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Cationic Copolymerization of Propylene Oxide with Tetrahydrofuran. X. Variation of Reactivity Ratios with Different Reaction Parameters

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ABSTRACT

The effects of different reaction parameters, such as catalyst, cocatalyst, and temperature, on reactivity ratios have been studied for the case of the copolymerization of propylene oxide (M_1) with tetrahydrofuran (M_2). The reactivity ratios were found to vary with the type of catalyst and cocatalyst used; however, the product of their values, $r_1 r_2$, remained essentially constant. For the three catalysts studied, viz., 1) triphenylmethyl cations, $(C_6H_5)_3C^+$, in combination with three different gegenions (hexafluorophosphate, PF_6^- ; hexafluoroarsenate, AsF_6^- ; and hexafluoroantimonate, SbF_6^- ; 2) antimony pentachloride, $SbCl_5$; and 3) borontrifluoride etherate, $BF_3 \cdot (C_2H_5)_2O$, the values of r_1 , calculated on the basis of constant reactivity ratio products, were found to increase with temperature in the range -10 to $20^\circ C$. However, for $BF_3 \cdot (C_2H_5)_2O$ initiated copolymerizations, the values of r_1 decreased between -30 and $-10^\circ C$. The magnitude of this increase or decrease depends on the concentration of the diol cocatalyst used. The energetics of the propagation reactions studied, as obtained from

plots of $\ln r_1$ and $\ln r_2$ vs $1/T$, showed that the concentration of diol had practically no effect on the thermodynamic parameters, ΔH and ΔS . Based on activation enthalpy ($\Delta H_{11} - \Delta H_{12}$) and entropy ($\Delta S_{11} - \Delta S_{12}$) differences for increasing reactivity of PO, the catalysts were found to lie in the following order with respect to their relative reactivities: $(C_6H_5)_3C^+SbF_6^- > (C_6H_5)_3C^+AsF_6^- > SbCl_5 > (C_6H_5)_3C^+PF_6^- > BF_3 \cdot (C_2H_5)_2O$. The different activation enthalpy and entropy values obtained in the two temperature ranges mentioned above are attributed to the presence of different ion-pairs.

INTRODUCTION

The role of several parameters (basicity of monomers [1, 2], dielectric constant of the medium [3-19], nature of the catalysts [3-7, 20-24] and cocatalysts used [24-56], and temperature of reaction [4, 16-20, 57-60]) in controlling the reactivity of monomers in cationic polymerization and copolymerization systems has been extensively dealt with in the literature. Two comprehensive articles dealing with this subject [61, 62] have also been published in which the individual role played by each of these parameters on copolymerization reaction systems is more clearly studied. Based on a comparison of data published on cationic and free-radical copolymerizations, it was noted that, unlike in radical copolymerizations, the reactivity ratio products obtained, r_1r_2 , with cationic copolymerizations do not always have a value close to 1. Furthermore, of the reaction parameters studied, the influence of the dielectric constant of the medium on r_1r_2 [3-18] appears to be the one which is the most unpredictable. The variation of other parameters, such as the type of catalyst or cocatalyst used, can change individual reactivity ratio values, but r_1r_2 remains much the same. As for the effect of temperature on r_1r_2 , constant values are observed only at low temperatures in the -78 to $0^\circ C$ range.

To shed more light on the influence of the above-mentioned parameters on r_1r_2 associated with copolymerization reactions, data obtained on copolymerizations of PO with THF carried out in this laboratory [25-33] has been reevaluated in the light of more recent developments in the field of cationic copolymerizations. Reactivity ratios have been calculated using the classic Mayo-Lewis equation [63] in a modified form [64-66]. Variations of the values on changing the catalyst, on adding a cocatalyst, and on raising the temperature have been studied with modified and additional new data. The results which have been obtained are the subject of this paper.

RESULTS

Equations for the Computation of Reactivity Ratios

In the work published earlier from this laboratory, reactivity ratios were computed from the well-known Mayo-Lewis [63] equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (1)$$

More recently, it has been reported [64, 65] that Eq. (1) may be used in the form:

$$\frac{d[M_1]}{d[M_2]} = K \left[\frac{[M_1]}{[M_2]} \right]^a \quad (2)$$

where K and a are constants which depend on the system being studied. For any two comonomer feed compositions, X_1 and X_2 , where $X_1 = [M_1]_1/[M_2]_1$ and $X_2 = [M_1]_2/[M_2]_2$, the values of r_1 and r_2 according to O' Driscoll and co-workers [66] may be evaluated from the expressions:

$$r_1 = - \frac{KX_1^{(a-2)} X_2^{(a-2)} (X_1 - X_2)}{X_1^{(a-2)} - X_2^{(a-2)}} - \frac{X_1^{(a-1)} - X_2^{(a-1)}}{X_1 X_2 (X_1^{(a-2)} - X_2^{(a-2)})} \quad (3)$$

and

$$r_2 = - \frac{X_1^{(a-1)} - X_2^{(a-1)}}{X_1^{(a-2)} - X_2^{(a-2)}} - \frac{X_1 - X_2}{KX_1 X_2 (X_1^{(a-2)} - X_2^{(a-2)})} \quad (4)$$

The constant "a" can be evaluated from the slope of a log-log plot of $d[M_1]/d[M_2]$ vs $[M_1]/[M_2]$; K , by setting $[M_1]/[M_2]$ in Eq. (1) equal to 1.

Thus

$$K = (r_1 + 1)/(r_2 + 1) \quad (5)$$

Evaluation of Reactivity Ratios for Different Catalyst-Cocatalyst Systems with the Modified Experimental Data of Refs. 25 to 33

The $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ /Diol Systems (1,2-Propane, 1,3-Propane, and 1,4-Butane Diols)

In an earlier study [25], plots of comonomer concentrations vs time were presented for three different diols. Initial rates of polymerization were estimated from tangents drawn to the curves. With these rates and the Mayo-Lewis equation, monomer reactivity ratios were calculated using the intersection method. In the present study, initial rates were computed from the linear portions of $\ln C_0/C$ vs time plots. The results, including initial comonomer concentrations for each case, are presented in Table 1. With this data, log-log plots of $d[M_1]/d[M_2]$ vs $[M_1]/[M_2]$ were drawn (see Fig. 1). From these, values for a and K were obtained which, on substitution into Eqs. (3) to (5), yielded values for r_1 and r_2 . These are listed in Table 2.

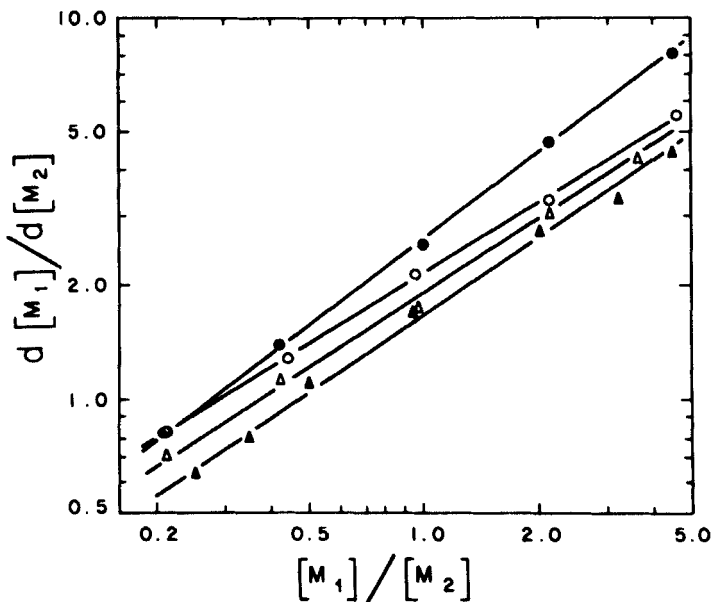


FIG. 1. Log-log plots of $d[M_1]/d[M_2]$ vs $[M_1]/[M_2]$ from which a and K are evaluated for the system PO-THF-DCE involving $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ and four cocatalysts: (\circ), 1,2-propane diol; (\bullet), 1,4-butane diol; (Δ), 1,3-propane diol; and (\blacktriangle) 1,2,3-propane triol.

TABLE 1. The Effect of Initial Comonomer Concentrations on the Initial Rates of Copolymerizations Carried Out at 0°C with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ in the Presence of Different Diols and of Dichloroethane as Solvent^a

Cocatalyst	$[\text{PO}]_0$ (mole/liter)	$[\text{THF}]_0$ (mole/liter)	$-\frac{d[\text{PO}]_0}{d\theta} \times 10^3$ [mole/(liter)(min)]	$-\frac{d[\text{THF}]_0}{d\theta} \times 10^3$ [mole/(liter)(min)]
1,2-Propane diol	5.25	1.15	27.77	5.00
	4.30	2.00	19.55	5.92
	3.00	3.20	9.00	4.16
	1.95	4.40	6.73	5.26
1,3-Propane diol	1.10	5.25	4.50	5.55
	5.40	1.50	51.66	11.80
	4.15	1.95	31.95	10.44
	3.15	3.25	20.00	11.64
1,4-Butane diol	1.75	4.20	5.95	5.25
	1.10	5.25	2.50	3.50
	5.40	1.20	17.00	2.14
	4.25	2.00	10.00	2.14
	3.00	3.00	5.50	2.14
	1.80	4.25	3.50	2.50
	1.10	5.25	2.00	2.50

^aOther conditions: $[\text{catalyst}]_0 = 7.0 \times 10^{-4}$ mole; $[\text{cocatalyst}]_0 = 2.4 \times 10^{-2}$ mole; $[\text{solvent}]_0 = [\text{PO} + \text{THF}]_0$ mole. (All three catalyst systems contain, besides diol, 0.09 mole/liter of water.)

TABLE 2. Reactivity Ratios and Other Values for Different Catalyst-Cocatalyst Systems^a

Catalyst	Cocatalyst	DC	a	K	r_1 (PO)	r_2 (THF)	$r_1 r_2$ range
BF ₃ ·(C ₂ H ₅) ₂ O	1,2-Propane diol	32.0	0.63	2.10	1.10 ± 0.05	0.08 ± 0.01	0.07-0.10
BF ₃ ·(C ₂ H ₅) ₂ O	1,3-Propane diol	35.0	0.65	1.92	1.00 ± 0.05	0.09 ± 0.01	0.08-0.10
BF ₃ ·(C ₂ H ₅) ₂ O	1,4-Butane diol	-	0.75	2.50	1.66 ± 0.05	0.05 ± 0.01	0.06-0.10
BF ₃ ·(C ₂ H ₅) ₂ O	1,2,3-Propane triol	-	0.68	1.66	0.85 ± 0.05	0.11 ± 0.01	0.08-0.11
BF ₃ ·(C ₂ H ₅) ₂ O*	Water*	80.4	0.65	0.70	0.26 ± 0.01	0.80 ± 0.05	0.19-0.23
SbCl ₅	1,2-Propane diol	32.0	0.66	1.85	1.00 ± 0.05	0.09 ± 0.01	0.08-0.10
SbCl ₅	1,2-Butane diol	-	0.82	2.50	1.70 ± 0.05	0.055 ± 0.01	0.07-0.11
(C ₆ H ₅) ₃ C ⁺ PF ₆ ⁻	None	-	0.65	0.70	0.26 ± 0.01	0.80 ± 0.05	0.19-0.23

^aOther conditions: [BF₃·(C₂H₅)₂O]₀ = 1.0 × 10⁻² mole/liter; [SbCl₅]₀ = 1.0 × 10⁻² mole/liter; [(C₆H₅)₃C⁺PF₆⁻]₀ = 6.5 × 10⁻³ mole/liter; [diol]₀ = 0.38 mole/liter; [water]₀* = 2.10 × 10⁻² mole/liter; [BF₃·(C₂H₅)₂O]₀* = 1.52 × 10⁻² mole/liter. DC is the known dielectric constant of the cocatalyst.

The $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/1,2,3\text{-Propane Triol System}$

With the data given in Ref. 28, a similar procedure was followed (see Fig. 1) from which values for a , K , r_1 , and r_2 were eventually obtained. These are also listed in Table 2.

The $\text{SbCl}_5/\text{Diol Systems (1,2-Propane and 1,2-Butane Diols)}$

The copolymerization of PO and THF with the $\text{SbCl}_5/1,2\text{-propane diol}$ catalyst-cocatalyst system has been reported on earlier [29]. Initial rates of reaction and consequent reactivity ratios were calculated in a fashion similar to that described in Ref. 25. An alternative approach was used in this work to calculate the initial rates of the copolymerizations ($\ln C_0/C$ vs t plots). The results from one or other method should be the same; however, this was not always the case. In Fig. 2 are shown monomer concentration vs time curves for the SbCl_5 -initiated copolymerization reaction, using alternatively 1,2-propane and 1,2-butane diols as cocatalysts. It should be noted that, at the beginning of each reaction, the consumption of PO and THF is rapid, but after this the disappearance of comonomers slows down considerably. The reactivity ratio results reported in Refs. 29 and 30 were calculated from tangents drawn to these curves. In the present study, other rate values were obtained when use was made of the initial linear parts of $\ln C_0/C$ vs time plots. Additional data with 1,2-butane diol has been added and is shown in Table 3. This data enabled log-log plots of $d[M_1]/d[M_2]$ vs $[M_1]/[M_2]$ to be drawn (see Fig. 3) from which values of a and K were obtained. These led to the calculation of new values of r_1 and r_2 listed in Table 2.

The $(\text{C}_6\text{H}_5)_3\text{C}^+\text{PF}_6^-$ and the $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/\text{Water Systems}$

Table 2 also lists, for comparison purposes, reactivity ratios values obtained by the revised $\ln C_0/C$ vs t method for $(\text{C}_6\text{H}_5)_3\text{C}^+\text{PF}_6^-$ -initiated copolymerizations [31] and $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/\text{water}$ -initiated reactions [32].

After establishing the values of r_1 and r_2 and $r_1 r_2$ for the different systems, the variations of these values with different parameters were studied with the help of the Mayo-Lewis equation. The initial rates of comonomer disappearance were calculated in each experiment for equimolar concentrations of the comonomers. This had the effect of reducing Eq. (1) to the form:

$$d[M_1]/d[M_2] = (r_1 + 1)/(r_2 + 1) \quad (6)$$

With the knowledge of $d[M_1]/d[M_2]$ and of $r_1 r_2$, values for r_1 and r_2 could easily be obtained. Alternatively, one may have preferred to

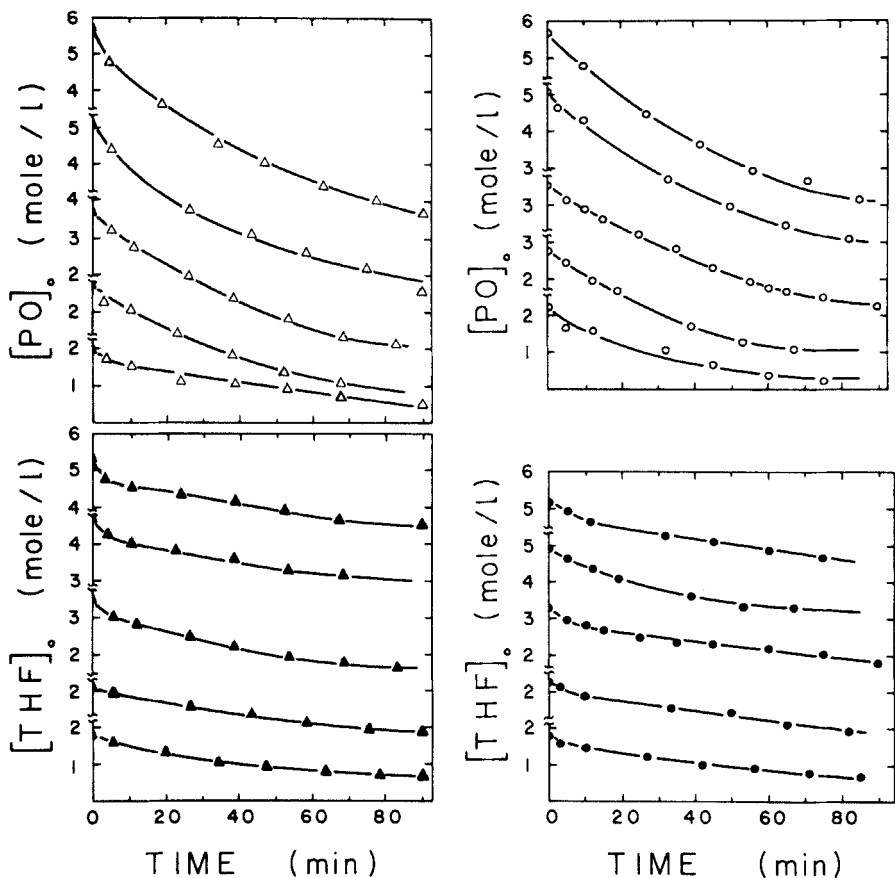


FIG. 2. Concentration vs time curves for PO and THF copolymerizations initiated with SbCl_5 and two different cocatalysts: (Δ , \blacktriangle), 1,2-butane diol; and (\circ , \bullet), 1,2-propane diol.

use the trial and error method by assigning values to r_1 in Eq. (6) and calculating the corresponding value for r_2 . In this way, numerous pairs of r_1 - r_2 values could be obtained for a single $d[M_1]/d[M_2]$ ratio, but only one pair can be retained: that which yields a reactivity ratio product in agreement with that obtained experimentally for the system.

TABLE 3. The Effect of Initial Comonomer Concentrations on the Initial Rates of Copolymerizations Carried Out at 0°C with SbCl_5 in the Presence of Different Diols and of Dichloroethane as Solvent^a

Cocatalyst	$[\text{PO}]_0$ (mole/liter)	$[\text{THF}]_0$ (mole/liter)	$\frac{-d[\text{PO}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]	$\frac{-d[\text{THF}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]
1,2-Propane diol	5.72	1.80	10.82	2.70
	5.07	2.26	9.38	4.30
	3.55	3.32	7.45	3.80
	2.75	4.91	7.24	4.80
	2.25	5.17	5.27	4.91
1,2-Butane diol	5.70	1.80	13.03	2.16
	5.10	2.10	12.24	2.40
	3.76	3.48	9.60	3.55
	2.75	4.70	5.74	3.70
	2.00	5.30	4.33	4.00

^aOther conditions: $[\text{catalyst}]_0 = 1.0 \times 10^{-2}$ mole/liter; $[\text{cocatalyst}]_0 = 0.38$ mole/liter; $[\text{solvent}]_0 = [\text{PO} + \text{THF}]_0$ mole/liter.

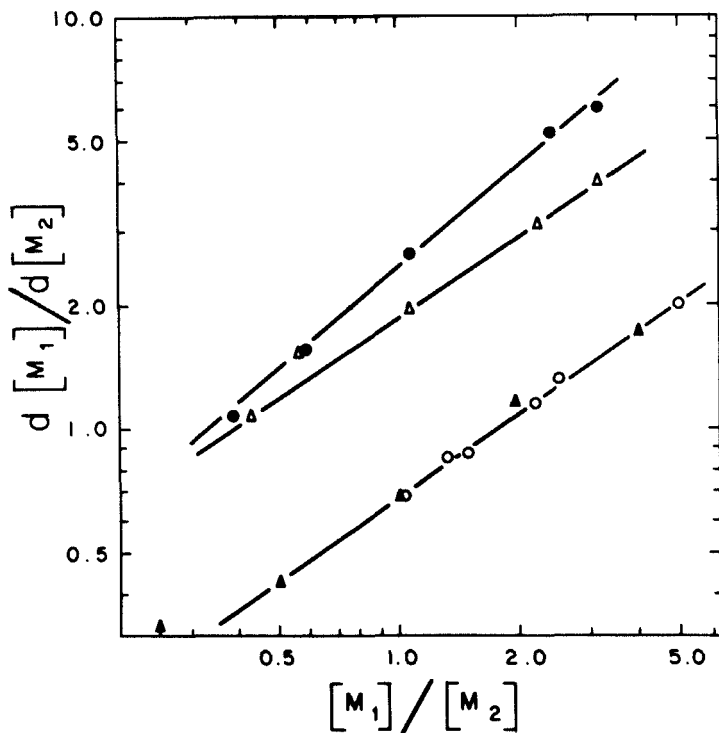


FIG. 3. Log-log plots of $d[M_1]/d[M_2]$ vs $[M_1]/[M_2]$ from which a and K are evaluated for systems involving different catalyst-cocatalyst combinations: (○), $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ -water; (●), SbCl_5 -1,2-butane diol; (Δ), SbCl_5 -1,2-propane diol; and (▲), $(\text{C}_6\text{H}_5)_3\text{C}^+\text{PF}_6^-$.

DISCUSSION

Variation of Reactivity Ratios under Different Reaction Conditions

Effect of the Catalyst

It was mentioned earlier that the effect of catalyst on reactivity ratios in cationic copolymerizations has been looked into by many groups. Though most of these centered their efforts on styrene and its derivatives, which are admittedly much different in nature from PO and THF, the comonomers used in this study, it was thought imperative for comparison purposes and general remarks that some of this data be tabulated here. Table 4 therefore lists,

along with the results obtained in the present study, values of r_1 , r_2 and r_1r_2 for different catalyst systems as reported by Florin [4], Overberger [6, 7], Okamura [14, 15], Furukawa [16-18], and Marechal [19]. It is to be noted that the reactivity ratios do indeed vary with the catalyst used; however, except for the work of Marechal et al. [19], the range of variations for the reactivity ratio products is relatively limited. For the copolymerization of styrene with p-chlorostyrene at 0°C [6, 7], all of the r_1r_2 values lie within ± 0.2 of 0.9. In the case of styrene with 3,4-dichlorostyrene at -78°C [4], all of the r_1r_2 values, except that obtained with $ZnCl_2$ (at 30°C), are, within ± 0.3 , equal to 1.8. In yet another case, styrene with p-ter-butyl styrene at -10°C [18], the r_1r_2 values fall within ± 0.02 of 0.25. It is obvious that r_1r_2 is different for each of the three cases discussed above; however, for each of the catalyst systems used within a given comonomer pair, the r_1r_2 values are quasi-unique. The criterion of a constant reactivity ratio product is not restricted to the cationic copolymerization of styrene with its own derivatives. In the present study on the cationic copolymerization of PO and THF with $SbCl_5$ and with $BF_3:(C_2H_5)_2O$ in the presence of diols as cocatalyst and of 1,2-dichloroethane as solvent, the values of r_1r_2 lie within ± 0.02 of 0.09. The idea that r_1r_2 is constant for the system has been used extensively to investigate the reactivity of other catalysts toward this copolymerization reaction.

In the copolymerization of PO and THF with $(C_6H_5)_3C^+PF_6^-$ as the catalyst [31, 33], the r_1r_2 value was found to be 0.21. Keeping this as the criterion for the PO-THF system involving $(C_6H_5)_3C^+$ cations in combination with AsF_6^- and SbF_6^- as the gegenions, the values of r_1 and r_2 at four different temperatures were determined (see data in Table 5). The values of r_1 and r_2 with the gegenions PF_6^- and AsF_6^- are much the same, whereas those with SbF_6^- show higher values for r_1 and consequently lower values for r_2 .

It has been reported that during the copolymerization of styrene with vinyl acetate [3a], with methyl methacrylate [3b], and with p-chlorostyrene [6, 7], catalyst concentration does not affect reactivity ratio values nor reactivity ratio products, these remaining constant. Marechal et al. [19] observed, however, that during the cationic copolymerization of styrene with 4-vinyl biphenyl, reactivity ratios decreased somewhat with increasing catalyst concentration, from which it follows that r_1r_2 decreased slightly.

Using the constant reactivity ratio product criterion, reactivity ratio values were calculated in the present study with various catalysts at four different concentrations. The results are presented in Table 6 where it can be seen that r_1 and r_2 do not change with changing catalyst concentration in the systems $BF_3:(C_2H_5)_2O/1,2$ -propane diol, $BF_3:(C_2H_5)_2O/water$, and $(C_6H_5)_3C^+PF_6^-$;

TABLE 4. The Effect of the Gegenions on Reactivity Ratios

Catalyst	Solvent	M ₁	M ₂
SbCl ₅	Dichloroethane	Propylene oxide	Tetrahydrofuran
BF ₃ ·(C ₂ H ₅) ₂ O	Dichloroethane	Propylene oxide	Tetrahydrofuran
SnCl ₄	Nitrobenzene	Styrene	p-Chlorostyrene
TiCl ₄	Nitrobenzene	Styrene	p-Chlorostyrene
AlBr ₃	(1:1) Nitrobenzene: carbon tetrachloride	Styrene	p-Chlorostyrene
TiCl ₄	(1:1) Nitrobenzene: carbon tetrachloride	Styrene	p-Chlorostyrene
AlBr ₃	(1:1) Nitrobenzene: carbon tetrachloride	Styrene	p-Chlorostyrene
SnCl ₄	(1:1) Nitrobenzene: carbon tetrachloride	Styrene	p-Chlorostyrene
AlBr ₃	Carbon tetrachloride	Styrene	p-Chlorostyrene
FeCl ₃	(1:4) Nitrobenzene: carbon tetrachloride	Styrene	p-Chlorostyrene
AlCl ₃	Carbon tetrachloride	Styrene	3,4-Dichlorostyrene
AlBr ₃	Carbon tetrachloride	Styrene	3,4-Dichlorostyrene
TiCl ₄	Carbon tetrachloride	Styrene	3,4-Dichlorostyrene
BF ₃ ·(C ₂ H ₅) ₂ O	Carbon tetrachloride	Styrene	3,4-Dichlorostyrene
ZnCl ₂ (30°C)	Carbon tetrachloride	Styrene	3,4-Dichlorostyrene
TiCl ₄	n-Hexane:methylene chloride (25 + 75%)	Styrene	Isobutene

of Various Cationic Comonomer-Solvent Systems

r_1	r_2	$r_1 r_2$ range	Comments
1.1 ± 0.05	0.08 ± 0.01	0.07-0.10	This work
1.0 ± 0.05	0.09 ± 0.01	0.08-0.10	This work
2.2 ± 0.2	0.45 ± 0.02	0.9-1.1	Overberger et al. [6, 7], 0°C
2.2 ± 0.2	0.45 ± 0.02	0.9-1.1	Overberger et al. [6, 7], 0°C
2.3 ± 0.4	0.36 ± 0.05	0.6-1.1	Overberger et al. [6, 7], 0°C
2.2 ± 0.2	0.45 ± 0.02	0.9-1.1	Overberger et al. [6, 7], 0°C
2.0 ± 0.2	0.34 ± 0.05	0.5-0.9	Overberger et al. [6, 7], 0°C
1.7 ± 0.2	0.55 ± 0.05	0.75 ± 1.1	Overberger et al. [6, 7], 0°C
1.5 ± 0.05	0.40 ± 0.02	0.6-0.7	Overberger et al. [6, 7], 0°C
2.0 ± 0.1	0.43 ± 0.03	0.8-1.0	Overberger et al. [6, 7], 0°C
3.1 ± 0.1	0.48 ± 0.08	1.2-1.8	Florin [4], 0°C
2.8 ± 0.2	0.45 ± 0.10	0.9-1.65	
6.8 ± 0.8	0.0 ± 0.2	0.0-1.5	Florin [4], 0°C
7.2 ± 0.5	0.38 ± 0.2	1.2-4.4	Florin [4], 0°C
5.9 ± 0.2	0.27 ± 0.07	1.1-2.1	Florin [4], 0°C
4.2 ± 0.2	0.10 ± 0.05	0.2-0.7	Florin [4], 0°C
1.70 ± 0.07	4.11 ± 0.19	6.4-7.6	Okamura et al. [14], -78°C

(continued)

TABLE 4 (continued)

Catalyst	Solvent	M ₁	M ₂
SnCl ₄	n-Hexane:methylene chloride (25 + 75%)	Styrene	Isobutene
TiCl ₄	Dichloroethane	Styrene	4-Vinyl biphenyl
SnCl ₄	Dichloroethane	Styrene	4-Vinyl biphenyl
BF ₃ :(C ₂ H ₅) ₂ O	Methylene dichloride	2-Chloroethyl vinyl ether	p-Methylstyrene
SnCl ₄ .tri-chloro acetic acid (TCA)	Methylene dichloride	2-Chloroethyl vinyl ether	p-Methylstyrene
BF ₃ :(C ₂ H ₅) ₂ O	Toluene	2-Chloroethyl vinyl ether	α-Methylstyrene
SnCl ₄ . (TCA)	Toluene	2-Chloroethyl vinyl ether	α-Methylstyrene
SnCl ₄	Nitrobenzene	Styrene	p-ter-Butylstyrene
AlBr ₃	Nitrobenzene	Styrene	p-ter-Butylstyrene
BBr ₃	Nitrobenzene	Styrene	p-ter-Butylstyrene
SnCl ₄	Dichloroethane	Styrene	p-ter-Butylstyrene
AlBr ₃	Dichloroethane	Styrene	p-ter-Butylstyrene
BBr ₃	Dichloroethane	Styrene	p-ter-Butylstyrene

r_1	r_2	$r_1 r_2$	Comments
1.92 ± 0.41	3.75 ± 0.45	5.0-9.9	Okamura et al. [14], -78°C
0.8 ± 0.1	0.7 ± 0.1	0.4-0.7	Marechal [19], -78°C
1.4 ± 0.1	1.0 ± 0.1	1.2-1.65	Marechal [19], -78°C
8.80 ± 0.45	0.40 ± 0.03	3.1-4.0	Okamura et al. [15], -78°C
2.31 ± 0.17	1.12 ± 0.06	2.3-2.9	Okamura et al. [15], -78°C
5.72 ± 0.70	0.31 ± 0.05	1.30-2.3	Okamura et al. [14], -78°C
3.46 ± 0.25	0.46 ± 0.07	1.25-2.0	Okamura et al. [14], -78°C
0.85 ± 0.02	0.35 ± 0.02	0.27-0.32	Furukawa et al. [18], -10°C
0.68 ± 0.03	0.31 ± 0.04	0.18-0.25	Furukawa et al. [18], -10°C
0.78 ± 0.02	0.32 ± 0.03	0.22-0.28	Furukawa et al. [18], -10°C
0.58 ± 0.05	1.17 ± 0.07	0.58-0.78	Furukawa et al. [18], 57°C
0.86 ± 0.07	1.11 ± 0.09	0.88-1.1	Furukawa et al. [18], 57°C
0.62 ± 0.15	1.13 ± 0.22	0.43-1.0	Furukawa et al. [18], 57°C

TABLE 5. The Effect of the Gegenions, Associated with the Trityl Cations, on Reactivity Ratios Determined at Different Temperatures^a

Temperature (°C)	Gegenion	[PO] ₀ (mole/liter)	[THF] ₀ (mole/liter)	$\frac{d\theta}{d\theta} \times 10^3$ [mole/(liter)(min)]	$\frac{-d[\text{THF}]_0}{d\theta} \times 10^3$ [mole/(liter)(min)]	r ₁ (PO)	r ₂ (THF)
-10	PF ₆ ⁻	3.40	3.40	1.70	2.80	0.21	1.00
-10	AsF ₆ ⁻	3.36	3.36	1.60	2.60	0.21	1.00
-10	SbF ₆ ⁻	3.36	3.36	1.60	2.20	0.26	0.80
0	PF ₆ ⁻	3.60	3.60	4.50	6.50	0.26	0.80
0	AsF ₆ ⁻	3.60	3.60	7.20	10.00	0.26	0.80
0	SbF ₆ ⁻	3.60	3.60	8.20	8.20	0.46	0.46
10	PF ₆ ⁻	3.50	3.50	13.00	16.40	0.32	0.66
10	AsF ₆ ⁻	3.60	3.60	18.60	21.80	0.38	0.55
10	SbF ₆ ⁻	3.36	3.36	28.00	19.80	0.79	0.27
20	PF ₆ ⁻	3.50	3.50	34.00	37.80	0.38	0.55
20	AsF ₆ ⁻	3.50	3.50	60.80	50.40	0.61	0.34
20	SbF ₆ ⁻	3.60	3.60	86.00	52.80	1.00	0.21

^aOther conditions: [DCE]₀ = [PO + THF]₀ mole/liter; [catalyst]₀ = 6.5 × 10⁻³ mole/liter; [cocatalyst]₀ = 0.00 mole/liter.

TABLE 6. Variations of Reactivity Ratios with Catalyst Concentration for Different Catalyst-Cocatalyst Systems Operating at 0°C in DCE. $[DCE]_0 = [PO + THF]_0$ mole/liter.

Catalyst	[Catalyst] $_0 \times 10^2$ (mole/liter)	Cocatalyst	[Cocatalyst] $_0$ (mole/liter)	[PO] $_0$ (mole/ liter)	[THF] $_0$ (mole/ liter)	$\frac{d\theta}{d\theta}$ (mole/(liter (min))	$\frac{-d[PO]_0 \times 10^2}{d\theta}$ (mole/(liter (min))	$\frac{-d[THF]_0 \times 10^2}{d\theta}$ (mole/(liter (min))	r_1	r_2
BF $_3$:(C $_2$ H $_5$) $_2$ O	0.24	1,2-Propane diol	0.38	3.35	3.26	0.44	0.31	0.31	0.65	0.14
SbCl $_5$	0.24	1,2-Propane diol	0.38	3.88	3.70	1.63	1.11	1.11	0.60	0.15
(C $_6$ H $_5$) $_3$ C $^+$ PF $_6^-$	0.24	None	-	3.25	3.25	0.33	0.50	0.50	0.24	0.87
BF $_3$:(C $_2$ H $_5$) $_2$ O	0.24	Water	0.01	4.48	4.08	0.13	0.21	0.21	0.20	1.05
BF $_3$:(C $_2$ H $_5$) $_2$ O	0.50	1,2-Propane diol	0.38	3.43	3.31	1.16	0.76	0.76	0.70	0.13
SbCl $_5$	0.50	1,2-Propane diol	0.38	3.90	3.55	3.86	2.10	2.10	0.90	0.10
(C $_6$ H $_5$) $_3$ C $^+$ PF $_6^-$	0.50	None	-	3.25	3.25	0.40	0.60	0.60	0.24	0.87
BF $_3$:(C $_2$ H $_5$) $_2$ O	0.50	Water	0.01	4.48	4.08	0.32	0.50	0.50	0.21	1.00
BF $_3$:(C $_2$ H $_5$) $_2$ O	1.00	1,2-Propane diol	0.38	3.40	3.35	2.16	1.38	1.38	0.75	0.12
SbCl $_5$	1.00	1,2-Propane diol	0.38	3.55	3.32	7.45	3.80	3.80	1.00	0.09
(C $_6$ H $_5$) $_3$ C $^+$ PF $_6^-$	1.00	None	-	3.25	3.25	0.63	0.80	0.80	0.31	0.68
BF $_3$:(C $_2$ H $_5$) $_2$ O	1.00	Water	0.01	4.48	4.08	0.85	1.18	1.18	0.25	0.84
BF $_3$:(C $_2$ H $_5$) $_2$ O	1.50	1,2-Propane diol	0.38	3.31	3.36	3.20	2.18	2.18	0.70	0.13
SbCl $_5$	1.50	1,2-Propane diol	0.38	3.89	3.32	14.82	6.14	6.14	1.34	0.07
(C $_6$ H $_5$) $_3$ C $^+$ PF $_6^-$	1.50	None	-	3.25	3.25	1.00	1.17	1.17	0.35	0.60
BF $_3$:(C $_2$ H $_5$) $_2$ O	1.50	Water	0.01	4.48	4.08	1.82	2.25	2.25	0.30	0.70
BF $_3$:(C $_2$ H $_5$) $_2$ O	1.50	Water	0.05	4.42	3.66	2.21	2.03	2.03	0.43	0.49

however, with SbCl_5 as catalyst, the values of r_1 increased with increasing catalyst concentration. As a consequence, that of r_2 decreased. The reason why the reactivity of PO should increase with increasing SbCl_5 concentration is perhaps best explained by invoking changes in the nature of the active centers produced in the presence of different catalyst concentrations. This possibility takes its origin from the fact that, in polymerizations initiated with metal halides in the presence of a cocatalyst, there are two ways of producing reactive centers: 1) by a process of self-ionization [44], and 2) by the reaction of the catalyst with a cocatalyst [47-56]. The extent to which one or the other of these ways is more important may be a function of the catalyst concentration. This would undoubtedly cause changes in the initial reactivities of the active centers and hence in the reactivity ratios.

Effect of the Cocatalyst

The role of the cocatalyst in cationic copolymerizations has always been a point of controversy. The necessity of a cocatalyst to initiate the reaction has been questioned repeatedly [44-46]. Some believe that certain catalysts, e.g., aluminum halides [44], can self-ionize ($4\text{AlX}_3 \rightleftharpoons \text{Al}_2\text{X}_5^+ + \text{Al}_2\text{X}_7^-$) into reactive cations. A situation of this type may occur even when a potential cocatalytic solvent, such as an alkyl halide, is present. Others [47-56] believe that the presence of a cocatalyst is essential to the initiation process and that it is the reaction between the cocatalyst and the catalyst which generates the active cations. In some systems the two mechanisms may be operative simultaneously, the extent of each depending on the absence or the presence of a cocatalyst.

This role of the cocatalyst on the reactivity ratios of the comonomers, PO and THF, has been studied in considerable detail in this laboratory [25-33]. The recalculated values of the reactivity ratios for this copolymerization system using different catalyst-cocatalyst arrangements are presented in Table 2. With $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ -initiated copolymerizations in the presence of four different diols, the reactivity ratios are different. Similarly, the SbCl_5 -initiated copolymerization of PO with THF in the presence of 1,2-propane or 1,2-butane diols yields different reactivity ratios. The reactivity ratios of copolymerizations initiated with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ in the presence of water may not be compared with those prepared in the presence of diols because the two sets of data were obtained under different reaction conditions. The effect of diols and water as cocatalyst are therefore discussed separately.

Effect of Diols. Keeping in mind the importance of the role played by diol cocatalysts, it is of interest to correlate the

effect of the bulk size of the diol and the effect of its concentration with the relative reactivities of the comonomers. It was mentioned earlier that the reactivity ratios of PO and THF are affected when a different diol is used (see Table 2); one should note, however, that the reactivity ratio product in the case of the systems $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/\text{diols}$ and $\text{SbCl}_5/\text{diols}$ remains constant, within ± 0.02 , at 0.09. The various values of the constants a and K , listed in Table 2, are slightly different but they all satisfy the criterion defined by O'Driscoll et al. [66], who suggested that, for $K > 0$ and $0 < a < 1$ with $0 < r_1 r_2 < 1$, the copolymerization products must be rich in alternate copolymer. This indicates that, in spite of different reactivity ratios, the nature of the copolymer product does not change. It would seem nevertheless that the comonomer PO has certain preferences for some diols over others. For instance, 1,4- and 1,2-butane diols increase the reactivity of PO (see Table 2) whereas 1,2- and 1,3-propane diols do not appear to have any effect. On changing from a diol to a triol, the reactivity of PO is also found to decrease. The role of the bulk size of diols is further explored in the case of SbCl_5 -initiated copolymerizations, as is shown in Table 7. Once again, the constant reactivity ratio product criterion has been used in the calculation of comonomer reactivity ratios with some of the diols. From Table 7, one notes that the reactivity of PO is highest with 1,2-ethane diol. It is somewhat lower with other diols and shows practically no dependence on the position of the hydroxyl groups.

Table 8 lists data showing the effects of diol concentration on the reactivity ratios of the comonomers. The calculation of this data is based on the criterion of constant values of $r_1 r_2$ for the system. It should be noted that the reactivity ratios of the comonomers vary considerably when the concentration of the diol in the reaction mixture is increased. This is believed to be the principal cause behind the different reactivity ratios reported in the literature for the copolymerization of PO with THF [25-33, 36, 37, 39]. Other effects of diols and their concentration on the copolymerization have been discussed earlier [30] and need not be repeated here.

Effect of Water. The role of water in the initiation reaction of the PO-THF copolymerization is thought to be much the same as that of a diol. It has been suggested [30, 56] that only one OH group of a diol or triol cocatalyst molecule reacts at any one time with the catalyst to generate reaction cations. Elsewhere [32, 33], the role of water in controlling the reactivity of the comonomers has been further discussed. It was found that the relative reactivity of PO increased with increasing water concentration and this with both of the catalyst systems studied

TABLE 7. The Effect of Bulk Size of the Cocatalysts on Reactivity Ratios for SbCl_5 -Catalyzed Copolymerizations^a

Cocatalysts	$[\text{PO}]_0$ (mole/liter)	$[\text{THF}]_0$ (mole/liter)	$-\frac{d[\text{PO}]_0}{d\theta} \times 10^2$ [mole/(liter)(min)]	$-\frac{d[\text{THF}]_0}{d\theta} \times 10^2$ [mole/(liter)(min)]	r_1 (PO)	r_2 (THF)
1,2-Ethane diol	3.83	3.51	13.30	2.90	3.40	0.026
1,2-Propane diol	3.55	3.32	7.45	3.80	1.00	0.090
1,2-Butane diol	3.76	3.48	9.60	3.55	1.80	0.050
2,3-Butane diol	4.28	3.60	7.50	4.00	0.82	0.110
1,3-Butane diol	3.76	3.48	6.50	2.90	1.28	0.070
1,4-Butane diol	3.80	3.48	8.50	4.20	1.05	0.086
1,5-Pentane diol	3.80	3.50	7.30	2.60	1.80	0.050

^aOther conditions: $[\text{catalyst}]_0 = 1.0 \times 10^{-2}$ mole/liter; $[\text{cocatalyst}] = 0.38$ mole/liter; solvent = $[\text{DCE}]_0 = [\text{PO} + \text{THF}]_0$ mole/liter; temperature = 0°C .

TABLE 8. Variation of Reactivity Ratios with Diol Concentration for Different Catalyst-Cocatalyst Systems Operating at 0°C in DCE^a

Catalyst	Cocatalyst	[Cocat] ₀ (mole/ liter)	[PO] ₀ (mole/ liter)	[THF] ₀ (mole/ liter)	$\frac{-d[PO]_0}{d\theta} \times 10^2$ [mole/(liter (min))]	$\frac{-d[THF]_0}{d\theta} \times 10^2$ [mole/(liter (min))]	r ₁ (PO)	r ₂ (THF)
BF ₃ :(C ₂ H ₅) ₂ O	1,2-Propane diol	0.00	3.48	3.40	1.04	1.13	0.38	0.55
BF ₃ :(C ₂ H ₅) ₂ O	1,2,3-Propane triol	0.00	3.50	3.70	0.70	0.75	0.42	0.50
SbCl ₅	1,2-Propane diol	0.00	3.30	3.33	0.63	0.90	0.15	0.60
BF ₃ :(C ₂ H ₅) ₂ O	1,2-Propane diol	0.20	3.40	3.35	1.67	1.23	0.60	0.15
BF ₃ :(C ₂ H ₅) ₂ O	1,2,3-Propane triol	0.20	3.50	3.75	1.35	1.10	0.48	0.19
SbCl ₅	1,2-Propane diol	0.20	3.48	3.49	2.37	2.03	0.41	0.22
BF ₃ :(C ₂ H ₅) ₂ O	1,2-Propane diol	0.38	3.40	3.35	2.17	1.37	0.75	0.12
BF ₃ :(C ₂ H ₅) ₂ O	1,2,3-Propane triol	0.38	3.50	3.70	2.20	1.25	1.00	0.09
SbCl ₅	1,2-Propane diol	0.38	3.90	3.55	3.86	2.10	0.90	0.10
BF ₃ :(C ₂ H ₅) ₂ O	1,2-Propane diol	0.59	3.35	3.25	2.20	1.15	1.10	0.08
BF ₃ :(C ₂ H ₅) ₂ O	1,2,3-Propane triol	0.59	3.50	3.70	2.75	1.25	1.50	0.06
SbCl ₅	1,2-Propane diol	0.59	3.46	3.36	5.45	2.24	1.50	0.06
BF ₃ :(C ₂ H ₅) ₂ O	1,2-Propane diol	0.75	3.35	3.25	2.50	1.30	1.05	0.08
BF ₃ :(C ₂ H ₅) ₂ O	1,2,3-Propane triol	0.75	3.50	3.70	3.15	1.25	1.80	0.05
SbCl ₅	1,2-Propane diol	0.75	3.46	3.36	7.00	2.35	2.05	0.04

^aOther conditions: [BF₃:(C₂H₅)₂O]₀ = 1.0 × 10⁻² mole/liter; [SbCl₅]₀ = 0.5 × 10⁻² mole/liter; [DCE]₀ = [PO + THF]₀ mole/liter; the [BF₃:(C₂H₅)₂O]/1,2-propane diol system contains around 0.09 mole/liter of water, besides the diol.

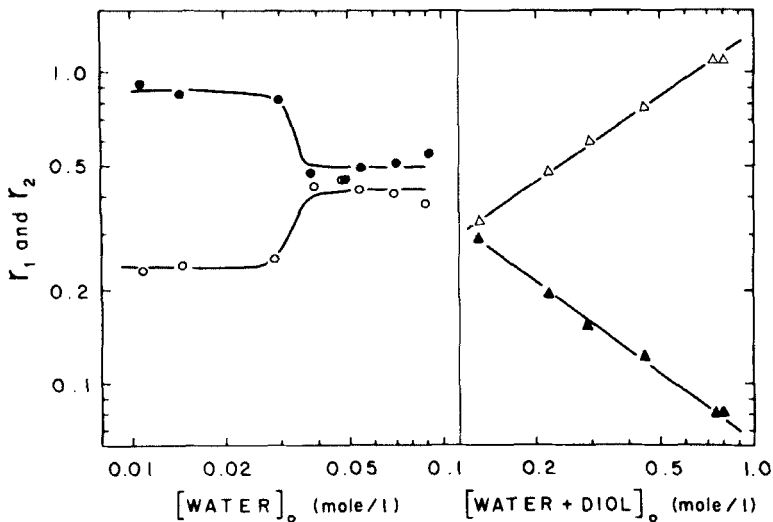


FIG. 4. Log-log plots of reactivity ratio vs initial cocatalyst concentrations: (○), PO; (●), THF-water as cocatalyst; (△), PO; and (▲), THF-water + diol as cocatalyst.

[$\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/\text{water}$ and $(\text{C}_6\text{H}_5)_3\text{C}^+\text{PF}_6^-/\text{water}$]. The results obtained with the $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/\text{water}$ system showed that with a catalyst concentration of 1.52×10^{-2} mole/liter the reactivity ratio values remained constant at 0.24 ± 0.01 for water concentrations between 1.2×10^{-2} and 3.0×10^{-2} mole/liter. At a water concentration of 3.7×10^{-2} mole/liter, the PO reactivity ratio increased abruptly to 0.45 and remained constant thereafter, within ± 0.01 , up to a water concentration of 5.3×10^{-2} mole/liter. The curves are shown in Fig. 4. It would appear that beyond an initial $[\text{water}]_0/[\text{catalyst}]_0$ ratio of 2.0 the nature of the active centers changes. To compare the role of water with that of an equivalent concentration of diol, a log-log plot was traced of the reactivity ratios as a function of the initial water plus diol concentration (see Fig. 4). It is noted that as this concentration increases, the reactivity ratio of PO increases linearly while that of THF decreases, indicating that the magnitude of the reactivities for equivalent initial concentrations of water and of diol is much the same. It must be added that this equivalence of reactivity would appear to be valid only for the lower concentrations of water since, at higher values, the role of water and diol may be different because of the higher dielectric constant (80) of water [67] compared to that (~ 37) of the diol.

Effect of Temperature

The influence of temperature on the reactivity ratios of the comonomers may be established with the help of Eqs. (7) and (8) drawn from the literature [18, 61, 62]. These relate the reactivity ratios with the energy of activation and may also be extended [18] to involve the thermodynamic parameters: activation enthalpy (H) and activation entropy (S):

$$\ln r_1 = \ln \frac{k_{11}}{k_{12}} = - \frac{1}{RT} (E_{11} - E_{12}) = - \frac{\Delta H_{11} - \Delta H_{12}}{RT} + \frac{\Delta S_{11} - \Delta S_{12}}{R} \quad (7)$$

and

$$\ln r_2 = \ln \frac{k_{22}}{k_{21}} = - \frac{1}{RT} (E_{22} - E_{21}) = - \frac{\Delta H_{22} - \Delta H_{21}}{RT} + \frac{\Delta S_{22} - \Delta S_{21}}{R} \quad (8)$$

In most cases the selectivity of a monomer in copolymerization reactions is controlled by its entropy of activation. Furukawa and co-workers [18] studied the copolymerization of styrene with p-substituted styrenes and showed that, although the activation enthalpy and the activation entropy are dependent on the solvent and the catalyst, ΔH and ΔS are interrelated by a relationship of the type $\Delta H = m'\Delta S + n'$, where the coefficient m' is related to the process of desolvation in the transition state of the reaction (and is independent of the catalyst and the solvent but not of the monomers) and n' is associated with the effects of conjugation or steric hinderances in the transition state of the active monomer-catalyst complex.

Very limited data on the temperature dependence of reactivity ratios is available in the literature to establish a universal relationship between the two parameters. In Table 9 are listed reactivity ratios and their products as reported by Alfrey [57], Smets [58], Imoto [59], Pepper [60], Marechal [19], and Furukawa [18] for various catalyst-comonomer systems at different reaction temperatures. In all of the reactions studied, the reactivity ratio of one of the comonomers decreases with increasing temperature while that of the other increases such that their product remains essentially constant, especially at low temperatures. The reactivity ratio products may be different for each system, but for any one system the value is unique. For example, in the copolymerization of n-butyl vinyl ether with acenaphthalene [59], an average value of 0.8 ± 0.1 covers all of the $r_1 r_2$ values obtained between -78 and 30°C . Similarly, for the copolymerization of styrene with p-chlorostyrene [21, 57] or α -methylstyrene [18], $r_1 r_2$ values

TABLE 9. Variation of Reactivity Ratios with Temperature

Catalyst system	Solvent	M ₁	M ₂
BF ₃ :(C ₂ H ₅) ₂ O	Toluene	n-Butyl vinyl ether	Acenaphthalene
BF ₃ :(C ₂ H ₅) ₂ O	Toluene	n-Butyl vinyl ether	Acenaphthalene
BF ₃ :(C ₂ H ₅) ₂ O	Benzene	n-Butyl vinyl ether	Acenaphthalene
BF ₃ :(C ₂ H ₅) ₂ O	Benzene	n-Butyl vinyl ether	Acenaphthalene
SnCl ₄	None	α-Methylstyrene	p-Chlorostyrene
SnCl ₄	None	α-Methylstyrene	p-Chlorostyrene
SnCl ₄	Carbon tetrachloride	Styrene	p-Chlorostyrene
SnCl ₄	Carbon tetrachloride	Styrene	p-Chlorostyrene
SnCl ₄	Carbon tetrachloride	Styrene	p-Chlorostyrene
TiCl ₄	Dichloroethane	α-Methylstyrene	4-Vinyl biphenyl
TiCl ₄	Dichloroethane	α-Methylstyrene	4-Vinyl biphenyl
BF ₃ :2HoAc	Dichloroethane	Styrene	2-Chloroethyl vinyl ether
BF ₃ :2HoAc	Dichloroethane	Styrene	2-Chloroethyl vinyl ether
BF ₃ :2HoAc	Dichloroethane	Styrene	2-Chloroethyl vinyl ether
SnBr ₄	Dichloroethane	Styrene	p-Methylstyrene
SnBr ₄	Dichloroethane	Styrene	p-Methylstyrene
BBr ₃	Dichloroethane	Styrene	p-Methylstyrene
BBr ₃	Dichloroethane	Styrene	p-Methylstyrene
SnBr ₄	Nitrobenzene	Styrene	p-Methylstyrene
SnBr ₄	Nitrobenzene	Styrene	p-Methylstyrene

for Various Cationic Catalyst-Cocatalyst Systems

Temperature (°C)	r_1	r_2	$r_1 r_2$	Ref.
-78	20.00 \approx	0.04 \pm 0.02	0.8	Imoto et al. [59]
-20	6.0 \pm 1.0	0.14 \pm 0.03	0.8-1.1	Imoto et al. [59]
0	4.2 \pm 0.8	0.24 \pm 0.04	0.7-1.4	Imoto et al. [59]
30	1.3 \pm 0.3	0.38 \pm 0.04	0.4-0.7	Imoto et al. [59]
-78	28.0 \pm 2.0	0.12 \pm 0.03	2.3-4.5	Smets et al. [58]
0	15.5 \pm 1.5	0.35 \pm 0.05	4.2-6.8	Smets et al. [58]
-20	2.5 \pm 0.4	0.3 \pm 0.03	0.6-1.0	Alfrey et al. [57]
0	2.5 \pm 0.5	0.3 \pm 0.03	0.6-1.0	Overberger et al. [21]
32	2.2 \pm 0.3	0.35 \pm 0.1	0.6-0.9	Alfrey et al. [57]
-78	1.0 \pm 0.1	1.0 \pm 0.1	0.8-1.2	Marechal et al. [19]
25	0.6 \pm 0.1	1.0 \pm 0.1	0.45-0.8	Marechal et al. [19]
-30	0.75 \pm 0.07	2.0 \pm 0.2	1.5-1.8	Pepper et al. [60]
0	0.48 \pm 0.04	3.9 \pm 0.15	1.65-2.1	Pepper et al. [60]
25	0.07 \pm 0.01	4.5 \pm 0.5	0.2-0.4	Pepper et al. [60]
-30	0.59 \pm 0.10	2.39 \pm 0.37	1.0-1.9	Furukawa et al. [18]
60	0.38 \pm 0.20	3.50 \pm 1.09	0.4-2.7	Furukawa et al. [18]
-30	0.64 \pm 0.05	2.20 \pm 0.15	1.2-1.6	Furukawa et al. [18]
60	0.51 \pm 0.10	3.27 \pm 0.48	1.1-2.3	Furukawa et al. [18]
-5	0.51 \pm 0.05	1.96 \pm 0.17	0.8-1.2	Furukawa et al. [18]
80	0.47 \pm 0.05	3.12 \pm 0.22	1.2-1.7	Furukawa et al. [18]

of 0.75 ± 0.15 and 1.2 ± 0.2 , respectively, may be applicable for the complete span of temperatures studied. At the higher temperatures (25°C), the constant reactivity ratio product criterion no longer appears to hold as is indicated by the results obtained in the copolymerization of α -methylstyrene with 2-chloroethyl vinyl ether [60]; however, in the copolymerizations of *n*-butyl vinyl ether with acenaphthalene [59], of styrene with *p*-methylstyrene [18], or 4-vinyl biphenyl [19], this criterion holds even at the higher temperatures. Based on this, the reactivity ratio products obtained at 0°C for the copolymerization of PO and THF were therefore used to compute r_1 and r_2 values at other temperatures.

In Table 10 are shown the reactivity ratios obtained at different temperatures with the catalyst-cocatalyst system: $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/1,2$ -propane diol: 1) in the absence of a diol (series A), 2) with 0.13 mole/liter of diol (series B), and 3) with 0.38 mole/liter of diol (series C). In series A, the PO reactivity ratios decrease between -25 and -13°C but increase constantly at higher temperatures. In series B, the trend for the reactivity of PO remains the same between -25 and -13°C ; however, the magnitude of the increase between -13 and 20°C is higher. In series C, the reactivity of PO increases constantly between -20 and 20°C . From these studies it appears that, at any given temperature, the absence or presence of a diol influences the reactivity of PO and, furthermore, that the effect of the diols is more pronounced at the higher temperatures.

In Table 11 are shown the different values of the reactivity ratios obtained at four different temperatures with the $\text{SbCl}_5/1,2$ -propane diol catalyst-cocatalyst system. It can be seen that the reactivity of PO increases with temperature while that of THF decreases. A comparison of the $\text{SbCl}_5/1,2$ -propane diol system with the $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}/1,2$ -propane diol system shows that, between -10 and 20°C and under identical operating conditions, the magnitude of the increase in the reactivity of PO is much greater in the case of the former catalyst-cocatalyst system.

The authors feel that if the reactivity ratios, listed in Tables 5, 10, and 11 for each of the temperatures studied, were exact values as calculated, for instance, from experimental data obtained with four or five different comonomer concentrations, it would be possible to provide true energetics for the propagation reactions with the use of Eqs. (7) and (8); however, as the r_1 and r_2 values have been calculated by using the constant reactivity ratio product concept, they only yield trends and not absolute values. Nevertheless, these values can be used in Eqs. (7) and (8) to establish the order of magnitude of the enthalpy of activation and of the entropy of activation for the copolymerization of PO with THF. The effect of different catalysts and of different cocatalysts on these two parameters can also be evaluated.

TABLE 10. Variation of Reactivity Ratios for the $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}/1,2\text{-Propane Diol Catalyst-Cocatalyst System}$ Operating at Different Temperatures and Various Diol Concentrations in Dichloroethane^a

Series	Temperature (°C)	[Cocat] ₀ (mole/liter)	[PO] ₀ (mole/liter)	[THF] ₀ (mole/liter)	$\frac{-d[\text{PO}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]	$\frac{-d[\text{THF}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]	r ₁ (PO)	r ₂ (THF)
A	-25	0.00	3.35	3.30	0.08	0.09	0.38	0.55
	-20	0.00	3.50	3.50	0.14	0.19	0.29	0.72
	-13	0.00	3.70	3.60	0.39	0.27	0.25	0.84
	-6	0.00	3.55	3.60	0.55	0.67	0.34	0.62
	0	0.00	3.48	3.40	1.00	1.12	0.38	0.55
	10	0.00	3.20	3.20	2.08	2.20	0.42	0.50
B	20	0.00	3.35	3.35	4.34	4.40	0.45	0.47
	-25	0.13	3.50	3.50	0.10	0.09	0.38	0.24
	-20	0.13	3.30	3.35	0.21	0.21	0.30	0.30
	-13	0.13	3.55	3.60	0.42	0.46	0.24	0.38
	-6	0.13	3.55	3.45	0.83	0.80	0.32	0.28
	0	0.13	3.40	3.35	1.81	1.46	0.48	0.19
C	10	0.13	3.35	3.25	3.11	2.34	0.53	0.17
	20	0.13	3.15	3.15	6.65	5.00	0.58	0.15
	-30	0.38	3.40	3.35	0.07	0.04	0.90	0.10
	-20	0.38	3.25	3.13	0.24	0.16	0.67	0.13
	-10	0.38	3.54	3.41	0.75	0.49	0.70	0.13
	0	0.38	3.40	3.35	2.37	1.37	0.75	0.12
C	7	0.38	3.29	3.08	3.36	2.00	0.80	0.11
	20	0.38	3.44	3.24	11.20	6.30	0.90	0.10

^aOther conditions: $[\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}]_0 = 1.0 \times 10^{-2}$ mole/liter and $[\text{DCE}]_0 = [\text{PO} + \text{THF}]_0$ mole/liter. (Series A, B, and C contain 0.09 mole/liter of water, besides the diol.)

TABLE 11. Effect of Temperature on the Reactivity Ratios of the Comonomers with the SbCl_5 /1,2-Propane Diol Catalyst-Cocatalyst System Operating in DCE^a

Temperature (°C)	$[\text{PO}]_0$ (mole/liter)	$[\text{THF}]_0$ (mole/liter)	$\frac{-d[\text{PO}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]	$\frac{-d[\text{THF}]_0 \times 10^2}{d\theta}$ [mole/(liter)(min)]	r_1 (PO)	r_2 (THF)
-10	3.48	3.49	1.30	0.90	0.65	0.14
0	3.90	3.55	3.86	2.10	0.90	0.10
10	3.48	3.49	9.30	4.30	1.30	0.07
20	3.82	4.07	20.00	8.80	1.50	0.06

^aOther conditions: $[\text{SbCl}_5]_0 = 5.0 \times 10^{-3}$ mole/liter; $[\text{1,2-propane diol}]_0 = 0.38$ mole/liter; $[\text{DCE}]_0 = [\text{PO} + \text{THF}]_0$ mole/liter.

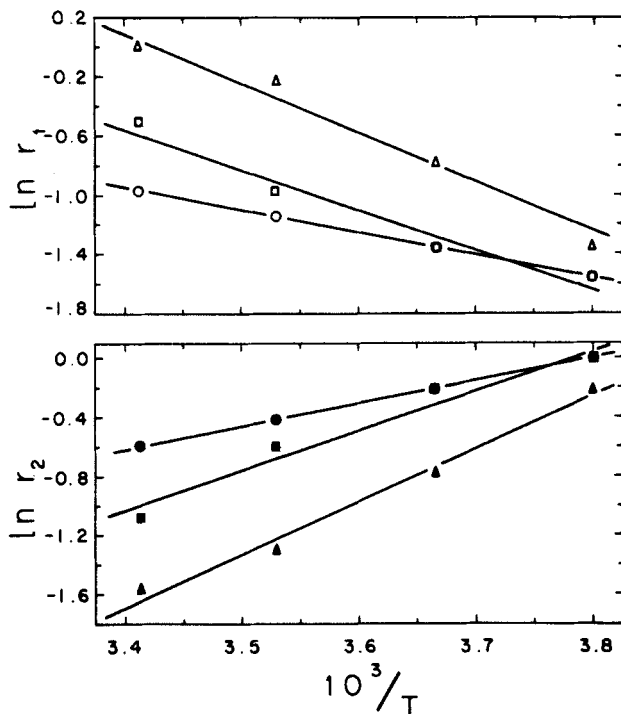


FIG. 5. Plots of $\ln r_1$ and $\ln r_2$ vs $1/T$ for PO-THF copolymerizations initiated with triphenyl methyl cations involving different gegenions: (Δ), PO; (\blacktriangle), THF-SbF₆⁻ as gegenion; (\square), PO; (\blacksquare), THF-AsF₆⁻ as gegenion; (\circ), PO; and (\bullet), THF-PF₆⁻ as gegenion.

Figures 5, 6, and 7 show plots of $\ln r_1$ and $\ln r_2$ vs $1/T$ for copolymerizations carried out with trityl ions associated with three distinct gegenions, viz., PF₆⁻, AsF₆⁻, and SbF₆⁻, with SbCl₅/1,2-propane diol (data of Table 11) and with BF₃:(C₂H₅)₂O/1,2-propane diol (data of Table 10), respectively. Thermodynamic parameters obtained from these figures are presented in Table 12. One notes that, under identical operating conditions, different catalysts yield different values for the activation enthalpy and the activation entropy differences. The order of increasing enthalpic differences ($\Delta H_{11} - \Delta H_{12}$) obtained for PO with different catalyst is as follows: (C₆H₅)₃C⁺SbF₆⁻ > (C₆H₅)₃C⁺AsF₆⁻ > SbCl₅ > (C₆H₅)₃C⁺PF₆⁻ > BF₃:(C₂H₅)₂O. This may best be explained by invoking the different nature of the oxonium salts which are formed between the epoxides and these catalyst as

TABLE 12. Thermodynamic Parameters for Copolymerizations of PO and THF Initiated with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, $(\text{C}_6\text{H}_5)_3\text{C}^+$ Cations and SbCl_5 (-10 to +20°C)

Catalyst	$\Delta H_{11} - \Delta H_{12}$ (kcal/mole)	$\Delta H_{22} - \Delta H_{21}$ (kcal/mole)	$\Delta S_{11} - \Delta S_{12}$ [cal/(mole)(deg)]	$\Delta S_{22} - \Delta S_{21}$ [cal/(mole)(deg)]
$\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$	1.98	-1.60	5.20	-7.00
$(\text{C}_6\text{H}_5)_3\text{C}^+ \text{PF}_6^-$	3.05	-3.08	8.46	-11.72
SbCl_5	4.50	-4.10	16.20	-19.50
$(\text{C}_6\text{H}_5)_3\text{C}^+ \text{AsF}_6^-$	5.43	-5.31	17.33	-20.13
$(\text{C}_6\text{H}_5)_3\text{C}^+ \text{SbF}_6^-$	6.55	-7.15	22.38	-27.72

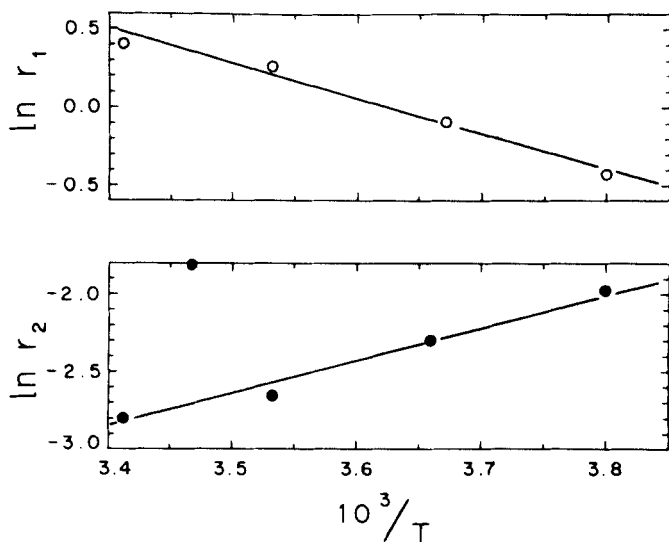


FIG. 6. Plot of $\ln r_1$ and r_2 vs $1/T$ for PO-THF copolymerizations initiated with SbCl_5 in the presence of 1,2-propane diol as cocatalyst: (○), PO; and (●), THF.

reported in the literature [68-71]. The higher reactivity of SbCl_5 -initiated copolymerizations over those initiated with $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ has been attributed [70] to the presence of a depropagation reaction present in both systems where the effect with the latter catalyst is far more pronounced than it is with SbCl_5 . Consequently, with $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ the rates of comonomer disappearance tend to be lower. In a recent review article on the depolymerization of THF [71], it has been suggested that the processes of initiation with $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$, SbCl_5 , and trityl ions are quite different. It is thus more than possible that the resulting oxonium salts have quite different reactivities.

In Table 13 are listed values of the thermodynamic parameters obtained from copolymerizations initiated with $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$ and varying concentrations of 1,2-propane diol. Table 13a covers the temperature range -10 to 20°C ; Table 13b covers that between -30 and -10°C . It should be noted that the parameters do not vary much in the presence of little or more diol (0.13 or 0.38 mole/liter), but are different for each of the temperature ranges studied. It would appear that the nature of the reactive species, in each of the ranges, may not be the same. If it were, one should obtain a single value for the enthalpy of activation and a single value for the entropy of

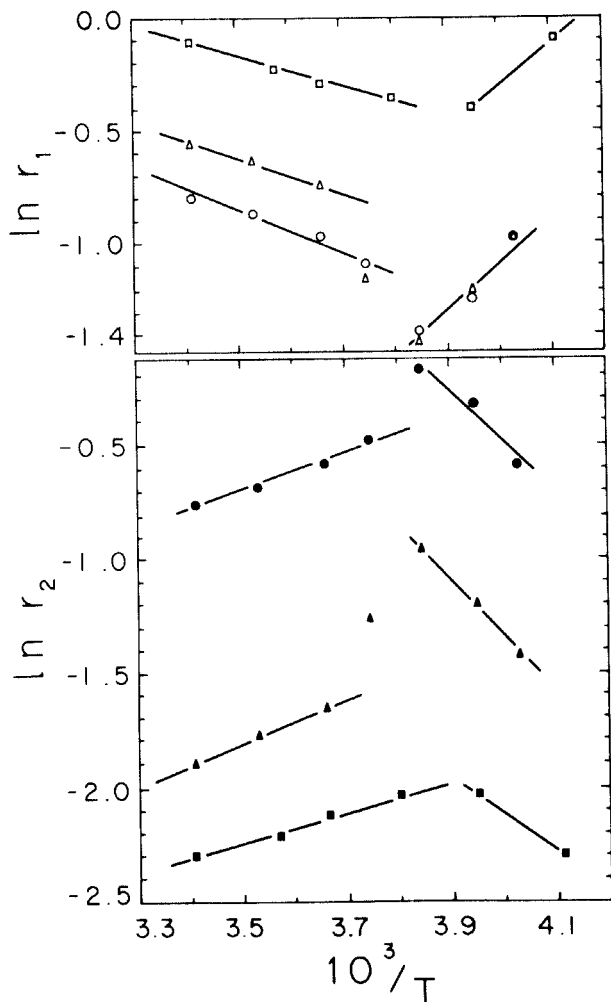


FIG. 7. Plots of $\ln r_1$ and $\ln r_2$ vs $1/T$ for PO-THF copolymerizations initiated with $\text{BF}_3:(\text{C}_2\text{H}_5)_2\text{O}$: (○), PO; (●), THF in the absence of diol; (△), PO; (▲), THF with 0.13 mole/liter diol; and (□), PO; (■), THF with 0.38 mole/liter diol.

TABLE 13a. Thermodynamic Parameters for Copolymerizations of PO and THF Initiated with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ in Different Concentrations of 1,2-Propane Diol (-10 to +20°C)

[Cocatalyst] ₀ (mole/liter)	$\Delta H_{11} - \Delta H_{12}$ (kcal/mole)	$\Delta H_{22} - \Delta H_{21}$ (kcal/mole)	$\Delta S_{11} - \Delta S_{12}$ [cal/(mole)(deg)]	$\Delta S_{22} - \Delta S_{21}$ [cal/(mole)(deg)]
0.00	1.98	-1.60	5.20	-7.00
0.13	1.52	-1.91	4.10	-10.30
0.38	1.52	-1.26	5.10	-8.88

 TABLE 13b. Thermodynamic Parameters for Copolymerizations of PO and THF initiated with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ in Different Concentrations of 1,2-Propane Diol (-30 to -10°C)

[Cocat] ₀ (mole/liter)	$\Delta H_{11} - \Delta H_{12}$ (kcal/mole)	$\Delta H_{22} - \Delta H_{21}$ (kcal/mole)	$\Delta S_{11} - \Delta S_{12}$ [cal/(mole)(deg)]	$\Delta S_{22} - \Delta S_{21}$ [cal/(mole)(deg)]
0.00	-4.11	4.34	-18.80	16.50
0.13	-4.11	4.82	-18.80	16.60
0.38	-3.96	3.96	-16.35	11.50

activation which would cover the entire range -30 to $+20^{\circ}\text{C}$. The concept of different types of reactive species, viz., free ions, solvent separated ion-pairs, and contact ion-pairs said to exist in anionic living polymerizations, is well known and has been discussed in detail by Szwarc [72]. It is believed possible that a similar situation might prevail in the case of cationic polymerizations. Indeed, such observations have been made in the case of the cationic polymerization of isobutene [73], of indene [74], and of cyclopentadiene [75] where negative activation energies were obtained and the presence of different reactive species was suggested as being responsible for these. Similar results were also reported from this laboratory [56] for the copolymerization of styrene oxide with propylene oxide when initiated with $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$.

Further studies on the variation of reactivity ratios with different variables are being carried out and will be reported on as they become available.

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