The Influence of Water on the Degradation of $FeCl_3$-doped Polyacetylene

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The degradation rate of $FeCl_3$-doped polyacetylene in air and argon is dependent on the water content of the gas phase.

The greatest shortcoming of polyacetylene (pac), in both the undoped and the doped state, is its sensitivity to air.[1] The effect of air (oxygen) on pristine polyacetylene is well established.[2] For doped pac no such comprehensive studies on the effect of air have been published.

It has been commonly accepted that doped pac and water are incompatible, but recent work[3] has shown that doped pac can maintain its conductivity in certain aqueous solutions.

From our studies with doped pac (*e.g.* $FeCl_4^-$, $InCl_4^-$, $CF_3SO_3^-$) we know that water has a deleterious effect on the polymer's conductivity. To quantify this observation we have studied the influence of air and argon of variable humidity on $FeCl_3$-doped pac.

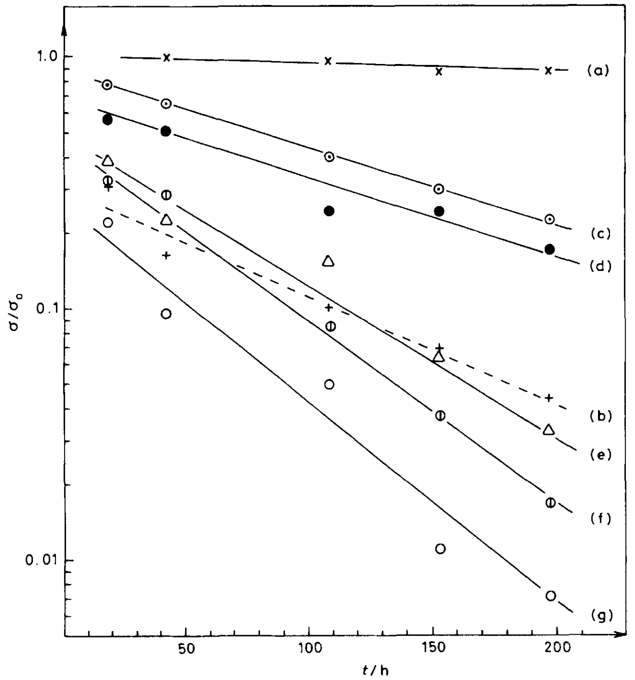

Figure 1. Conductivity (σ/σ_0) *vs.* exposure time for $FeCl_3$-doped polyacetylene that was exposed to air or argon of given relative humidity (%). (a) Ar, 0; (b) Ar, 76; (c) air, 0; (d) air, 35; (e) air, 55; (f) air, 76; (g) air, 92.

The experiments were carried out by exposing the doped pac samples at room temperature to air or argon of fixed relative humidity (established by saturated solutions of various salts).† After exposure, adsorbed water and oxygen were removed *in vacuo*. The samples were transferred to a glove-box‡ to measure mass and conductivity (four probe

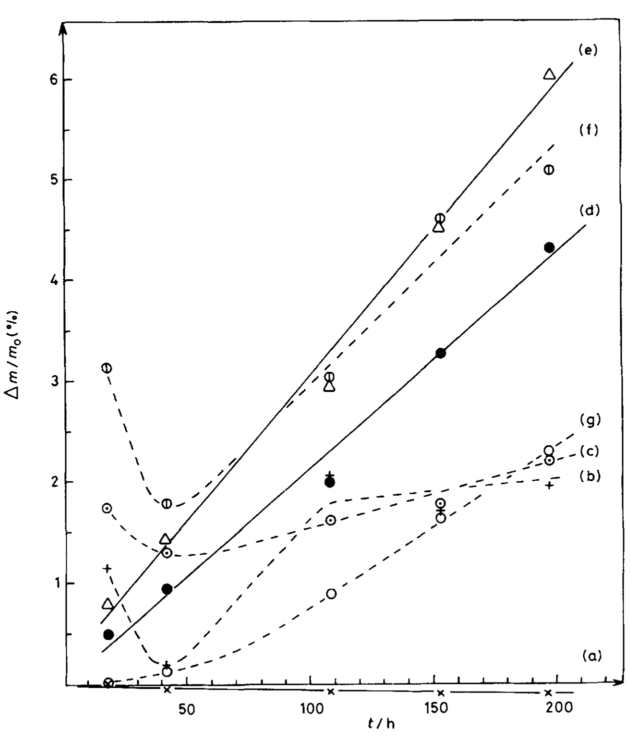

Figure 2. Relative mass uptake ($\Delta m/m_0$) *vs.* exposure time for $FeCl_3$-doped polyacetylene that was exposed to air or argon of given relative humidity (see Figure 1 for a—g).

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† Merck: Tables for the Chemical Laboratory. 92%: $Na_2CO_3 \cdot 10H_2O$; 76%: NaCl; 55%: $Ca(NO_3)_2 \cdot 4H_2O$; 35%: $CaCl_2 \cdot 6H_2O$; 0%: P_2O_5 (dry).

‡ During this procedure the samples were exposed to the laboratory atmosphere for about 30 s.

Table 1. g-Factor and linewidth (G) of the e.s.r. signals of $FeCl_3$-doped pac after 196 h exposure to air or argon of given moisture and additional two weeks storage in a glove-box.

Sample atmosphere and relative humidity		σ/σ_o (%)	Fe-signal			S1[b]		S2	
			g[a]	ΔH_{pp}	A/B	g	ΔH_{pp}	g	ΔH_{pp}
Ar	0%	86.6	1.9720	510	2.0	—	—	—	—
Ar	76%	4.4	2.0298	430	1.0	—	9	2.0027	0.5
Air	0%	22.6	1.9988	520	1.45	—	—	2.0026	<1[c]
Air	35%	17.4	2.0048	500	1.2	2.0025	10	—	—[d]
Air	55%	3.4	2.0189	510	1.0	—	9	2.0026	0.5
Air	76%	1.7	2.0244	480	1.0	—	10	2.0027	0.4
Air	92%	0.7	2.0345	440	1.0	2.0029	10	2.0027	0.4

[a] For asymmetric spectra an apparent g-factor was determined as for the symmetrical spectra (at $\Delta H_{pp}/2$ which was identical with the intercept of the spectrum with the baseline). [b] Because of the superposition of S1 and S2 it was not possible to evaluate unambiguously both g-factors, but they appear to be equal. [c] The signal was very weak, therefore it was necessary to use a large modulation width which resulted in line broadening. [d] S2 was not resolved from S1.

method) in an argon atmosphere. This procedure was repeated several times.

The measurements show clearly that the degradation of the conducting polymer (measured by the change in conductivity) is directly related to the water content of the surrounding gas phase (see Figure 1). The higher the humidity the faster the degradation. Interestingly, dry air does not degrade $FeCl_3$-doped pac as fast as moist argon does.

The weight uptake of the samples (Figure 2) show unusual behaviour. The relationship between weight uptake and humidity is not as evident as for the conductivity. We believe this can be explained by a combination of three effects: reaction with oxygen, hydration of the ions,§ and hydrolysis of the anion $FeCl_4^-$, with the measured result depending on which of these prevail. From the comparison of the two 76% samples it is obvious that oxygen causes a great deal of the weight uptake. However, the underlying reactions involved are not clear yet. Remarkably, the weight uptake in air of the $FeCl_3$-doped pac is less than for undoped pac.[4]

Changes in the e.s.r. spectra of the samples after exposure corresponded to the decrease in conductivity with the signal becoming more symmetrical (A/B goes from 2.2 to 1.0) and smaller. In addition, two new, rather weak, signals (S1, S2) appeared (imposed upon the broad dominating Fe^{3+} signal) which grew in intensity on increasing water exposure.

We are not sure of the origin of the new lines: the smaller one S2 may come from residual undoped, or slightly doped, pac that was not perceptible because of the skin-depth, but we have not found a pac signal with such a small linewidth in any of our previous experiments on $FeCl_4^-$-doped pac. The signal S1 may be due to compensated pac (*e.g.* $pac^+ + H_2O \rightarrow pac\text{-}OH + H^+$) where the spin is trapped compared to pristine pac. The e.s.r. results are in Table 1.

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§ On the 76 and 92% samples small droplets could be seen which left white spots on pumping.