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Chemical Modification of Polymers. 19.[1-3] Oxidation of Polyacetylene

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ABSTRACT: The kinetics of oxidation of polyacetylene by ambient air under fluorescent room lighting and by dry air in the absence of ultraviolet light at 25 °C have been established by weight uptake and by infrared and elemental analyses. In the absence of UV light, following an induction period of ~10 h, two pseudo-first-order oxidation regimes are observed; the oxidation has no effect upon cis–trans isomerization rate. Under ambient conditions (fluorescent lighting) the oxidation kinetics are comprised of two pseudo-first-order domains; cis–trans isomerization also shows two pseudo-first-order domains. The two regimes in each case are attributed to "surface" and "bulk" oxidation of the fibrils. The rapid initial isomerization under ambient conditions may be due to UV or singlet oxygen induced isomerization. The effect of oxygen upon conductivity and tensile properties of polyacetylene is rationalized by these oxidation kinetics.

Introduction

The prospect of combining the mechanical properties of polymers with the electrical properties of metals has caused a resurgence of interest in electrically conductive polymers in recent years. Polyacetylene, $-(\mathrm{CH{=}CH})-_n$, has led this resurgence. The key element was the ability to prepare films of this polymer in situ during polymerization.[4,5] This led to many new prospective applications relative to the powdered form prepared by variants of the Natta method,[6] even though the powder had been shown to be dopable.[7] The studies of the University of Pennsylvania group led to the discovery of metallic conductivity in polyacetylene doped with a number of novel dopants.[8]

These efforts stimulated interest in other laboratories. Now a number of polymers capable of high conductivity in the doped state are known: poly(1,6-heptadiyne),[9] poly(*p*-phenylene),[10] poly(*p*-vinylenephenylene),[11] poly(*p*-phenylene sulfide),[12,13] poly(*p*-phenylene oxide),[13] polypyrrole,[14] and poly(2,5-thienylene).[15]

In order to utilize conductive polymers for many applications, stability to ambient conditions (air, light, and water) is required. Our concern over this aspect of these unique polymers has led us to study the effects of oxygen on polyacetylene. We have shown that oxygen initially dopes polyacetylene and eventually degrades its conductivity.[3] With the objectives of (1) correlating the changes in electrical behavior with changes in chemical structure and (2) understanding the nature of the attendant chemical processes, a study of the oxidation was undertaken. That study is the subject of the present report.

Oxidation of polyacetylene powder was reported by Hatano, Kambara, and Okamoto[16] and by Berets and Smith,[7] who described the doping effect of oxygen on conductivity as well. More recently, Snow, Brant, Weber, and Yang[17] described the effects of oxygen on the ESR spectrum of polyacetylene film. Bernier et al. have also investigated the effect of oxygen on the ESR spectrum,[18] as have Karasz et al.[19] Shirakawa and Ikeda reported that air exposure resulted in the presence of carbonyl bands in the infrared spectrum of polyacetylene films.[4] Druy et al. described the effect of oxygen on the tensile properties of polyacetylene films.[20]

Summary of Our Previous Work. Earlier publications by us have described the effect of oxygen on polyacetylene in terms of dielectric relaxation processes, electrical conductivity, and oxygen uptake.[1,3,21] Dielectric measurements revealed enhanced dc conductivity and interfacial polarization upon short exposure to oxygen; the effect is partially reversible.[21] The electrical conductivity of polyacetylene increases upon exposure to oxygen and then drops precipitously, falling several orders of magnitude in a period of several hours.[1,3] Simultaneous oxygen uptake data show that the maximum conductivity occurs at 16 wt % at 91 °C.[3]

Table I
Oxidation of Polyacetylene[a] in Dry Air in a Glovebox in the Absence of UV Light

exposure time, h	% O[b]	composition x in $(\mathrm{C_2H_2O}_x)_n$
21.8	trace	<0.002
45[c]	6.39	0.111
48.8	5.16	0.0885
72.0	8.26	0.147
96.2	9.03	0.162
339.2	20.31	0.415
5 months[d]	45.68	1.38

[a] Sample initially 70 μm thick, 58% cis unless otherwise noted. [b] By elemental analysis after vacuum ($\leqslant 10^{-4}$ torr) treatment for 1 h. Remainder of sample C and H in 1.00:1.00 ratio. [c] In absence of visible light. [d] Sample initially 60 μm thick, 53.0% cis.

Table II
Oxidation of Polyacetylene[a] in Air under Ambient Conditions

exposure time, h	% O[b]	composition x in $(\mathrm{C_2H_2O}_x)_n$
0.50	2.70	0.0452
1.08	2.40	0.0401
3.00	2.08	0.0347
10.00	2.64	0.0442
28.3	5.12	0.0884
28.3[c]	5.88	0.102
28.3[d]	5.74	0.0997
100.0	9.18	0.169
199.5	18.38	0.366
672.0	29.14	0.679

[a] Sample initially 170 μm thick, 54% cis unless otherwise noted. [b] By elemental analysis after vacuum ($\leqslant 10^{-4}$ torr) treatment for 1 h. Remainder of sample C and H in 1.00:1.00 ratio. [c] Sample initially 63 μm thick, 77% cis. [d] Sample initially 81 μm thick, 60% cis.

Discussion

Evidence for Oxidation. (a) Elemental Analysis. Samples of polyacetylene have been exposed to air or oxygen for specific periods of time, subjected to dynamic

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Table III
Oxidation of *trans*-Polyacetylene[a] in Pure Oxygen (1 atm) at 91 °C

exposure time, min	% O[b]	composition x in $(C_2H_2O_x)_n$
3.0	3.22	0.0543
5.0	8.08	0.144
58.3	11.26	0.207
100	17.17	0.338
156	25.16	0.550

[a] Prepared by isomerization of 70% *cis*-polyacetylene at 200 °C for 98 min in vacuo; initially 70 μm thick. [b] By elemental analysis after vacuum ($\leq 10^{-4}$ torr) treatment for 1 h. Remainder of sample C and H in 1.00:1.00 ratio.

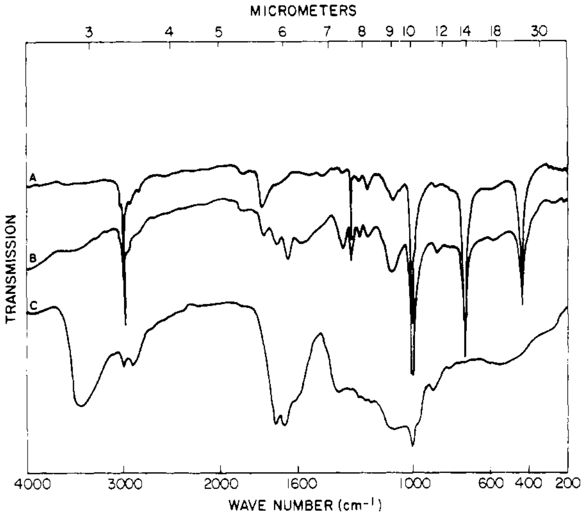

Figure 1. Infrared spectra of polyacetylene: (A) 45% *trans*-polyacetylene; (B) sample A after 5 h of exposure to ambient air, humidity, and light at 25 °C; (C) sample A after 49 days of exposure to ambient air, humidity, and light at 25 °C.

vacuum to remove any adsorbed oxygen, and analyzed for oxygen content. These results are given in Tables I–III. Clearly, oxygen is chemically incorporated into the polyacetylene.

(b) Weight Uptake. Exposure of polyacetylene to air results in substantial weight increase, which, as will be shown, correlates directly with the oxidative process.

(c) Infrared Spectroscopy. Figure 1A is the spectrum of ~45% *trans*-polyacetylene. Figures 1B and 1C are the spectra that result from exposure of the sample to air under ambient conditions for 5 h and 49 days. Several new absorption bands result. There are two carbonyl bands, one at 1665 cm^{-1} and one at 1720 cm^{-1}, as reported by Shirakawa and Ikeda.[4] These may be assigned to α,β-unsaturated ketone and isolated ketone chromophores, respectively.[22a] There is also an absorption at 3450 cm^{-1}. This band corresponds to a hydroperoxy group (OOH)[23] and also a hydroxy moiety.[22b] Peaks also appear at 1140 cm^{-1} (C–O stretch) and 887 cm^{-1} (peroxide, epoxide).[22c] Peaks at 1790, 1327, and 446 cm^{-1} disappear.

There are several mechanisms of oxidation that may apply. These depend on the nature of the oxygen, whether singlet or triplet. Singlet oxygen can react with olefins by several mechanisms as recently discussed by Frimer:[24] 1,2 addition to form a dioxetane, 1,3 addition (ene reaction) across the double bond and an allylic methylene group, or 1,4 addition to a cis diene (endoperoxide formation). Much is still in question regarding these reactions. Triplet oxygen, however, can apparently only react by attack on an existing carbon radical.[25] The resulting hydroperoxy radical is then capable of a number of reactions that lead to hydroperoxy, hydroxy, and carbonyl functionalities.

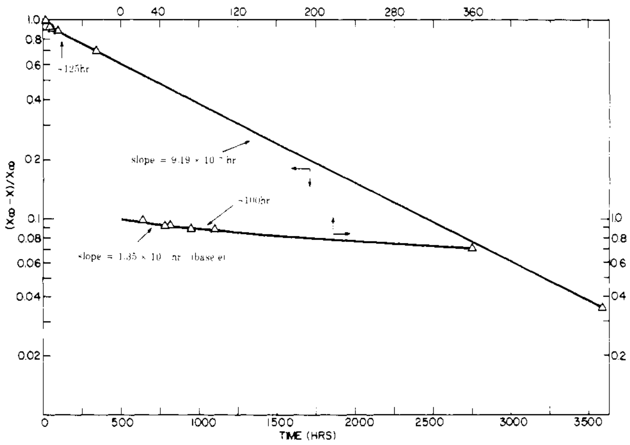

Figure 2. log (reduced oxygen content) of polyacetylene (initially 58% cis, 70 μm thick) vs. exposure time to dry air in the absence of ultraviolet light at 25 °C. $x_\infty = 1.43$.

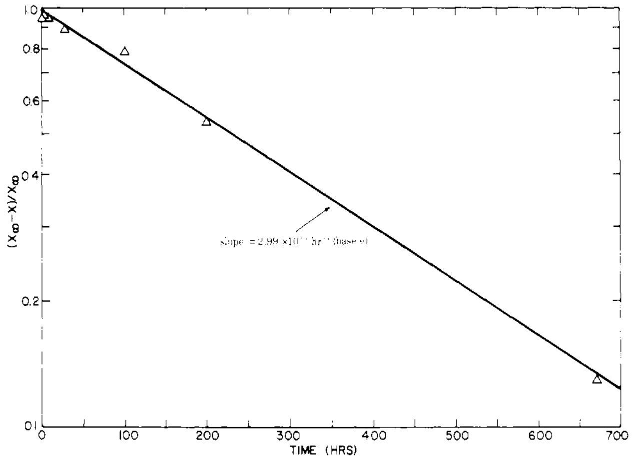

Figure 3. log (reduced oxygen content) of polyacetylene (initially 54% cis, 170 μm thick) vs. exposure time to ambient air, humidity, and light at 25 °C. $x_\infty = 0.780$.

It is not our intent in the present work to delineate the mechanism(s) of oxidation of polyacetylene. We have, however, carried out the oxidation under two sets of conditions: (1) under ambient conditions in which fluorescent lights can lead to some singlet oxygen formation directly or via excitation of polyacetylene and (2) in a glovebox filled with dry air and equipped with a $^1/_4$-in. Plexiglass window to minimize, if not eliminate, ultraviolet light.

Kinetics of Oxidation. The kinetics of oxidation of polyacetylene have been examined by three techniques in the present study. First, the oxygen chemically incorporated into the polymer was determined, as described above, as a function of oxidation time. Second, direct mass increase upon exposure to air was measured on a microbalance. Third, the time evolution of carbonyl, hydroperoxy, and cis/trans bands was monitored by infrared spectroscopy.

(a) Oxygen Content. The composition data of Table I are plotted in Figure 2. Note that the semilogarithmic plot of $(x_\infty - x)/x_\infty$ vs. time is comprised of two linear regimes of slightly different slope. This means that the oxidation process in the absence of UV light is first order or pseudo first order.[26a] This result is significant because it shows that oxidation is not controlled by diffusion of oxygen into the polymer, which would show a $t^{1/2}$ or t dependence.[27] Note the induction time of >22 h (Table I). The kinetics of the oxygen uptake under ambient

Table IV
Weight Uptake of Polyacetylene[a] Exposed to Ambient Air in the Absence of UV Light

time, h	weight increase,[b,c] mg	time, h	weight increase,[b,c] mg
0.00	0.00	308.0	0.36
0.62	0.00	330.0	0.38
2.00	0.00	400.0	0.43
6.67	0.01	500.0	0.48
23.3	0.04	567.0	0.53
26.7	0.04	617.0	0.55
46.7	0.08	717.0	0.63
53.3	0.09	867.0	0.66
68.3	0.12	950.0	0.71
75.0	0.13	1017.0	0.74
142.0	0.19	1117.0	0.82
167.0	0.23	1217.0	0.84
197.0	0.25	1300.0	0.84
217.0	0.28	1500.0	0.86
225.0	0.30		

[a] Initial conditions: weight 1.81 mg, 54% *cis*-polyacetylene, 140 μm thick. [b] Perkin-Elmer AD-22 autobalance. [c] Weight increase at infinite times estimated to be 1.70 mg for use in Figure 5 by Guggenheim fit of data for $t > 333$ h.

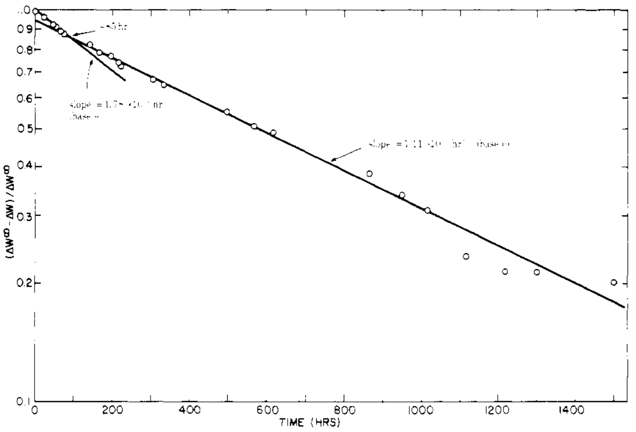

Figure 4. log (reduced weight uptake) of polyacetylene (initially 54% cis, 140 μm thick, 1.81 mg) vs. exposure time to ambient air and humidity in the absence of ultraviolet light at 25 °C. ΔW_∞ = 1.70 mg (see Table IV).

conditions (Table II, Figure 3) are similar to those in the absence of UV light except that there is no induction time in the former, nor are there two distinct regimes.

Visible light is shown in Table I to have no effect upon the oxidation rate. It was also shown (Table II) that total sample thickness has only a small effect upon total oxygen uptake under ambient conditions. The thickest film took up less oxygen. This does not address the issue of diffusion, however, in view of the fibrillar character of polyacetylene.

Oxidation of *trans*-polyacetylene in oxygen in the absence of UV light (Table III) also displays pseudo-first-order kinetics for the limited data set.

(b) Weight Uptake. Mass increase for polyacetylene as a function of exposure time (Table IV) to ambient air without UV light is shown in Figure 4. Two points are noteworthy. First, there is a short induction time of a few hours. Second, the weight uptake is comprised of two pseudo-first-order regimes, the break point occurring at about 90 h, in agreement with the result of Figure 2 in dry air. The initial and final slopes are comparable to those of Figure 2 for oxygen content kinetics.

(c) Infrared Analysis. (1) Carbonyl Formation. Figures 5 and 6 show the 1665-cm^{-1} carbonyl absorbance, assigned to the α,β-unsaturated functionality, as a function of time for air exposure under ambient conditions and in the absence of ultraviolet light. Note that the data reveal two first-order regimes in each case. The break point time increased by an order of magnitude in the absence of UV light and the rate constants decrease by 5-fold for the final line and 10-fold for the initial line.

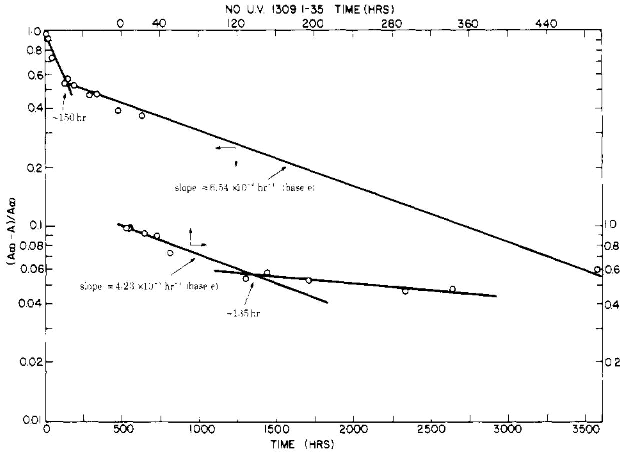

Figure 5. log (reduced 1665-cm^{-1} absorbance) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to dry air in the absence of UV light at 25 °C. A_∞ = 0.520.

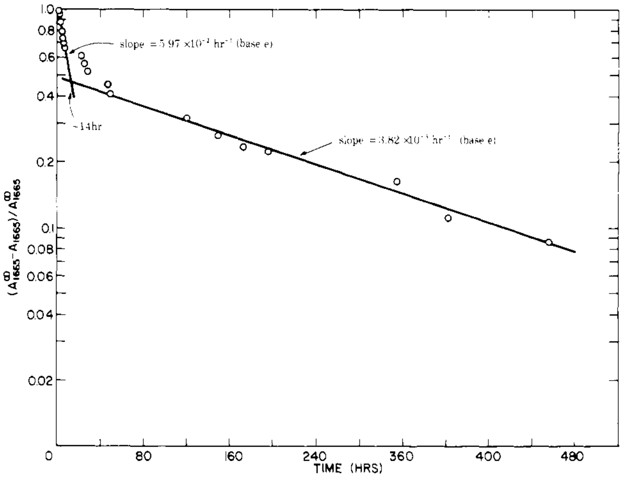

Figure 6. log (reduced 1665-cm^{-1} absorbance) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to ambient air, humidity, and light at 25 °C. A_∞^{1665} = 0.640.

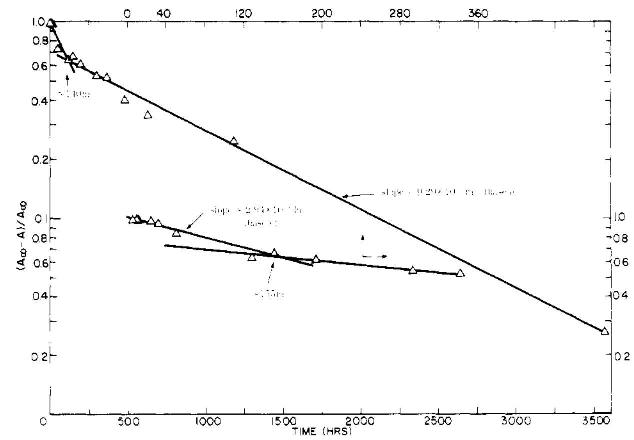

Figure 7. log (reduced 1720-cm^{-1} absorbance) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to dry air in the absence of ultraviolet light at 25 °C. A_∞ = 0.520.

Figures 7 and 8 are similar plots for the 1720-cm^{-1} peak, assigned to isolated carbonyl groups. Again, the break

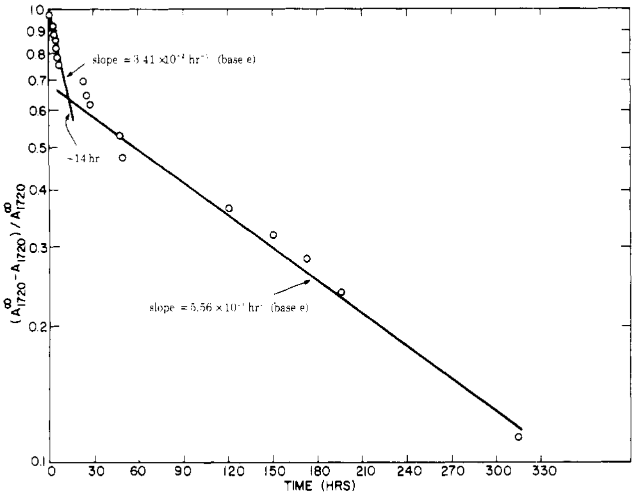

Figure 8. log (reduced 1720-cm^{-1} absorbance) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to ambient air, humidity, and light at 25 °C. $A_{\infty} = 0.530$.

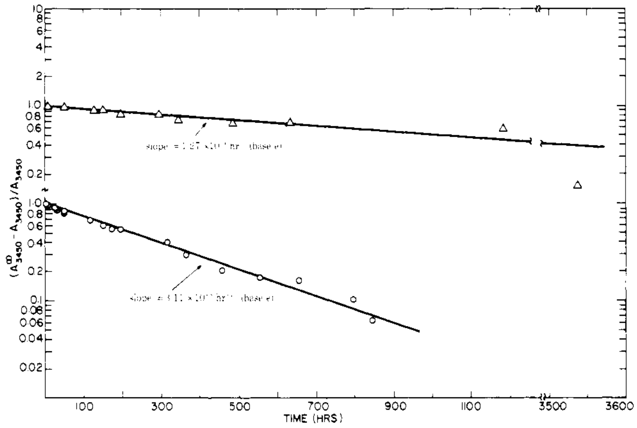

Figure 9. log (reduced 3450-cm^{-1} absorbance) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to air at 25 °C: (○) ambient light and humidity ($A_{\infty} = 0.380$); (Δ) dry air in the absence of ultraviolet light ($A_{\infty} = 0.590$).

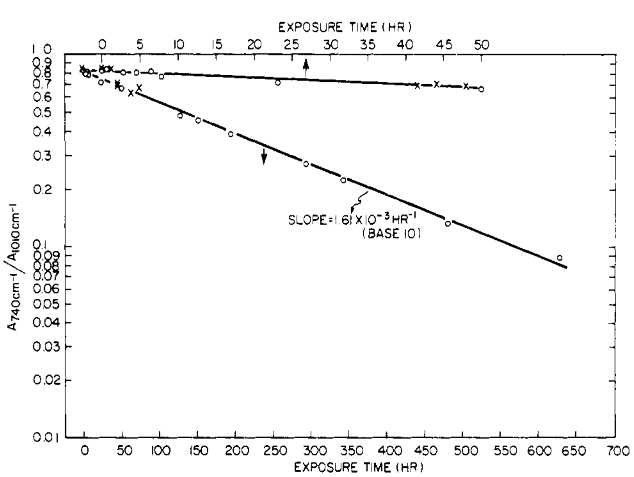

Figure 10. log (A^{740}/A^{1010}) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time at 25 °C: (○) dry air in the absence of ultraviolet light; (×) in the absence of both air and ultraviolet light.

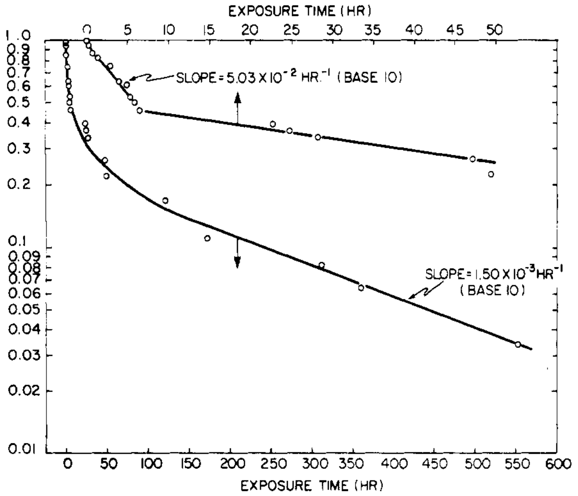

Figure 11. log (A^{740}/A^{1010}) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to ambient air, humidity, and light at 25 °C.

point between the two first-order regions increased by a factor of 10 and the rates decreased by 5-fold (final line) or 10-fold (initial line) in the absence of UV light.

A comparison of Figures 5 and 7 reveals that in the absence of UV light the 1665-cm^{-1} peak grows more rapidly than the 1720-cm^{-1} peak initially, but the order is reversed in the slower first-order regime. The same effects are observed in the ambient oxidation (compare Figures 6 and 8).

(2) Hydroperoxy and Hydroxy Formation. Curves for the 3450-cm^{-1} peak reveal, as shown in Figure 9, no break points either under ambient conditions or in the absence of ultraviolet light. The slopes of the lines indicate only a factor of 3 difference in rates under the two sets of conditions. This peak may contain the initially formed OOH group as well as the OH product moiety.

(3) Cis/Trans Ratio. Another feature of the oxidation process that can be probed by infrared spectroscopy is the change in the cis/trans ratio. We have followed the changes in the cis/trans ratio under ambient and glovebox conditions mentioned above. In Figure 10 the data for the oxidation in the glovebox (no ultraviolet light) are presented. The plot can be represented by a single straight line whose slope is identical with the thermal isomerization rate in argon, as also shown in Figure 10. In Figure 11 a semilogarithmic plot of the cis/trans ratio vs. ambient air exposure time is presented. Again, two distinct linear regions are observed, differing by a factor of 3 in rate. Note that the final slope of Figure 11 is identical with the slope of Figure 10, i.e., the thermal isomerization rate.

(d) Interpretation. The kinetic data described above indicate the following:

1. In the absence of ultraviolet light, air oxidation at room temperature, after an induction time of about 10 h, is a first-order process comprised of two distinct regimes, the break occurring at 90–150 h, depending upon the analytical probe employed.

2. Under ambient conditions, the air oxidation process shows no induction time but displays two first-order regimes, the break occurring at about 14 h.

It thus appears that in the absence of UV light the oxidation involves triplet oxygen which can interact only with existing free radicals.[25] The induction period for carbonyl formation is attributable to a buildup of a charge-transfer complex of oxygen with the polyene, as observed for aromatic systems.[28] The fact that oxygen uptake shows a short or zero induction time (Figure 4) is consistent with this view. The overall process is thus a series pseudo-first-order process[26b] in which the oxidation steps follow complexation, most likely via the usual path:[26c]

$$O_2 + R\cdot \rightarrow ROO\cdot$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

$$\mathrm{ROOH} \rightarrow \;>\!\mathrm{C{=}O} + \;>\!\mathrm{CH(OH)}$$

In the presence of UV light the oxidation is most likely complicated by the intervention of excited-state species in addition to the above-described ground-state process. The excited-state species could be associated with the polyene or with oxygen. There are, thus, three possible reactions: excited polyene–$^3O_2$, excited polyene–$^1O_2$, and ground-state polyene–$^1O_2$. The data of Table II, which show that under ambient conditions a thick film oxidizes more slowly, probably reflect the fact that the UV light reaches a smaller fraction of thicker films.

Reaction of triplet oxygen with free radical sites in the absence of UV light is consistent with the isomerization data of Figure 10. Oxygen has no effect upon the isomerization rate. At room temperature the production of free radicals during isomerization is insignificant compared to the radical population at these compositions. Thus, once triplet oxygen reacts with the radical sites, the resultant hydroperoxy radical reacts with cis and trans sites with equal facility. This also explains why in the ambient oxidation the isomerization rate (Figure 11) ultimately becomes equivalent to the thermal isomerization rate in the later stages where UV light is not a factor. No photoisomerization[29] of polyacetylene was observed during exposure to a 3-W UV lamp at a distance of 1 cm. This suggests that under ambient conditions the initial rapid loss of cis content is due to photoassisted selective oxidation of the higher energy cis isomer. Once the isomerization depth reaches the absorption limit of the actinic radiation, the process becomes thermal only and thus, the slope matches the slope obtained in the absence of ultraviolet radiation.

We turn now to the origin of the break points observed for the kinetics determined from elemental analyses, weight uptake, and 1720- and 1670-cm^{-1} infrared absorptions under both sets of oxidation conditions. These breaks are most simply attributed to "surface" and "bulk" oxidation of the polyacetylene fibrils. The situation is similar to other chemical reactions of solid polymers.[30] Thus, the higher initial rate corresponds to "surface" oxidation and the slower second rate to "bulk" oxidation. In view of the absorbance levels at the break points and their identity under the two sets of conditions this assignment is reasonable. Note that this description does not preclude that the surface region is disordered or amorphous and the bulk region ordered or crystalline, as proposed recently.[31]

Correlation with Other Data. Comparison of the present results with previous studies of electrical properties provides a means of identification of the chemical processes involved in the alteration of physical properties.

Figure 12 is a plot that shows the relationship between carbonyl absorbance and conductivity[3] by plotting both as a function of exposure time to air in the absence of ultraviolet light. Several features are noteworthy. First, the initial increase in conductivity occurs on a time scale during which there is no detectable increase in carbonyl absorption. Second, the decrease in conductivity corresponds approximately to the point in time at which carbonyl functionalities begin to form. Third, even when the carbonyl absorption has reached the break point level, the conductivity is still in excess of the initial value before air exposure. However, this point corresponds to a change (increase) in slope of the conductivity loss curve on a log (current) vs. time plot.[3]

All of these results are consistent with the oxidation process and model previously suggested.[3] In this model the doping process is a charge-transfer interaction of oxygen with the polyene. The loss of conductivity is due to the onset of oxidation of the polyene, although the loss of conductivity is a stochastic process that lags significantly behind the kinetics of the oxidation, which as shown here are pseudo first order and involve two distinct regions of the polymer. Thus, the change in slope of the conductivity curve can be ascribed to a changeover from oxidation of the surface to bulk regions of the polymer which contribute most strongly to the conductivity.

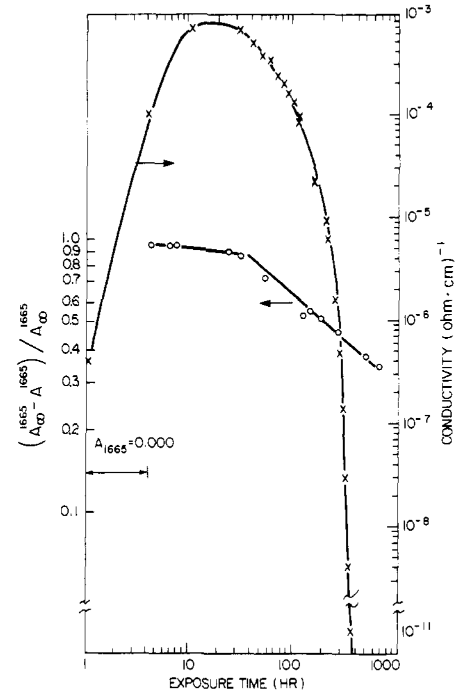

Figure 12. log (reduced 1665-cm^{-1} absorbance) and log (conductivity) of polyacetylene (initially 53% cis, 60 μm thick) vs. exposure time to dry air in the absence of ultraviolet light at 25 °C.

Druy et al. have examined the effect of air exposure on the tensile properties of 85% *cis*-polyacetylene.[20] They found that the ultimate extension ratio decreased as an exponential function of time. It was argued that cross-linking of the polymer was involved initially. A break in a plot of log (extension ratio) vs. log (air exposure time) occurred at about 1 h.

There is a correlation between the present oxidation kinetics and results for tensile properties. The growth of carbonyl groups in the bulk may account for mechanical property changes since the rate of loss of tensile properties increases in the region of the changeover from surface to bulk oxidation. Thus, it is not surprising that "ultraviolet light either in argon or air has no significant effect" on the extension ratio,[20] since mechanical properties are not very sensitive to surface modifications but are sensitivie to bulk changes.

Conclusions

In the absence of ultraviolet light, air oxidation of polyacetylene at 25 °C, after a 10-h induction period, is a pseudo-first-order process (not diffusion limited) comprised of two distinct regimes, a surface reaction and a bulk reaction; the cis–trans isomerization rate is unaffected. In the presence of UV light, air oxidation of polyacetylene at 25 °C also reveals two distinct first-order kinetic regimes, though of higher rate; the isomerization process reveals two first-order processes, but the ultimate kinetics are identical with those in the absence of UV light. Degradation of conductivity and tensile properties by oxygen are correlated to these chemical processes.

Experimental Section

Polyacetylene. Polyacetylene films were synthesized from acetylene gas by the method of Shirakawa.[5] Anal. Calcd for $-(\mathrm{CH}{=}\mathrm{CH})-_n$: C, 92.26; H, 7.74. Found: C, 91.44–92.25; H, 7.71–7.94. These and other elemental analytical data were obtained from Spang Microanalytical Laboratory. Samples were stored under argon in sealed containers at −80 °C (high cis content) or at 25 °C in a glovebox ($[\mathrm{O}_2] < 0.8$ ppm).

Oxidation. Samples of polyacetylene were exposed to ambient air in the laboratory under fluorescent light fixtures or to dry air ($[\mathrm{H_2O}] \sim 100$ ppm) in a glovebox (Labconco) having a $^1/_4$-in.-thick Plexiglass window. Samples for elemental analysis were exposed to dynamic vacuum ($\leq 10^{-4}$ mm) for 1 h to remove adsorbed oxygen and sealed in glass ampules. The mass uptake experiment was conducted in ambient air with a Perkin-Elmer Model AD-2Z autobalance with the glass doors closed to eliminate UV light.

Infrared Analyses. Infrared spectra were recorded on a Perkin-Elmer Model 283 instrument. For ambient oxidation the polyacetylene film was attached with adhesive tape across the opening of a cell holder, care being taken that no tape was in the beam. For oxidation in the absence of ultraviolet light the sample was removed from the glovebox (see above) in a sealed KBr cell. Most spectra were recorded in the transmission mode. Transmission data were converted to absorbance data manually.[32] The base line for the 3450-cm^{-1} peak was established in one of two ways. At the low A^{3450} values (<0.1) it was taken by drawing a line between the transmission maxima at 3200 and 3700 cm^{-1}. For higher A values (>0.1) the base line was drawn from ~2500 to 3700 cm^{-1}. The base line for the 1720- and 1665-cm^{-1} bands was taken as the maximum transmission at ~2000 cm^{-1}. Absorbance values for the 3450-, 1720-, and 1665-cm^{-1} bands were corrected for apparent values before oxygen exposure. The base line for the 1010-cm^{-1} (trans) band was drawn between transmission maxima at ~910 and ~1050 cm^{-1}. Likewise for the 740-cm^{-1} peak the base line was drawn between ~600 and 850 cm^{-1} for higher A^{740} values and later in the oxidation between ~700 and 800 cm^{-1}.

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References and Notes

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