Reductive Allylation of Poly(chlorotrifluoroethylene)

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ABSTRACT

Treatment of poly(chlorotrifluoroethylene) with allyltin reagents results in the clean replacement of chlorine by the allyl group under free-radical–chain conditions (AIBN, allyltributyltin), affording about a 10% degree of functionalization. An improved method using one-electron reduction of the polymer with cobalt(II) (generated by reduction of chloro(pyridine)bis(dimethylglyoximato)cobalt(III) with Mg) and allyltributyltin gives 50% functionalization. Further modification of the allyl group is realized through hydroboration-oxidation to the alcohol and subsequent Cr(VI) oxidation to the acid. A mechanistic discussion is provided. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

For some time, our group [1] as well as others [2–6] has been engaged in efforts to carry out the controlled functionalization of poly(chlorotrifluoroethylene) (PCTFE). Reactions involving halogen–metal exchange lead to elimination, and the resulting unsaturated surface can be subjected to functionalization reaction via the olefinic sites [7–15].

In a crucial contribution to this current work, Cais and Kometani [16] showed that the treatment of PCTFE with tri-n-butyltin hydride affords polytrifluoroethylene quite cleanly. Using reactions that have been shown to involve similar radical intermediates, we [17,18] reported a method to effect substitution of PCTFE with heteroatom nucleophiles. In this article, we report on our efforts to induce similar substitutions eventuating in the formation of carbon–carbon bonds [19].

RESULTS

Kel-F 6061 (3M), a solid homopolymer of PCTFE, was subjected to conditions that previously had been reported to lead to the generation and trapping of free radicals using organic halides as starting materials [20]. Most conditions for generation of the radicals (AIBN, n-Bu$_3$SnH, Bu$_3$SnSnBu$_3$, and combinations thereof) and traditional trapping agents (acrylonitrile and ethyl acrylate) proved disappointing. PCTFE was generally recovered unchanged. When conditions were developed to minimize side reactions in solution, a protocol for the substitution of an allyl group for the chlorine in PCTFE was developed. Treatment of a slurry of PCTFE in benzene with AIBN and allyltributyltin at reflux for 96 hours (Equation 1, method A) resulted in isolation of a white solid with little change in appearance.
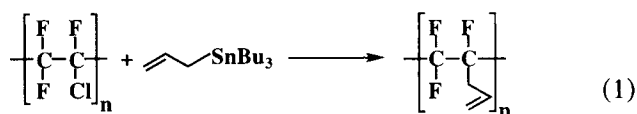
Method A: AIBN, refluxing in benzene, 96 h.
Method B: 0.1 eq Co(III), excess Mg, refluxing in THF, 12 d.

IR analysis showed attentuation of the C–Cl stretching band at 950 cm^{-1} and concomitant appearance of bands characteristic of the allyl group at 3020, 3010, and 2980 cm^{-1}. Elemental analysis was consistent with approximately 10% functionalization. While such a degree of functionalization might

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seem adequate for some purposes, we continued to search for improved methods of radical generation.

We were attracted to recent reports by Hu and Qiu [21], in which a soluble Co catalyst, either Co(I) or Co(II) (formed by treatment of bromo(pyridine)bis(dimethylglyoximato)cobalt(III) with zinc metal), promoted reductive addition of perfluoroalkyl groups to Michael acceptors. To the extent that the proposed organocobalt intermediates display radical character, such a system might be applied to the functionalization of PCTFE. We chose to generate the green solution of the Co(II) by treatment of chloro(pyridine)bis(dimethylglyoximato)cobalt(III) with magnesium metal. The reaction of Kel-F 6061, the Co(II) solution, and allyltributyltin in THF (Equation 1, method B) afforded the same allylated derivative as reported previously. IR analysis showed appearance of a C=C band at 1643 cm^{-1} and indicated a higher degree of functionality, which was determined to be 50% by elemental analysis. The nearly white appearance of the polymer was consistent with minimal side reaction, which the spectral and analytical data confirmed.

The pendant allyl groups could be subjected to further reaction. Hydroboration-oxidation (BH$_3$–THF; H$_2$O$_2$–OH$^-$) afforded the terminal alcohol, and subsequent oxidation with pyridinium dichromate (Scheme 1) yielded the carboxylic acid.

EXPERIMENTAL

General

IR spectra were recorded on a Biorad FTS-7 spectrophotometer. Elemental analyses were carried out by Galbraith Laboratories, Inc. (Knoxville, TN).

Kel-F 6061, 80–100 mesh, was provided by 3M Corporation. Allyltributyltin, chloro(pyridine)bis(dimethylglyoximato)cobalt(III), and magnesium (turnings) were purchased from Aldrich Chemical Company.

THF was dried by distillation from sodium benzophenone ketyl under nitrogen immediately prior to use. All other chemicals were of reagent grade and were used without additional purification. Magnesium (turnings) was ground into small pieces with an oven-dried mortar and pestle prior to use.
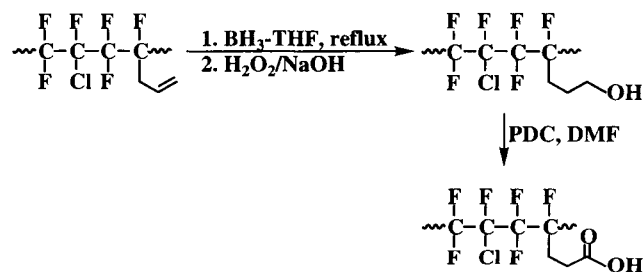
SCHEME 1

Reactions of PCTFE with Allyltributyltin

Method A. Into 5 mL of benzene was suspended Kel-F 6061 (0.8759 g, 7.55 meq). AIBN (0.1248 g, 0.761 mmol) and allyltributyltin (2.34 mL, 7.55 mmol) were added, and the slurry was heated at reflux with vigorous stirring. The AIBN addition was repeated (on the same scale) twice over 48 hours and the reaction continued at reflux for a total of 96 hours. The solvent was distilled off, and the reaction mixture was triturated with 15 mL of pentane. The resulting solid was then treated with hexanes in a Soxhlet apparatus. The solid was dried in an Abderhalden apparatus under refluxing toluene and reduced pressure to afford the allylated product. IR(KBr) 3020, 3010, 2980 cm^{-1}. Anal. found.: C, 23.18%; H, 0.65%; F, 47.42%; Cl, 27.70%; N, 0.05%; Sn, 0.17%.

Method B. A mixture of chloro(pyridine)bis(dimethylglyoximato)cobalt(III) (0.2018 g, 0.50 mmol) and ground magnesium (0.4896 g, 20.1 mmol) in anhydrous THF (10 mL) was refluxed with stirring under nitrogen. After refluxing for about 2 hours to obtain a brownish-green color, Kel-F 6061 (0.5825 g, 5.00 meq) and allyltributyltin (2.8 mL, 9.0 mmol) were added. The resulting slurry was heated to reflux and stirred under nitrogen for 12 days. The product mixture was filtered on a Buchner funnel, and the precipitate washed with hexanes, acetone, methanol, water, and methanol, successively. The solid was dried in an Abderhalden apparatus under refluxing toluene and reduced pressure to afford the allylated product. IR(KBr) 3087, 2982, 2886, 1643, 1443, 1379, and 1351 cm^{-1}. Anal. found: C, 34.48%; H, 2.32%; Cl, 13.28%; F, 46.97%.

Preparation of PCTFE-1-propanol

A suspension of allylated PCTFE (0.1002 g) in BH$_3$–THF (10 mL) was refluxed with stirring under nitrogen for 24 hours. The reaction mixture was treated with H$_2$O$_2$ (30% wt/wt)/NaOH (1.0 M) (1:1) solution (15 mL) in an ice bath and stirred at room temperature for 1 hour. The resulting polymer was filtered off on a Buchner funnel and washed with water, saturated NaHSO$_3$, water, acetone, methanol, water, and methanol. The polymer was then dried in an Abderhalden apparatus under refluxing toluene and reduced pressure for 24 hours. IR(KBr) 3445(broad), 2964, 2894, 1026 cm^{-1}.
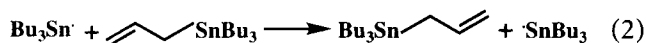
Preparation of PCTFE-propanoic Acid

A mixture of PCTFE-1-propanol (0.0840 g) and pyridinium dichromate (0.2020 g, 0.54 mmol) in DMF (7.0 mL) was stirred at room temperature for 3 days. The resulting polymer was filtered off on a Buchner funnel and washed with water, then methanol. The polymer was dried in an Abderhalden apparatus

under refluxing toluene and reduced pressure for 24 hours. IR(KBr) 3439(broad), 2967, 2893, 1656(broad) cm^{-1}.
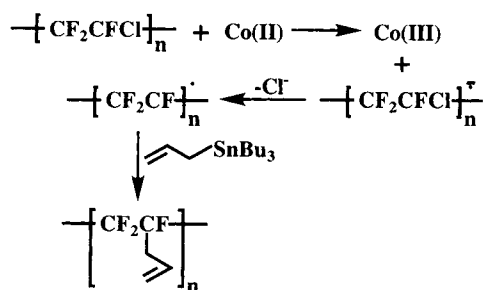
DISCUSSION

The principal difficulty in using traditional trapping agents to bring about the free-radical–promoted modification of PCTFE lies in its heterogeneity. Initiator species will react with the trapping agent present in solution, thus relegating chlorine abstraction from the PCTFE to a minor process.

The use of allyltributyltin as a trapping candidate relies on the recognition that a radical reaction with it does not terminate the chain. Instead, allyl transfer and release of tin radical (which can continue the chain) would arise (Equation 2). In the experiment, a 10% degree of functionalization is realized, a dramatic improvement over the use of other trapping agents.

$$Bu_3Sn\cdot \ + \ \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown SnBu_3 \longrightarrow Bu_3Sn\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown + \ \cdot SnBu_3 \qquad (2)$$

An even more impressive functionalization is observed when the polymeric species is subjected to modification through the use of the Co(II) species (Scheme 2). Clearly, solution reactions are further limited by this strategy.

We chose to use the chloro(pyridine)bis(dimethylglyoximato)cobalt(III) as a starting material rather than the precedented bromo derivative because of its availability. In order to carry out the formation of this Co(II) species, we needed to use Mg turnings rather than Zn. Since PCTFE and Mg are both solids, the two-electron processes were not observed. Once the allyl group is anchored onto the polymer, double-bond modifications are routine, albeit slightly sluggish.

$$-\!\!\left[CF_2CFCl\right]_n\!\!- \ + \ Co(II) \longrightarrow Co(III)$$
$$+$$
$$-\!\!\left[CF_2CF\right]_n\!\!\cdot \ \xleftarrow{\ -Cl\ } -\!\!\left[CF_2CFCl\right]_n^{\tau}$$
$$\Big\downarrow \diagup\!\!\diagdown\!\!\diagup SnBu_3$$
$$-\!\!\left[CF_2CF\atop \diagdown\!\!\diagup\right]_n\!\!-$$

SCHEME 2

This allylation procedure provides a clean route to carbon–carbon bonded modifications. We are working on additional strategies to extend this approach.

ACKNOWLEDGMENTS

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