

# Corona inhibition by photochemical dissolution of Al films by polymeric composition

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Received 27 June 2000; accepted 12 September 2000

## Abstract

Conductivity dependence on time for the 'exposed to ultra-violet light' polymeric composition of poly(*N*-epoxypropylcarbazole) (PEPC) with CBr<sub>4</sub> on Al film substrate was measured. Photochemical reaction takes place under ultra-violet irradiation, which leads to dissolving of vacuum deposited Al film and organometallic complexes formation in polymer bulk. Inhibition of Al dissolving by positive corona charge of outer polymer surface was found. © 2001 Elsevier Science B.V. All rights reserved.

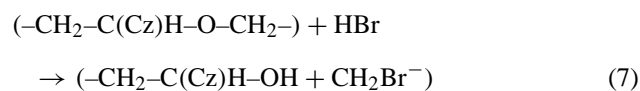
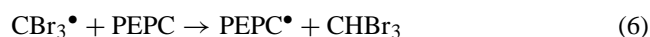
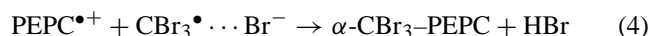
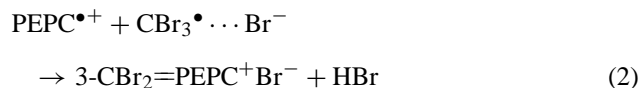
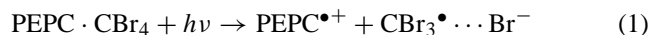
*Keywords:* Dark discharge; Photochemical reactions; Metal etching; Organometallic complex; Conducting polymers

## 1. Introduction

In our previous papers, we considered dry etching of metallic (Bi, Al, Cu and Ni) films [1–3] by intermediate and final photolysis products formed in polymeric layers deposited onto these films. It was established that photochemical etching of metallic films is due to its dissolving in exposed polymeric layers [4]. In the practical aspect, photochemical doping of polymers with organometallic compounds can be used to prepare the layers containing conducting latent image that can be visualized by toner and multiply reproduced by electrographic master. In the present work it is established that corona charging during dark conductivity measurements by electrographic technique can lead to inhibition of metal film dissolution in polymeric layers.

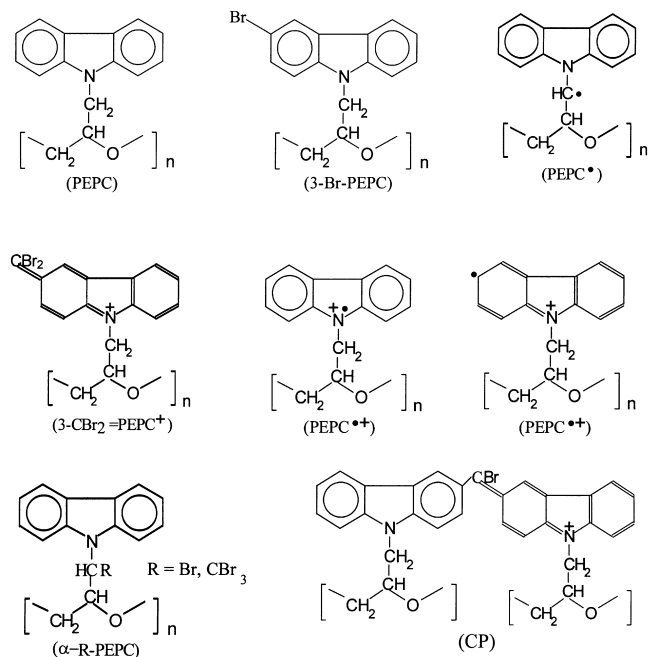
A weak charge transfer complex (PEPC·CBr<sub>4</sub>) between the carbazolyl group of PEPC as the donors and CBr<sub>4</sub> as the acceptor is formed at introduction of the electrophilic additive CBr<sub>4</sub> to poly(*N*-epoxypropylcarbazole)

(PEPC). The complex has a maximum in absorption spectrum in UV-region at  $\lambda = 405$  nm [5,6]. Photoexcitation of the complex results in the formation of a radical PEPC<sup>•</sup>, acid HBr, bromoform CHBr<sub>3</sub>, etc. [5] by reactions, which, following analogy with the reaction of CBr<sub>4</sub> with poly(*N*-vinylcarbazole) described in the paper by Smets et al. [6], may be written as

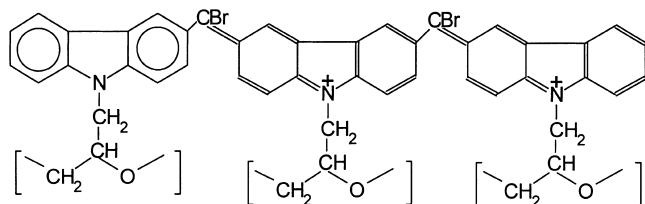


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where



An absorption band arises thus with a maximum  $\lambda = 670$  nm [7] which must be attributed to the formation of coloured product. Dark interchain reactions also occur [5,7], resulting in electronic reorganization in carbazoyl groups and formation of new, various conjugated configurations of interconnected carbazoyl groups. The extended tail in low energy area up to 2000 nm was attributed to the formation of dication of structure [5]:



Acids formed by reactions (2)–(5) and (7), etch the vacuum deposited aluminium layer and form intermediate aluminium-containing compounds in the interface zone [10]:



Then follows slow (some hours) moving of aluminium compounds inside of the polymer layer as a result of organometallic complexes formation [1–3]. These complexes can serve as generation or/and transport centres for charge carriers [4].

## 2. Experimental

Polymeric composition consisting of a solution of PEPC (2 wt. parts) and  $\text{CBr}_4$  (1 wt. part) in chloroform was spin

cast on the poly(ethylene terephthalate) (PET) substrate, on which the semitransparent aluminium (Al) layer was previously thermally deposited using a vacuum chamber. The obtained samples after drying in the dark in air at room temperature, were exposed to light of a mercury lamp HPQ 125 W. The radiation intensity was  $0.01 \text{ W/cm}^2$ . The exposure time was 1 h. The thickness of the polymeric layers was  $\sim 0.5 \mu\text{m}$ .

The electrographic curves of surface potential decay were measured using an electrometer TR-84M (Takeda Riken). The experiment was performed in air. Samples  $\sim 1.0 \times 1.0 \text{ cm}^2$  were charged by a negative or positive corona. The potential saturation level of 80–90% was reached during time interval of  $\sim 5$  s. The charge source comprised six parallel fine wires 0.05 mm in diameter placed at a distance of  $\sim 7$  mm from the sample. Voltage 7 kV was applied to these wires. A screen grid at a potential of  $\sim 450$  V was placed between the wires and the sample. The Al residue that remained after photochemical etching of the aluminium film was used as a ground electrode. After corona charging the sample was electromechanically removed from the coronator and placed before the wire probe of electrometer. The conductivity of the layer was determined by surface potential decay using formula  $\sigma = \epsilon\epsilon_0 \ln 2/\tau_{1/2}$  (S/cm), where  $\tau_{1/2}$  is the surface potential half-decay time. The optical spectra were registered using a spectrophotometer DU-7 (Beckman). Absorption optical density (OD) of aluminium film at  $\lambda = 830$  nm is linearly proportional to the thickness of the aluminium layer:  $d$  (nm) =  $16.2 \text{ OD}$  [1]. Thus, the decrease of optical density of the layer at  $\lambda = 830$  nm from the initial value  $\text{OD}_0$  down to OD as a result of photochemical etching means reduction of thickness of the aluminium film by  $\Delta d$  (nm) =  $16.2(\text{OD}_0 - \text{OD})$ .

## 3. Results and discussion

The conductivity increased from  $10^{-16}$  to  $10^{-13}$  S/cm due to ultra-violet light irradiation of the samples Al/PEPC +  $\text{CBr}_4$ . After this, first rapidly and then slowly, the conductivity decreased during several days of storage after switching-off the irradiation. The conductivity was estimated from surface potential decay curves of positive or negative corona charged samples. If only the negative corona was used and the samples were not charged by positive corona, some increase of the conductivity in a day or two of the storage in the dark was observed. The thickness of the aluminium film also decreased, as it was seen from optical density measurements. The initial increase of conductivity is associated with formation of holes by photoreaction (1), and the decrease — with consumption of radical cations by reactions (2), (4) and (5). The subsequent increase of the conductivity in a day or two of the storage in the dark, as it is known [4], is associated with dissolution of aluminium and formation of organometallic complexes.

It was revealed, that the noticeable changes of the conductivity value occur with increase of the number of the conductivity measurements carried out. That is, the conductivity depends on the number of positive corona charging and subsequent discharging of the sample. The effect, however, did not take place for the negative corona charging.

The dependence of optical density of the samples at  $\lambda = 830$  nm and conductivity on the number of positive corona charging are shown in Fig. 1. The measurements were carried out on the fourth day after the exposure of the samples by ultra-violet light.

After exposure for an hour by ultra-violet light, optical density of the samples at  $\lambda = 830$  nm decreased by some percentage, that indicates partial etching of the aluminium already during the exposure.

All samples were divided into four groups. The first group (I) containing the samples was charged by positive corona and discharged from 6 to 10 times within an hour at once after the exposure by ultra-violet light (strongly inhibited samples). In the second group (II), the samples were charged two times (poorly inhibited samples). In the third group (III) the samples were charged once (very poorly inhibited samples). And some of the samples (IV) were not inhibited by positive corona at all. As it is seen in Fig. 1, optical density at  $\lambda = 830$  nm of the non-inhibited samples in comparison with the inhibited ones, that is, the thickness of the layer of aluminium after 4 days of storage decreased by more than 25%. But the difference in conductivity for this time has reached one order.

In Fig. 2 the dependence of optical density at  $\lambda = 830$  nm on the storage time in darkness for the four groups of the exposed samples is presented: curves 1, 2, 3 and 4 for groups I, II, III and IV, respectively. For group I the insignificant increase of optical density at  $\lambda = 830$  nm within the second and third day of storage in darkness is observed. It is associated with the formation of a coloured product (CP) as a result of photolysis of PEPC with  $\text{CBr}_4$ . CP has a broad

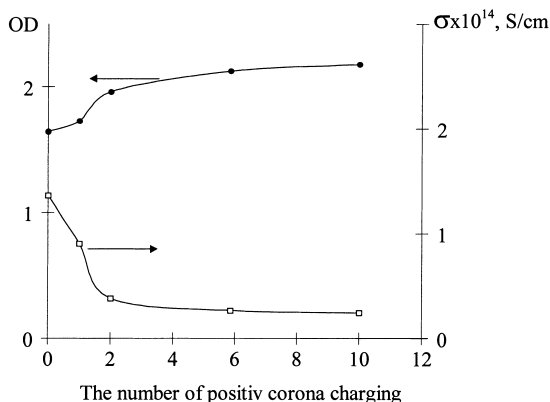


Fig. 1. Dependence of optical density of samples at  $\lambda = 830$  nm and conductivity of layers PEPC +  $\text{CBr}_4$  on the number of positive corona charging; the measurements were carried out at the fourth day after the exposure to UV light.

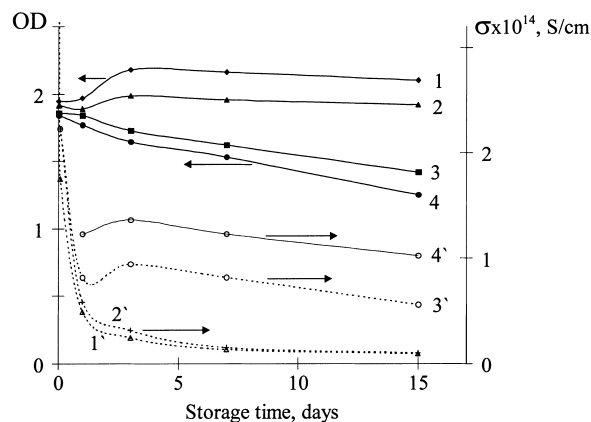


Fig. 2. Dependencies of optical density at a wavelength of 830 nm and conductivity changes on the storage time in darkness for four groups of samples: (1, 1') for I group; (2, 2') for II; (3, 3') for III; and (4, 4') for IV group.

absorption band at  $\lambda_{\text{max}} = 476$  nm and a weak absorption band at  $\lambda_{\text{max}} = 670$  nm [5,7]. The tail of absorption in low energy area is spreading up to  $\lambda = 2000$  nm [5]. For IV group the formation of CP also occurs. The decrease of optical density at  $\lambda = 830$  nm with the time for the III and IV samples is caused by effective dissolution of aluminium by the polymeric composition. The formation of organometallic complexes increases the dark conductivity of polymeric layers. That is, simultaneously with the fall of conductivity for the I and II group of samples (curves 1' and 2'), there is a growth of conductivity during the second and third days due to the formation of organometallic complexes for groups III and IV of samples (curves 3' and 4' in Fig. 2).

As inhibition is associated with positive corona charging but not negative, the process can be caused by using aluminium film as a cathode. The interaction of injected electrons with radical cation  $\text{PEPC}^{\bullet+}$  must lead to inhibition of formation of both the CP and the acid, and consequently to terminating the first step of Al dissolution (8). The interaction of electrons with the intermediate aluminium containing compounds



can only cut-off the organo-aluminium complex production but does not exert influence on the CP formation.

The change of optical density at  $\lambda = 830$  nm for the inhibited samples is due to the CP formation only (see curve 1 in Fig. 2). But for the non-inhibited layers it is concealed by the diminution of optical density due to dissolving the Al film. The conductivity change of the non-inhibited layers reveals two processes: the first is associated with the consumption of radical cations by reactions (2), (4) and (5), that is with the reduction of a hole concentration and the second with the formation of organometallic complexes (see curves 3 and 4 in Fig. 2). The inhibited layers show only reduction of conductivity (see curves 1' in Figs. 2 and 3). Therefore the approximate coincidence of kinetics of the formation of

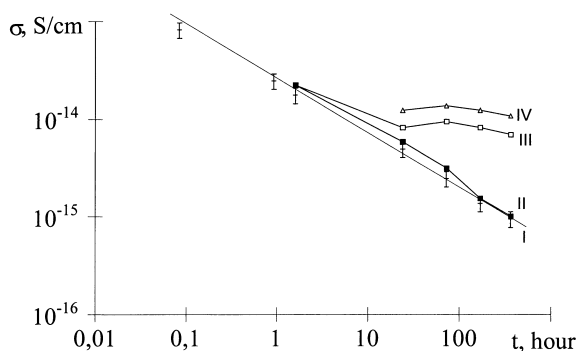


Fig. 3. Dark conductivity decay curves after the termination of exposition to ultra-violet light for four groups of samples.

organometallic complex and CP (curve 1 and curve 4' in Fig. 2) allows one to make an assumption, that organometallic complex has a structure of CP·Al.

In accordance with common conceptions, it is within reason to suggest that the  $-N<$  containing PEPC fragment and  $-OH$  containing  $-CH_2-C(Cz)H-OH$  fragment produced in reaction (7) participate in the formation of organo-aluminium complex.

To determine kinetics of the conductivity, curves 1'–4' are presented in a log–log scale in Fig. 3. The slope of the conductivity decrease for the I group of samples is  $\alpha \approx 0.6$ . That is, the conductivity obeys the dependence:  $\sigma \propto t^{-\alpha}$  where  $t$  is the storage time after switching-off the UV-exposure and  $\alpha$  the so-called dispersive parameter. Such dependence is within the framework of the theory of Arkhipov–Rudenko, which describes drop of photoconductivity after a step generation of charge carriers [8] and which was observed by us earlier in poly-hydroxyamino esters [9]. For the group III and IV samples the time dependence of conductivity is definitely a competition between the drop described by the above expression and the increase of conductivity due to formation of organometallic complexes.

The time dependence of the absorption spectrum was measured to evaluate the kinetics of the coloured product and organometallic complex formation in the polymeric composition PEPC + CBr<sub>4</sub>. Some curves are presented in Fig. 4. The curves 1–4 represent absorption spectra of polymeric composition PEPC + CBr<sub>4</sub> spin cast onto PET substrate without Al film (first set). Curve 1 represents spectrum before exposition to ultra-violet light; curve 2, at once after 10 min exposition to UV light with  $\lambda = 365$  nm of a mercury lamp; curve 3, after 20 min of storage; and curve 4, after 4 h of storage. The curves 1'–5' represent absorption spectra of polymeric composition PEPC + CBr<sub>4</sub> spin cast on PET substrate with previously vacuum deposited semitransparent Al film (second set): 1', before exposition to UV light; 2', 20 min after 10 min exposition to light with  $\lambda = 365$  nm; 3', after 1.5 h of storage; 4', after 4 h of storage; and 5', after 24 h of storage when Al film is appreciably dissolving in the polymer.

Immediately after UV-light exposure, a complex spectrum arises for polymeric composition PEPC + CBr<sub>4</sub> on PET

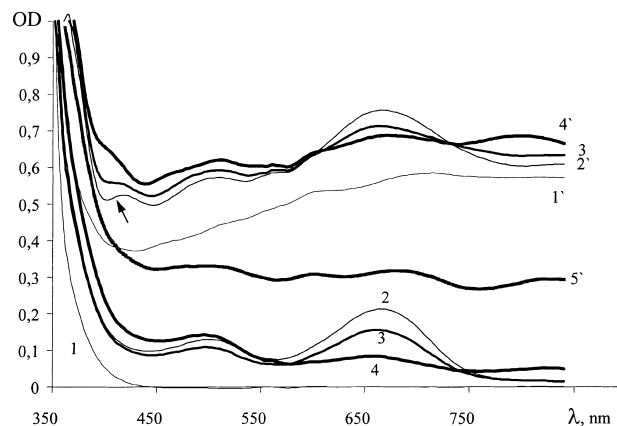


Fig. 4. A set of spectrum curves for optical density of a spin cast polymeric composition PEPC + CBr<sub>4</sub> on PET substrate without Al film (first set — untrimmed); and with previously deposited in vacuum semitransparent Al film (second set — primed): (1, 1') before exposition to ultra-violet light; (2) at once after 10 min exposition to ultra-violet light; (2', 3) 20 min after exposition to light; (3') after 1.5 h of storage; (4) after 4 h of storage; (5') after 24 h of storage.

substrate, and analogous situation is also observed for the composition with previously vacuum deposited semitransparent Al film. These spectra represent absorption spectrum of CP. During storage time the absorption band with  $\lambda_{max} = 655$  nm diminishes exponentially for both polymeric composition without Al film, and for the one with semitransparent Al film with the same time constant approximately equal to 6 h. Absorption at  $\lambda = 360, 500$  and  $800$  nm increases simultaneously with this until Al film dissolving ends. The kinetics of the absorption increase is the same for both polymeric compositions with and without semitransparent Al film.

The essential difference of the first set of spectrum from the second is marked by a cursor in Fig. 4. This absorption band in the spectrum should be assigned to complex CP·Al. As it is seen in Fig. 5, the maximum of this absorption band shifts first to the long wavelengths area from 410 nm up to 425 nm during first 50 min, then to the short wavelengths to 390 nm. The amplitude of this band increases

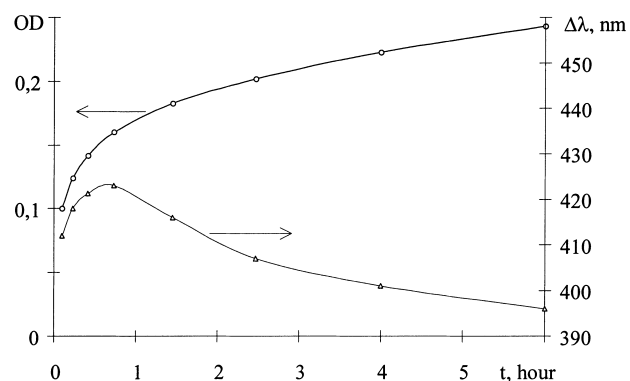


Fig. 5. Absorption band amplitude of organometallic Al complexes and its frequency shift as a function of samples storage time.

exponentially with the time constant  $\sim 1.3$  h during first 50 min, and also exponentially with time constant  $\sim 12$  h after 50 min. Therefore the formation of the organometallic complex has rather composite nature, and structure of the coloured product varies with time.

#### 4. Conclusions

1. Under irradiation by UV light of the polymeric composition PEPC + CBr<sub>4</sub> simultaneously with photochemical reactions the generation of mobile charge carriers occurs. The excess conductivity caused by these charges after switching-off the irradiation falls down according to a power law.
2. Photochemical reactions in polymeric composition PEPC + CBr<sub>4</sub>, lead to accumulation of the photoacid and the coloured product. The slow aluminium film dissolution in exposed polymeric layer in the presence of photoacid is associated with the formation of organometallic complex. The exposed areas of the polymer layer containing organometallic complex have higher conductivity. In the practical aspect, photochemical doping of polymers with organometallic compounds can be used to prepare the layers containing conducting latent image that can be visualized by toner and multiply reproduced by electrographic master.
3. The formation of the organometallic complex has rather composite nature, and coloured product varies with time.
4. Charging of polymeric layers by a positive corona just after exposure inhibits the aluminium film dissolution and consequently formation of organometallic complexes. The presumable mechanism of inhibition is associated with using the aluminium film as a cathode. It apparently

consists in the interaction of electrons with the intermediate aluminium-containing compounds in interfacial zone:  $Al^{n+}(H \cdots Br^-)_n + ne^- \rightarrow Al^0 \cdots (H \cdots Br^-)_n$ , which prevents the following organometallic complex formation.

#### Acknowledgements

The work was executed using financial support of the Russian Fund of Basic Researches (Project No. 99-03-32111) and the International Science and Technology Centre (Grant 872-98).

#### References

- [1] A.V. Vannikov, A.D. Grishina, M.G. Tedoradze, J. Photochem. Photobiol. A: Chem. 92 (1995) 223–228.
- [2] A.D. Grishina, M.G. Tedoradze, A.V. Vannikov, Sci. Appl. Photo. 38 (1996) 25–36.
- [3] A.D. Grishina, M.G. Tedoradze, A.V. Vannikov, Sci. Appl. Photo. 38 (3) (1997) 283–296.
- [4] A.D. Grishina, M.G. Tedoradze, O.V. Kurii, V.A. Kolesnikov, A.V. Vannikov, Sci. Appl. Photo. 39 (4) (1998) 321–328.
- [5] O.V. Kolniov, V.V. Kolesnikova, V.K. Milinchuk, Polymer Sci. USSR A 32 (3) (1990) 413–419.
- [6] G.J. Smets, J. Thoen, A. Aerts, J. Polym. Sci.: Sympos. 51 (1975) 119–134.
- [7] O.V. Kolniov, V.K. Milinchuk, E.G. Strukov, V.V. Kolesnikova, Polym. Sci. USSR A 22 (9) (1980) 2042–2049.
- [8] V.I. Arkhipov, J.A. Popova, A.I. Rudenko, Phil. Mag. B 48 (5) (1982) 401–410.
- [9] V.A. Kolesnikov, A.V. Sterlikova, A.D. Grishina, A.V. Vannikov, Sci. Appl. Photo. 39 (2) (1997) 173–181.
- [10] A.D. Grishina, M.G. Tedoradze, V.A. Kolesnikov, M.A. Brusentceva, A.V. Vannikov, High Energy Chem. 33 (1999) 457 (In Russian).