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The synthesis and characterization of polymer-bound diaryliodonium salts and their use in photo and thermally initiated cationic polymerization

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Summary

A new method for the synthesis of polymer-bound diaryliodonium salts has been developed which facilitates the preparation of these polymeric initiators. The polymer-bound diaryliodonium salts were used in both photo and thermally initiated cationic polymerizations.

Introduction

The use of diaryliodonium salts bearing anions of low nucleophilic character as photoinitiators for cationic polymerization has been described in several publications from this laboratory (CRIVELLO and LAM 1977; CRIVELLO, LAM and VOLANTE 1977) as well as by Smith at the 3M Company (SMITH 1974). By virtue of the fact that these photoinitiators liberate strong protonic acids on photolysis, they are capable of initiating the polymerization of virtually all cationically polymerizable monomeric substrates. The use of these same diaryliodonium salts in combination with a copper cocatalyst and reducing agents to thermally induce cationic polymerizations has also been reported by us (CRIVELLO and LAM 1981; CRIVELLO, LOCKHART and LEE 1983).

Recently, we have been investigating the possibility of preparing polymer-bound iodonium salts. Such materials would be of considerable interest as photo and thermal initiators for a number of reasons. First, such polymeric catalysts would be expected to have a low order of toxicity owing to the general inability of high molecular weight aromatic polymers to be absorbed and metabolized by mammalian digestive systems. Secondly, such polymer-bound catalysts would be conveniently isolated after synthesis by typical polymer isolation techniques such as precipitation, filtration and washing. On photolysis or thermolysis, a polymer-bound initiator would be expected to produce less undesirable volatile byproducts since at least half of the initiator fragments would be attached to the backbone of a polymer chain. Lastly, since the active catalyst is bound to a resin, it may be viewed as being extended in an inert carrier. Little difficulty should, therefore, be encountered in obtaining homogeneous liquid or solid dispersions of this type of catalyst as opposed to those encountered in attempting to uniformly disperse a small amount of the monomeric diaryliodonium salt.

With these objectives in mind, we began to investigate various routes to the preparation of polymer-bound diaryliodonium salts.

Experimental

All the reagents and starting materials used in preparation of the polymer-bound diaryliodonium salts were reagent grade and were used without purification. Epichlorohydrin was dried over CaH_2, decanted and then fractionally distilled. Molecular weight measurements were made in $CHCl_3$ with the aid of a Waters 244 gel permeation chromatograph and are based on polystyrene standards. A Varian EM 390 90-MHz spectrometer was used to record the ^1H-NMR spectra.

The Iodination of Polystyrene

Into a 2 L three necked round bottomed flask there were dissolved 52 g polystyrene (Shell Chemical Co.) having a $\overline{M}_n$ = 62,000 g/mol, 51 g iodine, 19 g HIO_3, in a mixture of 50 mL CCl_4, 50 mL 50% H_2SO_4 and 1.5 L nitrobenzene. The reaction vessel was fitted with a paddle stirrer, reflux condenser, thermometer and nitrogen inlet. Using an oil bath the temperature of the reaction mixture was brought to 90°C and iodination continued for a total of 50 hours. The polymer was isolated by pouring the reaction mixture into a large volume of methanol containing $NaHSO_3$. It was redissolved in CH_2Cl_2 and reprecipitated into methanol followed by drying in a vacuum oven at 60°C. There was obtained 84 g (73% yield) of iodinated polystyrene which had an elemental analysis of: %C, 50.09; %H, 3.92; %I, 45.02 indicating that the extent of iodination was 82%. Using ^1H-NMR spectroscopy it was determined that the position of substitution of the iodine in the polystyrene was predominantly para (>90%). GPC analysis of the iodinated polystyrene gave a $\overline{M}_n$ = 60,140 and a $\overline{M}_w$ = 162,500 g/mol.

Preparation of Polymeric Iodonium Salts

There were dissolved 11.5 g iodinated polystyrene in 100 mL CH_2Cl_2 and to this solution was added dropwise at 20°C with stirring 13.3 g (0.06 mol) 35% peracetic acid. The reaction temperature was maintained at 20°C during the addition with the aid of an ice bath. After completion of the addition, the reaction mixture was stirred for 2 h and then 4.76 g (0.025 mol) p-toluenesulfonic acid monohydrate was added. The mixture was stirred for 30 min and then 4.3 g (0.04 mol) anisole was added. A viscous polymer separated and the mixture was allowed to stir at room temperature overnight. The reaction mixture was divided into two parts and each part was dissolved in 200 mL of a solution of acetonitrile containing 20% methanol. To one portion (polymer 1) there was added 2.85 g (0.0125 mol) $KAsF_6$ and to the other (polymer 2), 2.3 g (0.0125 mol) KPF_6. The mixtures were allowed to stir for 2 h and then poured into water to precipitate the polymers. After isolation by filtration and washing with water, the polymers were redissolved in acetonitrile, the solutions filtered and the polymers reprecipitated into water and dried in vacuo at 30°C. Elemental analysis of polymer 1 showed that it contained 7.39% arsenic which amounts to 1.0×10^{-3} equivalents of diaryliodonium salt groups per gram of polymer. Similarly, polymer 2 had a phosphorus content of 3.45% amounting to 1.1×10^{-3} equivalents of diaryliodonium salt groups per gram of polymer.

Photoinitiated Cationic Polymerization of Epichlorohydrin

There were dissolved 0.1444 g of the above two polymer-bound diaryliodonium salts in 15 mL (0.191 mol) epichlorohydrin. Two mL (2.37 g) aliquots of the above solution were transferred to quartz photolysis tubes, flushed with nitrogen and sealed with a rubber septum. The quartz tubes were irradiated while immersed in a water bath at 20°C using a Hanovia 450 W medium pressure mercury arc lamp. The samples were withdrawn at appropriate irradiation times, quenched by adding a solution of 5% NH_4OH in methanol and then precipitated and washed with methanol. The polyepichlorohydrin was dried overnight at 60°C in vacuo and weighed.

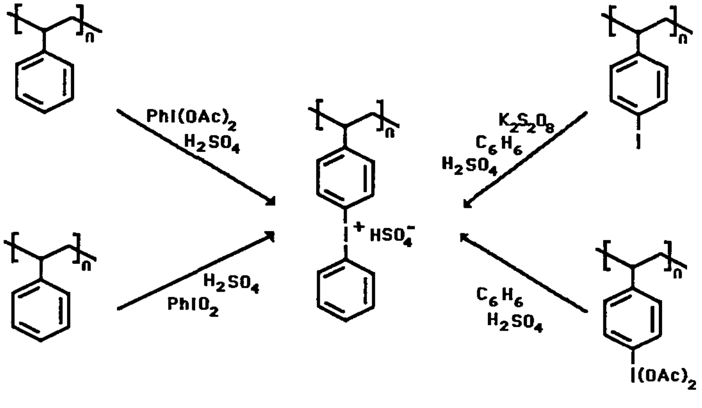
Thermally Initiated Cationic Polymerization of Epichlorohydrin

Dissolved in 10 mL (0.127 mol) epichlorohydrin were 0.9450 g of the polymer-bound diaryliodonium salt containing the AsF_6^- counterion (polymer 1) and 0.506 g (1.25×10^{-5} mol) stannous octoate. Aliquots (2.55 g) of the above solution were transferred to dry vials fitted with polyethylene liners and 0.0189 g (6.18×10^{-5} mol) cupric benzoate was added to each vial. The vials were then immersed in an oil bath at 50°C. At appropriate intervals the vials were withdrawn and the polymerization quenched by the addition of approximately 1 mL 5% NH_4OH in methanol. The polymers were precipitated with methanol and then washed five times with methanol to remove unreacted monomer. Finally, the polymers were dried overnight at 60°C in vacuo and then weighed.

Results and Discussion

Previously, polymeric diaryliodonium salts based on polystyrene were described by Yamada and Okawara (YAMADA and OKAWARA 1972). Employing the usual synthetic reactions shown in Scheme 1 used for the preparation of diaryliodonium salts, they were able to prepare polystyrene carrying the diaryliodonium bisulfate moieties as pendant groups. Subsequent metathesis to the corresponding trifluoroacetate, bromide and thiocyanate were performed. The polymer-bound salts were not employed as thermal or photochemical cationic initiators. Further, it would not be expected on the basis of what is presently known about diaryliodonium salts that the polymeric iodonium salts possessing the nucleophilic $CF_3CO_2^-$, Br^-, or SCN^- anions would be useful initiators. Initially, we sought to employ the above methods followed by metathesis of the resulting bisulfates with the alkaline or alkaline earth salts of the BF_4^-, PF_6^-, AsF_6^-, or SbF_6^- anions to prepare the active polymer-bound iodonium salt catalysts. Although

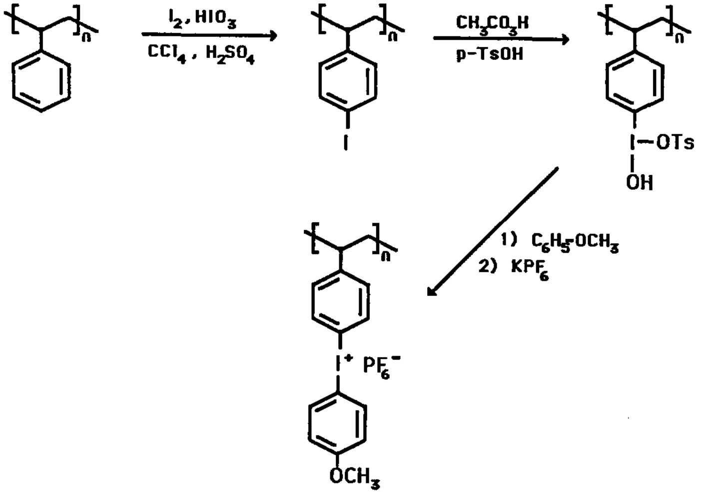
Scheme 1



these polymers were initiators for cationic polymerization, the methods shown in Scheme 1 generally appeared to be irreproducible and to lead to the incorporation of only a small number of active diaryliodonium salt groups onto the polystyrene backbone.

Instead, a new method of diaryliodonium salt synthesis (KOSER and WETTACH 1980) which gives higher yields under milder conditions, was adapted for the preparation of the polymer-bound initiators. The synthesis of polystyrene carrying pendant diaryliodonium salt moieties by this method is detailed in Scheme 2.

Scheme 2



Polystyrene was iodinated predominantly in the para position as previously described (BRAUN and WIRTH 1960) to the extent of 82% substitution. Treatment of the latter polymer with peracetic acid and p-toluenesulfonic acid gave the polymeric hydroxytosylate derivative which was coupled directly with anisole to give the polymeric iodonium tosylate salt. Lastly, metathesis of the tosylate with $KAsF_6$ or KPF_6 gave the desired polymer-bound diaryliodonium salt catalyst. It was found that it was necessary to keep the level of iodonium salt incorporation in the polymer below 50% to avoid problems of insolubility of the polymeric catalyst in both monomers and in polymerization solvents. Thus, the polymers we have prepared and examined in this study are, in fact, terpolymers of styrene, 4-iodostyrene, and 4-vinyl-4'-methoxydiphenyliodonium salts.

The polymer-bound iodonium salts are excellent photo and thermal initiators for cationic polymerization and can be used to carry out the polymerization of vinyl type monomers as well as those heterocyclic compounds which undergo ring opening polymerizations. Figure 1 shows an example of the use of the two polymeric initiators which have been prepared to carry out the photoinitiated polymerization of epichlorohydrin. As has been noted for the monomeric diaryliodonium salts (CRIVELLO and LAM

1977), the AsF_6^- containing polymer is a more efficient photoinitiator for the polymerization of oxirane monomers than the corresponding PF_6^- containing polymer. Depicted in Figure 2 is a study of the thermally initiated cationic polymerization of epichlorohydrin using the polymer-bound diaryliodonium salt bearing the AsF_6^- counterion. In this polymerization cupric benzoate is employed as a cocatalyst and stannous octoate as the reducing agent (CRIVELLO and LEE 1983). At 50°C polymerization is initially very rapid to about 28% conversion but then the increase in the rate of conversion slows markedly. The reasons for this behavior are not completely understood; however, in previous investigations of these types of catalyst systems the copper compound was observed to exhibit inhibiting or terminating characteristics at the concentration levels used in this experiment.

Polymer-bound diaryliodonium salts in which the iodonium salt moieties are attached as pendant groups are an easily synthesized class of materials whose capabilities as thermal and photochemical initiators compare favorably with those of their monomeric analogs. In addition, binding the diaryliodonium salt groups to a polymeric backbone confers a number of useful characteristics which can be used to advantage in the application of these polymers as initiators of cationic polymerization.

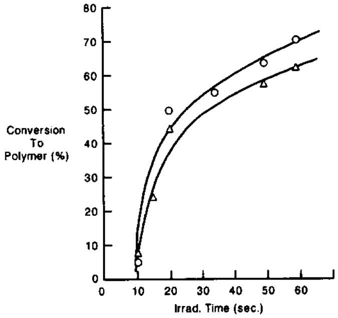


Figure 1. Photoinitiated cationic polymerization of epichlorohydrin (0.191 mol) using 0.144 g polymer-bound diaryliodonium salts: o AsF_6^-; Δ PF_6^-.

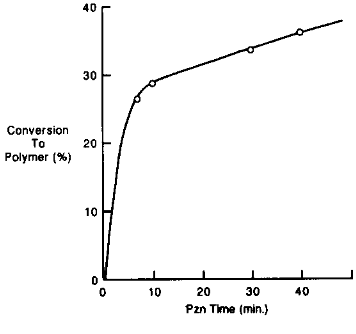


Figure 2. Polymerization of epichlorohydrin at 50°C using 0.025 mol epichlorohydrin, with a polymeric initiator containing 0.265×10^{-4} equivalents of diaryliodonium AsF_6^- groups; 0.25×10^{-5} mol stannous octoate; and 0.62×10^{-4} mol cupric benzoate.

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