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ON THE CONFIGURATION AND OXIDATION OF $(CH)_x$ OBTAINED BY LUTTINGER'S CATALYST

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Polyacetylene (PA) obtained by isothermal or non-isothermal polymerization using Luttinger's catalyst was studied by IR and Raman spectroscopy. It was found that the cis/trans content depends on the thickness of the films obtained. It was supposed that the population of trans-cisoid isomer in cis-rich films is probably larger than the population of trans-transoid isomer. Oxygen increases the cis-trans izomerization rate. The oxidation of cis-isomer probably proceeds with higher rate than the oxidation of lower energy trans-isomer.

INTRODUCTION

It is well known that the polymerization of acetylene at low temperature (-80°C) in the presence of a soluble Ziegler-Natta catalyst, $Ti(OC_4H_9)_4$ - $Al(C_2H_5)_3$, using the techniques developed by Shirakawa, primarily yields cis-PA (more than 95%) which is the thermodynamically unstable form and which can be isomerized into all-trans-PA by heating. Molecular structure of PA was studied by means of IR and Raman spectroscopy. Comparison of calculated vibrations with observed spectra leads to the conclusion, that cis and trans forms of PA are cis-transoid (c-t) and trans-transoid (t-t), respectively[1,2]. The trans-cisoid (t-c) structure was not proved experimentally, but was considered as an intermediate state in the thermal cis-trans isomerization[3,4].

The kinetics of oxidation and cis-trans isomerization of PA obtained by Shirakawa's techniques (S-PA) was studied by IR analyses. In the absence of UV light two pseudo-first-order oxidation regimes were observed. It was found that oxidation had no effect upon cis-trans isomerization rate[5].

Lieser et al.[6] showed that low-temperature polymerization of acetylene in the presence of Luttinger's catalyst yields cis-PA. The parameters of the orthorombic unit cell were determined using electron diffraction and X-ray experiments.

IR spectrum of powder sample of PA obtained by Luttinger's catalyst (L-PA) with cis-trans ratio 1:1 was published by Haberkorn et al.[7].

In this paper IR and Raman spectra of cis-rich films of L-PA and data for their cis/trans content, isomerization and oxidation are presented and discussed. Limited data for trans-PA obtained by thermal isomerization of cis-rich PA in high vacuum are given as well.

EXPERIMENTAL

Films of cis-rich L-PA were prepared as described earlier[8], by isothermal or non-isothermal polymerization of acetylene with $NaBH_4$-$Co(NO_3)_2$ as catalyst. All-trans samples were obtained by annealing of cis-rich films in vacuo (10^{-6} mm. Hg) at 150°C for 1 hr. IR spectra of films applied on KRS-5 (mixed crystal of TlBr-TlI) windows were measured using Karl-Zeiss UR-20 spectrometer. Raman spectra were taken on the spectrometer Coderg LRDH-800, recorded and accumulated using the PDP-11 computer in the Tracor system.

All oxidation experiments were carried out by exposure of the samples to ambient air at room temperature in the absence of light.

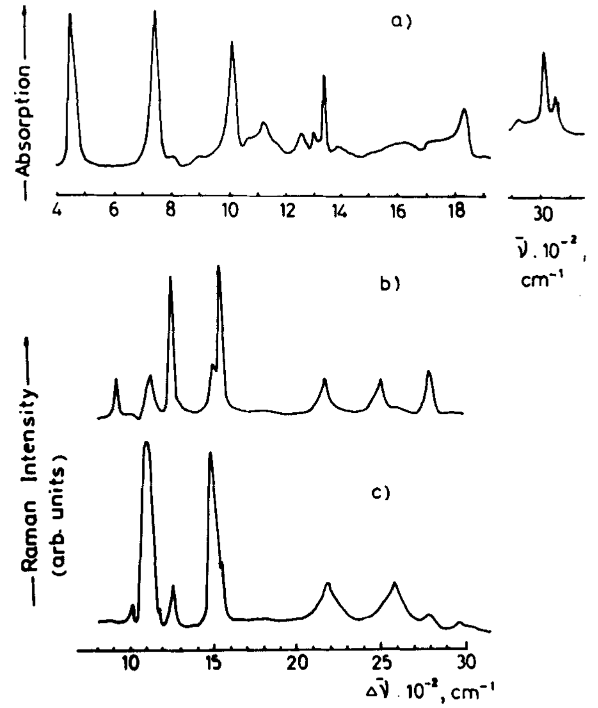

FIGURE 1. Infrared and Raman spectra of (CH)$_x$ obtained by Luttinger's catalyst
a) Infrared spectrum of cis-rich L-PA
b) Raman spectrum of cis-rich L-PA at 133°K
c) Raman spectrum of trans-rich L-PA at 173°K

RESULTS AND DISCUSSION

IR and Raman spectra of L-PA films are shown in Fig.1.They are identical to the corresponding spectra of S-PA films[1,9]. It was found that the cis/trans content determined by the procedure of Ito et al.[10], depends on the thickness of the films obtained. Lower cis-content was always observed in thicker areas than in thinner parts of the same film. Under isothermal (-80°C) or non-isothermal polymerization conditions the highest cis-content of about 85-90% was obtained when the film thickness was approximately 2-3 μm or lower.

It was found that the cis-content decreases to 70-75% on increasing film thickness up to about 40 μm. This trend of increasing trans-content with increasing film thickness in the exothermic polymerization of acetylene probably is due to the more intensive local superheating of the catalyst solution in thicker layers.

According to Ito et al.[10], S-PA obtained at -18°C and 0°C exhibits cis-content of about 95% and 79%, respectively. Evidently, when Luttinger's catalyst was used under our experimental conditions, PA with higher trans-content was obtained at considerably lower temperature.

It is plausible, however, that the higher trans-content determined by the IR procedure in L-PA to be due to the formation of t-c isomer. The calculated total energies of c-t and t-c isomers are very similar[11],i.e. the probability of formation of both less stable isomers is nearly equal. In calculation of the cis/trans content using absorbances of the C-H out-of-plane deformation bands, the t-c isomer should be assigned to the trans form[12], whereas in X-ray and electron diffraction measurements of the crystalline structure this isomer should be isomorphous with the c-t form and ought to be related to cis crystalline lattice. Since the reflections characteristic of the trans PA[10], are missing in the X-ray diffraction patterns of our samples containing up to 30% trans form determined by the IR procedure, it follows that the population of t-c isomer in cis-rich L-PA is probably larger than the population of t-t isomer. Haberkorn et al.[7] reached to similar conclusions for 50% cis L-PA powder.

The changes in cis-trans ratio of cis-rich L-PA films in argon and under oxidation conditions were followed by changes in absorbances (A) of the IR bands at 740 cm^{-1} and 1014 cm^{-1} characteristic of cis and trans PA, respectively. In contrast to the results of Gibson and Pochan[5] for S-PA, we have found that: (a) the semilogarithmic plots of A_{740}/A_{1014} vs. exposure time to ambient air in the absence of both air and light were not linear (Fig.2); and (b) the decrease in cis content (Fig.3) and in cis/trans ratio (Fig.2) in argon is much slower than in air. Furthermore, as shown

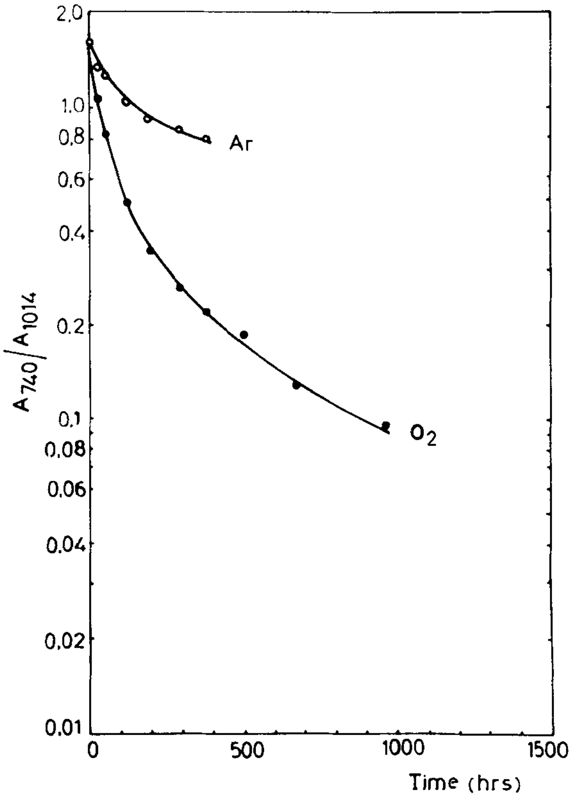

FIGURE 2. log(A_{740}/A_{1014}) of L-PA (initially 70% cis) vs. exposure time at room temperature in the absence of light
(●) ambient air; (o) argon)

in Fig.3, in the initial stages (up to 50 hrs) the increase in trans content in air is higher than in argon. From these results follows that oxygen increases the cis-trans isomerization rate.

The semilogarithmic plot of A_{740} of PA initially 70% cis vs. exposure time to ambient air (Fig.4, curve 1) is comprised of two linear regimes the break point occuring at about 200 hr. The cis-content decrease in the first region

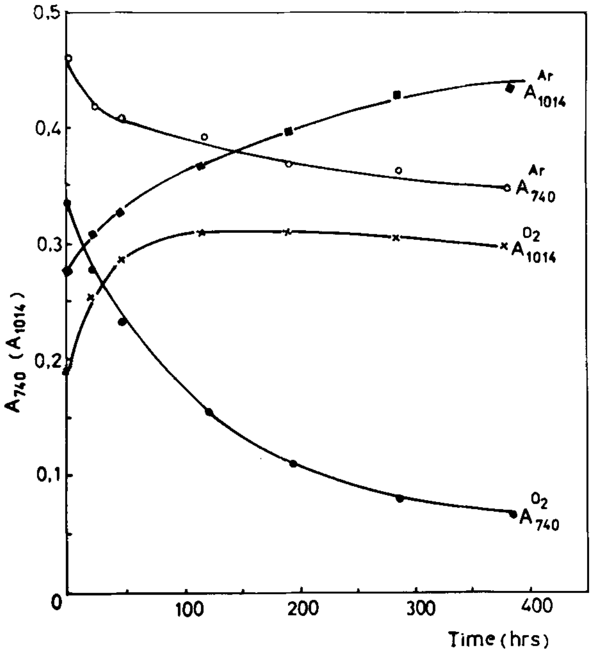

FIGURE 3. A_{740} and A_{1014} of L-PA (initially 70% cis) vs. exposure time at room temperature in the absence of light
(●) and (x) - ambient air; (o) and (■) - argon;

is determined by two parallel reactions - isomerization and oxidation. The rate in the second, lower slope region is probably due mainly to oxidation of the cis isomer.

In the plot of log(A_{1014}) vs. exposure time to ambient air of the same sample (Fig.4, curve 2) the initial sharp increase of the trans-content due to isomerization is followed by linear region (at about 200 hr) where the rates of isomerization and oxidation are equal, i.e d [trans] /dt = 0. The slope of the next, final region matches the slope of log(A_{1014}) of trans-PA sample (98% trans) vs. exposure time to ambient air (Fig.4, curve 3). Therefore, this final region could be assigned mainly to oxidation of trans-PA.

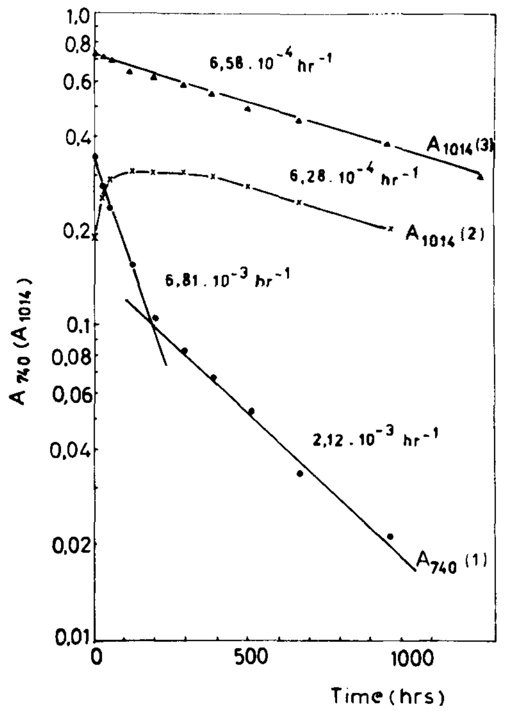

FIGURE 4. log(A_{740}) and log(A_{1040}) of L-PA vs. exposure time to ambient air in the absence of light at room temperature
1(●) and 2(x) - initially 70% cis; 3(▲)-98% trans

Comparing the final slopes of curves 1 and 2 in Fig. 4 we can suppose that probably the oxidation of the cis-isomer proceeds with higher rate than the oxidation of lower energy trans-isomer.

In addition, the kinetics of oxidation of cis-rich L-PA during exposure to ambient air was followed by changes in absorbances of the IR bands at 1665 cm^{-1}, 1720 cm^{-1} and 3450 cm^{-1} assigned to α,β-unsaturated keton, α-diketon and OOH+OH groups, respectively[5]. Semilogarithmic plots of reduced absorbances vs. time (Fig. 5) are comprised of three linear regimes of pseudo-first-order, the

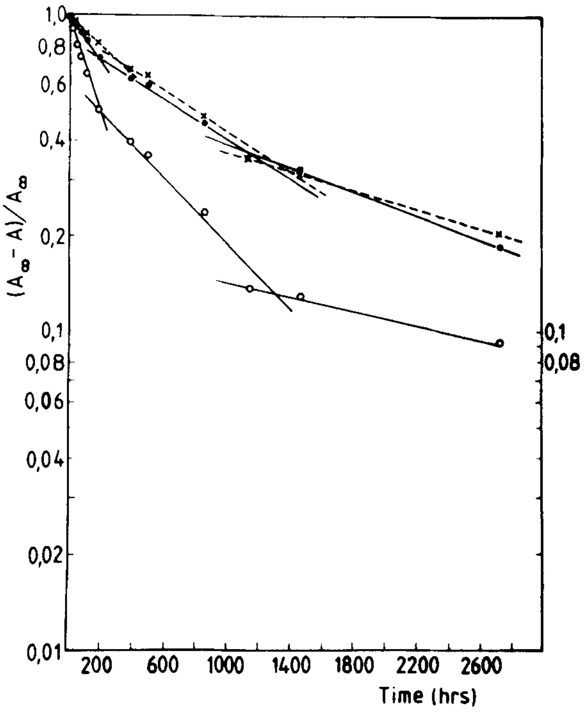

FIGURE 5. log(reduced absorbances) of L-PA (initially 70% cis) vs. exposure time to ambient air at room temperature in the absence of light

(o) 1665 cm^{-1}; (●) 1720 cm^{-1}; (x) 3450 cm^{-1};

$A^{\infty}_{1665}=0,560$ $A^{\infty}_{1720}=0,480$ $A^{\infty}_{3450}=0,480$

	SLOPES, hr^{-1} (base e)		
	0-200 hr	200-1200 hr	1200-2700 hr
(o) 1665 cm^{-1}	$3,61.10^{-3}$	$1,17.10^{-3}$	$2,55.10^{-4}$
(●) 1720 cm^{-1}	$1,63.10^{-3}$	$7,28.10^{-4}$	$4,20.10^{-4}$
(x) 3450 cm^{-1}	$1,10.10^{-3}$	$7,39.10^{-4}$	$3,41.10^{-4}$

break points occuring at about 200 hr and 1150 - 1250 hr. The values of the slopes of the two former linear regions are comparable to those obtained for oxidation of S-PA in dry air in the absence of UV light[5]. This two regions could be assigned to "surface" and "bulk" oxidation of PA fibrils according to Gibson and Pochan[5]. The third linear region in our plots could be explained by retarding of oxidation in later stages due to sharp decrease of oxidizing sites and possible steric hindrance of keto- and hydroperoxy- groups formed.

It should be noted the identity of the break points at about 200 hr in the carbonyl absorbances (Fig. 5) and in cis- and trans- isomer absorbances (Fig. 4). This is in agreement with our assumption for the higher oxidation rate of the cis-isomer.

CONCLUSIONS

- Cis-content in L-PA decreases on increasing film thickness.
- Population of t-c isomer in cis-rich L-PA is probably larger than the population of t-t isomer.
- Oxygen increases the cis-trans isomerization rate.
- The oxidation of the cis-isomer probably proceeds with higher rate than the oxidation of lower energy trans-isomer.

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