Polymerization of Tetrahydrofuran with Triethyloxonium Hexafluorophosphate

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Recently it was shown that when tetrahydrofuran (THF) was polymerized using triethyloxonium tetrafluoroborate as an initiator, the reactive chain end was mostly in the form of ion pairs, but with appreciable ionization to free ions.[1] Both of these species contributed to the propagation reaction, with the free ion having a higher rate constant. The dissociation constants of the reactive chain end ion pairs formed from most of the normally used initiators in this polymerization could be expected to be similar. Hence as it has been remarked that the overall rate constant of propagation varies little from counterion to counterion,[2] the free ion propagation reaction is likely to be a feature common to most THF cationic polymerizations. To confirm that it was not a unique feature of the tetrafluoroborate anion, a similar study has been made using triethyloxonium hexafluorophosphate as initiator.

Experimental Section

The techniques of conductance, reaction rate measurement, and reactant purification were essentially those used before.[1]

Results

Conductivities were measured for solutions of triethyloxonium hexafluorophosphate and tetrabutylammonium hexafluorophosphate in methylene chloride. The conductance was also measured for a solution of a short chain polytetrahydrofuran containing the active trialkyloxonium chain end, as in the previous study. But as was found before, the measured trialkyloxonium salt present was only half that expected from the added initiator, and so perhaps these measurements should be treated with reserve. The results are tabulated in Table I. There is a reasonable agreement with the values given by Plesch[3] for the oxonium salt. These salts have slightly higher dissociation constants than the corresponding tetrafluoroborates, perhaps to be expected from what is probably a larger anion.

The propagation rate was measured dilatometrically at 0° both in the presence and absence of the common ion salt tetrabutylammonium hexafluorophosphate. The results are plotted in Figure 1 according to the method of Szwarc et al.[4] and indicate that there is in fact both reaction with the ion pair and the free ion. The calculated rate constants are given in Table II. Once again it is found that there is good agreement between the dissociation constant of the growing chain end ion pair measured kinetically and that measured conductiometrically.

There is not such good agreement between the free ion rate constant found here and that found in the previous study. In principle they should be the same. There are various sources of error in these experiments, notably the instability of the tetrafluoroborate oxonium salts.[5] Moreover, with that counterion the apparent contribution of the free ion reaction to the overall rate was usually less than 30%, so errors in rate measurement were magnified when the free ion rate constant was extracted.

The discrepancy between the two values is probably no more than could be expected. Nevertheless, the contribution by the free ion reaction is again demonstrated. The ratio between the free ion and ion pair rate is small compared with the large ratios found in anionic polymerization[4] and comparable to that found in the cationic polymerization of episulfides.[6]

Table I
Conductance Data at 0° in Methylene Chloride Solution

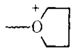
Salt	Λ_0	$K_D \times 10^6$
$Bu_4N^+PF_6^-$	100	50.2
$Et_3O^+PF_6^-$	105	9.9
 PF_6^-	82	8.2

Table II
Kinetic Data for THF Propagation Reaction at 0° in CH_2Cl_2

K_D (kinetic)	8.0×10^{-6}	
$k_{p\pm}$ (ion pair)	8.7×10^{-4}	M^{-1} sec^{-1}
k_{p+} (free ion)	2.1×10^{-2}	M^{-1} sec^{-1}
k_{p+} (ref 1)	1.0×10^{-2}	M^{-1} sec^{-1}

The change of counterion from BF_4^- to PF_6^- causes the minor changes in $k_{p\pm}$ of 1.4×10^{-3} to 8.7×10^{-4} M^{-1} sec^{-1}, in accord with others[2] who suggest only minor effects of counterion. Moreover, as it is not to be expected that there will be large changes in K_D with counterion, under particular conditions k_p overall will also be insensitive to counterion.

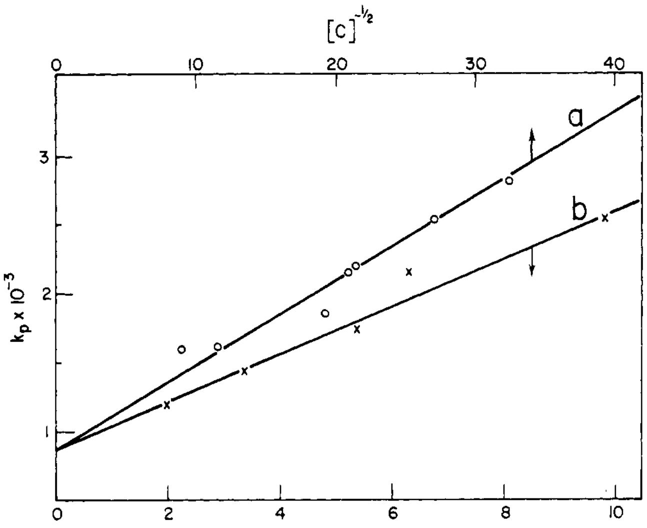


Figure 1. Rate constants in the propagation reaction of THF polymerization: (a) in the absence of tetrabutylammonium hexafluorophosphate; (b) in the presence of tetrabutylammonium hexafluorophosphate.

Penczek[2] gives a value of $k_{p\pm}$ of 4.6×10^{-2} M^{-1} sec^{-1} in a reaction mixture 65% THF and 35% CCl_4 at 25°. Assuming a reasonable activation energy, this rate constant appears to be higher at lower dielectric constants in accord with Penczek's suggestion.

References and Notes

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