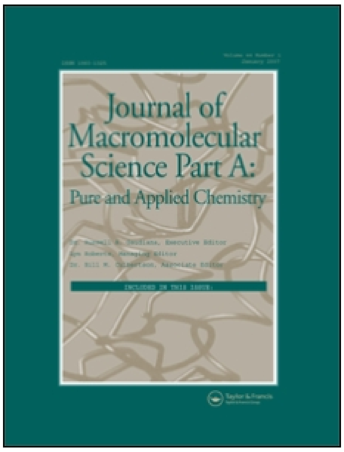

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Cationic Copolymerization of Propylene Oxide with Tetrahydrofuran. XI. Calculation of Individual Rate Constants.

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ABSTRACT

Rate constants (k_i, k_{11}, k_{12}, k_{22}, k_{21}, and k_t) for various steps involved in the copolymerization of propylene oxide (PO) with tetrahydrofuran (THF) have been calculated from reaction rate data obtained with the following catalyst system: (a) triphenylmethyl cations ($(C_6H_5)_3C^+$) associated with hexafluorophosphate (PF_6^-), hexafluoroarsenate (AsF_6^-) and hexafluoroantimonate (SbF_6^-) gegenions; (b) antimony pentachloride ($SbCl_5$); and, (c) boron trifluoride etherate, $BF_3{:}(C_2H_5)_2O$. The latter two systems were studied in the presence of cocatalysts. The effects of several parameters (the cocatalyst concentration and bulk size, the nature of the solvent, and the reaction temperature) on the rate constants are highlighted. The role of entropy in the initiation, propagation and termination steps is discussed in terms of solvation and desolvation processes. Based on termination activation energy considerations, the order of

stability for the gegenions used in the copolymerization of PO with THF was found to be: $AsF_6^- > SbF_6^- > HOBF_3^- \geq PF_6^- > SbCl_6^-$

INTRODUCTION

The cationic copolymerization of propylene oxide (PO) with tetrahydrofuran (THF) has been reported on extensively in the literature [1-16]. Recently, an empirical model was developed [17] for the determination of kinetic parameters for this system where the ratio of the disappearance of PO and THF is related, via their reactivity ratios r_1 and r_2, to the rate constants $k_i k_{12}[H^+]$, k_t, K_{PO}, and K_{THF}. On the basis of the assumption that initiation takes place rapidly, a method is also suggested for separating the initiation rate constant k_i from the expression $k_i k_{12}[H^+]$. To compute the above rate constants for different catalyst, cocatalyst, and temperature conditions, it was necessary to determine in what manner the reactivity ratios, r_1 and r_2, change with these conditions. The question is discussed in another publication [18], in which it is shown that the six-parameter equation developed earlier [17] can be reduced to a four-parameter equation which can be solved by optimization techniques [19-21] and the Monte Carlo simulation method [22-23]. A detailed diagram of the steps involved in these calculations is given in the earlier publication [17]. By using the model mentioned in this reference on data published from this laboratory [1, 3, 8-11, 14-16], it was possible to calculate the values of the rate constants k_i, k_{11}, k_{12}, k_t, K_{PO}, and K_{THF} for different catalyst, cocatalyst, temperature, and solvent conditions. In the present study, a new scheme has been developed to separate the propagation constants k_{22} and k_{21} which had not been achieved earlier. The rate constants K_{PO} and K_{THF} have, therefore, been dropped and only k_i, k_{11}, k_{12}, k_{22}, k_{21}, and k_t are discussed. The results obtained in this study form the subject of the present communication.

The Mathematical Model

The principal important steps retained in the proposed empirical model for the determination of kinetic parameters in the copolymerization of PO with THF have been discussed in detail earlier [17].

These are summarized here that the reader may be made fully aware of the precise meaning of each rate constant discussed further on in the text.

Initiation:

$$H^+ + PO \xrightarrow{k_i} PO^+ \qquad (A)$$

Propagation:

$$PO^+ + PO \xrightarrow{k_{11}} PO^+ \qquad (B)$$

$$PO^+ + THF \xrightarrow{k_{12}} THF^+ \qquad (C)$$

$$THF^+ + THF \xrightarrow{k_{22}} THF^+ \qquad (D)$$

$$THF^+ + PO \xrightarrow{k_{21}} PO^+ \qquad (E)$$

Termination:

$$PO^+ \xrightarrow{k_t} H^+ + \text{reaction products} \qquad (F)$$

The rate constants in the above steps have been correlated with the rates of disappearance of both PO and THF. This is shown in Eqs. (1) and (2).

$$[PO] = [PO]_0 \exp \left\{ - k_{12} A \left[\frac{r_1}{k_t} (1 - \exp\{- k_t t\}) - \frac{r_1}{K_{PO}} (1 - \exp\{-K_{PO} t\}) + \frac{[THF]_0}{[PO]_0} \frac{1 - \exp\{-K_{THF} t - k_t t + K_{PO} t\}}{K_{THF} + k_t - K_{PO}} - \frac{[THF]_0}{[PO]_0} \frac{1 - \exp\{-K_{THF} t\}}{K_{THF}} \right] \right\} \qquad (1)$$

and

$$
\begin{aligned}
[\mathrm{THF}] = [\mathrm{THF}]_0 \exp \Bigg\{ - k_{12} A \Bigg[& \frac{1}{k_t} (1 - \exp \{-k_t t)\} \\
& - \frac{1}{K_{PO}} (1 - \exp\{- K_{PO} t\} \\
& + r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \; \frac{1 - \exp\{- K_{THF} t - k_t t + K_{PO} t\}}{K_{THF} + k_t - K_{PO}} \\
& - r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \; \frac{1 - \exp\{- K_{THF} t\}}{K_{THF}} \Bigg] \Bigg\}
\end{aligned}
\tag{2}
$$

In these equations,

$$A = k_i [\mathrm{PO}]_0 [\mathrm{H}^+] / (K_{PO} - k_t)$$

K_{PO} is obtained from the approximation:

$$[\mathrm{PO}] = [\mathrm{PO}]_0 \exp \{- K_{PO} t\}$$

K_{THF} is obtained from:

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp \{- K_{THF} t\}$$

the reactivity ratios r_1 and r_2 are defined as

$$r_1 = k_{11}/k_{12}$$

and

$$r_2 = k_{21}/k_{22}$$

and finally k_i and k_t are the rate constants of the initiation and the termination steps, respectively.

When rapid initiation occurs, Eqs. (1) and (2) may be rewritten as Eqs. (3) and (4), respectively.

$$[PO] = [PO]_0 \exp\left\{ - k_{12}[H^+]_0 \left[\frac{r_1}{k_t} (1 - \exp\{- k_t t\}) + \frac{[THF]_0}{[PO]_0} \frac{1 - \exp\{- K_{THF}t - k_t t + K_{PO}t\})}{k_t + K_{THF} - K_{PO}} \right] \right\} \quad (3)$$

$$[THF] = [THF]_0 \exp\left\{ - k_{12}[H^+]_0 \left[\frac{1}{k_t} (1 - \exp\{- k_t t\}) + r_2 \frac{[THF]_0}{[PO]_0} \frac{(1 - \exp\{-K_{THF}t - k_t t + K_{PO}t\})}{k_t + K_{THF} - K_{PO}} \right] \right\} \quad (4)$$

Values of r_1 and r_2 for different reaction conditions are calculated separately by the means discussed in detail earlier [18].

Equations (1) and (2) can now be solved with the help of optimization techniques [19-21] and the Monte Carlo simulation method [22, 23]. This has led to the calculation of values for the rate constants $k_i k_{12}[H^+]$, k_t, K_{PO}, and K_{THF}.

The values of k_t, K_{PO}, and K_{THF} were substituted into Eqs. (3) and (4) in order to compute the rate constant k_{12} with which $k_i[H^+]$ in the expression $k_i k_{12}[H^+]$ was evaluated for different initial catalyst concentrations $[H^+]_0$. Generally, it was found that the value of $k_i[H^+]/[H^+]_0$ was a constant from which it was possible to evaluate k_i.

With a knowledge of r_1 and k_{12}, the evaluation of k_{11} posed no serious problem; though, a different approach had to be developed to separate the constants k_{22} and k_{21}. This is dealt with in detail in the following section.

Separation of the Propagation Rate Constants k_{22} and k_{21}

Basing the development on reactions (B) to (E) given earlier, the rates of comonomer disappearance may be written as:

$$d[PO]/dt = - k_{11}[PO]\,[PO^+] - k_{21}[PO]\,[THF^+] \tag{5}$$

and

$$d[THF]/dt = - k_{12}[THF]\,[PO^+] - k_{22}[THF][THF^+] \tag{6}$$

Dividing Eq. (5) by Eq. (6) leads to:

$$\frac{d[PO]/dt}{d[THF]/dt} = \frac{[PO]}{[THF]}\left\{\frac{k_{11}[PO^+] + k_{21}[THF^+]}{k_{12}[PO^+] + k_{22}[THF^+]}\right\} \tag{7}$$

On letting d[PO]/dt and d[THF]/dt in Eq. (7) be represented hereafter, for the sake of convenience, by D_1 and D_2 and replacing the rate constants k_{22} by $k_{21}r_2$ and k_{11} by $k_{12}r_1$, Eq. (7) will now read:

$$\frac{\dfrac{D_1[THF]}{D_2[PO]} - r_1}{1 - \dfrac{D_1[THF]}{D_2[PO]}\,r_2} = \frac{k_{21}[THF^+]}{k_{12}\,[PO^+]} \tag{8}$$

If the sum of the concentrations of active centers, at any time t is assumed to be equal to the initial catalyst concentration [5, 6, 13] one can write:

$$\sum^{t} \left\{[THF^+] + [PO^+]\right\} = [H^+]_0 \tag{9}$$

Earlier [17], the value of $[PO^+]$ for the case of fast initiation was calculated by Eq. (10):

$$[PO^+] = [H^+]_0 \exp\{-k_t t\} \qquad (10)$$

where k_t is the individual rate constant for the termination step.

Combining Eqs. (9) and (10) leads to:

$$[PO^+]/[THF^+] = 1/(\exp\{k_t t\} - 1) \qquad (11)$$

Substituting in Eq. (8) the expression for $[PO^+]/[THF^+]$ on the right-hand side of Eq. (11) yields:

$$\frac{\dfrac{D_1[THF]}{D_2[PO]} - r_1}{1 - \dfrac{D_1[THF]}{D_2[PO]} r_2} = \left\{\frac{k_{21}}{k_{12}} (\exp\{k_t t\} - 1)\right\} \qquad (12)$$

where, upon taking logarithm of both sides of this equation, one arrives at:

$$\ln\left(\frac{\dfrac{D_1[THF]}{D_2[PO]} - r_1}{1 - \dfrac{D_1[THF]}{D_2[PO]} r_2}\right) = \ln(\exp\{k_t t\} - 1) + \ln\frac{k_{21}}{k_{12}} \qquad (13)$$

which, if plotted (the term on the left-hand side versus that on the right), will yield a line from which the value of $\ln(k_{21}/k_{12})$ may be obtained. With the value of k_{12} calculated earlier, k_{21} can then be determined; likewise, knowing k_{21}, k_{22} may next be computed from the relationship: $k_{22} = k_{21}r_2$.

RESULTS AND DISCUSSION

The $BF_3:(C_2H_5)_2O$/(Water and 1,2-Propanediol) Catalyst–Cocatalyst System

In Table 1 are listed, as a function of the initial catalyst concentration, six rate constants for the $BF_3:(C_2H_5)_2O$/water catalyst-

TABLE 1. Effect of Catalyst Concentration on the Rate Constants of Copolymerizations carried out at 273° K in DCE with a BF_3:$(C_2H_5)_2O$/(Water and 1,2-Propanediol) Catalyst-Cocatalyst System [a,b]

No.	$[Catalyst]_0 \times 10^2$ (mole/liter)	$[Water]_0 \times 10^2$ (mole/liter)	$[Diol]_0 \times 10^2$ (mole/liter	Rate constants (liter/mole-min and 1/min)					
				$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
B-1	0.25	1.17	0.0	4.56	0.18	0.92	0.88	0.84	115.30
B-2	0.51	1.17	0.0	4.45	0.16	0.78	0.70	0.70	92.14
B-3	0.75	1.17	0.0	3.75	0.12	0.53	0.47	0.51	49.66
B-4	1.01	1.17	0.0	4.95	0.10	0.40	0.32	0.38	32.48
B-5	1.26	1.17	0.0	4.96	0.12	0.43	0.26	0.34	16.14
B-6	1.52	1.17	0.0	5.30	0.12	0.41	0.22	0.32	14.95
S65-14	0.24	9.0	0.38	6.80	0.26	0.41	0.04	0.25	19.44
S65-05	0.50	9.0	0.38	5.94	0.70	1.00	0.13	1.05	21.04
S65-02	1.00	9.0	0.38	8.57	0.52	0.70	0.17	1.45	14.40
S65-04	1.50	9.0	0.38	5.71	0.70	1.00	0.24	1.85	24.68

[a] Other conditions: series B, $[PO]_0$ = 4.48 mole/liter, $[THF]_0$ = 4.08 mole/liter, $[DCE]_0$ = 4.88 mole/liter; series S65, $[PO]_0$ = 3.40 mole/liter, $[THF]_0$ = 3.35 mole/liter, $[DCE]_0$ = $[PO + THF]_0$ mole/liter.

[b] Data of Blanchard et al. [3, 15].

cocatalyst system in dichloroethane (DCE) as solvent (series B). Increases in the catalyst concentration (from 0.25×10^{-2} to 1.52×10^{-2} mole/liter) with a fixed cocatalyst concentration (1.17×10^{-2} mole/liter) has no appreciable effect on the initiation rate constant k_i. It appears that the PO$^+$-based active centers formed by the reaction of the catalyst with PO under different experimental conditions are a direct function of the catalyst concentration. The termination rate constant k_t, however, decreased with increasing catalyst concentration, as one might normally expect in a system where side reactions with the solvent, monomer or cocatalyst are prominent. This effect is more pronounced under conditions where the number of active centers is relatively small. As the number of active centers increases (with increasing catalyst concentration) their rate of disappearance would be expected to decrease because there are now comparatively fewer deactivated species. The propagation rate constants k_{11}, k_{12}, k_{22}, and k_{21} all decrease as the catalyst concentration is increased. But before analyzing the data, it must be remembered that k_t also decreases with increasing catalyst concentration. Thus, the ideal situation would be to note the effect of increases in the catalyst concentration on the ratios k_{11}/k_t, k_{12}/k_t, k_{22}/k_t, and k_{21}/k_t which in fact show a definite increase when the catalyst concentration is raised. This indicates that the reactivity of the active centers increases with catalyst concentration due, it is thought, to a possible increase in the number of active centers.

In Table 1 are listed other results dealing with rate constant variations caused by increases in the catalyst concentration. In the experiments (series S65) leading to these results, the molarity of the water present in the solution was 0.09 mole/liter; that of the diol, 0.38. One notes that the values of k_i and k_t are relatively constant. In the case of k_i, this would indicate that the PO$^+$-based active centers are directly proportional to the initial catalyst concentration. As for the values of k_t, these would appear to be normal considering the high concentrations of both water and diol used in the experiments. It would seem that once the cocatalyst concentration exceeds a certain limit, the reaction solutions behave identically in so far as the termination step is concerned. As regards the values of k_{11}, k_{12}, k_{22}, and k_{21}, all increase with catalyst concentration. As the values of k_t are constant in this series, the values of k_{11}/k_t, $k_{12}/_t$, k_{22}/k_t, and k_{21}/k_t should show the same trend with increasing catalyst concentration.

The effects of increasing cocatalyst concentration on the rate constants in copolymerizations carried out with a $BF_3:(C_2H_5)_2O$/(water and 1,2-propanediol) catalyst–cocatalyst system are summarized in Table 2. In series C, where a fixed catalyst concentration of 1.52 $\times 10^{-2}$ mole/liter was used in conjunction with initial water concentrations which varied from 1.17×10^{-2} to 5.31×10^{-2} mole/liter, the initiation and termination rate constants k_i and k_t remained practically constant though the propagation rate constants k_{11}, k_{12}, k_{22}, and k_{21} all increased with increasing concentrations of water. This would indicate that either the reactivity of PO^+-based active centers or their number increases with cocatalyst concentration. The effects of the initial cocatalyst concentration $(\text{water} + \text{diol})_0$ on the rate constants are also shown in Table 2 (series S65, where the cocatalyst mixtures were made up of a constant concentration of water and varying concentrations of diol). One notes that the initiation rate constant k_i increases slightly with diol concentration, indicating that the formation of PO^+-based active centers is enhanced in its presence [26]. The termination rate constant k_t, however, changes little with changing diol concentration. It appears that water and diol act in a similar manner in the termination process in so far as killing of the reactive centers is concerned. The propagation rate constant k_{11} increases while k_{22} decreases, indicating that homopolymerization leading to the formation of poly(propylene oxide) is favored over the reaction that leads to the formation of polytetrahydrofuran. The other two constants k_{12} and k_{21} remain more or less constant, suggesting that, in the copolymer, the probability of chains ending with PO or THF does not depend on the cocatalyst concentration.

The effects of temperature on the rate constants of the copolymerization are summarized in Table 3. The study was divided into three sets of experiments. In the three cases the concentration of water is the same (0.09 mole/liter) while that of diol varies from zero in the first, to 0.13 mole/liter in the second and on to 0.38 mole/liter in the third. In all of these experiments, the rate constants increase with temperature and the magnitude of the increase is, in general, a function of the diol concentration.

Based on data taken from Table 3, kinetic and thermodynamic parameters for the $BF_3:(C_2H_5)O$/(water and diol) catalyst–cocatalyst system are presented as a function of the diol concentration in Table 4. One notes that the initiation activation energy E of 12.20 kcal/mole, when only water (0.09 mole/liter) is used as cocatalyst, decreases to 10.27 kcal/mole on the addition of 0.13 mole/liter of diol and to 8.9 kcal/mole on the addition of 0.38 mole/liter of diol.

TABLE 2. Effect of Cocatalyst Concentration on the Rate Constants of Copolymerizations Carried out by 273° K in DCE with a BF_3: $(C_2H_5)_2O$/(Water and 1,2-Propanediol) Catalyst-Cocatalyst System[a,b]

	$[\text{Catalyst}]_0 \times 10^2$	$[\text{Water}]_0 \times 10^2$	$[\text{Diol}]_0 \times 10^2$	Rate constants (liter/mole-min and 1/min)					
No.	(mole/liter)	(mole/liter)	(mole/liter)	$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
C-1	1.52	1.17	0.0	4.70	0.12	0.41	0.22	0.32	14.95
C-2	1.52	1.43	0.0	5.70	0.11	0.46	0.21	0.25	7.45
C-3	1.52	2.89	0.0	7.40	0.14	0.59	0.28	0.34	13.10
C-4	1.52	3.73	0.0	5.55	0.26	0.59	0.20	0.43	15.46
C-5	1.52	4.75	0.0	6.20	0.27	0.59	0.30	0.66	15.48
C-6	1.52	5.31	0.0	6.20	0.25	0.59	0.32	0.66	15.60
S65-17	1.0	9.0	0.0	4.17	0.26	0.70	0.55	1.01	16.00
S65-23	1.0	9.0	6.0	4.00	0.25	0.80	0.23	0.84	12.70
S65-19	1.0	9.0	13.0	6.40	0.48	1.00	0.21	1.10	15.70
S65-15	1.0	9.0	21.0	6.60	0.48	0.80	0.08	0.55	19.40
S65-02	1.0	9.0	38.0	8.57	0.52	0.70	0.17	1.45	14.40
S65-24	1.0	9.0	65.0	8.77	1.00	0.90	0.10	1.35	15.44
S65-22	1.0	9.0	71.0	12.80	0.86	0.78	0.12	1.56	17.60

[a] Other conditions: series C, $[PO]_0 = 4.42$ mole/liter, $[THF]_0 = 4.08$ mole/liter, $[DCE]_0 = 4.60$ mole/liter; series S65, $[PO]_0 = 3.40$ mole/liter, $[THF]_0 = 3.35$ mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter.

[b] Data of Blanchard et al. [3, 15].

TABLE 3. Effect of Temperature on the Rate Constants of Copolymerizations Carried out in DCE with a $BF_3:(C_2H_5)_2O$/(Water and 1,2-Propanediol) Catalyst-Cocatalyst System[a,b]

No.	Temperature (°K)	$[\text{Water}]_0 \times 10^2$ (mole/liter)	$[\text{Diol}]_0 \times 10^2$ (mole/liter)	Rate constants (liter/mole-min and 1/min)					
				$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
S65-32	248	9.0	0.0	0.67	0.04	0.10	0.01	0.02	9.30
S65-40	254	9.0	0.0	0.80	0.05	0.17	0.06	0.09	9.40
S65-36	260	9.0	0.0	1.54	0.08	0.33	0.16	0.19	16.00
S65-38	267	9.0	0.0	4.73	0.19	0.55	0.22	0.36	20.00
S65-17	273	9.0	0.0	4.14	0.27	0.70	0.55	1.01	16.00
S65-34	283	9.0	0.0	10.00	0.38	0.90	1.00	1.98	20.00
S65-30	293	9.0	0.0	11.71	1.57	3.50	1.88	4.00	34.00
S65-33	248	9.0	13.0	0.24	0.15	0.39	0.09	0.39	9.90
S65-41	254	9.0	13.0	1.52	0.04	0.15	0.04	0.15	9.70
S65-37	260	9.0	13.0	2.40	0.05	0.23	0.08	0.21	10.00
S65-39	267	9.0	13.0	4.42	0.12	0.38	0.15	0.53	11.00
S65-19	273	9.0	13.0	6.40	0.48	1.00	0.20	1.10	15.70
S65-35	283	9.0	13.0	8.73	0.82	1.55	0.55	3.25	10.75
S65-31	293	9.0	13.0	27.11	1.56	2.70	0.70	4.72	12.74
S65-09	253	9.0	38.0	3.35	0.15	0.23	0.01	0.10	24.00

S65-11	263	9.0	38.0	6.76	0.24	0.34	0.07	0.53	19.00
S65-02	273	9.0	38.0	8.57	0.52	0.70	0.17	1.45	14.40
S65-13	280	9.0	38.0	19.00	0.80	1.00	0.12	1.15	27.00
S65-10	293	9.0	38.0	38.75	2.16	2.40	0.48	4.80	29.00

[a] Other conditions: $[PO]_0$ = 3.50 mole/liter, $[THF]_0$ = 3.50 mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter, and $[BF_3{:}(C_2H_5)_2O]_0 = 1.0 \times 10^{-2}$ mole/liter.

[b] Data of Blanchard and Baijal [3].

TABLE 4. Effect of Cocatalyst Concentration on the Kinetic and Thermodynamic Parameters of Copolymerizations Carried out with a BF_3:$(C_2H_5)_2O$/(Water and 1,2-Propanediol) Catalyst–Cocatalyst System[a,b]

Rate constants (liter/mole-min and 1/min)	[Water]$_0$ × 10^2 (mole/liter)	[Diol]$_0$ × 10^2 (mole/liter)	A (same units as k)	E (kcal/mole)	ΔH (kcal/mole)	-ΔS (cal/° K-mole)
k_i	9.0	0.0	2.45×10^7	12.20	11.83	34.05
	9.0	13.0	1.09×10^6	10.27	10.40	38.36
	9.0	38.0	1.60×10^5	8.90	8.55	43.94
k_{11}	9.0	0.0	1.01×10^9	11,96	12.54	23.02
	9.0	13.0	7.93×10^9	11.50	11.20	25.00
	9.0	38.0	4.70×10^8	11.20	10.65	28.83
k_{12}	9.0	0.0	0.56×10^9	11.02	11.57	24.30
	9.0	13.0	2.23×10^9	10.63	10.58	28.61
	9.0	38.0	0.64×10^8	9.96	9.33	33.06
k_{22}	9.0	0.0	20.50×10^9	13.36	13.35	19.33
	9.0	13.0	9.34×10^8	11.97	11.70	26.42
	9.0	38.0	2.38×10^8	11.70	11.60	28.51
k_{21}	9.0	0.0	1.33×10^{12}	15.30	14.70	13.21
	9.0	13.0	1.55×10^{10}	12.78	13.19	18.12
	9.0	38.0	2.33×10^{10}	13.00	12.90	19.51

k_t	9.0	0.0	100.20	4.67	3.57	61.22
(1/min)	9.0	13.0	0.53	2.03	1.80	68.58
	9.0	38.0	0.36	1.48	1.10	69.74

[a] Other conditions: $[PO]_0$ = 3.50 mole/liter, $[THF]_0$ = 3.50 mole/liter, $[DCE]_0$ = $[PO + THF]_0$ mole/liter, and $[BF_3{:}(C_2H_5)_2O]_0 = 1.0 \times 10^{-2}$ mole/liter.

[b] Data of Blanchard et al. [3, 15].

This clearly shows that the presence of diol facilitates initiation. The differences in the initiation activation energies obtained in experiments with water alone and with (water + diol) mixtures correspond to the energy differences for the formation of oxonium ions directly from hydronium ions ($H_3{}^+O$) in reaction (G).

$$BF_3{:}(C_2H_5)_2O + 2\,H_2O \rightleftharpoons H_3O^+ + HOBF_3^- \tag{G}$$

$$BF_3{:}(C_2H_5)_2O + 2(HO - R - OH) \rightleftharpoons HORO^+H_2 + HOROBF_3^- \tag{H}$$

or from an oxonium ion intermediate such as $HORO^+H_2$ shown in reaction (H). At the same time, if one analyzes the activation energies E required for the termination step, one notes that these also decrease on the addition of diol. The E value of 4.67 kcal/mole, obtained for the termination step when only water (0.09 mole/liter) is used as cocatalyst, changes to 2.03 kcal/mole when diol (0.13 mole/liter) is also added with the water. When the diol concentration was raised to 0.38 mole/liter, the E value dropped still further to 1.48 kcal/mole. Thus, on the one hand, the addition of diol is of help in the initiation step while, on the other, it hinders the growth of polymer chains by facilitating termination at an early stage. The values of E for the various propagation steps involving k_{11}, k_{12}, k_{22}, and k_{21} also show a similar trend: decreasing with increasing diol concentration. This would mean that the role of the diol is not limited to the initiation process [26] but also affects propagation in a similar manner.

According to Entelis and Korovina [13], the presence of excess water or diol results in nucleophilic solvation of the cationic ends with a consequent reduction of their activity. The physical nature of the active centers, according to these authors, changes from one of contact ion-pairs to one of solvent separated ion-pairs. This would mean that because of different extents of solvation of the ion pairs under various reaction conditions, the enthalpy of activation ΔH should also be different. This has been found to be true in the present studies as can be seen from the data in Table 4. Values of the Arrhenius constant A follow patterns which are similar to the increases and decreases observed in the case of E. The thermodynamic parameters: enthalpy of activation ΔH and entropy of activation ΔS, were calculated from Eq. (14):

$$\log (k/T) = \log (k^*/h) + (\Delta S/2.303R) - (\Delta H/2.303R)(1/T) \tag{14}$$

where k is the rate constant; h, the Planck constant (6.6256×10^{-27} erg-sec.) and k*, the Boltzmann constant (1.3805×10^{-16} erg/deg.). From the data given in Table 4, one notes that ΔH varies in a similar fashion to the variations of E; however, the entropies of activation for the initiation and the termination steps show interesting trends. For the initiation process, an activation entropy of -34.05 cal/°K-mole was calculated for the case where 0.09 mole/liter of water alone is present. On addition of 0.13 mole/liter of diol in combination with the 0.09 mole/liter of water, a ΔS value of -38.86 cal/°K-mole was calculated, and when the diol concentration was raised to 0.38 mole/liter, ΔS decreased further to -43.94 cal/°K-mole. One notes that the magnitude of these entropy values is substantial. Yamashita and co-workers [27] and Aoki et al. [28, 29], during their study on the correlation of cationic copolymerization parameters with basicity [27, 28] and ring strain [29], have stressed the importance of entropy in the process of initiation when water or diol are used in combination with $BF_3{:}(C_2H_3)_2O$. The role of ΔS along with that of ΔH takes its shape in the form of the free energy term ΔG in the equation proposed by Aoki to relate the reactivity ratio r_1 for PO with the basicity (pKb) of THF. Thus, according to Aoki,

$$\log (1/r_1) = -0.036\ \Delta G - 0.31\ (\text{pKb}) + \text{constant} \tag{15}$$

The ΔS values associated with the propagation steps in the copolymerization also decrease when diol is added as cocatalyst; however, the magnitude of these entropy values is not as high as that obtained for the initiation step. Furukawa and co-workers [30], during their studies on the copolymerization of styrene with its derivatives, encountered similar situations. They explained that, when monomer selection is entropy-controlled and when the enthalpy of activation is but a few kilocalories, the process turns out to be a desolvation-controlled phenomenon. The solvated growing cationic species may be desolvated in the transition state but the process requires energy to do so and the liberated solvent yields its entropy to the medium. It is plausible that similar hypotheses may be put forth to explain the results obtained in the present study, though the magnitude of the ΔH values is not as small as that observed by Furukawa [30].

The entropy of termination in the present studies with the $BF_3{:}(C_2H_5)_2O$ catalyst is very high, being in the range of -60 to -70 cal/°K-mole. Before relating these values to any specific step, it is necessary to know the exact mode of termination. The molecular weight distributions of the products obtained at the end of these copolymerizations have been found to be bimodal [3, 7]. The low molecular weight species are cyclic in structure [7] and have an average $\overline{DP}$ of 4 to 5; the structure of the high molecular weight species has yet to be fixed, though it would seem safe to assume, as a first approximation, that these are linear rather than cyclic copolymers. Thus, the enthalpy and entropy of activation for the termination step reflect the combined effects of both cyclization and transfer reactions in the solution. The decrease in enthalpy with increasing concentration of diol suggests that the major contribution comes from the reaction of diol with growing chain ends, while that from cyclization is not judged to be so important. The entropy changes, however, are not so marked as those associated with enthalpy and they remain in the vicinity of -60 to -70 cal/°K-mole. Szwarc [31] has emphasized the role played by solvation and desolvation processes in propagation as well as termination reactions. It is quite possible that the high magnitude of the entropy for termination in the present system may be the sum of two entropy terms: one arising out of a hydrolysis reaction between water or diol present in the system with active chain ends and the other from cyclization which may be a desolvation controlled phenomenon.

The $SbCl_5$/1,2-Propanediol Catalyst–Cocatalyst System

Table 5 contains rate constants calculated from data obtained at different catalyst concentrations with the $SbCl_5$/1,2-propanediol catalyst–cocatalyst system in DCE as solvent. A fourfold increase in the catalyst concentration (from 0.25×10^{-2} to 1.0×10^{-2} mole/liter) in the presence of 0.38 mole/liter of cocatalyst, had no effect on k_i. The magnitude of k_i with this $SbCl_5$/1,2-propanediol catalyst–cocatalyst system is much the same as that obtained with the BF_3:$(C_2H_5)_2O$ catalyst system studied earlier. This is not surprising if one keeps in mind the fact that the mechanism of initiation by which oxonium ions are formed is the same for the two catalysts; however, for a catalyst concentration of 1.5×10^{-2} mole/liter, k_i is too high. It could be that the nature of the active centers changes beyond a certain catalyst concentration. This factor does not intervene, however, in the present results, since most of the experiments were carried out with a catalyst concentration of 1.0×10^{-2} mole/liter. The termination constant k_t is likewise unaffected by changing catalyst concentration though its values are higher than those obtained for the same copolymerization when carried out with the BF_3:$(C_2H_5)_2O$/(water–1,2-propanediol) catalyst system. According to Eastham [34], the

TABLE 5. Effect of Catalyst Concentration on the Rate Constants of Copolymerizations Carried out at 273° K in DCE with a $SbCl_5$/1,2-Propanediol Catalyst–Cocatalyst System[a,b]

No.	$[Catalyst]_0 \times 10^2$ (mole/liter)	Rate constants (liter/mole-min and 1/min)					
		$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
22	0.25	7.50	1.80	3.00	0.76	5.10	58.51
35	0.50	8.14	2.16	2.40	0.26	2.60	82.39
26	1.00	8.75	2.33	2.33	0.28	3.11	80.25
27	1.50	26.10	3.12	2.33	0.21	3.02	65.72

[a] Other conditions: $[PO]_0 = 3.90$ mole/liter, $[THF]_0 = 3.55$ mole/liter, [1,2-propanediol] = 0.38 mole/liter, and $[DCE]_0 = [PO + THF]_0$ mole/liter.

[b] Data of Alvarez, Hornof, and Blanchard [10].

difference with the two catalysts arises from the relatively greater number of chain transfer and catalyst destruction reactions observed in the $SbCl_5$-catalyzed system. The propagation rate constants k_{11}, k_{12}, k_{22}, and k_{21} are also unaffected by catalyst concentration changes. Their values however are higher than those reported with the $BF_3(C_2H_5)_2O$/water–1,2-propanediol system. This is explained by the absence of depropagation reactions in the $SbCl_5$-catalyzed reactions which are a definite possibility in BF_3-initiated polymerizations [33].

The effects of diol concentration on the rate constants are shown in Table 6. As in BF_3-initiated polymerizations, with $SbCl_5$, k_i increases with diol concentration, stressing the importance of diol as an aid in the initiation process. The value of k_t in the absence of diol is slightly lower than that obtained when 0.20 mole/liter of diol is present in the solution. Beyond that, additional diol has no further effect on the process of termination. The rate constant k_{11} increases with the diol concentration while k_{21} decreases. The other two, viz., k_{12} and k_{22}, remain essentially constant. Similar increases in the values of k_{11} were also observed in the $BF_3{:}(C_2H_5)_2O$-initiated copolymerizations (see Table 2).

The effects of cocatalyst bulk size on $SbCl_5$ initiated copolymerizations are shown in Table 7. The diols are not listed in the order of their bulk size, since k_i and k_t values obtained with them showed no definite trends with the changing bulk size of diol. Rather, they are presented here in decreasing order of their reaction terminating ability. 1,2-Propanediol gives the lowest value of k_i but the maximum for k_t. 1,2-Butanediol, on the other hand, shows the highest value for k_i and the lowest for k_t. Values for the other diols fall between those of 1,2-propanediol and 1,2-butanediol.

Values of the rate constants with increasing temperature are shown in Table 8. All are found to increase. Based on these data, kinetic and thermodynamic parameters for the $SbCl_5$/1,2-propanediol system are shown in Table 9. The initiation activation energy for the present system is 9.96 kcal/mole a value close to the 8.90 kcal/mole obtained for the $BF_3{:}(C_2H_5)_2O$/(water and 1,2-propanediol) system. The Arrhenius parameter A, the initiation enthalpy ΔH, and entropy ΔS of activation are also identical in the two systems, as are the kinetic and thermodynamic parameters for the termination step. Such is not the case, however, with propagation activation energies calculated from the values of k_{11} and k_{12} corresponding to the reaction of PO^+-based oxonium ions with PO and THF, respectively.

TABLE 6. Effect of Diol Concentration on the Rate Constants of Copolymerizations Carried out at 273° K in DCE with a $SbCl_5$/1,2-Propanediol Catalyst–Cocatalyst System[a,b]

No.	$[\text{Diol}]_0$ (mole/liter)	Rate constants (liter/mole-min and 1/min)					
		$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
16	0.00	11.56	0.22	1.50	2.55	1.53	36.96
28	0.20	34.50	0.90	2.20	3.30	0.78	44.64
29	0.59	52.00	3.60	2.40	3.60	0.21	34.11
30	0.75	60.70	5.95	2.90	2.20	0.09	44.17

[a] Other conditions: $[PO]_0 = 3.50$ mole/liter; $[THF]_0 = 3.50$ mole/liter; $[DCE]_0 = [PO + THF]_0$ mole/liter and $[SbCl_5]_0 = 5.0 \times 10^{-3}$ mole/liter.

[b] Data of Alvarez, Hornof, and Blanchard [11].

TABLE 7. Effect of Bulk Size of the Cocatalyst on the Rate Constants of Copolymerizations Carried out at 273° K in DCE with a $SbCl_5$/Diol Catalyst–Cocatalyst System[a,b]

		Rate constants (liter/mole-min and 1/min)					
No.	Diol used	$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{22}	$k_t \times 10^3$
26	1,2-Propanediol	8.75	2.33	2.33	0.28	3.11	80.25
43	1,2-Ethanediol	15.80	6.80	2.00	0.06	2.00	57.75
44	1,5-Pentanediol	17.60	2.97	1.65	0.10	1.90	46.93
39	2,3-Butanediol	15.00	1.40	1.70	0.18	1.70	32.08
40	1,3-Butanediol	18.00	1.40	1.10	0.15	2.20	23.28
42	1,4-Butanediol	15.90	1.36	1.30	0.17	1.95	11.08
41	1,2-Butanediol	19.40	1.62	0.90	0.03	0.56	7.12

[a] Other conditions: $[PO]_0 = 3.80$ mole/liter, $[THF]_0 = 3.50$ mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter, $[SbCl_5]_0 = 1.0 \times 10^{-2}$ mole/liter, and $[diol]_0 = 0.38$ mole/liter.

[b] Data of Alvarez, Hornof, and Blanchard [11].

TABLE 8. Effect of Temperature on the Rate Constants of Copolymerizations Carried out in DCE with a $SbCl_5$/1,2-Propanediol Catalyst–Cocatalyst System[a,b]

No.	Temperature (°K)	Rate constants (liter/mole-min and 1/min)					
		$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
31	263	3.85	0.42	0.65	0.08	0.60	18.32
35	273	8.24	2.16	2.40	0.26	2.60	82.24
32	283	11.43	9.10	7.00	0.34	4.90	100.00
33	293	27.78	13.50	9.00	0.73	12.15	112.50

[a] Other conditions: $[SbCl_5]_0 = 5.0 \times 10^{-3}$ mole/liter, $[\text{1,2-propane diol}]_0 = 0.38$ mole/liter, $[PO]_0 = 3.50$ mole/liter, $[THF]_0 = 3.50$ mole/liter, and $[DCE]_0 = [PO + THF]_0$ mole/liter.

[b] Data of Alvarez, Hornof and Blanchard [10].

TABLE 9. Kinetic and Thermodynamic Parameters for the $SbCl_5$/1,2-Propanediol Catalyst–Cocatalyst System[a]

Rate constants (liter/mole-min and 1/min)	A (same units as k)	E (kcal/mole)	ΔH (kcal/mole)	-ΔS (cal/mole-° K)
k_1	7.00×10^5	9.96	9.51	41.35
k_{11}	2.62×10^{18}	22.63	22.12	-15.93
k_{12}	2.16×10^{14}	17.50	16.74	3.60
k_{22}	6.66×10^7	10.71	10.45	31.61
k_{21}	4.1×10^{12}	15.45	14.60	11.90
k_t (1/min)	7.17	2.43	2.00	64.09

[a] Other conditions and source of data as in Table 8.

With the $SbCl_5$-initiated system (Table 9), these values are considerably higher than those obtained with the $BF_3:(C_2H_5)_2O$ catalyst system. As for THF^+, the k_{22} values lead to enthalpies and entropies of activation which are much the same with the two catalyst systems. It is worth mentioning here, that, in spite of the substantial differences noted in the propagation enthalpies and entropies of activation associated with PO^+ for each of the catalyst system considered, the ΔG values at 0° C calculated from the relationship $\Delta G = \Delta H - T\Delta S$, do not vary by much.

The Triphenylmethyl Salt (PF_6^-, AsF_6^-, and SbF_6^-) Catalyst System

Rate constants for copolymerizations carried out with the $(C_6H_5)_3C^+PF_6^-$ catalyst system are listed in Table 10. One notes that k_i values vary with the catalyst concentration, which could mean that the number of active centers is not directly proportional to the initial catalyst concentration but rather to the square root of this concentration because $k_i/[H^+]_0$ is constant for different $[H^+]_0$ values. It could also mean that the omission of k_{iTHF} in the mathematical model given in the literature [17] is not justifiable with the present catalyst system. This assumption arose from experimental observations made in this laboratory where the homopolymerization of THF with trityl salts could not be achieved. It must be mentioned, however, that Bawn and co-workers [33], as well as Kuntz and Melchior [26], did homopolymerize THF with antimony pentachloride-based trityl ions. It is not impossible therefore that in the value k_i (where $k_i = k_{iTHF} + k_{iPO}$), the contribution of k_{iTHF} may also be quite important as is that of k_{iPO} in the present system. In the absence of concrete experimental evidence to support these hypotheses, the results obtained with the present system were treated in the same fashion as those with the $BF_3:(C_2H_5)_2O$ and $SbCl_5$ catalyst systems. The termination rate constant k_t decreases from 99.52×10^{-3} 1/min to 20.07×10^{-3} 1/min as the catalyst concentration is increased from 0.26×10^{-2} to 1.30×10^{-2} mole/liter. Beyond this k_t remains constant. The propagation rate constants k_{11}, k_{12}, k_{22} and k_{21} decrease with increasing catalyst concentration as does k_t. The ratio of the propagation to termination rate constants as the catalyst concentration is increased, remains constant or increases but does not decrease per se. This

TABLE 10. Effect of Catalyst Concentration on the Rate Constants of Copolymerizations Carried out at 273°K in DCE with a $(C_6H_5)_3C^+PF_6^-$ Catalyst System[a,b]

No.	$[\text{Catalyst}]_0 \times 10^2$ (mole/liter)	Rate constants (liter/mole-min and 1/min)					
		$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
A-01	0.26	0.96	0.46	1.92	1.48	1.70	99.52
A-2	0.65	1.93	0.26	1.00	0.69	0.86	13.71
A-03	1.30	3.85	0.20	0.61	0.40	0.64	20.07
A-04	3.35	10.25	0.18	0.41	0.16	0.36	20.80

[a] Other conditions: $[PO]_0 = 3.25$ mole/liter, $[THF]_0 = 3.25$ mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter, $[(C_6H_5)_3C^+PF_6^-]_0 = 6.5 \times 10^{-3}$ mole/liter and $[\text{cocatalyst}]_0 = 0.00$ mole/liter.

[b] Data of Blanchard et al. [14].

means that the ratio of active to deactivated centers is not a function of the catalyst concentration as it was with the other catalyst systems, viz., $BF_3{:}(C_2H_5)_2O$ and $SbCl_5$, where this ratio was found to increase consistently with the catalyst concentration.

In Table 11 are presented copolymerization rate constants as a function of the initial cocatalyst (water) concentration. The initiation rate constant k_i increases with increasing water concentration, an observation which is similar to that which was made with the $SbCl_5$ catalyst system where k_i was found to increase with the diol concentration. It may be recalled that with the $BF_3{:}(C_2H_5)_2O$ catalyst system, when the concentration of water was raised from 1.17×10^{-2} to 5.31×10^{-2} mole/liter, k_i did not change by much.

The termination rate constant k_t does not change with increasing water concentration up to a value of 10^{-3} mole/liter; however, in the presence of 10^{-1} mole/liter of water, the value of k_t increased from 11.11×10^{-3} to 115.60×10^{-3} 1/min. This is totally different from the observation noted in the case of the $BF_3{:}(C_2H_5)_2O$ and $SbCl_5$ catalyst systems, where the addition of water or diol had no visible effect on k_t. The $(C_6H_5)_3C^+PF_6^-$/water system resembles the PF_5/water system studied by Sims [36] in the polymerization of THF. He suggested that two competing effects of water might be involved cocatalysis and destruction of the catalyst. GPC molecular weight distributions of polymers prepared in both the absence and the presence of (10^{-1} mole/liter) water were presented in an earlier publication from this laboratory [16]. It was shown that the molecular weight distributions were bimodal with the products obtained when water was absent from the reaction, and unimodal when the reactions were carried out in the presence of water. This is thought to be due to early termination of the growing polymer chains. A termination constant of 115.6×10^{-3} 1/min supports this concept.

In the presence of excess water, the ratios of the propagation to the termination rate constants clearly decrease, indicating the active destruction of catalyst centers or the domination of chain transfer reactions.

In Table 12 are summarized the effects of the different solvent conditions on the individual rate constants. In DCE as solvent and with a comonomer to solvent ratio of 1 to 2 (Expt. A-5), k_i shows a value of 4.46×10^{-3} liter/mole-min. On lowering the solvent concentration (Expt. A-2) with a consequent increase in the monomer concentrations, k_i decreases to 1.93×10^{-3} liter/mole-min. Because

TABLE 11. Effect of Water Concentration on the Rate Constants of Copolymerizations Carried out at 273° K in DCE with a $(C_6H_5)_3C^+PF_6^-$/Water Catalyst–Cocatalyst System[a,b]

No.	$[Water]_0$ (mole/liter)	Rate constants (liter/mole-min and 1/min)					
		$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
A-2	0.00	1.93	0.26	1.00	0.69	0.86	13.71
A-13	1×10^{-3}	2.30	0.10	0.69	0.29	0.37	11.11
A-14	1×10^{-1}	5.12	0.71	0.57	0.12	0.74	115.60

[a] Other conditions: $[PO]_0 = 3.25$ mole/liter, $[THF]_0 = 3.25$ mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter, and $[(C_6H_5)_3C^+PF_6^-]_0 = 6.5 \times 10^{-3}$ mole/liter.

[b] Data of Blanchard et al. [16].

TABLE 12. Effect of Solvent on the Rate Constants of Copolymerizations Carried out at 273°K with $(C_6H_5)_3C^+PF_6^-$ System[a,b]

		Rate constants (liter/mole-min and 1/min)					
No.	Solvent	$k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
A-5	DCE	4.46	0.70	0.77	0.20	0.87	17.43
A-2	DCE	1.93	0.26	1.00	0.69	0.86	13.71
A-6	Toluene	8.20	0.53	1.77	0.43	0.62	56.73
A-7	Bulk	3.83	0.33	2.07	0.84	0.64	72.88

[a] Other conditions: $[PO]_0 = [THF]_0 = 3.25$ mole/liter (expt A-2 and A-6), $[PO]_0 = [THF]_0 = 6.40$ mole/liter (expt A-7), $[PO]_0 = [THF]_0 = 1.65$ mole/liter (expt A-5), and $[(C_6H_5)_3C^+PF_6^-]_0 = 6.5 \times 10^{-3}$ mole/liter.

[b] Data of Blanchard et al. [16].

the rate of initiation R_i, shown in Eq. (16), is a direct function of the

$$R_i = k_i [M] [C^*] \tag{16}$$

monomer and the catalyst concentrations, for identical rates of initiation in the two experiments, one should observe for Expt. A-2, a k_i value of 2.3×10^{-3} liter/mole-min (i.e. one half of 4.46×10^{-3} liter/mole-min) on doubling the monomer concentration. The value predicted by the calculations (1.93×10^{-3} liter/mole-min) is indeed very close to the estimated value which clearly indicates, in the present case, that the number of active centers is not strictly dependent on the ratio of monomer to catalyst. Replacing DCE with toluene but retaining the same monomer to solvent proportions (1:2) brought about an increase in the value of k_i to 8.2×10^{-3} liter/mole-min. This suggests that the reactive proportions of the number of active centers produced from the same concentration of catalyst in toluene are less than in DCE. It has been assumed here that the rates of initiation in DCE and in toluene are of similar magnitude; however, it is quite possible that in toluene the rate of initiation may be low due to its low dielectric constant and thus the proportion of the number of active centers $[C^*]$ in this case may be still lower. Under bulk copolymerization conditions where the monomer concentration is twice that in toluene, the value of k_i (3.83×10^{-3} liter/mole-min.) is slightly less than half that computed for the case when toluene is present (8.2×10^{-3} liter/mole-min.). This would indicate that under bulk conditions the catalyst activity is of the same magnitude as that computed for conditions that include the presence of toluene as solvent.

The termination constant k_t, when DCE is the solvent, is 17.43×10^{-3} 1/min for comonomer to solvent proportions of 1:2. The value is slightly lower (13.71×10^{-3} 1/min) when the comonomer to solvent proportions are 1:1. This suggests that the concentration of solvent is not an important factor in the termination reactions. Based on evidence showing DCE to be an active transfer agent, one would expect a more important decrease in the values of k_t. On changing from DCE to toluene or on removing the solvent all together, an increase was observed in the calculated values of k_t while normally one would expect k_t to be lower in bulk conditions and in the presence of toluene. This was confirmed by the molecular weights obtained for the final copolymer products where these increased regularly from 589 in Expt. A-5 to 3925 in Expt. A-7 [17]. This discrepancy in the results obtained via two different approaches needs to be explained. In the computation of k_t it has been assumed that the initial concentration of the catalyst $[H^+]_0$ is equal to the number of active centers $[C^*]_0$, irrespective of the presence or absence of solvent and irrespective of the nature of the solvent used. It is quite likely that the relationship $[H^+]_0 = [C^*]_0$ is not applicable to bulk or toluene-solvent conditions. Thus, to compare k_t values in two identical systems, it is necessary to bear in mind the number of active centers $[C^*]$ involved in each of the system. If these are comparable in nature then only a comparison of k_t has any significant meaning because these are related to R_t, the rate of termination by the equation $R_t = k_t [C^*]$. In the present case, the higher values of k_t obtained in the presence of toluene or under bulk operating conditions result from low initial concentrations of active centers developed in them, whereas the lower k_t values encountered when DCE is the solvent are due to the higher concentration of active centers.

The values of k_{11} and k_{22} representing the propagation constants for the homopolymerizations of PO and THF, respectively, vary in opposite directions on decreasing the DCE solvent concentration, k_{11} decreasing and k_{22} increasing. The values of k_{12} and k_{21}, however, remain substantially the same. On changing from DCE (A-2) to toluene (A-6), k_{11} increases while k_{22} decreases. Once again, the importance of the number of active centers in the present case must be stressed. The PO homopolymerization reaction may be favored in toluene or even under bulk operating conditions, because the values of the constant k_{11} in dichloroethane, in toluene, and under bulk copolymerization conditions do not differ by more than a factor of two, whereas the corresponding number of active centers may differ by a factor greater than two. Similar arguments may be used to explain the apparent decrease in the THF homopolymerization constant k_{22} on changing from DCE to bulk operating conditions. The other two propagation constants, k_{12} and k_{21}, have similar magnitudes in toluene and under bulk operating conditions but when compared to DCE solvent conditions, there is a slight difference.

In Table 13 are shown the rate constants obtained as a function of temperature when using trityl ions with three different gegenions, viz., PF_6^-, AsF_6^-, and SbF_6^-, respectively. One notes that with increasing temperature all of the constants increase. Based on the results of Table 13, kinetic and thermodynamic parameters have

TABLE 13. Effect of Temperature and the Gegenions Associated with Trityl Ions on the Rate Constants of Copolymerizations Carried out in DCE[a,b]

No.	Temperature (°K)	Gegenion	Rate constants (liter/mole-min and 1/min) $k_i \times 10^3$	k_{11}	k_{12}	k_{22}	k_{21}	$k_t \times 10^3$
A-1	263	PF_6^-	1.68	0.05	0.25	0.23	0.23	10.00
25	263	ASF_6^-	3.89	0.03	0.12	0.50	0.50	10.00
26	263	SbF_6^-	2.69	0.04	0.15	0.07	0.09	10.48
A-2	273	PF_6^-	1.93	0.26	1.00	0.69	0.86	13.71
20	273	AsF_6^-	3.96	0.20	0.77	0.57	0.72	15.70
19	273	SbF_6^-	3.58	0.55	0.92	0.29	0.83	15.40
A-3	283	PF_6^-	4.47	0.49	1.54	1.67	2.54	11.29
28	283	AsF_6^-	11.30	0.74	1.95	1.00	1.83	40.16
27	283	SbF_6^-	13.35	1.21	1.54	0.33	1.23	42.86
A-4	293	PF_6^-	15.20	1.27	2.54	1.28	3.05	17.74
30	293	AsF_6^-	20.17	2.62	4.30	1.02	3.01	46.35
29	293	SbF_6^-	28.30	2.84	2.84	0.39	1.85	35.27

[a] Other conditions: $[PO]_0 = 3.25$ mole/liter, $[THF]_0 = 3.25$ mole/liter, $[DCE]_0 = [PO + THF]_0$ mole/liter, $[catalyst]_0 = 6.50 \times 10^{-3}$ mole/liter, and $[cocatalyst]_0 = 0.00$ mole/liter.

[b] Data of Blanchard et al. [16].

been calculated for the three systems. The results of these calculations are presented in Table 14, where the order of presentation follows a decreasing initiation activation energy or an increasing termination activation energy but not the bulk size of the gegenions in which case they would read PF_6^-, AsF_6^-, SbF_6^-, respectively. The value obtained (16.4 kcal/mole) for the activation energy for the initiation reaction with PF_6^- is higher than that obtained (11.9 kcal/mole) with SbF_6^- or that (8.76 kcal/mole) with AsF_6^-, though the last is of the same magnitude as that obtained with the BF_3:$(C_2H_5)_2O$/(water and 1,2-propanediol) and the $SbCl_5$ /1,2-propanediol catalyst systems. The termination activation energy (2.9 kcal/mole) obtained with the PF_6^- gegenion is lower than those (6.2 and 7.8 kcal/mole) obtained with SbF_6^- and AsF_6^-, respectively. The values, nevertheless, fall in the same range as those obtained with BF_3:$(C_2H_5)_2O$ and $SbCl_5$ catalysts. It must be mentioned here that the k_t value is taken as a measure of the stability of the gegenion [37]. In the present study, the order of stability of the various counterions on the basis of k_t values is $PF_6^- = AsF_6^- = SbF_6^- = BF_3{:}(C_2H_5)_2O > SbCl_5$. However, the authors feel that a comparison of the termination activation energy gives better information regarding the stable nature of the counterions. Thus, on the basis of this criterion for the three counterions involved in the present case, AsF_6^- is the most stable, followed by SbF_6^- and then PF_6^-. Bawn and co-workers [38], in their study of the polymerization of THF have indicated that with trityl salts, the PF_6^- counterion is more stable than the $SbCl_6^-$ one. Dreyfuss and Dreyfuss [33] pointed out that fluorine is more electronegative than chlorine, and as a result its compounds are relatively more stable. According to these authors, the order of gegenion stability (defined as the ability to avoid chemical reaction with the oxonium ion itself or with other components in the copolymerization mixture, such as water or solvent) in the polymerization of THF is $PF_6^- > BF_4^- > SbCl_6^-$. In the copolymerization of PO with THF, in the absence of cocatalysts, the results from this laboratory show the order to be $AsF_6^- > SbF_6^- > PF_6^-$. The termination energies obtained in the presence of water or diol may be compared separately and these are: $BF_4(C_2H_5)_2O$/(water) > BF_3:$(C_2H_5)_2O$/(water + 0.13 mole/liter diol) > $SbCl_5$ /diol > BF_3:$(C_2H_5)_2O$/(water + 0.38 mole/liter diol). The activation energies for the other four rate constants, viz., k_{11}, k_{12}, k_{22}, and k_{21}, are generally higher than those for the BF_3:$(C_2H_5)_2O$ system but comparable to those of $SbCl_5$ system.

The enthalpy of activation ΔH, the Arrhenius constant A, and the entropy of activation ΔS follow the trends of E: the enthalpy of activation for the copolymerization rate constants (19 kcal/mole)

TABLE 14. Kinetic and Thermodynamic Parameters of Copolymerizations Carried out with Trityl Ions Associated with Different Gegenions[a]

Rate constants (liter/mole-min and 1/min)	Gegenion	A (same units as k)	E (kcal/mole)	ΔH (kcal/mole)	$-\Delta S$ (cal/°K-mole)
k_i	PF_6^-	2.50×10^{10}	16.40	15.84	20.94
	SbF_6^-	2.17×10^{7}	11.94	11.44	34.73
	AsF_6^-	7.04×10^{4}	8.76	7.57	48.74
k_{11}	PF_6^-	3.78×10^{12}	16.65	15.93	11.84
	SbF_6^-	2.74×10^{19}	25.10	24.64	-20.80
	AsF_6^-	7.50×10^{18}	24.60	23.80	-16.81
k_{12}	PF_6^-	4.11×10^{10}	13.50	12.83	20.44
	SbF_6^-	2.12×10^{13}	16.95	16.60	7.15
	AsF_6^-	9.50×10^{15}	20.33	19.83	- 4.93
k_{22}	PF_6^-	3.11×10^{11}	14.59	14.09	15.84
	SbF_6^-	1.21×10^{8}	11.11	10.84	30.52
	AsF_6^-	4.24×10^{6}	8.60	8.10	39.78
k_{21}	PF_6^-	1.14×10^{14}	17.67	17.24	3.85
	SbF_6^-	6.50×10^{14}	19.10	18.74	0.00
	AsF_6^-	1.83×10^{11}	14.25	13.74	16.06

k_t (1/min)	PF_6^-	2.66×10^0	2.92	2.37	66.78
	SbF_6^-	1.39×10^3	6.18	5.56	34.63
	AsF_6^-	3.06×10^4	7.81	7.19	48.21

[a] Other conditions and source of data as in Table 13.

is different with different counterions (Table 14); however, the free energy ΔG at 0° C is the same for each step of the reaction though the counterions may be different. The low Arrhenius constants [31] as well as the negative activation entropy [30] are generally considered as representing the higher extent of solvation of the cations. In the present case, the entropy of activation plays a very important role, especially in the termination processes where $T\Delta S$ contributes more towards the value of the free energy, ΔG, than does ΔH.

Based on the different entropy values, one can define the role of solvation in each of the steps involved in copolymerization reactions, especially in the initiation and the termination reactions. The trends, however, in the values of the energy of activation with various counterions in the copolymerization reactions are difficult to interpret. One can only suggest that in homopolymerizations of PO the active centers of (PO*) are less solvated than those of (THF*) in corresponding THF homopolymerizations, for all three counterions. Earlier, it was mentioned that the variations of the kinetic and thermodynamic parameters with the different counterions do not rigorously follow the order of their bulk sizes. There are some other facets of triphenylmethyl salts which are puzzling. For instance, it is difficult to understand why $(C_6H_5)_3C^+AsF_6^-$ should require less energy for the process of initiation than does $(C_6H_5)_3C^+PF_6^-$. Furthermore, $(C_6H_5)_3C^+AsF_6^-$-initiated polymerizations are by far the most stable. If bulk size of the gegenion is so important, then the activation energy should be a maximum for SbF_6^- and it should be more stable than AsF_6^-. It is worthwhile adding that in the polymerization of isobutyl vinyl ether [39] and α-methylstyrene [40] the stereoregularity of the polymer is said to be controlled mainly by the bulk size of the gegenion. Dreyfuss and Dreyfuss [33] have suggested that the contribution of properties like the electronic structure of the elements involved in the counterion, their ionic structure, polarizability and their thermal stability, all add up to determine counterion reactivity. Based on their analyses of different counterions and making use of their criteria, they suggest that PF_6^- has a higher order of stability than SbF_6^-. In the present system as was mentioned earlier, PF_6^- has been found to be less stable than SbF_6^-.

The overall conclusions drawn by some [38-40] to the effect that trityl salts yield better polymers than those produced by $BF_3{:}(C_2H_5)_2O$ and $SbCl_5$ are likewise not in full agreement with the results of the present copolymerization system, where low molecular weight cyclic materials were always present along with the higher molecular weight polymers, irrespective of the type of catalyst used. Based on these results, one would have to say that the parameters responsible for the stability of the counterions suggested by Dreyfuss and Dreyfuss

[33] as well as Kunitake and co-workers [39, 40] are probably true, but the order of the stability for a given set of counterions in two different systems may not be the same. For the PO-THF copolymerization system with or without cocatalysts, the order of stability of the counterions based on their energies of termination would be the following: $AsF_6^- > SbF_6^- > HOBF_3^- \geqq PF_6^- > SbCl_6^-$.

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