The Chemical Reduction of Poly(tetrafluoroethylene)

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ABSTRACT: Poly(tetrafluoroethylene) is readily reduced to polyethylene by the action of lithium in liquid ammonia. The product is identified as high density polyethylene. A mechanism for the reduction sequence is proposed.

Introduction

In general, the carbon–halogen bond is highly susceptible to cleavage by metal–ammonia solutions.[1] Under suitable conditions the cleavage can be quantitative. The reaction has been employed to quantitatively determine halogen contents of organic compounds.[2-4] Some polyhalogenated compounds, especially fluorides, are reported to be incompletely reduced at the boiling point of liquid ammonia (−33 °C), but at elevated temperature in sealed tubes the reduction is complete.[5]

Poly(tetrafluoroethylene) (PTFE) is a remarkably chemically inert material;[6,7] however, PTFE will react with a variety of reducing agents, e.g., alkali metals in ammonia or amine solvents and radical anions, or electrochemically to produce, in most instances, black-colored products. These products have been variously described as consisting of carbon,[8-10] of having a carbon to oxygen ratio of ca. 1.0:0.3,[11,12] of containing carbon radicals and/or carbon–carbon double bonds,[11,13,14] as polymeric carbon interspersed with alkali-metal fluoride,[15] as amorphous carbon interspersed with alkali-metal fluoride,[16] as intercalated carbon,[17] as polymeric radical anions,[18] and as poly(fluoroacetylene) doped with alkali-metal fluoride.[19] The benzoin dianion is described as yielding PTFE surfaces with reflective metallic luster (silver or gold) instead of the black product produced with other reducing agents.[20] Both alkali-metal–ammonia solutions and the naphthalene radical anion have been utilized to "carbonize" PTFE surfaces for bonding.[8,21,22]

If it were possible to reduce PTFE to the corresponding hydrocarbon polyethylene (PE) and if cross-linking did not occur during the reduction, it should be possible to produce *linear, high molecular weight polyethylene* since PTFE is known to be an essentially linear molecule with molecular weight in the range of 5–20 million.[23-25] We report herein the chemical reduction of PTFE to PE.

Experimental Section

All microanalyses were conducted by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All analyses were performed as duplicates, and multiple samples were analyzed.

Starting Materials. Poly(tetrafluoroethylene) was obtained from Aldrich Chemical Co. The material, in the form of a powder, was subjected to continuous Soxhlet extraction with tetrahydrofuran for a period of 12 h to remove surface impurities. The resulting powder was dried to constant weight at 60 °C at 10 mm; mp 330 °C. Anal. Calcd for $-(CF_2)-$: C, 24.00; F, 76.00. Found: C, 24.18, 23.87; F, 75.96, 75.96.

Low-density polyethylene (LDPE) was obtained from Aldrich Chemical Co. in the form of powder. The powder was extracted with ethanol and vacuum dried. DSC data are presented in Table II.

High-density polyethylene (HDPE) was obtained from Aldrich Chemical Co. in the form of pellets. The pellets were dissolved in xylene and precipitated with ethanol to form a powder. DSC data are presented in Table II.

Reduction Procedure. A 500-mL three-necked flask was fitted with an ammonia inlet tube, a dry ice cold finger, and a stopper. Stirring was accomplished with a glass-encased magnetic stirring bar. Gaseous ammonia was passed through a barium oxide drying tower prior to condensation in the reaction flask. [Gaseous ammonia precludes the inclusion of metallic (ferric) impurities that can adversely effect the reducing properties of the metal–ammonia solutions.] Approximately 400 mL of ammonia was condensed and 1.00 g of cleaned PTFE was added to the solution. Lithium metal was added in small pieces over a period of ca. 15–20 min, and reaction times were 4–24 hours depending on the amount of lithium added (see Table I). At the end of the reaction the color of the solution varied from colorless (no excess lithium) to blue (excess lithium present). The ammonia was allowed to evaporate; the residue in the flask was white in color when excess lithium was not present and bronze in color when excess lithium was present. Ethanol (100–150 mL) was added, and the reaction mixture was refluxed for 1 h. Water (300 mL) was added, and the reaction mixture was refluxed for an additional hour. The solid product was removed by filtration and washed free of alkali. The solid product was stirred in 400 mL of 0.33 N HCl at 50 °C for 10 h to dissolve any residual LiF contained in the sample, washed free of acid with water, and dried at 40–50 °C at 10 mm. The appearance of the final product varied in color (see Table I); it should be noted that subsequent to reduction of PTFE with limited lithium the "reduced" PTFE was black in color, with the theoretical amount of lithium the "reduced" PTFE was gray in color, and with excess lithium the reduced PTFE was white in color and that the subsequent treatment of the reaction residue to isolate the reduced organic material free from lithium fluoride did *not* result in any perceptible color change of the respective products. The isolated yield of polyethylene from the reduction of PTFE *with excess lithium* is ca. 90% of theoretical.

At the request of one of the reviewers, infrared spectra were determined on prehydrolyzed reduced PTFE and of hydrolyzed reduced PTFE where the hydrolysis was conducted in DCl/D_2O; no differences are noted in the pre- and posthydrolysis samples with the exception that the prehydrolyzed sample contained more water than the posthydrolysis sample. Lithium fluoride in the prehydrolysis sample tends to tenaciously retain water. As expected, no deuterium incorporation was observed in the deuteriated hydrolysis sample.

Infrared Spectra. Diffuse reflectance and photoacoustic infrared spectra were obtained on a Digilab IR Model 40. Transmittance spectra (KBr pellets) were obtained on a Mattson Cygnus 100 spectrometer. The principal absorbances (transmission mode) of reduced PTFE (cm^{-1}) are 2918.2, 2850.5, 1472.9, and 718.9, for HDPE are 2918.6, 2850.8, 1472.8, and 718.9; for LDPE are 2896.5, 1466.0, 1369.1, and 719.5.

Solid-State ^{13}C NMR Spectra. Solid-state ^{13}C spectra were obtained on a Varian VXR-300 spectrometer at a frequency of 75 MHz operating in the CP/MAS mode. The spectral parameters were initially optimized (recycle delay of 2 s and a contact time of 0.5 ms) on a defluorinated PTFE sample; the same parameters were utilized on HDPE and LDPE. Although a spectrum could be obtained in four transients, a total of 256 transients were collected for each sample for good signal to noise ratios.

Differential Scanning Calorimetry. DSC was performed on Perkin-Elmer Model 2A differential scanning calorimeter.

Results

The complete reduction of a two-carbon poly(tetrafluoroethylene) segment requires 8 equiv of metal according to eq 1, i.e., each C–F bond requires 2 equiv of lithium for reduction. Experiments were conducted em-

$$-(CF_2CF_2)- + 8Li + 4NH_3 \rightarrow -(CH_2CH_2)- + 4LiF + 4LiNH_2 \quad (1)$$

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Table I[a]
Analytical Data for Reduced PTFE

	PTFE, equiv	Li, mol	color of product	anal. C	anal. H	anal. F	ash	sum C, H, F
1a	0.01	0.04	black	37.06	1.98	57.22	<0.36	96.26
1b	0.01	0.04	black	37.30	2.04	57.18	<0.43	96.52
2a	0.01	0.08	gray	63.13	8.13	27.70	<0.20	98.96
2b	0.01	0.08	gray	62.83	8.33	27.66	<0.25	98.82
3a	0.01	0.16	white	80.07	12.99	3.31	<0.15	96.37
3b	0.01	0.16	white	80.25	13.14	3.32	<0.15	96.71
4a	0.01	0.16	white	83.91	13.50	2.18	0.45	99.59
4b	0.01	0.16	white	83.98	13.27	2.54	0.48	99.79
5a	0.01	0.16	white	84.02	13.40	1.39	<0.06	98.81
5b	0.01	0.16	white	83.91	13.32	1.39	<0.06	98.62
6a	0.01	0.16	white	83.19	13.92	2.93	0.23	100.04
6b	0.01	0.16	white	82.87	13.64	2.93	0.17	99.44
7a	0.01	0.16	white	83.99	14.36	0.97	0.16	99.32
7b	0.01	0.16	white	84.23	14.29	0.97	0.16	99.49

[a] The a, b notation in column 1 refers to duplicate analyses of a numbered product; i.e., each product was analyzed twice. The numerals refer to separate reactions.

ploying 1, 2, and 4 equiv of lithium per C–F bond in the reactant. The results are presented in Table I.

In the first set of experiments, PTFE was reduced with a deficiency of lithium in liquid ammonia. The product, black in color, has empirical formula $C_3H_2F_3$, corresponding to approximately 18 deg of unsaturation per 100 carbon atoms. The material is insoluble in all common organic solvents and is extremely brittle, crumbling to a fine powder under pressure. It is this product that has previously been described as "carbonaceous" by other investigators even though it contains both hydrogen and fluorine. The fact that it does contain hydrogen indicates that some reduction is taking place even in the presence of limiting reducing agent. The sum of the constituent elements in the elemental analysis is approximately 96%; if this material contains oxygen, it is only a minor constituent (see below).

When PTFE is reduced in the presence of the theoretical amount of lithium, the solution discolors (blue to colorless) in a period of ca. 12 h. The product, gray in color, has empirical formula $C_{72}H_{113}F_{20}$, corresponding to approximately 10 deg of unsaturation per 100 carbon atoms. Extensive reduction of fluorine from the polymer has occurred, and it appears that reduction of some of the olefinic linkages is simultaneously occurring. This partially reduced PTFE is pressure moldable. Since the elemental analysis accounts for 99% of the total material in the sample, this product is, for all intents and purposes, devoid of oxygen.

With a twofold excess of reducing agent, the original blue color of the solution persists for at least 24 h. The product of this reduction, white in color, has empirical formula $C_{90}H_{179}F_1$. Within the experimental error of elemental analysis, this material is saturated. The elemental analyses account for 96–100% of the samples; if any oxygen is present in the reduced samples it is minimal. Attempts to dissolve the sample in solvents commonly employed to prepare solutions of polyethylene, e.g., benzene, toluene, xylene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene,[26] etc., met with failure. At elevated temperatures (150 °C) for extended times (18–24 hr) the supernatant discolored and the undissolved solid darkened. Although this behavior would appear to be incompatible with the identity of the reduced product as PE, the spectral and physical characterizations described below are only consistent with HDPE as the product.

Comparison of the photoacoustic infrared spectra of LDPE (d = 0.92; mp 115 °C), HDPE (d = 0.95, mp 125 °C), and the totally reduced product from PTFE shows

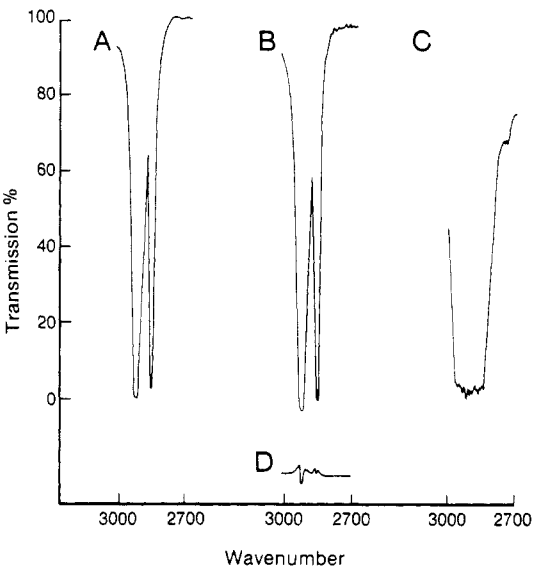

Figure 1. Transmission FT-IR spectra (CH stretch) of (A) reduced PTFE, (B) HDPE, (C) LDPE, and (D) difference spectrum (A – B).

that the reduction product is identical with HDPE. The complete absence of C–F absorption in the 1200 cm^{-1} region was also noted. Transmission Fourier transform infrared spectra of reduced PTFE, HDPE, and LDPE are presented in Figures 1, 2, and 3, respectively. A difference spectrum (reduced PTFE – HDPE) is presented in each Figure; only slight differences in the spectra are noted in the 3000, 1450 and 700 cm^{-1} regions. The reduced sample appears to be linear, HDPE.

Solid-state NMR (^{13}C) spectra of reduced PTFE, HDPE and LDPE are presented in parts b, a, and c, respectively, of Figure 4. The high-field region of the LDPE NMR spectrum exhibits an overlapping resonance to the main signal, indicative of chain terminations (methyl groups). Although a significantly reduced chain termination resonance is observed in the HDPE sample, this resonance is even more reduced in the reduced PTFE sample; i.e., the number of chain terminations is less in the reduced sample, indicative of higher molecular weight for the reduced sample than for the HDPE sample employed as a standard.

The DSC data for LDPE, HDPE, and reduced PTFE are presented in Table II. The reduced PTFE exhibits a very high melting point relative to the HDPE employed as a standard. The DSC data indicate that the reduced

Chart I
Reduction Sequence

$$-(CF_2CF_2)-_x + 2Li + NH_3 \rightarrow -(CF_2CF_2)_{x-1}\underset{\mathbf{1}}{CF_2CHF}- + LiF + LiNH_2$$

$$1 + NH_2^- \text{ (or } NH_3) \rightarrow -(CF_2CF_2)_{x-1}\underset{\mathbf{2}}{CF{=}CF}- + NH_3 + F^-$$

$$2 + 4Li + 2NH_3 \rightarrow -(CF_2CF_2)_{x-1}\underset{\mathbf{3}}{CH{=}CH}- + 2LiF + 2LiNH_2$$

$$3 + 2Li + NH_3 \rightarrow -(CF_2CF_2)_{x-2}\underset{\mathbf{4}}{CF_2CFHCH{=}CH}- + LiF + LiNH_2$$

$$4 + NH_2^- \text{ (or } NH_3) \rightarrow -(CF_2CF_2)_{x-2}\underset{\mathbf{5}}{CF{=}CFCH{=}CH}- + NH_3 + F^-$$

$$5 + 4Li + 2NH_3 \rightarrow -(CF_2CF_2)_{x-2}\underset{\mathbf{6}}{CH{=}CHCH{=}CH}- + 2LiF + 2LiNH_2$$

$$6 + 2Li + 2NH_3 \rightarrow -(CF_2CF_2)_{x-2}\underset{\mathbf{7}}{CH_2CH{=}CHCH_2}- + 2LiNH_2$$

$$7 + NH_2^- \text{ (or } NH_3) \rightarrow -(CF_2CF_2)_{x-3}\underset{\mathbf{8}}{CF_2CF{=}CHCH{=}CHCH_2}- + NH_3 + F^-$$

$$8 + 2Li + NH_3 \rightarrow -(CF_2CF_2)_{x-3}\underset{\mathbf{9}}{CF_2CH{=}CHCH{=}CHCH_2}- + LiF + LiNH_2$$

$$9 + 2Li + 2NH_3 \rightarrow -(CF_2CF_2)_{x-3}\underset{\mathbf{10}}{CF_2CH_2CH{=}CHCH_2CH_2}- + 2LiNH_2$$

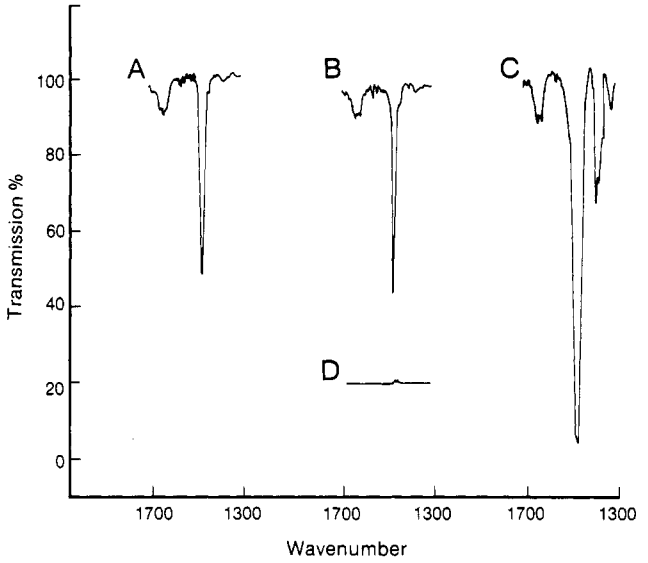

Figure 2. Transmission FT-IR spectra (CH band) of (A) reduced PTFE, (B) HDPE, (C) LDPE, and (D) difference spectrum (A – B).

Table II
DSC Results for LDPE, HDPE, and Reduced PTFE[a]

sample	T_M, °C	ΔH_{fus}, cal/g
LDPE	115.1	24.04
HDPE	124.6	43.40
reduced PTFE	136.0	40.05

[a] Standard benzoic acid: ΔH_{fus}(obsd) = 34.6 cal/g; ΔH_{fus}(lit.) = 33.9 cal/g [Andrews, D. H.; Lynn, G.; Johnston, J. *J. Am. Chem. Soc.* **1926**, *48*, 1274. Ke, B. *J. Polym. Sci.* **1960**, *42*, 15].

PTFE is linear, high molecular weight PE.

Thin films of reduced PTFE exhibit no absorption in the visible–ultraviolet region (800–200 nm).

To date, we have been unable to ascertain the molecular weight of the product PE.

Discussion

The reduction of PTFE can be envisioned as occurring in either or both of two modes, proceeding initially from an elimination of HF at a chain terminus (assuming such termini exist) or from a random chain interior reduction–elimination sequence. Subsequent steps after the initial elimination event are identical.

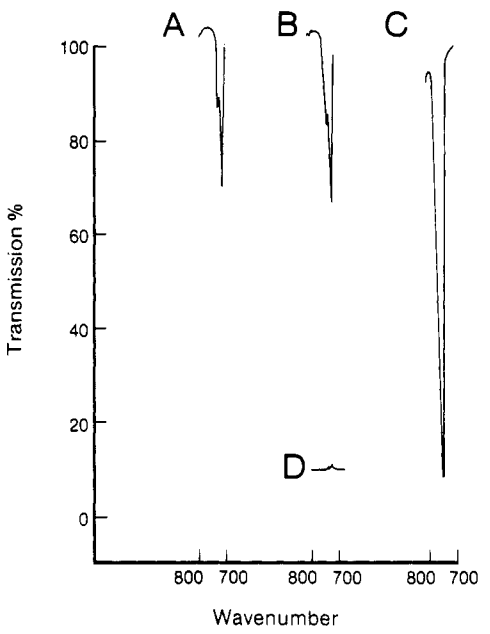

Figure 3. Transmission FT-IR spectra (CH wag) of (A) reduced PTFE, (B) HDPE, (C) LDPE, and (D) difference spectrum (A – B).

A plausible sequence accounting for the reduction of PTFE is presented in Chart I. If the fluorocarbon chain is terminated by a thermal disproportionation reaction leading to a terminal $-CF_2H$ group or if a random reduction event introduces a $-CHF-$ entity into the chain, the initial event is base-catalyzed elimination (either by ammonia itself or by amide ion produced in the reduction sequence) to generate a difluoro vinyl group (**2** in Chart I). The base-catalyzed dehydrofluorination of both poly(vinylidene fluoride) and poly(trifluoroethylene) have previously been observed. In the presence of *n*-butylamine at reflux poly(vinylidene fluoride) blackens in 4 h while the degradation of poly(trifluoroethylene) under the same conditions requires only 10 min. Perfluorinated polymers, e.g., PTFE and co-poly(tetrafluoroethylene–hexafluoropropylene) are, as expected, stable under these reaction conditions.[27]

The reduction of vinylic fluoride under dissolving metal conditions has also been previously observed; vinyl fluoride itself is quantitatively reduced by lithium–ammonia so-

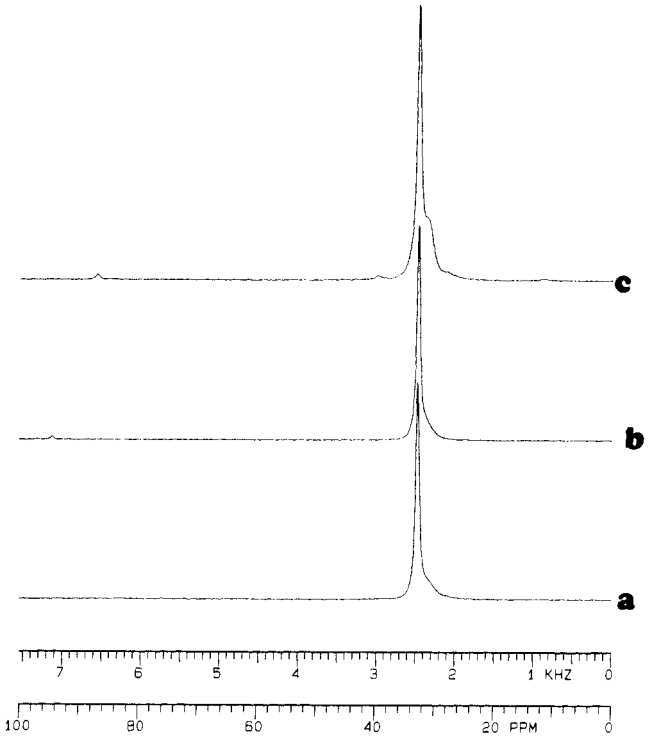

Figure 4. 75-MHz CP-MAS ^{13}C NMR spectra of (a) HDPE, (b) reduced PTFE, and (c) LDPE.

lutions at −33 °C.[28] Thus **2** is reduced to **3**. Allylic reduction follows, producing **4**, which is susceptible to base-catalyzed dehydrofluorination to produce a difluorodiene (**5**). Vinylic reduction produces diene **6** which is conjugately reduced[29] to produce **7**. The sequence outlined above is repeated: dehydrofluorination, vinylic reduction, conjugate reduction, dehydrofluorination, etc. If random chain reduction initiated the sequence, reduction could simultaneously occur in "both" directions along the chain from a reduction intermediate such as **7**.

The behavior of the reduced PTFE samples when dissolution in normal PE solvents was attempted (discoloration and, presumably, decomposition) indicates that these PE samples are abnormal. The abnormality may be a limited amount of cross-linking produced during the reduction process. Some cross-linking can be inferred from the unusually high melting point of the reduced PTFE sample, but the spectroscopic evidence (NMR and IR) indicates that the degree of cross-linking must be low.

It should be noted that the chemical reduction of PTFE to linear HDPE constitutes a structure proof of PTFE as an unbranched, high molecular weight polymer (as if such proof were needed). We are currently attempting to determine the unique chemical and physical properties of the polyethylene described herein, to reduce very high molecular weight PTFE to high molecular weight, linear PE, and to decrease reaction times by the utilization of amine solvents rather than ammonia.

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Registry No. PTFE, 9002-84-0; NH_3, 7664-41-7; Li, 7439-93-2.

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