Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 90, Number 2, April 1981, pp. 117-120.

Oxonium ions as initiators for vinyl polymerizations. A reappraisal

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MS received 19 September 1980; revised 19 January 1981

Abstract. Triethyl oxonium fluoroborate either preformed or prepared *in situ* by the reaction of boron trifluoride etherate with epichlorohydrin does not initiate the homo or copolymerization of vinyl monomers. Small conversions to copolymers by use of these initiators with low methyl methacrylate incorporation is ascribed to conventional vinyl copolymerizations, initiated by free boron trifluoride and/or protonic impurities in the system.

Keywords. Oxonium ions; vinyl polymerization; boron trifluoride; epichlorohydrin; initiator; homo-copolymerizations.

1. Introduction

Trialkyl oxonium salts can be regarded as specifically solvated alkyl cations ($R_3O^+ \rightleftharpoons R^+ + R_2O$) and consequently are powerful alkylating agents (Perst 1971). In view of this, they are also good initiators for cyclic ether polymerizations (Tsukamoto and Vogl 1971). Initiation of cationic vinyl polymerization can also be regarded as an electrophilic alkylation of a double bond and is most efficient when the initiating and propagating ions are of roughly equal stabilities. Using this criterion one cannot preclude the ability of an oxonium ion to initiate vinyl polymerization.

However, there has been no attempt so far to study the initiating ability of either preformed or *in situ* generated trialkyl oxonium salts for vinyl polymerizations. It has been reported that usually no random copolymerization takes place between monomers propagating through carbenium ions (e.g., styrene) and through oxonium ions (e.g., tetrahydrofuran, 3, 3-*bis* (chloromethyl) oxetane) (Tsukamoto and Vogl 1971). In a limited sense this could be inferred as evidence that oxonium ions cannot initiate vinyl polymerizations. More recently it has been reported that boron trifluoride etherate in conjunction with epichlorohydrin in benzene at 50° C initiates in low yield the copolymerization of styrene and methyl methacrylate (Pavlyunchenko *et al* 1971). However, these authors did not recognize the interesting possibility that their initiator combination could lead to *in situ* generation of triethyl oxonium fluoroborate.

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In view of our interest in the study of oxonium ions as initiators for carbenium ion polymerizations, we have examined triethyl oxonium fluoroborate as a polymerization initiator. This paper reports the results of such a study.

2. Experimental

2.1. *Materials*

All solvents and monomers used in this study were dried by distillation over CaH_2 (ethyl ether over sodium) and stored in serum-capped bottles under a positive pressure of nitrogen at − 20° C. Boron trifluoride etherate was purified according to the published procedure (Brown and Zwiefel 1963). Triethyl oxonium fluoroborate was prepared as reported (Meerwein 1966), m.p. 90–91° and was stored in a screw-capped bottle at − 20° C.

2.2. *Polymerizations*

Polymerizations were conducted in a three-neck flask fitted with a mechanical stirrer, dropping funnel and reflux condenser and constantly swept by a slow stream of high purity nitrogen. All liquids were transferred using dry hypodermic syringes using a neoprene rubber septum and under a positive pressure of nitrogen. Solid additions were done in an inert atmosphere box swept by a stream of high purity nitrogen. A typical experimental procedure is given below :

Epichlorohydrin (0·32 ml, 3 mmol) dissolved in 10 ml dry benzene was placed in the reaction vessel and boron fluoride etherate (0·75 ml, 6 mmol) dissolved in 10 ml benzene was added dropwise. The mixture was heated to 50° C for 1 hr. After cooling, a mixture of styrene and methyl methacrylate (0·2 mol each) dissolved in 30 ml benzene was added with stirring. After complete addition, the reaction mixture was once again heated to 50° C and maintained for 2 hr. The polymer was precipitated by the addition of methanol, filtered and purified by reprecipitation. The purified polymer was dried *in vacuo* for 8–10 hr (50° C, 1 torr). Polymer yield 1·4 g (3·5% conversion).

2.3. *Characterization*

Polymers were characterized by their IR spectra in HCB using a Beckman 4220 IR spectrophotometer. Elemental analyses were performed on a Coleman analyzer. The intrinsic viscosities of the polymers were determined in cyclohexane at 30° C (theta conditions).

3. Results and discussion

Styrene was homopolymerized and copolymerized with methyl methacrylate with boron trifluoride etherate alone and with different molar proportions of epichlorohydrin as well as with preformed triethyl oxonium fluoroborate. The results are summarized in table 1. Boron trifluoride etherate is a good initiator for

Table 1. Polymerization of styrene and methyl methacrylate using boron trifluoride etherate-epichlorohydrin initiator systems[a]

Expt. No.	Initiator, mmol $Et_3O^+BF_4^-$	$BF_3 \cdot Et_2O$	ECH	Solvent	Yield[b] g	Conv. %	$[\eta]$[c]
1[d]	..	6	..	Benzene	10	48·5	0·073
2[e]	..	6	..	Benzene	0	0	..
3	..	6	..	Benzene	4	9·9	0·034
4[d]	..	6	3	Benzene	5	24·1	0·056
5	..	6	3	Benzene	1·4	3·5	0·037
6	..	6	3	None	2·1	5·2	..
7	..	6	8	Benzene	0·7	1·7	..
8	..	60	30	Benzene	5·9	14·6	0·021
9[d]	6	..	..	Benzene	0·3	1·4	..
10[d]	6	..	..	Nitrobenzene	0·1	0·5	..
11	6	..	..	Benzene	0·6	1·5	..
12[f]	6	..	..	Dichloromethane	0·3	0·7	..
13	6	..	..	Nitrobenzene	0·4	1·0	..

[a] Each charge consists of 0·2 moles each of both monomer in 30 ml of solvent, unless otherwise mentioned; reaction time 2 hr, temperature 50° C.

[b] Yield based on total monomers charged.

[c] In cyclohexane at 30° C.

[d] 100% styrene charged.

[e] 100% MMA charged.

[f] refluxing solvent temperature.

styrene polymerization; however it fails to polymerize methyl methacrylate When styrene and methyl methacrylate are copolymerized in the presence of boron trifluoride etherate there is a reduction in both yield and molecular weight. Such an observation has been made before with aluminium chloride (Gaylord *et al* 1975). The composition of the copolymer as determined from elemental composition and confirmed by IR, showed the presence of 6·6% MMA.

The polymerization of styrene and copolymerization with methyl methacrylate was attempted under two different stoichiometries of boron trifluoride etherate and epichlorohydrin (ECH), namely,

$$4\,ECH + 3\,BF_3 \cdot Et_2O + 2Et_2O \rightarrow Et_3O^+BF_4^- + (Cl\text{-}CH_2\text{-}CH(CH_2OEt)\text{-}O\text{-})_3\,B$$

$$3\,ECH + 6\,BF_3 \cdot Et_2O \rightarrow Et_3{}^+OBF_4^- + 2BF_3 + (Cl\text{-}CH_2\text{-}CH(CH_2OEt)\text{-}O\text{-})_3\,B$$

Under these conditions where the oxonium ion is expected to be formed *in situ*, no appreciable homo or copolymerization occurred. However, the copolymer showed slight incorporation (2–3%) of MMA, presumably arising out of the adventitious presence of free BF_3 or protonic impurities in the reaction system.

Preformed triethyl oxonium ion did not give any homo or copolymerization even in high dielectric media where it was anticipated that some oxonium–carbenium equilibrium could probably exist. Substantially higher concentration of boron trifluoride etherate and epichlorohydrin (60 and 30 mmol respectively) gave rise to higher conversions (~ 15%). The copolymers showed evidence of MMA incorporation (~ 6%).

Our results establish that (a) preformed triethyl oxonium ions are not initiators of cationic vinyl polymerization nor do they induce copolymerization of styrene with methyl methacrylate and (b) where boron trifluoride etherate and epichlorohydrin are mixed *in situ*, some homopolymerization or copolymerization occurs which can be simply explained as a Lewis acid initiated homo or copolymerization of vinyl monomers (Kennedy 1975; Gaylord *et al* 1975). The inability of triethyl oxonium fluoroborate to initiate vinyl polymerization implies that the initiator oxonium ion is substantially more stabler than the propagating styryl carbocation. This has led us to a search of energetically more compatible oxonium ions (i.e., $R_3O^+ \rightleftharpoons R^+ + R_2O$ equilibrium shifted more to the right) capable of initiating vinyl polymerization. Preliminary studies now in progress indicate that *o*-methyldibenzofuranium fluoroborate (Copson *et al* 1972) may be a true initiator of vinyl polymerization. Details of this study will be reported elsewhere.

References

Brown H C and Zwiefel G 1963 *Org. Reactions* **13** 28

Copson A J, Heaney H, Logun A A and Sharma R P 1972 *Chem. Commun.* p. 315

Gaylord N G, Deshpande A B, Dixit S S, Maiti S and Patnaik B K 1975 *J. Polymer Sci. Chem. Ed.* **13** 467

Kennedy J P 1975 *Cationic polymerization. A critical inventory* (New York : Wiley Interscience) p. 231

Meerwein H 1966 *Org. Synthesis* **46** 113, 120

Pavlyuchenko N, Balaev G A, Solokov V N and Kondratenkov G P 1973 *Vysokomol. Soedin* **158** 87; *Chem. Abstr.* **79** 19183

Perst H 1971 *Oxonium ions in organic chemistry* (New York : Academic Press) p. 37

Tsukamoto A and Vogl O 1971 *Progress in polymer science* (ed. A D Jenkins) (New York : Pergamon) vol. 3, p. 199