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Topokinetics of the Polyene Formation in Poly(Vinyl Chloride) Films during Treatment with Nonoxidative Plasma

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Changes of the physical and chemical structure of a polymer solid during plasma treatment are mainly caused by two processes: the collision of ions, electrons and other particles with the polymer surface and the ultraviolet irradiation emitted by the plasma gas and absorbed by the polymer. The former process is limited to a very thin surface layer (only a few nanometers thick,¹ whereas the latter usually leads to a significant depth profile (up to $10\ \mu\text{m}^{1,2}$ or even more),³ depending on the kind of the plasma and the polymer investigated.

KEY WORDS Kinetics, poly(vinyl chloride), film, plasma

BACKGROUND

The ultraviolet irradiation emitted by the plasma consists of uv-B and uv-A irradiation and of a very strong uv-V (vacuum) irradiation in the range of $20\ \text{nm} < \lambda < 200\ \text{nm}^{2,4}$ causing $\sigma\text{-}\sigma^*$ excitation of the main chain bonds of the polymer. The penetration depth of uv irradiation depends not only on the absorption coefficient of the virgin polymer, but also on the absorption coefficient of the nonvolatile degradation products formed in the polymer. In the case of plasma treatment of poly(vinyl chloride) (PVC), the latter effect may be of great importance because the main degradation product in a nonoxidative atmosphere contain conjugated double bonds that absorb strongly in a broad spectral region from uv-V to uv-VIS. Thus, the expected main absorption bands of isolated double bonds, dienes and trienes are 158 nm, 235 nm and 285 nm, respectively, and the corresponding absorption coefficients in degraded PVC films are of orders of magnitude $20000\ \text{cm}^{-1}$, $70000\ \text{cm}^{-1}$ and $110000\ \text{cm}^{-1}$. For this reason, uv/VIS-spectroscopy is a widely used and is a very sensitive detection method for degradation processes in PVC.

The aim of this paper is to compare the time-dependence and the depth profile of polyene formation during treatment of PVC films using different nonoxidative gas plasmas (H_2 , Ar, NH_3). Figure 1 shows formation of polyenes with conjugation length up to about 10 (corresponding to $\lambda_{max} = 450$ nm) after only 15 min of plasma treatment. The sequence length distribution of the polyenes (as represented by the shape of the uv/VIS-spectra) seems to be independent of the kind of the plasma gas and corresponds to that of the photolytically and chemically initiated degradation of PVC below the glass-transition temperature.⁵ However, in the case of the plasma-treated films, the uv/VIS-spectra are without any fine structure, thus indicating a high degree of dehydrochlorination in a thin surface layer (some cross-linking cannot be excluded also).

The time-dependence of the polyene formation (for example, the formation of trienes; Figure 2) shows two characteristic stages: after a fast initial period the process is considerably retarded, or even stopped. Such a kinetic behavior is to be observed, if an irradiation initiated degradation process immediately leads to the formation of absorbing reaction products (self shielding effect). A strong quantitative comparison between the efficiency of the three plasma gases to initiate polyene formation in PVC is not possible, because there is only little knowledge on the emission spectra of the plasma gases and the absorption coefficients of polymers in the vacuum uv region. Nevertheless, according to our results the following relationship of this initiation efficiency is valid: $H_2 > NH_3 > Ar$. This result agrees with a conclusion drawn in a recent paper,⁶ that among nonpolymer-forming gases H_2 is most effective in preventing volatilization of plasticizer due to surface cross-linking by plasma treatment of flexible PVC sheets.

As mentioned above, the uv/VIS-spectra indicate the formation of a high con-

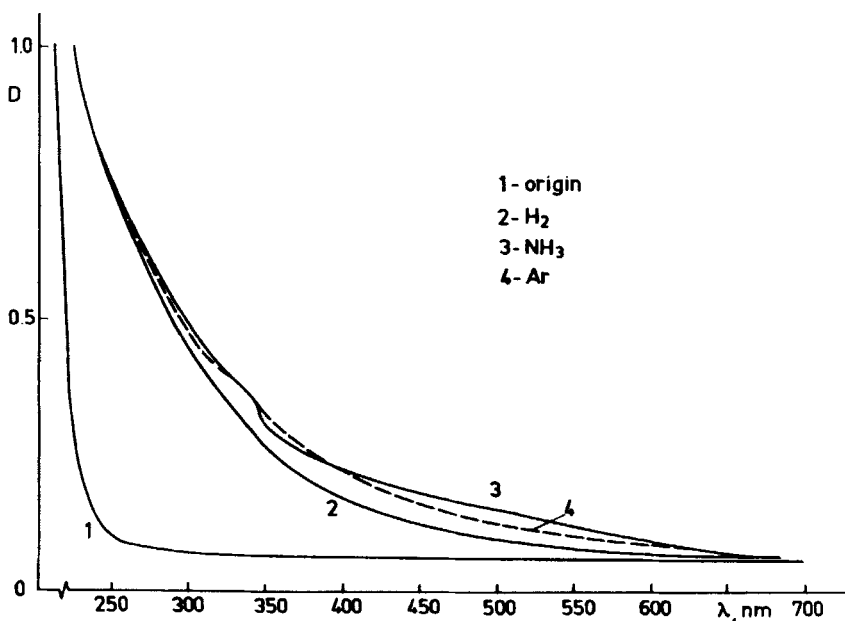


FIGURE 1 UV/VIS-spectra of PVC films (20 μ m) after 15 min of plasma treatment.

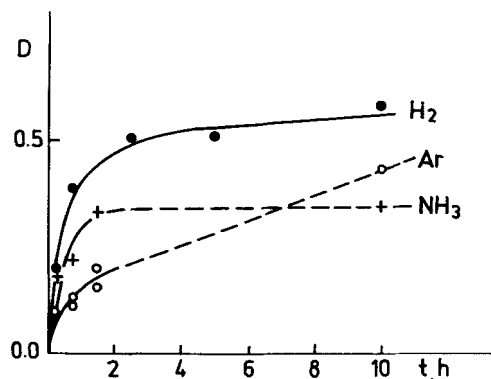


FIGURE 2 Time-dependence of the absorption at 285 nm of a PVC film (20 μm) during plasma treatment.

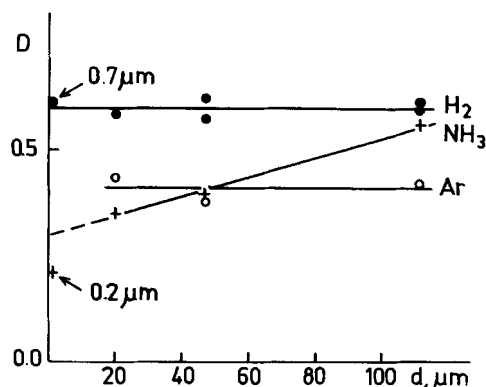


FIGURE 3 Absorption at 285 nm of PVC films after 10 h of plasma treatment in dependence on the film thickness.

centration of polyenes in a thin surface layer. To get more information on the depth profile we investigate PVC films of various thickness, keeping the conditions of plasma treatment constant (Figure 3). In the case of the H₂-plasma the overall absorption does not depend on the film thickness, i.e., the thickness of degraded layer is less than 1 μm . A similar conclusion should be drawn in the case of the Ar-plasma. However, in the case of the NH₃-plasma the absorption is nearly linear to the film thickness, thus indicating a uniform distribution of the formed polyenes even in a 100- μm sample. We have no definite explanation for that surprising effect. In some aspects it is possible to assume that the thermal exposure of the sample may be higher in the case of the NH₃-plasma because of the greater number of different particles that collide with the sample surface.

EXPERIMENTAL

The investigated films ($\geq 20 \mu\text{m}$) are prepared by casting a solution of PVC (a commercial suspension polymerized Scoviny S, VEB Buna-Werke, GDR) in 1,2-

dichlorethane on a glass plate. The thin films ($<1 \mu\text{m}$) are obtained by slow drawing out of a quartz plate from a concentrated PVC solution.

The plasma treatment is performed using a dc glow discharge with an energy density of about 5 W per cm^2 electrode area and at a pressure of 6 Pa. The samples were located on a frame made from glass and rotating across the discharge zone (floating potential).

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