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Effect of the Counterion on the Cationic Polymerization Rate of Ethylene Oxide by Trityl Salts

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ABSTRACT

The cationic polymerization of ethylene oxide by trityl salts (BF_4^-, $SbCl_6^-$, AsF_6^-, and PF_6^- as counterions) in nitrobenzene at different temperatures has been studied. The kinetic analysis was carried out by use of an automatic manometer, and it showed that the polymerization rate constant depends neither on the counterion type nor on the initial initiator concentration. These facts allowed us to conclude that macrocations and macroion pairs have the same reactivity.

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INTRODUCTION

The transformation of a low molecular weight monomer into a high molecular weight polymer through a cationic mechanism necessarily implicates the counterion except when the initiating system involves electron ejection from the monomer [2]. The propagation reaction can be accomplished by three different species, i.e., unpaired ions, paired ions, and covalent species, according to

$$\begin{tikzcd}
P_nA \arrow[r, leftrightharpoons] \arrow[d, "k_p^e"', "+M"] & P_n^+A^- \arrow[r, leftrightharpoons] \arrow[d, "k_p^{\pm}"', "+M"] & P_n^+ + A^- \arrow[d, "k_p^+"', "+M"] \\
P_{n+1}A \arrow[r, leftrightharpoons] & P_{n+1}^+A^- \arrow[r, leftrightharpoons] & P_{n+1}^+ + A^-
\end{tikzcd}$$

which results in different propagation rate constants according to the reactivity of each species.

The total rate of monomer consumption [3] is the sum of the reaction rates due to macrocations (unpaired ions), macroions (paired ions), and macrocovalent species, i.e.:

$$R = R^+ + R^{\pm} + R^e = (k_p^+[P_n^+] + k_p^{\pm}[P_n^+A^-] + k_p^e[P_nA])[M].$$

By an appropriate choice of experimental conditions it is possible to shift the above equilibria toward the desired side so that a given propagation species will predominate in the reaction medium. In our systems, covalent species have been avoided since anions from Lewis acids are incapable of forming a covalent bond by direct union with the carbocation [4].

When the propagating species are macrocations and macroions, the propagation rate can be expressed by

$$R = [k_p^+c\alpha + k_p^{\pm}c(1 - \alpha)][M],$$

where α is the degree of dissociation of paired ions and leads to the equilibrium

$$P_n^+A^- \overset{K_d}{\rightleftharpoons} P_n^+ + A^-.$$

This equilibrium is characterized by a dissociation constant defined in the approximate form of the Bjerrum-Fuoss equation [5] as

$$-\log K_d = A + \frac{B}{Ta\epsilon},$$

where "a" is the effective interionic distance and ϵ is the dielectric constant of the solvent. Thus, if a larger anion is replaced by a smaller one, K_d will decrease.

The choice of counterions in the cationic polymerization of cyclic ethers is restricted to complex anions having large radii [6]. The structure of the counterion is of paramount importance for the propagation kinetics, at least in anionic polymerization. There are only a few systematic studies about the influence of anions on the propagation rate constant of macroion pairs [7], and two different kinds of conclusions are reported: either k_p^+ and $k_p^\pm$ are indistinguishable or they differ by a factor of 2 or more [6].

From the dissociation constant of $Ph_3C^+A^-$ in nitrobenzene [8] it can be deduced that "a" has no great influence on K_d since the anions are bulky enough, except for BF_4^-, which is the smallest one. The values of ΔH_d and ΔS_d for triphenylmethylium salts are also close to those found for poly-THF and polyoxepane ion pairs [9], and, therefore, the degrees of dissociation were not taken directly from macroion dissociation studies but from trityl salts.

EXPERIMENTAL

The experimental technique has been previously described [1, 10], and the manometer calibration at the different reaction temperatures (279, 298, 313, and 328 K) was done as before [1]. The purity of the trityl salts used as initiators was checked by measuring the molar absorption at 412 nm in CH_2Cl_2 [11].

RESULTS AND DISCUSSION

Experiments were carried out as described previously [1]. Table 1 shows the results obtained at 298 K with AsF_6^- and $SbCl_6^-$ as counterions. Figure 1 shows an example of the first-order plots obtained; in all experiments the linearity of the propagation stage is maintained until the end of the polymerization reaction, as reported previously [1]. Successive monomer additions to the polymerization system after the first reaction was complete indicated that termination reactions are absent in our systems, i.e., no loss of active centers

TABLE 1. Initial Conditions and k_1 Values in Ph-NO_2 at 298 K

Experiment	$[M]_0$, mol/L	$[I]_0$, mmol/L	$k_1 \times 10^3$, min^{-1}
Sb0-1	0.167	2.28	4.93
Sb0-2	0.167	2.49	6.25
Sb0-3	0.130	0.752	1.64
Sb0-4	0.138	1.43	4.03
Sb0-5	0.153	0.854	2.02
Sb0-6	0.177	4.53	12.9
Sb0-7	0.218	5.05	14.1
Sb0-8	0.158	0.501	0.994
Sb1-8	0.135	0.501	1.25
Sb0-9	0.145	1.93	6.20
Sb1-9	0.150	1.93	6.00
As0-1	0.165	2.18	5.59
As1-1	0.166	2.18	5.60
As0-2	0.141	1.18	2.71
As1-2	0.142	1.18	3.23
As0-3	0.175	0.797	1.59
As0-4	0.175	3.05	6.07
As0-5	0.122	1.58	3.76

occurs. These results also indicate that k_p is almost the same after one or more successive monomer additions (for instance, in Table 1, Experiment Sb1-9 corresponds to a second addition of monomer after the first reaction, Sb0-9, has been completed).

By plotting the slope of the first-order plot (pseudofirst-order constant, k_1) vs initial initiator concentration, the propagation rate constant k_p is obtained (see Fig. 2). From this plot the following conclusions can be deduced.

a) The propagation rate constant, which can be expressed as

$$k_p = k_p^+\alpha + k_p(1 - \alpha),$$

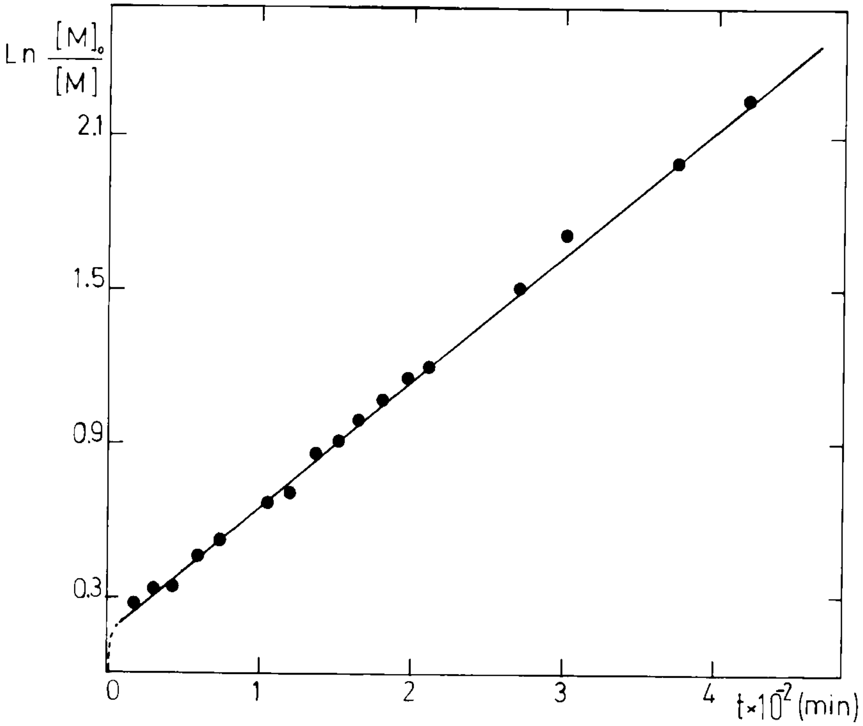

FIG. 1. First-order plot for Experiment SbO-1.

is constant in the whole range of initial initiator concentrations used ($[I]_0 = 10^{-2}$ to 10^{-4} mol/L). Since a change in the initial initiator concentration would shift the dissociation equilibrium for macroion pairs, changing its degree of dissociation, the constancy in the k_p values indicates that k_p^+ is equal to $k_p^\pm$. For the polymerization of THF [12], oxepane, and other cyclic ethers [6] with large anions like AsF_6^-, $SbCl_6^-$, etc., it has been shown that k_p^+ and $k_p^\pm$ also coincide. The opinion that macrocations are more reactive than macroion pairs in the polymerization of THF [13] does not seem valid today.

b) A high degree of purity for our systems is shown by the low values observed for the intercept on the $[I]_0$ axis in Fig. 2 [14].

Table 2 shows the k_p values for all the counterions and temperatures as well as the corresponding ranges for $[M]_0$ and $[I]_0$. An Arrhenius plot using these data (Fig. 3) allows us to obtain the

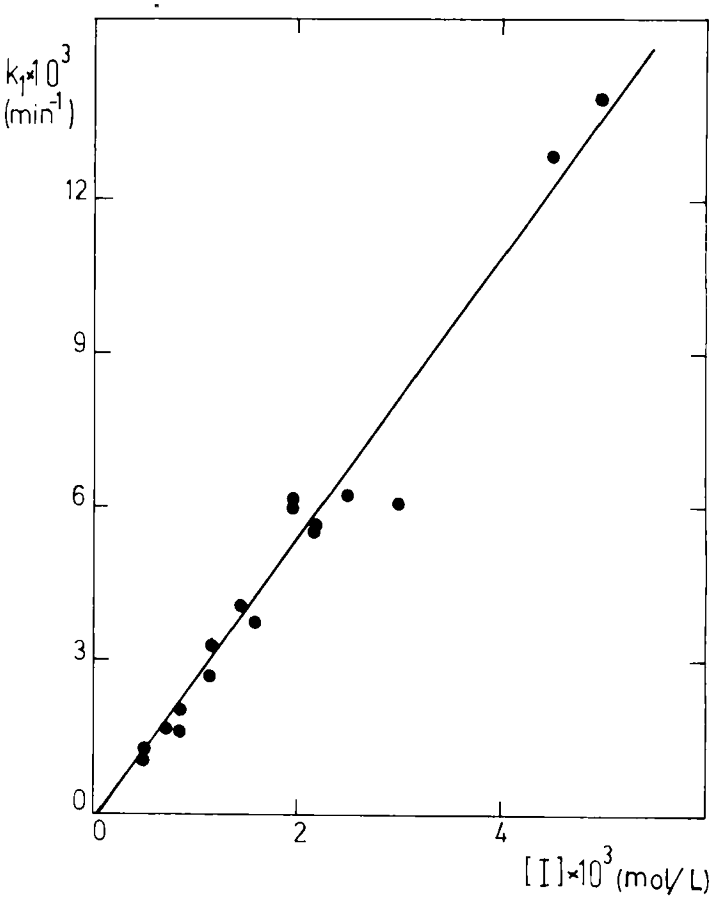

FIG. 2. Plot of k_1 vs $[I]_0$ at 298 K.

TABLE 2. k_p Values in Nitrobenzene

Counterion	T, °K	k_p (mol/L)$^{-1}$min^{-1}	$[M]_0$, mol/L	$[I]_0$, mmol/L
$SbCl_6^-$	279	0.335	0.37-0.42	3.78-8.68
$SbCl_6^-$	298	2.59	0.12-0.22	0.50-5.05
AsF_6^-	298	2.37		
$SbCl_6^-$	313	8.02	0.09-0.14	2.20-11.7
PF_6^-	313	7.75		
$SbCl_6^-$	328	24.7	0.07-0.14	0.086-0.648
AsF_6^-	328	32.0		

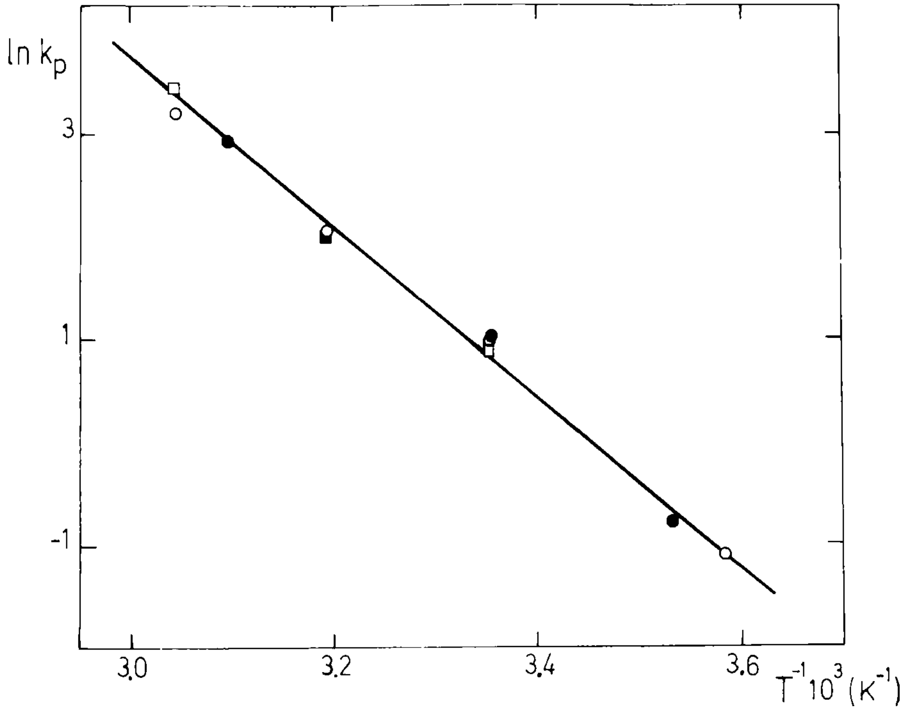

FIG. 3. Arrhenius plot (●, BF_4^- [1, 10]; ○, $SbCl_6^-$; □, AsF_6^-; ■, PF_6^-).

following values for the activation energy and the frequency factor:

$$E_a = 16.7 \text{ kcal/mol}$$

$$A = 1.83 \times 10^{10} \text{ (mol/L)}^{-1}\text{s}^{-1}$$

These values are in good agreement with those previously reported for the polymerization of cyclic ethers via an oxonium ion [15, 16].

The IR spectrum of the polymer (recovered with distilled water by conventional techniques) shows all the characteristic bands of poly(ethylene oxide) [17] and none corresponding to an aromatic ring is detected. On the other hand, triphenylmethane can be isolated and characterized from the organic layer after long evaporation. These facts allow us to propose that, in the polymerization of ethylene oxide with carbenium ions, initiation occurs through hydride abstraction, as it does for other cyclic ethers such as THF [18] and 1,3-dioxolane [19].

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