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ELECTROCHEMICAL INITIATION OF SURFACE DEHYDROHALOGENATION OF POLYVINYLCHLORIDE FILMS

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ABSTRACT

The possibility of indirect electrochemical dehydrohalogenation of polyvinylchloride (PVC) at the sacrifice of the reduction products of acetonitrile has been established and realized. A possible mechanism has been proposed. The described process may be used as the method of PVC surface dehydrohalogenation to obtain the semiconducting layers on the film surfaces.

INTRODUCTION

It is known that PVC is subjected to dehydrochlorination by action of various chemical agents and energetic exposures of different nature. This process is followed by formation of polyconjugated multiple bonds system [1]. The resulting material like the majority of polymers with the conjugated system possesses semiconducting properties and may be used in electrical engineering, microelectronic, etc.[2]. Of special interest is the creation of polyconjugated structures on PVC film surface from the point of view of possibility to obtain two-layer material with thin surface conducting layer and to retain physico-mechanical properties of PVC.

Such material has been achieved through the dehydrohalogenation of PVC film surface by electrochemical initiating process and reported here.

MATERIALS

The suspended PVC with the molecular weight $4 \cdot 10^4$ was used. The employed reagents were purified by procedures described in the literature: acetonitrile [3], tetrahydrofuran [4], tetrabutylammonium perchlorate (TBAP) [5]. The films for investigations (thickness 60 μm) were formed from the solution of PVC in tetrahydrofuran.

METHODS

Electrolysis of 0.05 M TBAP in acetonitrile was carried out under controlled potential within the interval of E values $-(1.8 \div 2.2)$ V (vs S.C.E.) in argon during 1 hr. The two-chamber sealed cell with cathodic and anodic spaces separeted by a Schott filter was used for this procedure. The platinum plates were used as the electrodes. The PVC film was placed in cathodic space before or after electrolysis. Then the films were dried in vacuum, their surfaces were investigated by infrared reflection absorption spectroscopy (IRRAS) with the spectrometer Specord M80. The PVC films and catholyte solution were studied by UV-spectroscopy with the spectrometer Specord M400. The specific surface conductivity of films was measured by two-probe method with the aid of high-ohmic voltmeter B7-26. The test for rupture strength was carried out with rupture machine RM-250.

RESULTS AND DISCUSSION

During the electrolysis the PVC film has been changing colour to dark-brown*. The investigation of PVC surface by IRRAS showed the considerable decreasing ofabsorption band intensity in the area of 600-700 cm^{-1} characteristic to the valency oscillation of C=C conjugated bonds [6] (fig.1). UV-spectrum of such PVC film is characterized by absorption curve in 280-600 nm area (fig.2) typical to the polyene structure [7].

During the electrolysis the catholyte solution also has been changing: its colour becoming yellow-brown, the absorption in 280-500 nm area in UV-spectrum appe-aring, the relative viscosity of solution increased by 5%. Perhaps, these changes take place due to removing of acetonitrile soluble low-molecular products of PVC reduction to catholyte.

The enumerated facts attest that during the electrolysis the PVC film surfaces layer is being subjected to dehydrochlorination. This process is followed by formation of polyconjugated C=C bonds, destruction and passing of low-molecular fragments to solution. Since the film was in solution and did not touch the cathode, we suppose that the process of dehydrohalogenation was initiated by anions $[CH_2CN]^-$, the possibility of their formation during the cathodic reduction of acetonitrile was shown [8].

The measuring electrical conductivity of the films subjected to electrolysis and dopped in iodine vapour was equal to $10^{-7}\,\Omega^{-1}cm^{-1}$. However, the conductivity of different parts of film is unequal. It is connected with changes during the electrolysis in concentration of particles initiating the

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*** Any changes of the controle PVC film after 1 hr of exposure in 0.05 M TBAP in acetonitrile was not fixed by UV- and IR-spectroscopy.**

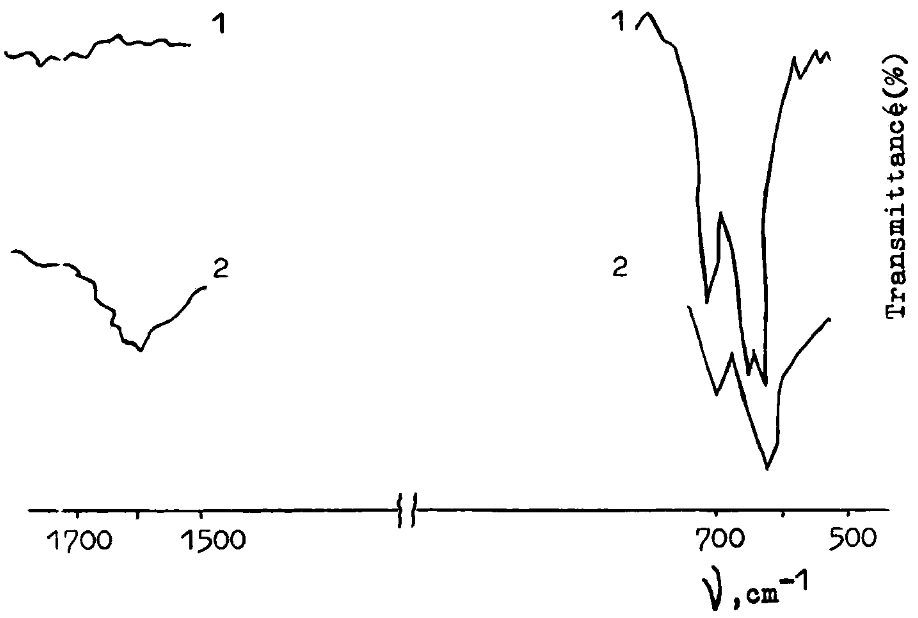


Fig.1. IRRAS of PVC films: (1)-starting, (2)-treated during electrolysis in catholyte (0.05 M TBAP in acetonitrile).

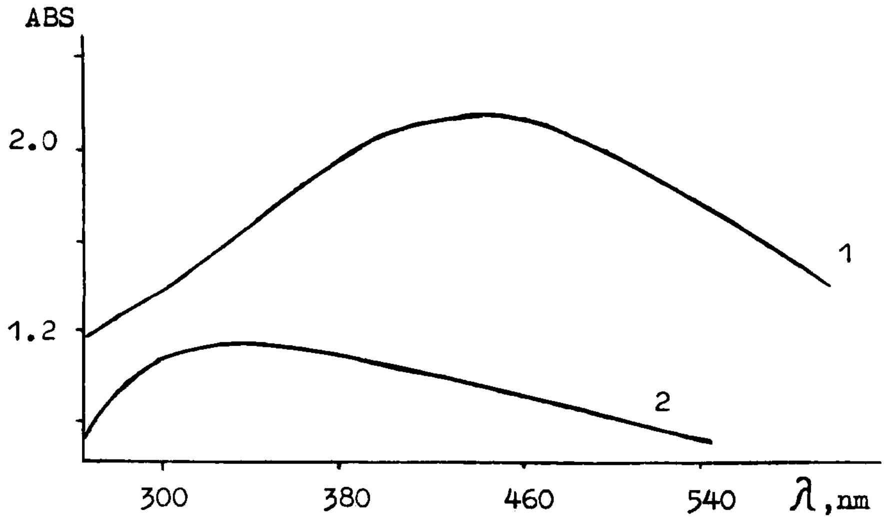


Fig.2. UV-spectra: (1)-PVC film after electrolysis in 0.05 M TBAP in acetonitrile, (2)-catholyte solution after removing PVC film.

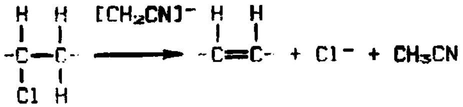
dehydrochlorination and correspondingly with the changes in intensity of their action on film surface. We suppose that the uniformity of the film properties would be higher if the film is treated by the electrolyzed catholyte. Such effect was established in DMFA [9]. Really, the changes which take place in PVC film treated by electrolyzed catholyte are analogous to the changes occured in film during electrolysis : turning dark-brown and UV- and IR-spectra of this film being similar to the described above.

The advantage is that the conductivity of the film producing by such way is equal over all surfaces.

The phisico-mechanical tests of the films with electrochemically dehydrohalogenated surfaces showed that the rupture strength of such treated films with thickness 60 μm is decreased by no more 10%.

So the possibility of indirect electrochemical dehydrohalogenation of PVC at the sacrifice of the reduction products of acetonitrile has been established and realized. It is supposed that $[CH_2CN]^-$ interact with PVC macromolecules, which leads to dehydrohalogenation and formation of multiple bonds:

$$2\ CH_3CN \xrightarrow{\bar{e}} 2\ CH_2CN^- + H_2\uparrow$$



$$-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \xrightarrow{[CH_2CN]^-} -\overset{H}{C}=\overset{H}{C}- + Cl^- + CH_3CN$$

The described process may be used as the method of PVC surface dehydrohalogenation to obtain the semicon-ducting layers on the film surfaces. The advantages of this process over well-known methods are better thermo-, photo-, dehydrohalogenation by action of alkails, etc. The indirect electrochemical dehydrohalogenation is realized in comparatively soft conditions at room temperature (that keeps side effects minimum). This approach permits to process only polymer surface and to obtain semiconductor layers practically without changes of shape and physico-mechanical properties of starting polymer.

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