

polymer communications

Initiation of cationic polymerization using *p*-methyl benzyl bromide

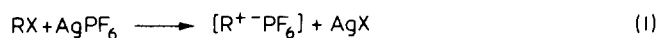
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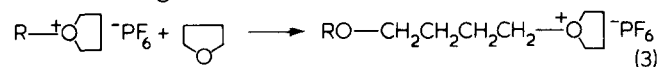
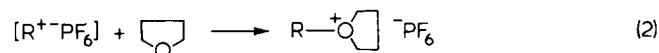
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In an earlier paper¹ we considered the reaction between organic halides and selected silver salts as a means of generating species capable of initiating cationic polymerization. Silver salts of strong acids such as the perchlorate, hexafluorophosphate and hexafluoroantimonate were used in order that the soluble product resulting from the metathetical reaction (equation 1) was sufficiently ionized to initiate effectively the monomer also present in the reaction mixture.



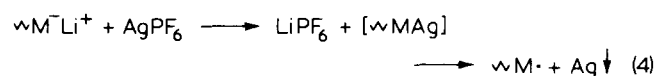
Many classes of halides were investigated using tetrahydrofuran (THF) as both monomer and solvent (equations 2 and 3). From this survey it was concluded that benzylbromide at the rather high concentrations used was capable of rapidly producing the benzyl carbonium ion which in turn was an efficient initiator of cationic polymerization:



This initiator was successfully used in subsequent work involving the reaction between polymeric anions and 'living' poly THF^{2,3} initiated by an equimolar (0.01 M) benzylbromide - silver hexafluorophosphate system. The red living anionic polymer solutions were titrated into polyTHF until the onset of a permanent colour, the titre being close to the calculated equivalence point based on complete consumption of the halide. Further g.p.c. traces of the component polymers showed that polyTHF was of the predicted molecular weight and was of the narrow polydispersity required of efficient initiation.

Subsequent experiments using different batches of benzyl bromide and silver hexafluorophosphate, under the same conditions have, however, failed to reproduce these results, the end-point being masked by a black precipitate of metallic silver. Precipitation was observed on titration up to 3 h after initiation of the TFH polymerization, although the quantity was inversely related to the time elapsed. Precipitation of silver can only occur if the reaction between equimolar

AgPF₆ and benzyl bromide is incomplete, leaving the silver salt to react with the anionic polymer as shown in equation (4). This reaction has been confirmed by the direct reaction of living polystyrene with AgPF₆ in THF.



Present evidence is therefore that initiation is comparatively slow, and further support for this view was obtained from experiments designed to study the reaction of living polyTHF with tertiary amines⁴. AgBr was regularly observed to form for a considerable period after the silver salt and halide were mixed.

These findings, now confirmed by a large number of experiments, although contradicting the results obtained and published earlier, are in line with the observations of other workers⁵. We are unable to account satisfactorily for the discrepancy between the two sets of results. Since we no longer found benzyl bromide to be a satisfactory coinitiator we were obliged to investigate the suitability of alternative halides and to confirm more quantitatively the slow reaction of benzyl bromide. This Communication briefly describes such investigations.

Results and discussion

In the published survey of the reactions of organic halides with silver salts¹ there were indications that *p*-methyl benzyl bromide was more reactive than benzyl bromide, consistent with the positive inductive effect of the methyl group on the C-Br bond. This compound therefore seemed a likely replacement for benzyl bromide in the initiating system, and a comparison of the reactivities of the two halides with AgPF₆ was undertaken. Three types of measurement were carried out: (1) the direct monitoring of unreacted organic halide with time by g.l.c., (2) gravimetric determination of the AgBr yield, and (3) measurement of polymer yield and molecular weight (g.p.c.) to estimate the efficiency of initiation. The experimental techniques and equipment were as described elsewhere¹⁻³. The reaction conditions, unless otherwise stated, were 0.01 M halide in THF at -10°C, a temperature at which it has been previously shown that living

non-transfer conditions prevail⁶.

The rates of consumption of the organic halides with equimolar and excess quantities of AgPF₆ at -10°C are shown in Figure 1. With benzyl bromide and 10% molar excess AgPF₆ about 25% of the halide remains unreacted after 2 h, and even with 120% excess AgPF₆ detectable amounts (~3%) remain at that time. The decay curves cannot be fitted to a second order process, the admittedly semi-quantitative results indicating a higher reaction order. These observations tally with those obtained in similar systems by Lee and Dreyfuss⁵ who, like ourselves, offer no explanation for this apparently complex kinetic behaviour.

The consumption of *p*-methyl benzyl bromide is very much faster, and under equimolar conditions the reaction is complete at -10°C after 1 h. On the basis of this data the *p*-methyl derivative seems the more suitable initiator for the cationic polymerization of THF.

The yields of AgBr and polymer listed in Table 1 are in general agreement with the halide consumption. Thus with benzyl bromide only about 75% yield of AgBr was obtained under equimolar reagent conditions after 2 h, whereas with *p*-methyl benzyl bromide the yield was about 95%. Interestingly, a very much higher yield was obtained with benzyl bromide when a fresh batch of AgPF₆ was used, suggesting that perhaps the discrepancy with the original results might be related to the condition of the silver salt (a deliquescent material). Against this, however, is the observation that reaction with AgClO₄ under the same conditions also gives only about 75% yield of AgBr. The data confirm that the rate of reaction and hence the rate of initiation can be

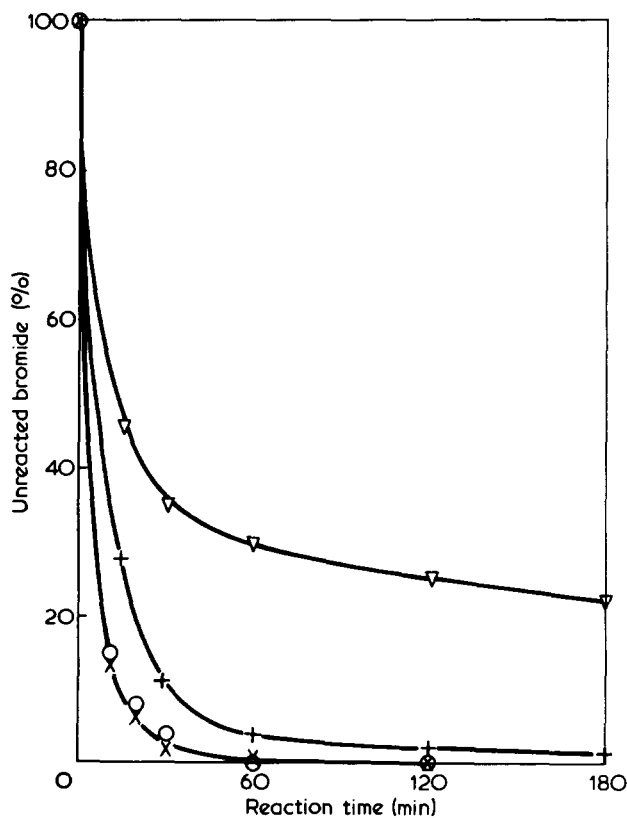


Figure 1 Unreacted bromide as a function of time: ▽, C₆H₅CH₂Br = 0.010 M, AgPF₆ = 0.011 M; +, C₆H₅CH₂Br = 0.010 M, AgPF₆ = 0.022 M; ○, CH₃C₆H₄CH₂Br = 0.010 M, AgPF₆ = 0.010 M; x, CH₃C₆H₄CH₂Br = 0.010 M, AgPF₆ = 0.010 M

Table 1 Reaction of benzyl bromide and of *p*-methyl benzyl bromide with AgPF₆ in THF at -10°C

	Bromide molarity	AgPF ₆ molarity	AgBr % yield after 2 h	Initiating efficiency (1 h)	Saegusa method
Benzyl bromide	0.010	0.010	68		
	0.010	0.010	79		
	0.010	0.010	75		
	0.010	0.010*	95		
	0.040	0.040	88		
	0.080	0.080	92		
<i>p</i> -Methyl Benzyl bromide	0.010	0.010	94		
	0.010	0.010	96		
	0.010	0.010		101	
	0.010	0.010		100	
	0.010	0.010		92.5	
	0.010	0.010		94.8	92
	0.010	0.013		94.7	87.2
	0.030	0.033		99.0 (2 h)	

* New batch AgPF₆

increased by mixing reagents at high concentration, the solution being subsequently diluted to concentrations convenient for propagation.

The yields of polymer using *p*-methyl benzyl bromide, obtained 1 h after mixing the reagents, are high enough to suggest 100% conversion efficiency of halide into active polymer chains. The direct estimate of the concentration of active ends was attempted in two cases using the technique of Saegusa and Matsumoto^{7,8} in which the living polyTHF is terminated with sodium phenoxide and the concentration derived from the u.v. absorbance of the isolated sample. The results are somewhat lower than those obtained from the polymer yield data. This is consistent with a small proportion of inadvertent termination, but also with the presence of a small molecule absorber for which there is some evidence from g.p.c. traces.

Experiments were carried out with *p*-methyl benzyl bromide in which AgSbF₆ was used as a precipitant. The results were very similar to those obtained with AgPF₆. Thus this halide reacts much more rapidly with silver salts than benzyl bromide; it initiates polyTHF chains with an efficiency ≥ 95%, and at 0.01 M equimolar concentration the initiation is complete within 1 h at -10°C. This initiator has now been used successfully to generate polyTHF which has subsequently been visually titrated with living polystyrene. Similarly, living polyTHF has been prepared by this means which has been reacted with tertiary amines without interference from unconsumed organic halide.

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