# Formation of poly-*p*-phenylene thin films and their composites with fullerene by discrete evaporation in vacuum

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The effect of parameters of discrete evaporation of poly-*p*-phenylene (PPP) and $C_{60}$ on quality of the films formed was studied. PPP and PPP/$C_{60}$ composite films and heterostructures based on these materials were prepared. It was established that the conjugation length of PPP macromolecules consists of ~9—10 units, and they can be electrochemically transformed into the radical cation state at a potential of 2.10 V. Glassy carbon—PPP—$C_{60}$—Al heterostructures with a rectification ratio of $10^6$—$10^8$ were formed.

**Key words**: poly-*p*-phenylene, vacuum deposition, diode, fullerene.

Preparation of thin films of poly-*p*-phenylene (PPP) and its composites (heterostructures) with fullerene is of interest due to the possibility of creating diodes and photodiodes based on these materials. In recent times, great attention has been given to electroluminescent diodes with blue luminescence and the $SnO_2$—PPP(or its derivative)—Al structures[1] and $SnO_2$—PPP—$C_{60}$—Al type heterostructures with the properties of diodes and photodiodes.[2] In addition, it is promising to create composite films based on conducting polymer—fullerene systems and $SnO_2$—composite—Al photodiodes. The photosensitivity of these elements with conducting polymer based on polythiophene and polyphenylenevinylene derivatives is compared to that of photodiodes based on silicon.[2]

Unlike polyphenylenevinylenes, PPP in the pure form is an insoluble material. Therefore, a technique of its deposition by discrete evaporation *in vacuo* has been suggested previously.[3] In this work, the effect of conditions of evaporation on quality of polymer films of poly-*p*-phenylene and fullerene and their composites was studied. The preliminary data on properties of heterostructures with fullerene with a high rectification ratio of $10^6$—$10^8$ were obtained.

## Experimental

Poly-*p*-phenylene was obtained by polymerization of benzene in the presence of $AlCl_3$ and $CuCl_2$ taken in a ratio of 2 : 1 at 35 °C according to the known procedure.[4] The polymer was subsequently washed with 5 *M* HCl, water, and acetone, dried in air, and heated *in vacuo* at 50 °C.

Fullerene containing 99% of the main substance was used without preliminary purification. Its purity was monitored by the IR spectrum (KBr), $\nu$/cm$^{-1}$: 1429, 1182, 576, and 527.

The equipment for discrete evaporation *in vacuo* (Fig. 1) includes a quartz evaporator *1*, a detachable block with substrates *2*, and a heater *3*. The polymer powder was injected through a quartz funnel *4* passed through a hole in the heater. The velocity of injection of the powder was monitored by the frequency of mechanical vibration of a feeder *5*.

IR spectra of the initial PPP were recorded on an IKS-29 spectrometer as pellets with KBr; pastes based on nujol were prepared from the material of the films. Similar pastes were used for recording absorption of the PPP powder in the visible and UV spectral regions on a Specord M-40 spectrophotometer. Absorption of polymer films in the UV region was determined directly on substrates of optical quartz.

To exclude background currents at high potentials, the oxidation potential of PPP was determined by the change in the transmission coefficient (at $\nu$ = 12000 cm$^{-1}$) of a long-wave absorption maximum appearing upon transformation of the polymer to the radical cation state.[6] Electrochemical studies were carried out in a quartz electrochemical cell in an argon atmosphere using a PI-50-1 potentiostat. The cell was placed in a window of the Specord spectrophotometer in such a way that light would pass through the quartz windows and the polymer film would be deposited on a transparent conducting electrode of tin dioxide on quartz. The resistance of the electrode was 20—30 Ohm cm$^{-1}$.

To estimate the properties of the heterostructure, a PPP film ~100 nm thick was deposited on the lower conducting electrode. Then fullerene was deposited as squares 2×2 mm$^2$ in size by evaporation through a screen. Aluminum as circles 1 mm in diameter was deposited on fullerene also through the screen. The top current lead was provided by a standard clamping electrode, whose surface was covered with a thin silver film to improve contact.

## Results and Discussion

The velocity of injection of PPP and the temperatures of the evaporator and substrate have a substantial effect on the quality of the coverings formed. It can be seen from Table 1 that an increase in the temperature of the evaporator from 655 to 870 °C results in substantial

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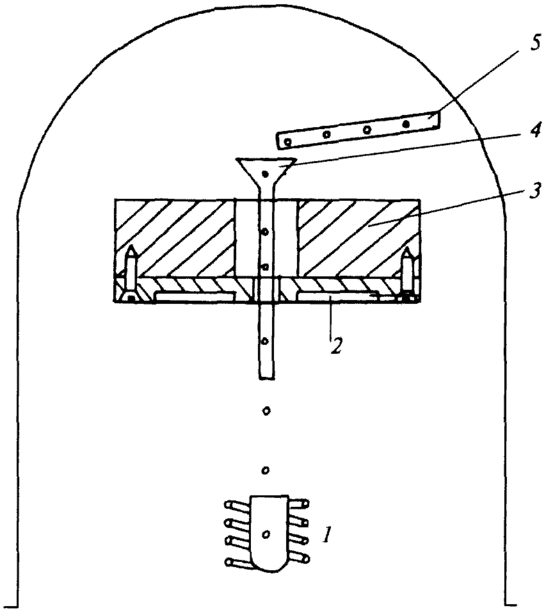

**Fig. 1**. Scheme of the installation for discrete evaporation *in vacuo*. *1*, evaporator, *2*, substrates, *3*, heater, *4*, quartz funnel, and *5*, feeder (transportation groove).

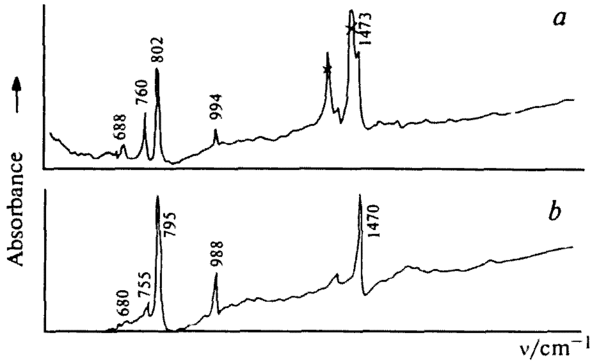

**Fig. 2**. IR absorption spectra of the material of films (*a*) and the initial PPP (*b*). Peaks of nujol are crossed.

worsening of quality of the films formed, and a decrease in the temperature to 500 °C decreases the efficiency of evaporation. An increase in the velocity of injection of the polymer from 9 to 97 mg $h^{-1}$ also has an unfavorable effect on the quality of PPP layers, which are porous and nonuniform at an excessive velocity of injection of the powder. A substrate temperature of ~100 °C is optimum for the formation of qualitative polymer layers. At higher temperatures of heating of a substrate in the range from 150 to 200 °C, PPP films evaporate at a noticeable rate. The optimum distance between the evaporator and substrate is 55 mm.

To determine the chemical composition of the films formed, the absorption spectra in the IR and UV regions of the initial and deposited PPP were compared. A set of bands in the IR spectrum (Fig. 2) indicates unambiguously that PPP is present both in the initial material and film. (The crossed peaks correspond to absorption of nujol.) Absorption at 1473 $cm^{-1}$ and a weakly pronounced peak at 1630 $cm^{-1}$ correspond to stretching vibrations of the carbon—carbon bonds of the aromatic ring, and the maxima at 802, 760, and 688 $cm^{-1}$ correspond to nonplanar vibrations of the C—H groups of di- and monosubstituted benzene ring. The existence of polyphenylene in the samples is also confirmed by a weak peak at 3030 $cm^{-1}$ corresponding to stretching vibrations of the C—H bond (not presented in the Figure). The spectra of the initial PPP and material of the film are almost identical, except for the ratio of intensities of absorption bands at 802, 760, and 688 $cm^{-1}$ corresponding to nonplanar vibrations of the C—H groups. A sharp shift of the maximum from 430 nm (23255 $cm^{-1}$, 2.9 eV) to 337 nm (29673 $cm^{-1}$, 3.7 eV) is observed in the UV region (Fig. 3).

The films obtained by discrete evaporation are thermally stable up to 150—200 °C, and their thickness decreases sharply as the temperature increases to 400 °C, which follows from the change in the optical density (Fig. 4).

Fullerene can be evaporated by both standard and discrete evaporation *in vacuo* in the temperature range

**Table 1**. Effect of parameters of discrete evaporation on quality of PPP films

| Number of experiment | $H$/mm | $T_1$/°C | $T_2$/°C | $t$/min | $h$/nm | $v$/mg $h^{-1}$ | Quality of films by their appearance |
|---|---|---|---|---|---|---|---|
| *1* | 55 | 660 | 75 | 50 | 71 | 20 | Good |
| *2* | 55 | 670 | 80 | 70 |  | 12 | Good |
| *3* | 55 | 655 | 85 | 25 | 24 | 13 | Excellent |
| *4* | 55 | 660 | 110 | 30 | 27 | 9 | Excellent |
| *5* | 35 | 665 | 87 | 85 | 110 | 12 | Good on quartz, rings |
| *6* | 55 | 720 | 77 | 23 | 135 | 45 | Satisfactory, rings, nonuniform films |
| *7* | 50 | 870 | 105 | 43 | 30 | 21 | Nonuniform films |
| *8* | 55 | 850 | 98 | 10 | 190 | 97 | Unsatisfactory |

*Note*. $H$ is the distance from the evaporator to the substrate; $T_1$ and $T_2$ are temperatures of the evaporator and substrate, respectively; $t$ is time of evaporation; $h$ is the thickness of films; and $v$ is the rate of evaporation. PPP with a particle size of 65—130 mm was used, vacuum was $5 \cdot 10^{-5}$ Torr.

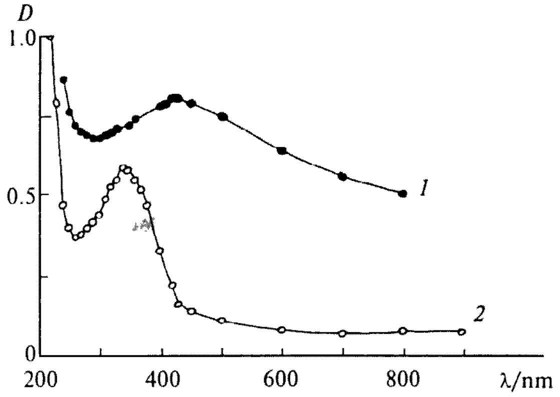

**Fig. 3.** UV absorption spectra of the initial PPP (*1*) and material of the film (*2*).

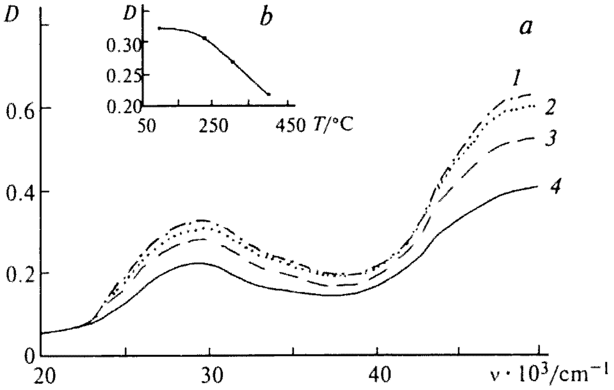

**Fig. 4.** *a.* UV absorption spectra of PPP films heated for 1 h at 100 (*1*), 200 (*2*), 300 (*3*), and 400 (*4*) °C. *b.* Temperature dependence of the optical density at 30000 cm$^{-1}$.

from 380 to 540 °C. A temperature of 400 °C is optimum, because fullerene is ejected from the evaporator at more intense heating. Several maxima (26800, 22700, 18500, and 15300 cm$^{-1}$) typical of fullerene are observed in the UV spectra of the layers formed. The quality of the PPP films and fullerene is sufficiently high, hence their thickness could be determined interferometrically without additional deposition of reflecting silver layers.

For preparation of composite PPP and fullerene films, the method of discrete evaporation was used at temperatures of the evaporator and substrate of 550 and 100 °C, respectively, velocity of injection of the mixture of 10—17 mg h$^{-1}$, evaporation time of 40—60 min, and distance between the substrate and evaporator of 55 cm. The content of fullerene in the initial mixture is 5, 10, 15, 20, and 30%, while in deposited composite films it is 21, 37, 44, 59, and 82%. The higher content of fullerene in the film compared to that in the initial composite is caused by incomplete evaporation of PPP and different rates of evaporation of components of the mixture.

An important characteristic of PPP is the oxidation potential of the film in acetonitrile, which is usually observed in the range of ~2 V relative to the standard Ag/AgCl electrode. Since this oxidation is accompanied by a change in color, the optical method of monitoring is used to exclude background currents. The change in the optical density at 12000 cm$^{-1}$ at different potentials is presented in Fig. 5.

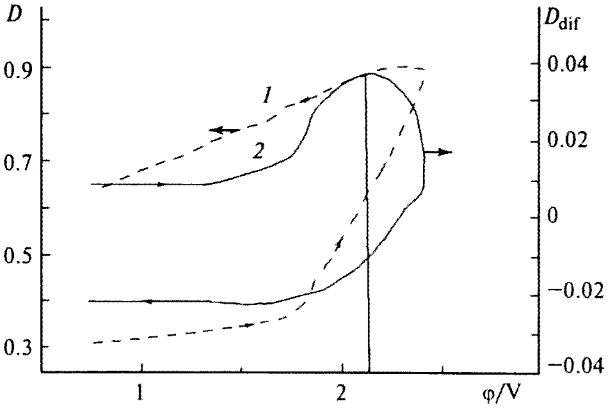

**Fig. 5.** Dependence of the optical density of the PPP film at 12000 cm$^{-1}$ on potential (*1*) and differential curve (*2*).

The curve obtained is integral relative to the classical electrochemical volt-ampere characteristic. Therefore, differentiation was performed (the Origin program followed by smoothing was used), the result of which is presented in Fig. 5. It follows from these data that the film formed can be transformed to the oxidized state, which, according to the available published data,[4] is a conducting radical cation salt.

The electric properties of the glassy carbon—PPP—$C_{60}$—Al structures are presented in Fig. 6. The unusually high value of the threshold potential ($\varphi \approx$ 10—15 V) should be mentioned. The dependence of the logarithm of current on potential consists of two linear regions. At high voltage, the direct currents are 6 to 8 orders of magnitude greater than the reverse currents, whose values do not exceed $10^{-12}$—$10^{-13}$ A cm$^{-2}$. The linear region of volt-ampere characteristics is shifted to lower voltage in the case of glassy carbon substrates.

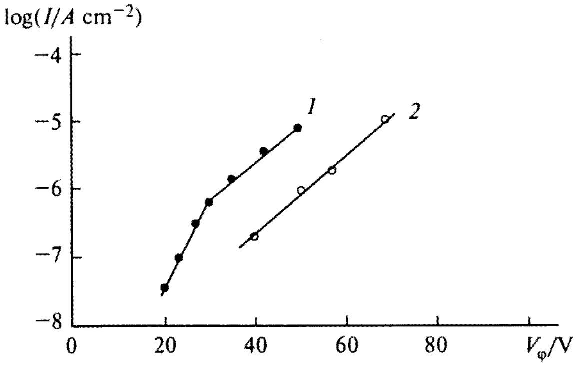

**Fig. 6.** Direct branch of the volt-ampere characteristic of glassy carbon—PPP—$C_{60}$—Al (*1*) and $SnO_2$—PPP—$C_{60}$—Al (*2*) heterostructures.

The results of optical studies indicate unambiguously that the films formed by discrete evaporation retain the PPP structure. At the same time, the shift of the absorption maximum in the UV spectrum[7] depends on the chain length according to the formula

$$E = 3.36 + 3.16/n \text{ (eV)},$$

where $E$ is the energy of a quantum corresponding to a peak in the absorption maximum and $n$ is the number of conjugated units in the chain. Thus it follows that molecules of evaporated PPP contain 9—10 conjugated units, which is the reason for the change in the ratio of intensities of nonplanar vibrations of the C—H bond in the IR spectra of the initial polymer and film. It is known[4] that the logarithm of the ratio of intensities of the peaks at 680 (or 760 $\text{cm}^{-1}$) and 800 $\text{cm}^{-1}$ depends on the length of the PPP chain.

The character of absorption spectra of the films does not change after heating to 400 °C (see Fig. 4), which indicates the unchanged character of the molecular-mass distribution of the film upon heating. At the same time, heating of PPP higher than 250 °C makes it possible to remove microadmixtures,[6] which can be introduced into a sample during polymerization and can be retained in the polymer during evaporation. Thus, annealing of the film allows one to obtain a more clean material and to vary its thickness toward lower values.

Evaporation of the polymer can occur both by breaking of the PPP chains followed by the interaction of residues on the substrate or due to evaporation of oligomer admixtures, which can exist in the initial material. Taking into account the wide spectral range of the initial polymer, it could be supposed that oligomers are already present in the PPP powder and they evaporate upon heating. It should be taken into account that the films evaporate *in vacuo* even at 200 °C, while, according to TGA data, mass loss begins at 430 °C, which points to the destructive character of evaporation of PPP.

The dependences of the optical density on the potential for the direct and reverse curves substantially differ, which is associated with irreversibility of the electrochemical oxidation of the films. This irreversibility can have a purely electrochemical character, *i.e.*, it can be caused by a low diffusion coefficient of an anion of an electrolyte in the film or by a low rate constant of electron transfer through the interface. However, the interaction of highly reactive PPP radical cations with microadditives of water or other substances in an electrolyte also cannot be excluded.

The distinctive specific feature of volt-ampere characteristics (VAC) of heterostructures based on PPP and $C_{60}$ is a high threshold potential, which is also mentioned in other works in which aluminum-based contacts are used. Probably, an insulating layer forms at the aluminum—PPP interface, which results in a strong decrease in voltage on the diode. At the same time, in the absence of fullerene, *i.e.*, in the C—PPP—Al system, no rectification characteristics are observed, and electroluminescence is observed only at alternative current at a voltage of 12 V. Thus, the presence of fullerene in the system is necessary for achievement of high rectification ratios. The VAC obtained for the heterostructure with a glassy carbon substrate are shifted to lower voltage compared to the systems based on tin dioxide.

The possibility to obtain rectification ratios of ~$10^4$ in the $SnO_2$—PPP—$C_{60}$—Al system has been shown previously.[8] The higher values obtained in our work are probably caused by the shift of the direct branch of the VAC at unchanged values of reverse currents.

Thus, optimum ratios of the evaporator and substrate temperatures and the velocity of injection of an evaporable material in the process of discrete evaporation of PPP are revealed. It is shown that the films formed are characterized by the conjugation region, which covers 9—10 elementary units. The evaporation technique suggested can be used for molding composites with fullerenes and heterostructures with a high rectification ratio of the direct current to reverse current.

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