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Notes

1,2-Dibromotetrafluoroethane as an Initiator for the Photopolymerization of Tetrafluoroethylene

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Since the discovery of poly(tetrafluoroethylene) there has been considerable interest in the photopolymerization of tetrafluoroethylene (TFE). Polymer has been produced in the mercury sensitized photolysis of gaseous TFE. However, analysis showed perfluorocyclopropane to be the main product in this reaction,[2] and at pressures less than 60 Torr it is reported to be the only product.[3] Photopolymerization of gaseous TFE has also been reported in the presence of mercury bromide,[4] phosgene,[5] and nitrous oxide.[6] Low molecular weight polymers are reported to be produced when trifluoroiodomethane,[7] tribromofluoromethane,[8] or trichlorobromomethane[9] are used as initiators in the photopolymerization of TFE. Direct photolysis of TFE results in surface photopolymerization at low monomer pressures[10] and solid polymer floc at monomer pressures above 8 Torr.[11]

This note reports that 1,2-dibromotetrafluoroethane is an efficient and novel initiator for the photopolymerization of tetrafluoroethylene. The solid polymer floc, which is the only product produced in the photolysis reaction, is very similar in structure to linear poly(tetrafluoroethylene) by chemical and infrared analysis. The polymer floc is obtained under reaction conditions where little or no polymer is produced if 1,2-dibromotetrafluoroethane is not present, and where oily telomers are the product if other halocarbons are used as initiators.

Experimental Section

Tetrafluoroethylene was obtained from Matheson Gas Products and was purified by distillation. 1,2-Dibromotetrafluoroethane (Du Pont Chemical Co., Freon 114B2) was purified by fractional distillation. Pentafluoroiodoethane and bromotrifluoromethane were obtained from PCR, Inc. Carbon tetrachloride, iodomethane, bromoethane, iodoethane, and bromine were reagent grade chemicals. The reaction chamber was constructed from a 3 l. Pyrex reaction flask[12] by sealing an optical grade quartz window (3 × 45 mm diameter) over a 3.5 cm hole drilled in the side wall of the flask at the point of largest circumference.

In preparation for a reaction, a tared polystyrene weigh tray (8.0 × 8.0 cm) was placed inside at the bottom of the chamber. The chamber was assembled, tested for leaks under reduced pressure, flushed with dry nitrogen, and evacuated to a pressure equal to atmospheric pressure less the desired monomer pressure. Freshly distilled TFE and initiator were introduced into the reaction chamber. The ultraviolet lamp (Hanovia Lamp Division, 140 W quartz utility lamp), which had thoroughly warmed up, was positioned directly 3 cm in front of the quartz window of the reaction chamber. The reaction was stopped at the end of the desired time interval by turning off the uv lamp and left undisturbed for 10 min to allow all of the polymer floc to settle. The chamber was then flushed with nitrogen and disassembled. The weight of polymer deposited on the plastic tray was determined.

Infrared spectra (KBr pellet) were obtained on a Perkin-Elmer 621 spectrophotometer. Mass spectra were measured using a Finnigan Model 1015 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

It can be seen from the data presented in Figure 1 that over the range of 0–8 mol % there is a direct correlation between the concentration of 1,2-dibromotetrafluoroethane and the amount of polymer produced. Observation of the reaction gives dramatic evidence of the effectiveness of 1,2-dibromotetrafluoroethane as an initiator. With no initiator present, no evidence of polymer formation is visible under these conditions. With as little as 1 mol % of 1,2-dibromotetrafluoroethane present, formation of solid white polymer floc is easily observed. The polymer, which appears to condense from the gas phase, deposits on the top side of all surfaces in the reaction chamber. It was necessary to carefully clean the chamber window between reactions and to limit the percentage of conversion to less than 10%. Complete kinetic analysis of this system has not been completed, but the conversion/time curve for this reaction is that expected of a heterogeneous polymerization, including the marked acceleration at the commencement of the reaction.[13] At a constant concentration of initiator (1.6 mol %), the rate of polymer deposition exhibited first-order dependence on monomer concentration (200 to 400 mm pressure range). Increasing the diameter of the quartz window from 3.5 to 10.8 cm increased the rate of polymer production by over 20-fold. No polymer formation was detected when a Pyrex filter was used in place of the quartz window, indicating that radiation of less than 300 nm is required for initiation. 1,2-Dibromotetrafluoroethane absorbs strongly

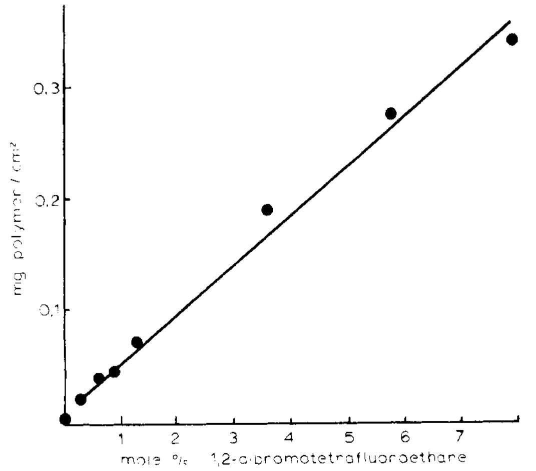

Figure 1. Dependence of polymer floc production on the mole percent of 1,2-dibromotetrafluoroethane. Results are average values from two or more experiments run with 300 mm partial pressure of TFE and a 20 min irradiation time. (Mole percent of initiator is calculated relative to total initiator and monomer.)

in the uv below 270 nm[14] and would be expected to undergo photodissociation of the carbon–bromine bond under irradiation.[8] The presence of air in the reaction chamber did not inhibit the reaction.

Wilkus and Wright[11a] report that the polymer floc produced in the direct irradiation of TFE showed considerable infrared absorption at 980 cm^{-1} due to the presence of either CF_3 groups or cyclic fluorocarbons. In this respect, their product differed from the linear form of poly(tetrafluoroethylene). The polymer floc that was produced when 1,2-dibromotetrafluoroethane was used as initiator showed no infrared absorption near 980 cm^{-1} and was identical with the published spectrum of linear poly(TFE)[11a] and with a spectrum of a sample of linear poly(TFE) powder.[15]

Analysis by mass spectroscopy of the gas phase during and after the 1,2-dibromotetrafluoroethane initiated photopolymerization showed no detectable amounts of cyclic fluorocarbons or other low molecular weight side products. This result is in contrast to the side products reported using other initiators or no initiator.[16]

The polymer floc produced in these reactions contained about 6% bromine by elemental analysis. After heating the floc at 60° under reduced pressure for 12 hr, the amount of bromine present was found to be less than 1.5%, and the carbon and fluorine analyses were 22.87 and 75.72%, respectively (Calcd for poly(TFE): C, 24.0; F, 76.0). Upon heating in air, the floc was found to fuse to a clear film above 200°, and after heating to 320° there was a 10% loss in material noted.

Other halocarbons were tested as initiators in this reaction: carbon tetrachloride, iodomethane, bromoethane, iodoethane, bromotrifluoromethane, and pentafluoroiodoethane. All of these materials did act as initiators, but the products were oils and no polymer floc was produced with any of these compounds. The introduction of bromine, which reacts rapidly with TFE to produce 1,2-dibromotetrafluoroethane, gave results which were identical with experiments using equal molar amounts of 1,2-dibromotetrafluoroethane. Direct gas phase photolysis of 1,2-dibromotetrafluoroethane in the absence of TFE gives a small amount of oily product, but no floc is formed.

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Polymerization of Methyl Methacrylate with *tert*-Butyl Hydroperoxide and Metal Acetylacetonates

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The decomposition of hydroperoxides catalyzed by metal salts and complexes has been extensively studied.[1-3] Several of these studies have used metal acetylacetonates.[2,4-8] In the present work, the effect of a small concentration of acetylacetonates on *tert*-butyl hydroperoxide initiated polymerization of methyl methacrylate in 1-chlorooctane medium has been investigated. To relate this work to that of Osawa et al.,[8] Co(II), Co(III), and Cu(II) catalyzed polymerizations have also been studied in benzene. The decompositon of *tert*-butyl hydroperoxide catalyzed by Co(II) and Co(III) acetylacetonates has been studied in the absence of the monomer as well, in both benzene and 1-chlorooctane media.

Experimental Section

Chemicals. Methyl methacrylate (Eastman Organic Chemicals) was treated with anhydrous Na_2SO_4 and distilled under vacuum. *tert*-Butyl hydroperoxide, Wallace and Tiernan, Inc. (Lucidol Division), was purified by distilling away lower boiling impurities (>95% by iodometric titration). 1-Chlorooctane (Aldrich Chemicals, Inc.) was distilled and its purity checked by gas chromatography. Metal acetylacetonates, McKenzie Chemical Corp., were recrystallized from chloroform, and their purity was ascertained from uv spectra. Spectroanalyzed benzene (Fisher Scientific Co.) was used without purification.

Kinetics. The reactions were performed using either of two techniques. In one, reactants introduced into Carius tubes were frozen at liquid nitrogen temperatures, evacuated, and degassed through three freeze–thaw cycles, sealed under vacuum, and thermostated. Alternately, reactants were saturated with nitrogen, mixed in a thermostated jacketed reactor under a nitrogen atmosphere, and aliquots taken. Rates of polymerization were measured by gravimetric determination of polymer precipitated with methanol. Hydroperoxide was determined by iodometric titration[9] using 0.01 *N* thiosulfate. At very low and at very high percent decomposition of hydroperoxide only an upper or lower limit could be determined. Number average molecular weights, $\bar{M}_n$, were determined viscometrically, using the relation[10]

$$[\eta] = 7.24 \times 10^{-5} \bar{M}_n^{0.76}$$

where $[\eta]$ is the intrinsic viscosity. Viscosities were measured at 30° in benzene.