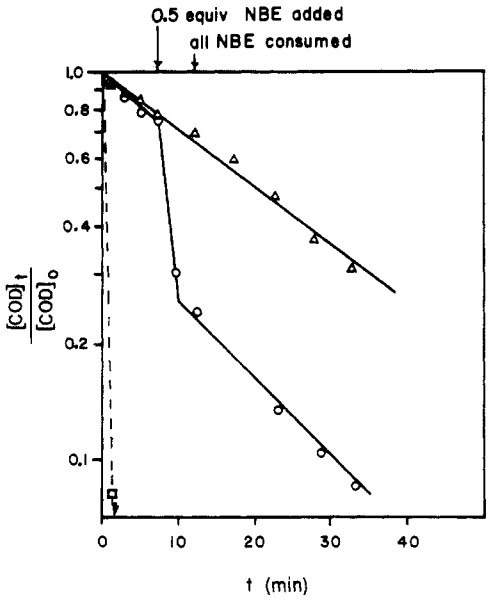


Figure 2. Homopolymerizations of NBE (□) and COD (△) and polymerization of COD to which 0.5 equiv of NBE was added at t = 10 min (○). $[NBE]_0$(homopolymerization) = 0.17 M, $[COD]_0$ = 0.35 M, T = 35 °C.

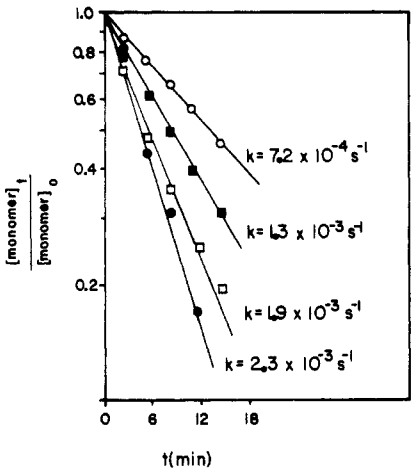
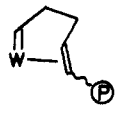


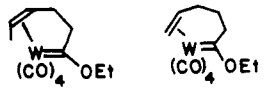
Figure 3. Homopolymerizations of COE (□) and COD (○) and copolymerization of COE (■) and COD (●): $[monomer]_0$ = 0.4 M, T = 80 °C.

side-by-side homopolymerizations, COE reacts 2.7 times as fast as COD, but in a copolymerization the relative reactivity switches: COD then reacts 1.8 times as fast as COE, presumably because it contains two double bonds. We conclude that **5** is more reactive than **6**. That **6** should



6

be a particularly unreactive olefin–carbene complex is shown by the fact that **7** has recently been isolated and its structure determined.[5,6] These authors also point out that **8** is less stable than **7**.



7 **8**

Acknowledgment. We are grateful to Exxon Chemical Co. for partial support of this work and C. Peter Lillya and Howard W. Turner for fruitful discussions.

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Surface Modification of Poly(tetrafluoroethylene) with Benzoin Dianion

Poly(tetrafluoroethylene) (PTFE) is a highly chemically resistant polymer, inert to a wide variety of reagents.[1,2] In contrast to its behavior with most chemicals, PTFE reacts readily with strong reducing agents,[3-11] particularly alkali metals, to produce black-colored materials which have been described as carbonaceous,[3,4] containing carbon and oxygen in a ratio of ~1:0.3,[5,6] containing carbon radicals and carbon–carbon double bonds,[5] amorphous carbon interspersed with alkali metal fluoride,[7] intercalated carbon,[8] polymeric carbon and alkali fluoride,[9] polymeric anion radicals,[10] and alkali fluoride doped poly(fluoroacetylene).[11] In this communication we report a new and significantly different reduction of PTFE which does not involve alkali metals as the reducing agent. The reduced polymer is likewise different from the alkali-reduced materials: the surface exhibits a reflective metallic lustre instead of the black color which is characteristic of reduced Teflon.

Experimental Section. Virgin PTFE film (Commercial Plastics/Du Pont Teflon) (5 mils) was extracted with tetrahydrofuran for 24 h in a Soxhlet extractor and dried under vacuum at 60 °C to constant weight. Benzoin was purchased from Aldrich and recrystallized twice from ethanol to a constant melting point of 96 °C and stored in a vacuum desiccator. Potassium *tert*-butoxide was purchased from Aldrich and used without further purification. Doubly distilled water (Gilmont still) was degassed by purging with nitrogen; THF was distilled from sodium benzophenone dianion; Me_2SO was distilled from CaH_2 at reduced pressure.

Gravimetric analyses were performed with a Cahn 29 electrobalance. Scanning electron micrographs of gold sputter-coated samples were obtained with a JEOL 100 CX. ESCA spectra were recorded using a Mg Kα source with a Kratos XSAM 800 spectrometer. UV–vis spectra were obtained directly from films using a Perkin-Elmer 100A with a virgin PTFE sample in the reference beam.

Reduction. Potassium *tert*-butoxide (4.0 g, 35 mmol) was dissolved in 35 mL of Me_2SO and added to a 5-mL Me_2SO solution of 0.27 g (1.3 mmol) of benzoin under nitrogen. A dark purple color (indicative of the radical anion of benzoin) forms, and this solution is transferred

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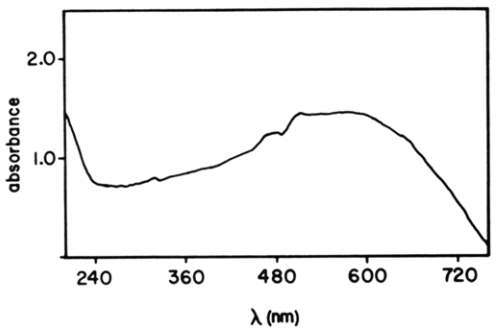

Figure 1. UV–vis spectrum of reduced PTFE.

to a Schlenk tube containing a 1 cm × 1 cm PTFE film sample. The Schlenk tube is placed in a 50 °C oil bath and the reaction allowed to proceed for 6 h, after which the solution is transferred from the tube and the film is washed successively with ten 25-mL portions of water and five 25-mL portions of THF (all under nitrogen).

This reduction procedure renders metallic, gold-colored films. On exposure to air the color fades—back to white after 1–2 days. Oxidation (for gravimetric analysis) was carried out by using 5% sodium hypochlorite solution for 12 h followed by successive washings with water and THF and then drying under vacuum to constant weight.

Results and Discussion. Exposure of PTFE film samples to Me_2SO solutions of the potassium salt of benzoin dianion produces changes consistent with reduction of PTFE to polymeric carbon (eq 1). Control experiments with

(1)

Me_2SO/benzoin and Me_2SO/potassium *tert*-butoxide under identical conditions exhibit no reaction. The presence of Me_2SO is not essential: the reaction proceeds in *N*-methylpyrrolidone as well. Equation 1 describes the net reaction; a large excess of reducing agent is used. A surface-confined dianion may serve as a two-electron reducing agent, but benzil would react with more dianion to form the radical anion product.[12] The most obvious change is visible to the eye: *the PTFE color changes from white to metallic gold.* Shorter reaction times produce silver-colored films. Larger reaction times render more highly converted samples, but the color remains gold. This as well as the morphology of the product (see below) indicates that the color is due to absorbance/reflectance and not interference. Figure 1 shows the UV–vis spectrum of a sample reacted for 6 h. The spectrum exhibits an absorbance with λ_{max} = 540 nm and little fine structure. Infrared spectra (transmission; ATR-Ge, KRS-5) are lucid only in their lack of non-PTFE absorbances. This points out that any reaction incorporating benzil or benzoin is minimal and not important. The films are air-sensitive and gradually lose their color (turn white) over 1–2 days. Oxidation can be accomplished more rapidly with stronger oxidants: the color is eliminated overnight by 5% sodium hypochlorite solution or in several hours by $KClO_3$/sulfuric acid solution.

The reduction is not surface-selective and is corrosive in nature. Figure 2 exhibits scanning electron micrographs of PTFE, reduced PTFE, and reduced and then oxidized ($KClO_3/H_2SO_4$) PTFE samples as well as a graphic representation of these data. Small unreacted PTFE "islands" are visible in the washed solutions of oxidized samples.

ESCA and gravimetric analysis attest to the stoichiometry of eq 1. Figure 3 shows the lucid regions of ESCA spectra for the reduction and oxidation ($KClO_3/H_2SO_4$) reactions. The reduced sample contains very little fluorine within the ESCA sampling depth. Gravimetric analysis[13] indicates the loss of ca. 3.8 fluorines per monomer, based on the percentage of the total weight loss (after oxidation) attributed to the reduction step. The unreacted PTFE "islands" depicted in Figure 2 would be expected to bias the fluorine loss low. The average depth of reaction after 6 h is ca. 2500 Å; longer reaction times yield more extensively reduced materials: a sample reduced for 6 days had an average depth of reaction of 1.7 μm.

We are presently investigating the structure and properties of the reduced material, particularly with regard to the chemical nature of the carbon and how it differs from alkali-reduced samples, none of which[1-11] have a well-characterized structure. Gold-colored samples react readily with chlorine and bromine, turning white and exhibiting C–X in ATR-IR and ESCA spectra. We have prepared sodium/naphthalene/THF, sodium/ammonia, lithium/ammonia, sodium amalgam, and electrochemically reduced

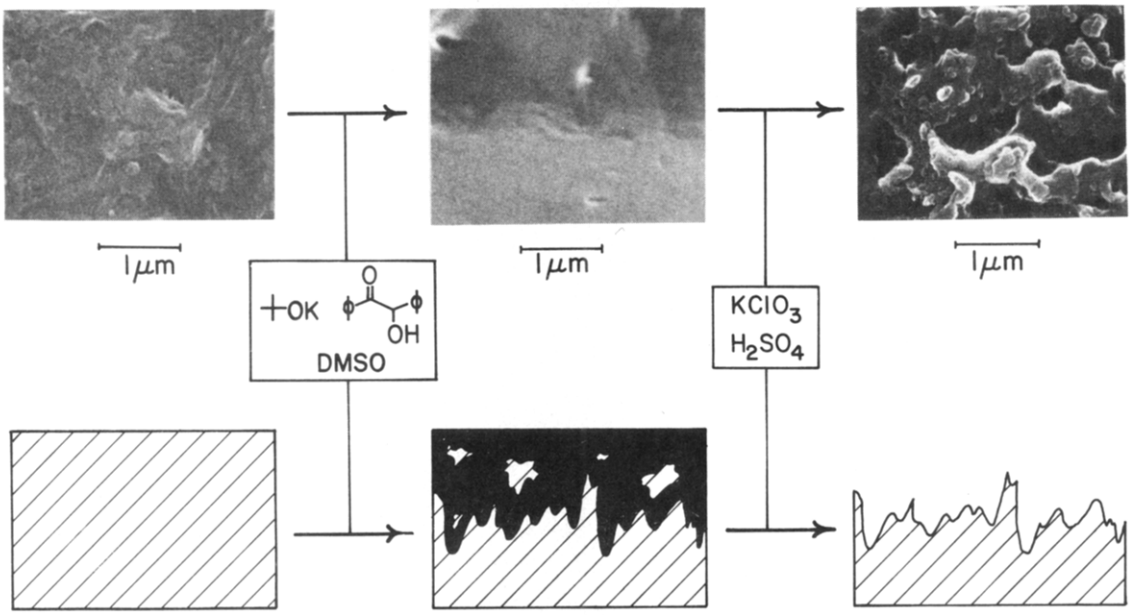

Figure 2. Scanning electron micrographs and graphic representation of reduction and oxidation reactions.

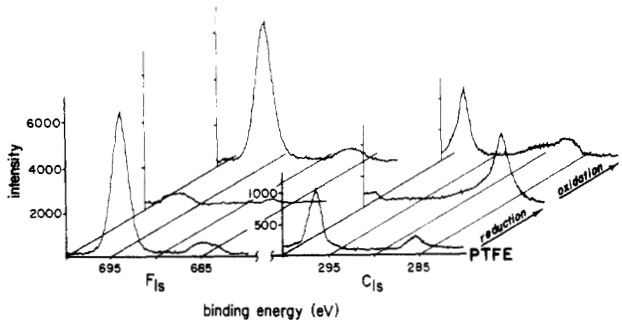

Figure 3. ESCA spectra for reduction and oxidation ($KClO_3/H_2SO_4$) reactions.

Teflon samples and none of them turn white (all remain black) in air.

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(13) 3.8 is the average of five experiments (6-h reduction), the results of which were determined as follows: A PTFE sample weighing 15.3145 mg (M_i) weighed 15.2673 mg (M_r) after reduction and 15.2497 mg (M_o) after oxidation. The value 0.76 is the predicted percentage weight loss for $CF_2 \rightarrow C$ (50 → 12 g/mol).

$$\frac{(M_i - M_r)(4)}{(M_i - M_o)(0.76)} = 3.83$$

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CORRECTIONS

Frank S. Bates,* Harvey E. Bair, and Mark A. Hartney: Block Copolymers near the Microphase Separation Transition. 1. Preparation and Physical Characterization of a Model System. Volume 17, Number 10, October 1984, p 1987.

M_w/M_n should be 1.15 for sample BB5 in Table I (p 1988).