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Study of the Ageing of Poly-9-vinylanthracene

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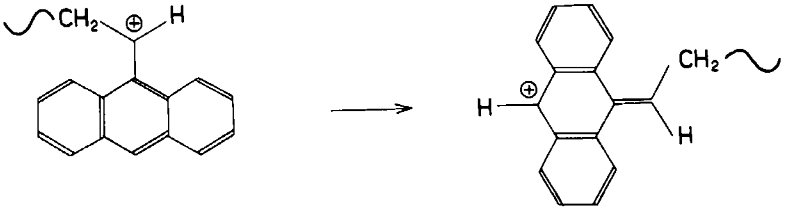
ABSTRACT

Degradation of poly-9-vinylanthracene obtained by cationic initiation has been studied under various experimental conditions. Polymerizations have been carried out in the dark and under nitrogen, but the evolution of the polymer has been studied in the dark or in daylight under nitrogen and in air. In daylight and in air a drastic and rapid change of the polymer is observed. Analysis of the breakdown products shows that they contain anthraquinone. A possible mechanism of the degradation is suggested.

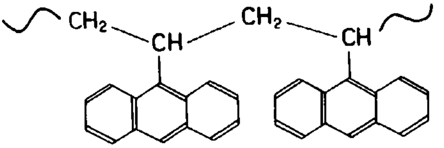
INTRODUCTION

The cationic polymerization of 9-vinylanthracene has been studied by various authors [1-6] who have examined the structure of the corresponding polymers. Most of them have reported that the main characteristics of the NMR and IR spectra could be explained only by assuming an isomerization of the cation [Eq. (1)]:

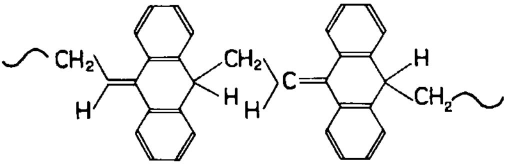


(1)

leading to the presence of structures I and II in the polymer chain.



I



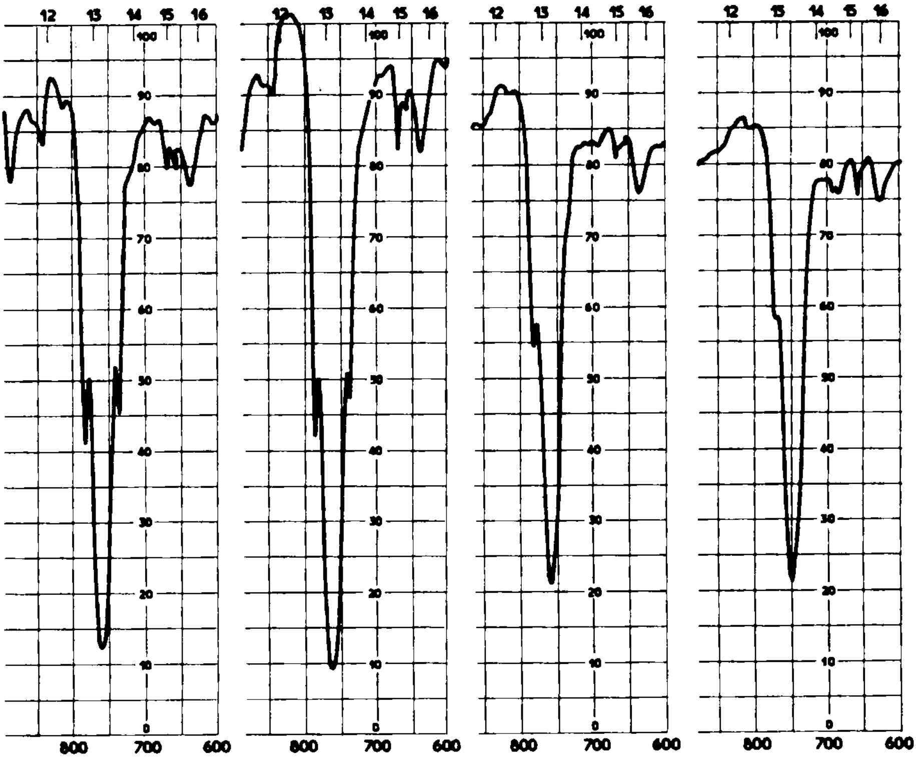
II

However, a close examination of the spectra makes us somewhat suspicious of this interpretation. All our conclusions will be published at a later date. However we can already say that this polymer degrades in the polymerization solution and that the shape of the spectra largely depends on the time which has elapsed between the end of the polymerization and recording. This preliminary note is devoted to the study of this phenomenon.

EXPERIMENTAL

9-Vinylanthracene was polymerized at -78°C by $TiCl_4$ in CH_2Cl_2 under oxygen-free nitrogen. After a contact time of 10 min between monomer and initiator, the active species are killed by methanol; the polymer precipitates. Both polymerization and killing are carried out in the dark. The suspension thus obtained is fractioned into four parts (A-D), and each of those fractions is treated in the following way: (A) kept under nitrogen in the dark; (B) kept under nitrogen in daylight; (C) exposed to air in the dark; (D) exposed to air in daylight.

From each fraction four samples are taken at the following times



D₁ D₂ D₃ D₄

FIG. 1. Change in the IR spectra (600-800 cm^{-1}) of sample D with time.

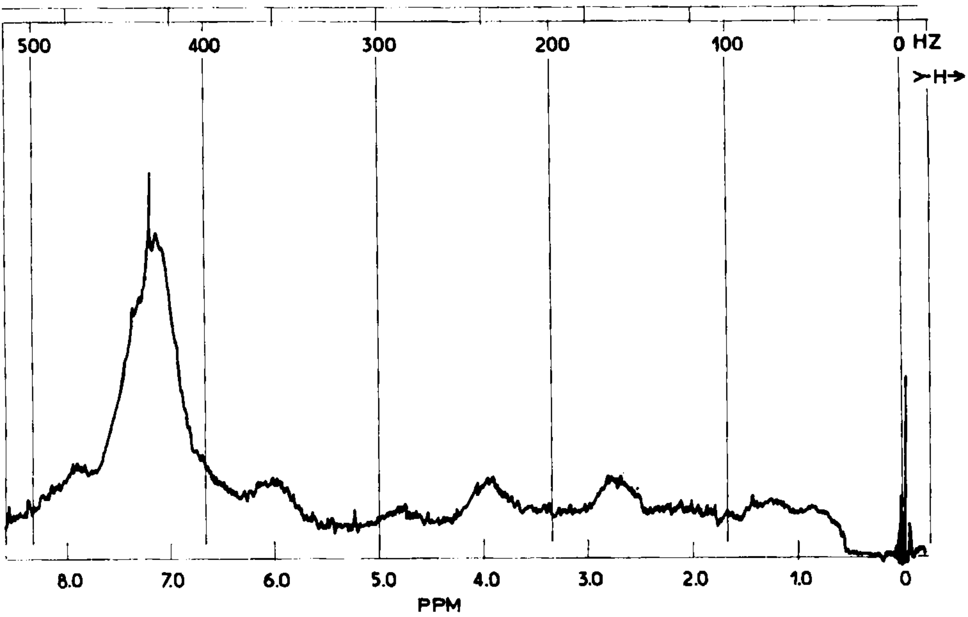


FIG. 2. NMR spectrum of sample D_4.

after killing: 1 (90 min); 2 (1 day); 3 (two days); and 4 (8 days). The polymer is separated from the suspension by filtration and dried in the dark. The filtrate is evaporated to dryness and the residual solid analyzed. Fraction D contains mainly anthraquinone; in the fractions A and C, no anthraquinone was found and only traces in the case of fraction B.

RESULTS AND DISCUSSION

Evolutive Aspect of the Suspension

In the case of fraction D the amount of precipitated polymer decreases with increasing time while the solution turns a deep yellow. The same kind of evolution is observed with fraction B but to a much smaller extent. No noticeable modification can be observed with fractions A and C.

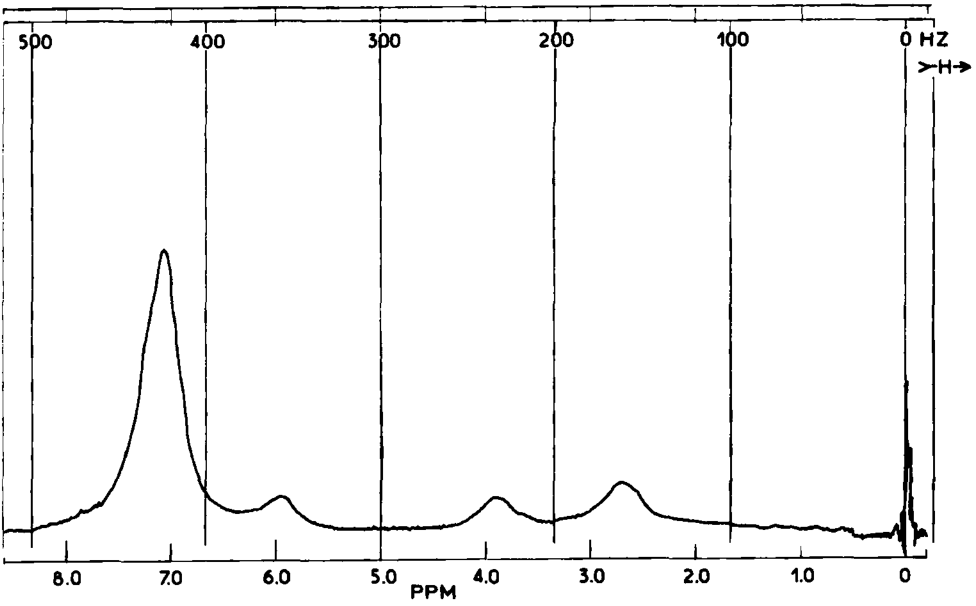


FIG. 3. NMR spectrum of sample D$_1$.

Infrared Spectroscopy

Two areas of the spectrum have been particularly examined: the bands at 700-800 cm^{-1} and 2800-3100 cm^{-1}. According to Michel, the bands at 735 cm^{-1} and 760 cm^{-1} are characteristic of structure I and structure II, respectively. However a dramatic evolution of these two bands can be observed, at least for some of the fractions.

For fractions A and C there is practically no change, and in all cases the ratio of the absorbances at 735 and 760 cm^{-1} remains unchanged.

For fraction D, as shown in Fig. 1, a rapid and drastic change is observed: the band at 13.7 μM decreases little by little and completely disappears in the last sample (8 days). The ratio aliphatic/aromatic increases (2800-3100 cm^{-1}).

NMR Spectroscopy

The spectra of poly-9-vinylanthracene published in the literature [1-3] have the general shape shown in Fig. 2. Michel [1, 2] ascribes this spectrum to structure II.

The spectra that we obtained (sample A, C, B_1, and D_1) are slightly different (see Fig. 3), since two supplementary patterns can be observed (7.9 and 4.8 ppm).

But a drastic change in the NMR spectra can be observed when the sample is exposed to air and to daylight. No visible change is observed for fractions A and C and only a small change is observed for fraction B, but the spectra of sample D recorded after 90 min and 1, 2, and 8 days show a progressive decrease of the features at 7.9 and 4.8 ppm; these features, originally present, are almost absent in fraction D_3 (after 2 days) and have completely disappeared in fraction D_4 (8 days) as shown in Figs. 2 and 3. The spectrum of sample D_4 is identical to the spectrum published by Michel.

Melting Points

The melting points range between 220 and 240°C before degradation and between 240 and 260°C after degradation.

Average Molecular Weights

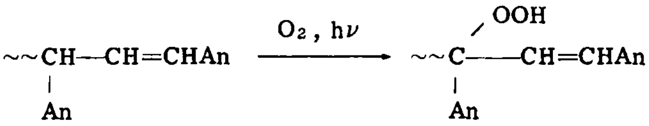
The number-average molecular weights (determined by vapor pressure measurements) are around 2000 ($\overline{x}_n \simeq 10$) and–whatever the conditions–do not change to a significant extent with respect to the time.

From the former results the following conclusion can be drawn. Ageing of poly-9-vinylanthracene has two main causes: light (fractions A and C do not change with the time) and oxygen. In all cases a rapid and drastic change of fraction D has been observed. The slow and weak change of fraction B could be due to oxygen traces present in the nitrogen, even after its deoxygenation.

The fact that the average molecular weights do not change to a significant extent proves that most of the photooxidative degradation takes place at the ends of the chains. Since the melting point increases with time it can be assumed that the degradation affects mainly short chains.

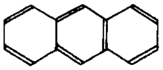
Analysis of the breakdown products shows that they contain anthraquinone. No anthraquinone is produced when solutions of 9-vinylanthracene and anthracene in CH_2Cl_2 + CH_3OH are added with $TiCl_4$ and kept under air in daylight in the same conditions as the polymer. This proves that anthraquinone results from the polymer degradation.

Assuming that endgroups are vinyl, the scheme (2) can be suggested [7, 8].

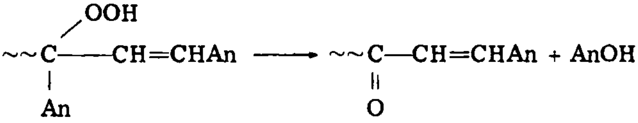


$$\sim\sim\underset{\mathrm{An}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH{=}CHAn}\xrightarrow{\mathrm{O_2},\ h\nu}\sim\sim\underset{\mathrm{An}}{\underset{|}{\overset{\mathrm{OOH}}{\overset{/}{\mathrm{C}}}}}-\mathrm{CH{=}CHAn} \qquad (2)$$

where

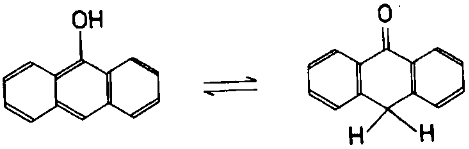
(An = )

followed by reaction (3).



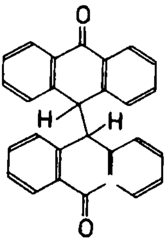
$$\sim\sim\underset{\mathrm{An}}{\underset{|}{\overset{\mathrm{OOH}}{\overset{/}{\mathrm{C}}}}}-\mathrm{CH{=}CHAn}\longrightarrow\sim\sim\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{CH{=}CHAn}+\mathrm{AnOH} \qquad (3)$$

From the tautomeric equilibrium (4)



(4)

anthrone is obtained. We have studied the behavior of anthrone in the degradation conditions used for the polymer and have observed that after a few hours it was changed into a mixture of anthraquinone and bis(10-anthronyl)(III) which then oxidizes into anthraquinone



III

This mechanism is supported by infrared spectrography. Undegraded polymer exhibits a band at 1625 cm^{-1} (vinyl endgroup). This band disappears when the degradation occurs and is replaced by a band at 1675 cm^{-1} (CO group) and a band at 1605 cm^{-1} (vinyl group conjugated to a CO group).

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