperature dependence has been demonstrated are listed in Table 2. Data showing small change of reactivity ratios with varying temperature are excluded. It has been assumed that the monomer [M_1] has a smaller e value in the Q-e scheme than the comonomer.

The product relation might be utilized to identify the mechanism by use of the parameters as indexes. For instance, as shown in Table 2, the radical copolymerization systems can be classified into two groups corresponding to the negative and the positive sign of β. Two types of mechanisms seem to influence interactions between a polymeric chain end and the comonomer. The magnitude of α for various systems is very scattered, whereas β is close to unity. These findings suggest that entropy character plays a major role in monomer selectivity in the radical copolymerization process.

Table 1. The Parameters α and β Interpreted with Thermodynamic Measurements According to Eqs. (5) and (6)

Parameters α or β	Conditions designated with differences of thermodynamic measurements	Remarks
$\beta = 1$	$(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12}) = -(\Delta^\ddagger_{22} - \Delta H^\ddagger_{21})$	$r_1 r_2 = \alpha$
$\beta = -1$	$(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12}) = (\Delta H^\ddagger_{22} - \Delta H^\ddagger_{21})$	$r_1/r_2 = \alpha$
$\beta = 1, \alpha = 1$	$(\Delta S^\ddagger_{11} - \Delta S^\ddagger_{12}) = -(\Delta S^\ddagger_{22} - \Delta S^\ddagger_{21})$	$r_1 r_2 = 1$
$\beta = -1, \alpha = 1$	$(\Delta S^\ddagger_{11} - \Delta S^\ddagger_{12}) = (\Delta S^\ddagger_{22} - \Delta S^\ddagger_{21})$	$r_1/r_2 = 1$
$\alpha = 1$	$(\Delta S^\ddagger_{11} - \Delta S^\ddagger_{12}) = -\beta(\Delta S^\ddagger_{22} - \Delta S^\ddagger_{21})$	$r_1 r_2{}^\beta = 1$
$\beta > 0$	$(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12}) \gtrless 0, (\Delta H^\ddagger_{22} - \Delta H^\ddagger_{21}) \lessgtr 0$	$r_1\uparrow r_2\downarrow$ or $r_1\downarrow r_2\uparrow$
$\beta < 0$	$(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12}) \gtrless 0, (\Delta H^\ddagger_{22} - \Delta H^\ddagger_{21}) \gtrless 0$	$r_1\uparrow r_2\uparrow$ or $r_1\downarrow r_2\downarrow$
$\alpha = 1$	$\frac{(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12})}{(\Delta H^\ddagger_{22} - \Delta H^\ddagger_{21})} = \frac{(\Delta S^\ddagger_{11} - \Delta S^\ddagger_{12})}{(\Delta S^\ddagger_{22} - \Delta S^\ddagger_{21})}$	Compensation effect
$\alpha \neq 1$	$\frac{(\Delta H^\ddagger_{11} - \Delta H^\ddagger_{12})}{(\Delta H^\ddagger_{22} - \Delta H^\ddagger_{21})} = \frac{(\Delta S^\ddagger_{11} - \Delta S^\ddagger_{12}) - R \ln \alpha}{(\Delta S^\ddagger_{22} - \Delta S^\ddagger_{21})}$	Compensation effect

On the other hand, most ionic systems show a positive sign for β , and these systems were classified by the temperature dependence of the reactivity ratios. The wide scatter of α and β values, which is contrary to the expectation of Landler [5], indicates both entropy and enthalpy terms seem to cooperate in the ionic mechanism. Since little quantitative work especially for cationic copolymerization has been done under systematic variation of physical conditions, the magnitude of α and β, as a guide, would not be dependable. However, in only Grignard reagent copolymerization (Group AI in Table 2) are the examined values of β close to unity. This case can thus be recognized as one in which the entropy term behaves predominantly as a function of conditions.

So-called pressure and solvent effects on the reactivity ratios should be reconsidered using this product relation, because Eq. (1) also might be found by derivation with the elimination of the pressure or concentration term, as in Eqs. (2) to (6).

In Table 3 are summarized α and β values for the reactivity ratios which depend on the pressure and the solvent. In radical copolymerization β values for pressure dependence usually have the negative sign, but in which two systems (Group PII in Table 3), β values have the positive sign for temperature dependence (see Table 2). It can not yet be confirmed whether the mechanism for the temperature dependence and for the pressure effect are different from each other or if the literature data involves some errors by the investigators.

The solvent effect on the reactivity ratios examined as a function of pressure has been recognized [10]. These reactivity ratios have the linear relation due to Eq. (1), yielding parameters which show the tendency for α to increase with decreasing β.

The solvent effect on cationic copolymerization is remarkably large as a general rule. The typical two cases [13, 14] in which reactivity ratios change with increasing dielectric constant of solvent display a fairly linear correlation between r_1 and r_2, though it is still not known what the α and β values calculated mean (Group SII in Table 3). This correlation suggests that the cationic mechanism on an active site in the various solvent molecules can be ascribed to "compensation effect" according to the equation cited in Table 1.

Consequently, the new product relation of the reactivity ratios variable with physical conditions is proposed as $r_1 r_2^{\beta} = \alpha$, i.e., it is a convenient means of identifying the various copolymerization mechanisms. More detailed discussions concerning the mechanism conferred by the parameter values will be made later with more precise data.

Table 2. The Parameters α and β Calculated for Some Reactivity Ratios Against Temperature Dependence. Data Quoted from Literature Tables [6]

Group No.	Comonomers		Parameters		Temperature dependence[b]		Remarks
	$[M_1]$	$[M_2]$	α	β	r_1	r_2	
		Radical Copolymerization					
RI	Vinyl acetate	Methyl acid maleate	0.12	-1.5	↑	↑	
	Styrene	Methyl methacrylate	1.27	-1.3	↑	↑	
	Styrene	Methyl acrylate	1.41	-0.37	↑	↑	
	Styrene	Diethyl fumarate	5.5	-1.1	↑	↑	
	N-Vinyl carbazol	Vinyl acetate	10	-0.64	↑	↑	
RII	Styrene	2,5-Dichlorostyrene	0.09	0.50	↑	↓	
	Styrene	Acrylonitrile	0.19	0.23	↑	↓	
	Allyl chloride	Methyl acrylate	0.20	0.62	↑	↓	
	Styrene	2-Fluorobutadiene	2.5×10^5	30	↑	↓	
RIII[a]	Methyl methacrylate	Acrylonitrile	0.72	0.28	↓	↑	
		Cationic Copolymerization					
CI	CEVE[c]	α-Methyl styrene[d]	0.15	4.0	↑	↓	$(SnCl_4 TCA)$ toluene
	CEVE	α-Methyl styrene[d]	0.87	2.2	↑	↓	$(BF_3 Et_2O)CH_2Cl_2$
	CEVE	α-Methyl styrene[d]	1.0	3.3	↑	↓	$(SnCl_4 TCA)CH_2Cl_2$

	CEVE	α-Methyl styrene	1.3	1.5	↑	↓	$(BF_3\,2AcOH)(CH_2Cl)_2$
	CEVE	p-Methyl styrene[d]	1.6	2.6	↑	↓	$(SnCl_4\,TCA)$ toluene
	CEVE	p-Methyl styrene[d]	5.0	3.7	↑	↓	$(SnCl_4\,TCA)CH_2Cl_2$
	CEVE	p-Methoxy styrene[d]	15	1.2	↑	↓	$(BF_3\,Et_2O)$ toluene
CII	N-Butyl vinyl ether	Acenaphthylene	0.91	0.96	↓	↑	$BF_3\,Et_2O$
	CEVE	p-Methoxy styrene[d]	4.6	0.52	↓	↑	$(SnCl_4\,TCA)CH_2Cl_2$
	α-Methyl styrene	p-Chlorostyrene	8.7	0.55	↓/	↑	$SnCl_4$
	CEVE	p-Methoxy styrene[d]	12	0.90	↓	↑	$(BF_3\,Et_2O)CH_2Cl_2$
CIII[a]	Isobutene	Styrene	2.3	−0.39	↑	↑	$AlCl_3$
CIV[a]	p-Methoxy styrene	o-Methoxy styrene	7.9	−3.2	↓	↓	$BF_3\,Et_2O$
	CEVE	Styrene	107	−0.59	↓	↓	$(BF_3\,2ACOH)(CH_2Cl)_2$
		Anionic Copolymerization					
AI	Methyl methacrylate	Acrylonitrile	0.06	0.82	↑	↓	PhMgI toluene
	Methyl methacrylate	Acrylonitrile	0.14	1.1	↑	↓	(PhMgBr·ether) toluene
	Methyl methacrylate	Acrylonitrile	0.15	1.2	↑	↓	PhMgBr toluene
	Styrene	Methyl methacrylate	0.39	1.1	↑	↓	(PhMgBr·ether) toluene
	Styrene	Methyl methacrylate	0.62	1.0	↑	↓	(PhMgBr·ether) ether
	Methyl methacrylate	Methacrylonitrile	1.08	0.51	↑	↓	(PhMgBr·ether) toluene

[a] RIII, CIII, and CIV are exceptional cases in their respective polymerization system.

[b] ↑ and ↓ denote that the reactivity ratio increases and decreases, respectively, with increasing temperature.

[c] 2-Chloroethyl vinyl ether.

[d] Ref. 9.

Table 3. The Parameters α and β Calculated for Some Literature Data Concerning Pressure Dependence [Upper] and Solvent Effect [Lower]

Group No.	Comonomers [M_1]	[M_2]	Reporter of r_i	Parameters α	β	Dependency[a] r_1	r_2	Remarks[b]
PI	Styrene	Methyl methacrylate	[10]	0.63	-0.51	↑	↑	R. 1-1000 atm, pyridine 50°C
	Styrene	Methyl methacrylate	[10]	0.84	-0.70	↑	↑	R. 1-1000 atm, $(CH_2Cl)_2$ 50°C
	Styrene	Methyl methacrylate	[10]	0.94	-0.98	↑	↑	R. 1-1000 atm, ethanole 50°C
	Styrene	Methyl methacrylate	[10]	1.3	-1.2	↑	↑	R. 1-1000 atm, benzene 50°C
PII	Styrene	Acrylonitrile	[11]	1.4	-0.50	↑	↑	R. 1-1000 atm, 90°C
	Methyl methacrylate	Acrylonitrile	[11]	2.0	-0.19	↑	↑	R. 1-1000 atm, 90°C
SI	Styrene	Methyl methacrylate	[12]	1.3	-1.2	↑	↑	R. Benzenes 60°C
SII	Isobutene	Styrene	[13]	4.6	0.33	↑	↓	$TiCl_4$, nC_6H_{12}-CH_2Cl_2, -78°C
	Isobutene	p-Chlorostyrene	[14]	1.5	8.5	↑	↓	$AlBr_3$, DK = 1.82-38, 0°C

[a] ↑ and ↓ denote that the reactivity ratio increases and decreases, respectively, with increasing pressure or polarity of solvent.

[b] R denotes radical initiation.

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Akira Yamada
Masaya Yanagita

Institute of Physical and Chemical Research
Yamato-Cho, Saitama, Japan

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