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Polyacetylene Formed by the Benzoin Dianion Reduction of Poly(tetrafluoroethylene)

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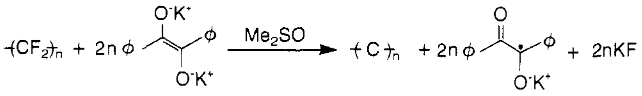
ABSTRACT: The reflective, gold-colored surface layer produced on reduction of poly(tetrafluoroethylene) (PTFE) films with benzoin dianion in dimethyl sulfoxide (Me_2SO) has previously been reported to be a reactive form of carbon. In this work the material has been prepared on the surfaces of polycrystalline PTFE films and powder. It was characterized by resonance-enhanced Raman scattering, photoacoustic Fourier transform infrared spectroscopy, and electron microscopy. The resonance Raman spectrum indicates that the reduced PTFE surface contains *trans*-polyacetylene (*trans*-$(CH)_x$) with polyene conjugation lengths consisting of 12–28 olefin units. *trans*-$(CD)_x$ is formed when Me_2SO-d_6 is used as the reaction solvent, indicating that the protons on the polyacetylene originate from the solvent used in the reduction reaction. Infrared spectra also show the presence of a lesser amount of a carbonaceous fraction composed of aromatic rings and C≡C bonds.

Introduction

Costello and McCarthy[1] recently reported that the reduction of poly(tetrafluorethylene) (PTFE, Teflon) by benzoin dianion in dimethyl sulfoxide (Me_2SO) gives a gold-colored, air-sensitive reactive surface film. This is in contrast to previous reports of black, carbonaceous surfaces produced on reduction of PTFE with strong reducing agents such as alkali metals[2,3] and alkali naphthalide.[4]

The benzoin dianion reduced PTFE film surfaces showed very little fluorine from ESCA measurements, to within a 30–100-Å sampling depth, and gravimetric analysis indicated the loss of ca. 3.8 fluorines per (C_2F_4) monomer.[1] The films are bleached on exposure to air and could be doped with iodine to obtain high electrical conductivities ($\sim$36 S cm^{-1}).[5] The formation of a carbon polymer was proposed[1] according to the following reaction:



(1)

In this paper we report on a detailed Raman and photoacoustic infrared spectroscopic and electron microscopic characterization of films and powders of PTFE reduced by the method of Costello and McCarthy.[1]

Experimental Section

The samples were prepared by treatment of either 130-μm-thick films or 3–8-μm particle diameter powder of PTFE (Polysciences) with either pure dimethyl sulfoxide (Me_2SO) or Me_2SO-d_6 (99.9 atom % D) solutions of undeuteriated benzoin and potassium *tert*-butoxide for 1–144 h at 50 °C, followed by successive washings with water and tetrahydrofuran, all under an argon atmosphere. The samples were dried under a vacuum for 24 h at 22 °C and then handled in an argon-filled drybox.

Details of the experimental procedure and the concentrations of the carefully purified reagents used were the same as those given by Costello and McCarthy.[1] Some of the PTFE films were sectioned after preparation and examined under an optical microscope in order to determine the average thickness of the gold-colored surface films. The film thicknesses were found to range from 5 to 7 μm.

Raman scattering experiments using various excitation wavelengths were performed on reduced PTFE films sealed under argon in flat, thin glass cells. Laser radiation (5 mW) at the sample and a 180° backscattering geometry were used for all the measurements. The scattered radiation was analyzed with a Spex 1401 double monochromator coupled to a Spex Datamate system. Photoacoustic infrared measurements were made on PTFE powders reduced for 144 h. A PAR 6003 photoacoustic sample cell, which was loaded in an argon atmosphere, and a Nicolet 170 SX Fourier transform infrared spectrometer were employed for the infrared measurements. Transmission electron microscopy was performed with a Hitachi H800 electron microscope on the edges of reduced PTFE films, which were sectioned orthogonal to the surface plane.

Results and Discussion

The Raman spectra of PTFE films reduced in Me_2SO and in Me_2SO-d_6 and excited with 4579- and 6471-Å laser radiation are displayed in Figure 1. The relative peak intensities and peak positions for these samples in both the fundamental mode region below 1600 cm^{-1} and the overtone and combination mode region above 1600 cm^{-1} and the observed shifts of the peak frequencies as a function of excitation wavelengths are in good agreement with previously published data on *trans*-polyacetylene (*trans*-$(CH)_x$)[6,7] and *trans*-$(CD)_x$,[8] respectively. This is particularly evident in a comparison of the Raman spectra excited at 4579 Å of PTFE reduced in Me_2SO with that of a sample of *trans*-$(CH)_x$ prepared in our laboratory using the Shirakawa method[9] (cf. parts a and b of Figure 2, respectively). The peak frequencies of three of the overtone and combination (multiphonon) modes are, however, downshifted by 20–30 cm^{-1} in reduced PTFE compared with the *trans*-$(CH)_x$ sample. Shifts of this magnitude are to be expected for multiphonon modes since their frequencies are related to critical points in the Brillouin zone and hence are sensitive to small changes in three-dimensional packing of the chains in different samples. The line shapes and intensities of the multiphonon bands are, however, the same for the reduced PTFE and *trans*-$(CH)_x$ samples and are in good agreement with the data in the multiphonon region for *trans*-$(CH)_x$ published by Lichtmann and Fitchen.[7]

These results indicate that the product of the benzoin dianion reduction of PTFE is not entirely a carbon polymer, as proposed in reaction 1, but rather a hydrogenated version of it which may result from protonation of an intermediate carbon polymer or its macromolecular radical via the solvent protons. Polymers containing polyene segments have been prepared by base-promoted dehydrohalogenation of poly(vinylidene fluoride)[10] and poly(vinyl chloride),[11] but the complete dehalogenation of PTFE to give polyacetylene probably occurs by a different mechanism which appears to be unique.

The peak frequencies from the Raman and infrared (see following discussion) spectra together with assignments are listed in Tables I and II. The observed frequencies of the

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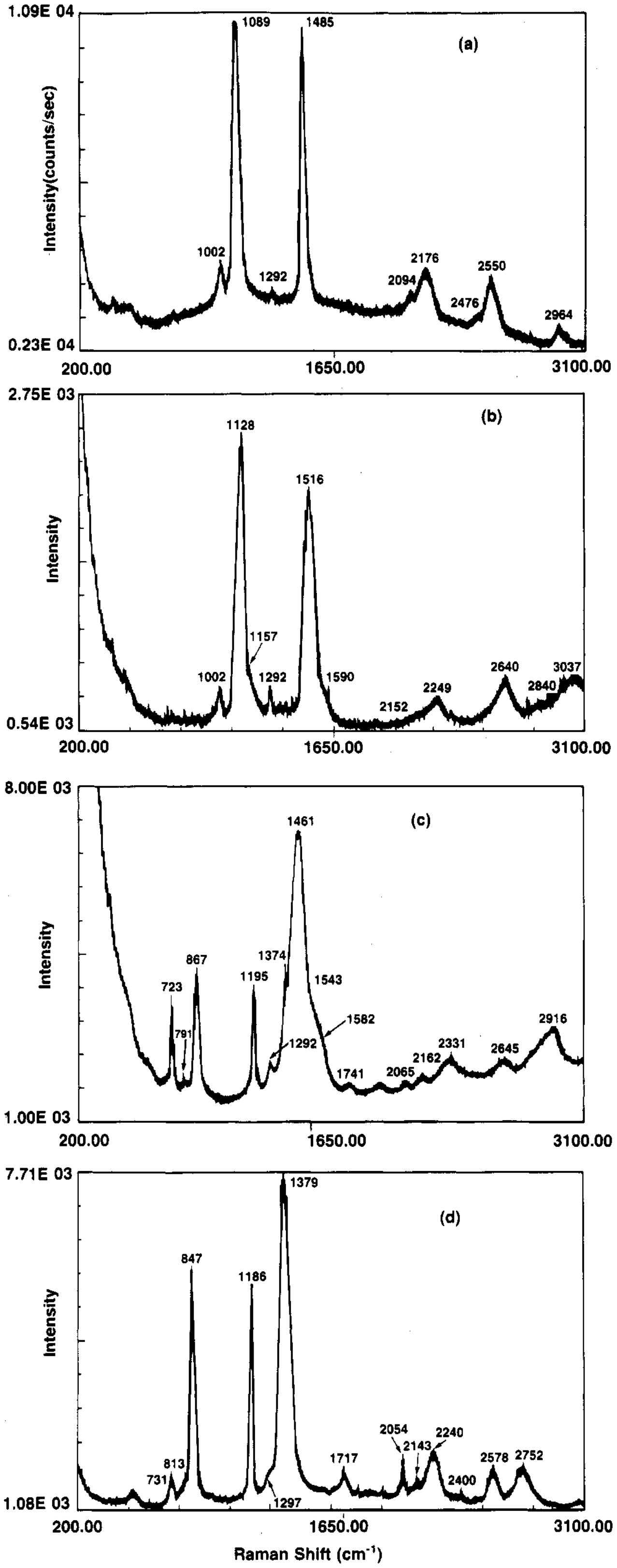


Figure 1. Resonance Raman spectra of reduced PTFE surfaces: (a) spectrum of PTFE reduced in Me_2SO, 6471-Å excitation; (b) spectrum of PTFE reduced in Me_2SO, 4579-Å excitation; (c) spectrum of PTFE reduced in Me_2SO-d_6, 4579-Å excitation; (d) spectrum of PTFE reduced in Me_2SO-d_6, 6471-Å excitation.

resonance-enhanced C—C and C═C stretching Raman-active vibrations (and their overtones and combinations) in *trans*-$(CH)_x$ and *trans*-$(CD)_x$ are known to be sensitive to conjugation length distributions. As extensively discussed in the literature,[6,8,12] the dispersion of the peak frequencies of the vibrational modes in *trans*-$(CH)_x$ and *trans*-$(CD)_x$ is associated with the photoselection of the long and short conjugation length distributions by longer and shorter laser wavelength excitation, respectively. An alternative explanation in terms of one-dimensional amplitude modes associated with different conjugation length segments[13] is essentially equivalent to the conjugation length distribution model.[12] The dispersion with excitation frequency exhibited in the spectra obtained on reduced PTFE samples, as evident from Figure 1, provides additional support for the identification of the surface material as *trans*-$(CH)_x$ and *trans*-$(CD)_x$. An estimate of the conjugation length (n), i.e., the number of olefin units over which conjugation is maintained without disruption by a

Table I
Raman and Infrared Peak Frequencies and Assignments for PTFE Film and Powder Reduced in Me_2SO

Raman peak frequencies, cm^{-1}		infrared peak frequencies, cm^{-1}	assignments[a]
4579 Å	6471 Å		
		900	*trans*-$(CH)_x$, soliton
		1012	*trans*-$(CH)_x$, IR-active $\delta(CH)$
1002	1002		*trans*-$(CH)_x$, Raman-active $\delta(CH)$
1128			*trans*-$(CH)_x$, $\nu_{(\mathrm{C{-}C})}$
1157	1089		
1292	1292		*trans*-$(CH)_x$, $\delta(CCH)$
		1380	*trans*-$(CH)_x$, soliton
	1485		*trans*-$(CH)_x$, $\nu_{(\mathrm{C{=}C})}$
1516			
1572			
1590			
		1505	$\delta(CH_2)$[b]
		1600	*a*-carbon,[c] $\nu_{(\mathrm{C{=}C})}$
	2094		*trans*-$(CH)_x$, $\delta CH + \nu_{(\mathrm{C{-}C})}$
2152		2150	*a*-carbon,[c] $\nu_{(\mathrm{C{\equiv}C})}$
2249	2176		*trans*-$(CH)_x$, $2\nu_{(\mathrm{C{-}C})}$
	2476		*trans*-$(CH)_x$, $\nu_{(\mathrm{C{-}C})} + \nu_{(\mathrm{C{=}C})}$
2640	2550		
2840	2964		*trans*-$(CH)_x$, $2\nu_{(\mathrm{C{=}C})}$
3037			
		2980	$\nu_{(CH_2)}$
		3020	*trans*-$(CH)_x$, $\nu_{(\mathrm{C{-}H})}$

[a] Assignments after Zannoni and Zerbi[23] and Peluso et al.[24]
[b] Associated with $-CH_2-$ defects in $(CH)_x$. (See text for discussion.)
[c] *a*-carbon represents the disordered carbon fraction.

Table II
Raman Peak Frequencies (cm^{-1}) and Assignments for PTFE Film Reduced in Me_2SO-d_6 and for *trans*-$(CD)_x$

reduced PTFE			
λ_{exc} = 4579 Å	λ_{exc} = 6471 Å	*trans*-$(CD)_x$[a] λ_{exc} = 6000 Å	assignments
723	731	744	$\delta(\mathrm{C{-}D})$
791	813	816	$\nu_{(\mathrm{C{-}C})}$
867	847	848	
1195	1186	1198	$\delta(CCD)$
1292	1297		*trans*-$(CH)_x$, $\delta(CCH)$
1374			$\nu_{(\mathrm{C{=}C})}$
1461	1379	1340	
1543			*trans*-$(CH)_x$, $\nu_{(\mathrm{C{=}C})}$
1582			$\delta(CD) + \nu_{(\mathrm{C{-}C})}$
1741	1717		$2\nu_{(\mathrm{C{-}C})}$
2065	2054		$\nu_{(\mathrm{C{-}C})} + \delta(CCD)$
2162	2143		$\delta(CD) + \nu_{(\mathrm{C{=}C})}$
2331	2240		$\nu_{(\mathrm{C{-}C})} + \nu_{(\mathrm{C{=}C})}$
	2400		$\nu_{(\mathrm{C{=}C})} + \delta(CCD)$
2645	2578		
2916	2752		$2\nu_{(\mathrm{C{=}C})}$

[a] From Lichtmann et al.[8]

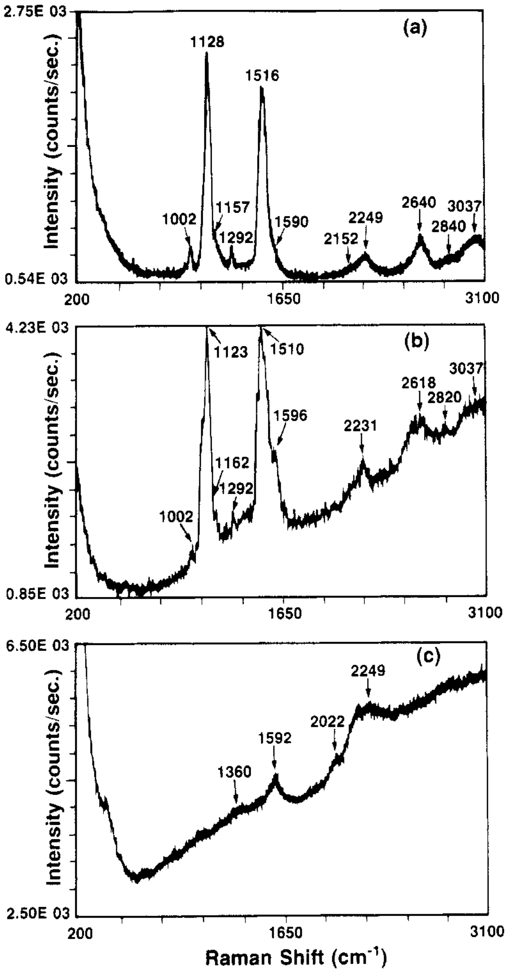


Figure 2. Resonance Raman spectra of (a) reduced PTFE in Me_2SO, 4579-Å excitation; (b) *trans*-$(CH)_x$ sample, 4579-Å excitation; and (c) reduced Aclar in Me_2SO, 4579-Å excitation.

chemical or structural defect, can be estimated from the equation[14]

$$\nu_{C=C} = 1460 + 700/n \text{ cm}^{-1} \qquad (2)$$

where $\nu_{C=C}$ is the observed C=C stretching frequency. From the peak positions for $\nu_{C=C}$ with excitation at 4579 and 6471 Å for reduced PTFE, the estimated conjugation lengths of the polyene segments are ~12 and 28 olefin units, respectively. This indicates that fairly good quality polyacetylene-containing films are produced on the PTFE surface, which is consistent with the observed golden color and ease of doping with iodine to high conductivities.[5]

The reduced PTFE surface was found to be extremely air-sensitive. On exposure of the surface to air it turned white (the color of the underlying pristine PTFE surface) after a few hours. Raman spectra recorded continuously over a period of 3 h in air showed decreasing intensity of the lines assigned above to *trans*-$(CH)_x$. After 3 h, lines associated with pristine PTFE are observed, but no Raman scattering from *trans*-$(CH)_x$ or an air-stable carbonaceous fraction (as observed on reduction of Aclar; vide infra) could be detected. This result suggests that the carbonaceous fraction in reduced PTFE is probably small.

A photoacoustic Fourier transform infrared (PA/FT-IR) spectrum of PTFE powder reduced in Me_2SO for 6 days, with the lines associated with pristine PTFE subtracted from the spectrum, is shown in Figure 3. The observed peak frequencies and probable assignments are indicated in Table I. Because of the surface-specific nature of the reduction of PTFE, PA/FT-IR spectroscopy rather than conventional IR methods was used to observe the IR-active vibrations of reduced PTFE. Also, since the absorption is measured directly, sample opacity and scattering do not interfere with the measurement.

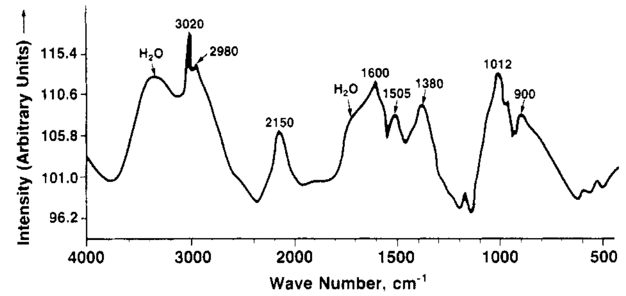


Figure 3. Photoacoustic Fourier transform IR spectrum of PTFE powder reduced in Me_2SO solution. The lines due to unreacted PTFE have been subtracted out.

The IR data indicate the presence of lines associated with *trans*-$(CH)_x$, consistent with the Raman results. In addition, there are other features in the spectrum, which will be discussed below. Two peaks at ~1650 and 3350 cm^{-1} are observed, which can be assigned to the bending and stretching modes, respectively, of H_2O, which is probably adsorbed on the surface of the reduced PTFE particles. Another interesting feature is the observation of dopant-induced soliton peaks of *trans*-$(CH)_x$ at 900 and 1380 cm^{-1} in the infrared spectrum. The observation of soliton peaks in the absence of significant electrical conductivity in the reduced PTFE is not surprising since relatively intense soliton lines have been observed in *trans*-$(CH)_x$ at extremely low dopant concentrations.[15] The reducing environment of the surface modification reaction would be expected to weakly donor-dope the *trans*-$(CH)_x$ formed on the PTFE surface.

The presence of absorption bands at 1600 and 2150 cm^{-1} points to the presence of an amorphous carbon fraction in the reduced PTFE surface in addition to the *trans*-polyacetylene component. The lines at 1600 and 2150 cm^{-1} can be attributed to aromatic rings and C≡C bonds, respectively, in the carbon fraction. The weak lines observed at 2980 and 1500 cm^{-1} can be assigned to the stretching and deformation modes of $-CH_2-$ groups that are perhaps produced on quenching the reaction with water (via protonation of donor-doped polyacetylene segments).

Aclar, a related polymer with a $(-CF_2CFCl-)$ repeat, produces only an air-stable black surface on benzoin dianion reduction.[16] The Raman spectrum of a reduced Aclar surface, recorded under exactly the same conditions as that for the reduced PTFE surface (Figure 2a), is shown in Figure 2c. From the spectra shown in Figure 2 it can be seen that there is no evidence for *trans*-$(CH)_x$ on the reduced Aclar surface, but there is appreciable scattering associated with the C≡C stretching mode of a carbon network, which is likely to be resonance-enhanced. The presence of a small Raman component due to C≡C bonds in reduced PTFE would, however, be masked by the multiphonon scattering at 2152 cm^{-1} from *trans*-$(CH)_x$.

Although details of the reaction mechanisms are unclear at this time, a few mechanistic possibilities are outlined in the scheme shown in Figure 4. An interesting question is just where in the course of the reaction the protons from the solvent are transferred to give *trans*-$(CH)_x$. The generation of intermediates containing **3** (linear carbon) provides a rationale for the existence of both *trans*-$(CH)_x$ (**4**) and a carbon fraction composed of condensed aromatic (**5**) and alkyne moieties. The difference in reaction products obtained from Aclar and PTFE could be related

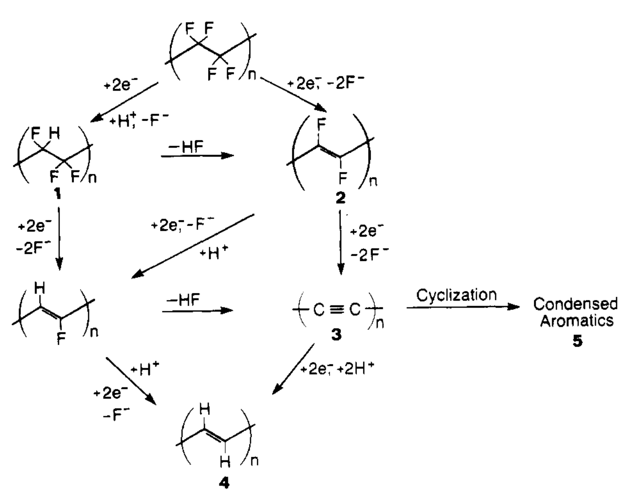
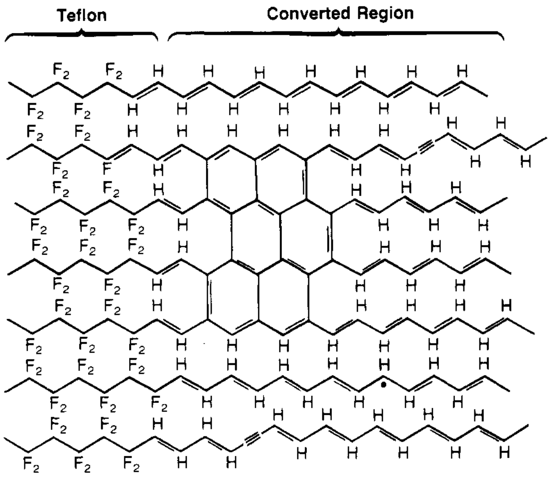


Figure 4. Possible PTFE reduction scheme in Me_2SO solution of benzoin and potassium *tert*-butoxide.

to the greater lability of Cl compared with that of F. In addition, the absence of crystallinity in Aclar might result in a different topotactic reaction course in Aclar compared with that in crystalline PTFE. A tentative two-dimensional model schematically portraying the observed products on the PTFE surface (where the converted region indicated represents the reduced surface) is shown below:



An examination of the surface of the reduced PTFE films by scanning electron microscopy shows that the surface material is fibrillar. The surface morphology may reflect the large loss of material volume on going from $(CF_2)_x$ to $(CH)_x$. Transmission electron microscopy of cross sections of reduced PTFE films also shows fibers on the PTFE surface. The fibrous material thus obtained was too thick to give reliable imaging and diffraction data.

Since the PTFE-reduced surface layer appears to be composed primarily of *trans*-$(CH)_x$, it should be dopable to conductive compositions. Chemical donor doping with sodium naphthalide and potassium naphthalide solutions in THF was carried out in an Ar atmosphere. We obtained a composition that had a conductivity of 4.8×10^{-2} S cm^{-1}, a value that is much lower than that observed for donor-doped *trans*-$(CH)_x$ ($\sim$50 S cm^{-1}).[17] By contrast, acceptor doping with I_2 was found to give a highly conductive surface. Costello and McCarthy[5] have obtained high conductivities on I_2 doping, but no measurable electrical conductivities on sodium naphthalide doping. The Raman spectrum of a K-doped reduced PTFE surface is shown in Figure 3 and compared with the spectra of K-doped $(CH)_x$ reported by Eckhardt et al.[18] The lines at 1135 and 1561 cm^{-1} correspond to those observed in K-doped $(CH)_x$ at 1140, 1550, and 1580 cm^{-1} using 4579 Å excitation. However, the sharp line at 1265 cm^{-1} observed by Eckhardt et al. and assigned to the A_g mode of the undimerized chain in highly crystalline K-doped $(CH)_x$ is visible only as a weaker component peaking at 1220 cm^{-1} in K-doped reduced PTFE. One rationale for this difference between the two spectra could be the absence of crystalline order in the $(CH)_x$ formed on the PTFE surface. Additionally a broad line at 1361 cm^{-1}, assignable to a disordered carbon,[19] is observed in K-doped reduced PTFE. A similar feature is seen in the Raman spectrum of reduced Aclar (Figure 2c), where a predominantly carbonaceous surface is obtained. These results suggest that potassium naphthalide doping of the *trans*-$(CH)_x$ on the PTFE surface may be complicated by the reaction of the alkali-metal dopant with the PTFE substrate to produce partially compensated $(CH)_x$ (resulting in the low observed conductivity) and an additional layer of disordered carbon.[2]

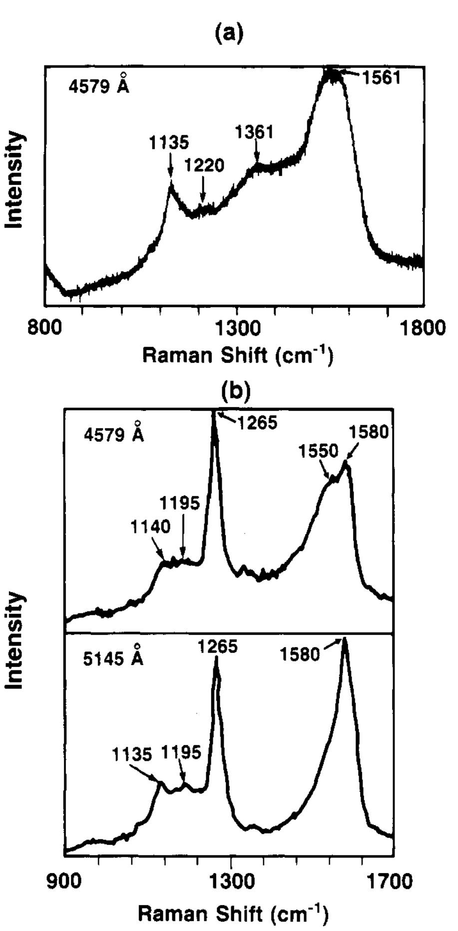


Figure 5. (a) Raman spectrum of potassium naphthalide doped reduced PTFE. Excitation is at 4579 Å. The electrical conductivity of the surface coating is 4.8×10^{-2} S cm^{-1}. (b) Resonance Raman spectra of electrochemically K-doped polyacetylene (12% doping level) (after Eckhardt et al.[18]).

In conclusion, we have presented data that strongly suggest that the surface material formed via the benzoin dianion reduction of PTFE films in Me_2SO consists primarily of *trans*-$(CH)_x$ and a small fraction of a disordered carbon. The conjugation lengths in the *trans*-$(CH)_x$ component range between 12 and 28 units. Identification of the main component of the surface layer as *trans*-$(CH)_x$ is consistent with its color, air reactivity, and conductivity on doping. Furthermore, this suggests that the surface layer can be subjected to reactions known to convert $(CH)_x$ into a variety of new chemical forms providing new layers on PTFE which may be potentially useful as conductors,[20] catalytic surfaces,[21] and battery electrodes.[22] Moreover, the formation of $(CH)_x$ from $(CF_2)_x$ poses interesting mechanistic questions concerning this chemical transformation.

Acknowledgment. We acknowledge stimulating initial discussions with T. J. McCarthy and thank both him and C. Costello for helpful information on the chemical procedures for the benzoin dianion reduction of PTFE. We also thank H. Eckhardt for discussions on the spectroscopic aspects of this work and J. Marti for his help in obtaining the electron microscope results.

Registry No. $(CH_3)_3CO_2K$, 865-47-4; I_2, 7553-56-2; benzoin, 119-53-9; sodium naphthalide, 3481-12-7; potassium naphthalide, 4216-48-2.

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Laser Desorption Time-of-Flight Mass Spectrometry of Low Molecular Weight Polymers

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ABSTRACT: A laser desorption time-of-flight mass spectrometer (LD-TOF-MS) has been used to examine a number of low molecular weight polymers. Laser desorption is provided by a high-power, moderately focused, pulsed CO_2 laser. A time-variable drawout pulse is used to selectively extract lower energy quasi-molecular ions, $[M + K]^+$, and thus reduce the abundances of the fragment ions that are observed. Reliable molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) were calculated from the $[M + K]^+$ ion relative intensities for a series of poly(ethylene glycol) and poly(propylene glycol) samples with oligomer molecular weights up to ~5000. Molecular weight averages determined for a series of poly(ethylene imine) samples were somewhat too low, however; this may be attributed to a thermal fragmentation effect. Two additional low molecular weight polymers with different structures were also qualitatively analyzed. The use of LD-TOF-MS to characterize oligomeric mixtures has been demonstrated.

A number of desorption ionization methods have been used for the direct mass spectral analysis of low molecular weight polymers.[1,2] "Direct" in this sense means that mass spectra are obtained that contain very high abundances of molecular (or quasi-molecular) ions with minimal contribution of ions due to fragmentation/decomposition processes. Methods that have been used, with varying degrees of effectiveness, include field desorption (FD-MS), electrohydrodynamic ionization (EH-MS), ^{252}Cf plasma desorption (PD-MS), laser desorption (LD-MS), fast atom bombardment (FAB-MS), and thermospray (TSP-MS). The major application areas have been (a) structural characterization of oligomeric mixtures (monomer types, end groups, and impurities), (b) identification of chromatographic (GC, LC, and GPC) effluents, and (c) determination of polymer molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$).

Polyglycols has been the class of low molecular weight polymers most often studied by desorption ionization mass spectrometry. Field desorption has been used to examine poly(propylene glycol) (PPG),[3–6] poly(ethylene glycol) (PEG),[5,6] and poly(tetrahydrofuran).[6] In FD-MS analysis, polyglycols generally yield protonated molecular ions $[M + H]^+$ of reasonable intensity, but fragment ions are also prominent, particularly at low masses. Alkali cation attachment is often employed to obtain enhanced quasi-molecular ion spectra. A number of PEG samples have also been analyzed by EH-MS.[7–9] Sodium attachment ions were dominant in EH spectra obtained from NaI/glycerol solutions,[7] and fragment ions were essentially absent.