DC Discharge Plasma Polymerization of 1-Naphthylamine

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Naphthalene and their derivatives such as 1-naphthylamine are very promising blocks for building high-quality conducting polymers due to the extended π-electron systems in their molecules [1], and plasma polymerization is of undoubted interest in this regard, since it allows for the synthesis of polymers in the form of thin films and coatings [2, 3]. There are some chemical and electrochemical methods for producing polymer from 1-naphthylamine [4 – 7].

In this work thin polymer films from 1-naphthylamine have been obtained for the first time by polymerization at the cathode and anode in DC discharge and studied the chemical structure and properties of this polymer.

1-naphthylamine (NA) was purified by recrystallization from ethanol prior to use, and its purity was checked by measuring the melting temperature (T_m=50°) using differential scanning calorimetry.

The setup and procedure for DC discharge plasma polymerization of compounds that are solid at room temperature are described by us elsewhere [8, 9]. A polymer from NA (PPNA) was obtained by DC discharge in the form of thin film on an aluminum foil, conducting single-crystalline silicon, or fused silica substrate. The process conditions were as follows: a temperature in the reaction chamber of 40°, an NA vapor pressure of 40 Pa, a discharge current of 5 mA, and a reaction time from 60 s to 420 s. The films thickness was measured by interferometry. The PPAN films neither dissolved nor swelled in ethanol, acetone, heptane, at all, but the films obtained at the cathode were easy detached from the aluminum foil substrate with ethanol. Kinetics of the formation of polymer films obtained by the DC discharge at the cathode has been investigated, and it is shown that the growth rate of polymer films increases from 3 nm/s to 6 nm/s with the film thickness from 100 nm to 1 μm; then, the growth rate becomes constant. The morphology of polymer films synthesized under various conditions was examined by SEM and AFM. It was shown that the films have granular structure and a size of these granules is ~ 50 nm. The presence of micron-size aggregates composed from granules was also established. The value of the surface roughness calculated from roughness profile obtained by AFM was increased from 4±1 nm for the film with the thickness of 90 nm to 35±12 nm for the film with the thickness of 1.5 μm. These data are in agreement with the results obtained in [5].

The elemental composition of PPNA was studied by pyrolysis chromatography using a Carlo-Erba IA 1108 CHNS analyzer. It is evident that the relative amount of hydrogen and nitrogen in polymer is lower than that in NA, and oxygen appears as well. Calculation of the empirical formula for C_{10} shows the amount of nitrogen in PPNA is reduced to 0.7 as compared to 1.0 in the initial compound.

Fig. 1 shows the FTIR absorption spectra of (***1***) NA and (***2***) PPNA obtained at the cathode.

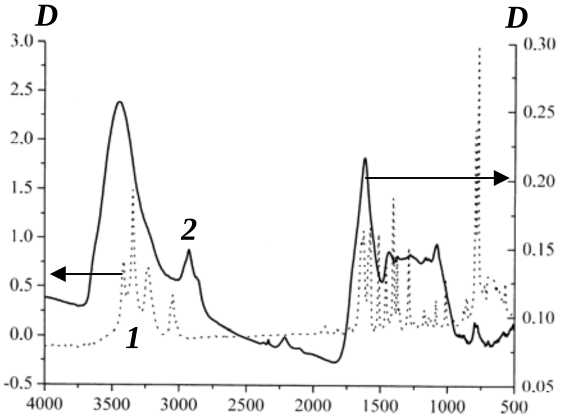

Fig. 1. FTIR absorption spectra of (*1*) NA and (*2*) PPNA synthesized at the cathode.

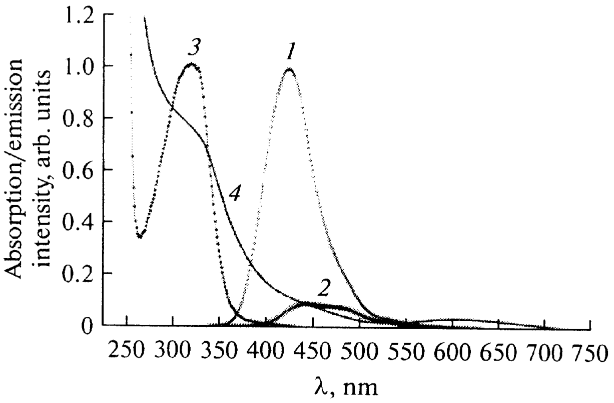

Fig. 2. Matching the (*1, 2*) luminescence and (*3, 4*) absorption spectra of (*1, 3*) NA and (*2, 4*) PPNA.

The broad band at 3370 cm^{-1} is associated with stretching vibrations of secondary amines, and the band at 1630 cm^{-1} is apparently due to stretching vibration of the imine group. The absorption bands at 1378 and 1260 cm^{-1} are associated with C–N stretching, and the absorption band peaked at 1141 cm^{-1} indicates the presence of the imine and secondary amine groups, i.e., benzenoid and quinonoid conjugated moieties in polymer chain. The absorption bands at 1445 and 1520 cm^{-1} correspond to C=C skeletal vibration of the aromatic rings, and the absorption bands at 720 and 879 cm^{-1} apparently indicate attachment of aromatic rings in the 1,4-position [7].

The luminescence spectra of NA in ethanol and (*2*) PPNA are shown in Fig. 2, as well (*3*) the monomer and (*4*) polymer absorption spectra. It is seen that the spectrum of (*2*) PPAN exhibits maximums close in position to the 240- and 325-nm peaks of (*1*) the NA spectrum and new maximums at 440 and 615 nm. In the case of excitation at a wavelength of 325 nm, week luminescence of the polymer at 400-600 nm is observed, roughly coinciding with the monomer luminescence. A comparison of the absorption spectra of PPNA and NA leads to the conclusion that this may be aminonaphthalene nucleus luminescence strongly attenuated by the 440-nm polymer absorption band (inner filter effect).

The data of FTIR and UV spectroscopy show that the PPNA chain is apparently made of units with two different structures. In one case, NA units are joined together without breaking the double bonds, as confirmed by the long-wavelength absorption and the absence of luminescence. In the other case, NA units are linked to one another by a spacer with broken conjugation.

The TGA measurements were shown that PPNA loses less than 20% of mass in an argon atmosphere when heated to 400°C, whereas the polymer undergoes oxidative degradation in air: a 50% of mass loss is observed upon heating to ~410°C and further heating leads to a rapid loss (up to 90% at ~470°C), and then slowly to the gradual complete degradation of the sample at 800°C. These data resemble those reported in [7] for the polymer synthesized by the chemical method.

Polymer synthesized by the DC discharge was investigated by ESR method. The typical ESR spectrum of PPNA is shown in Fig. 3.

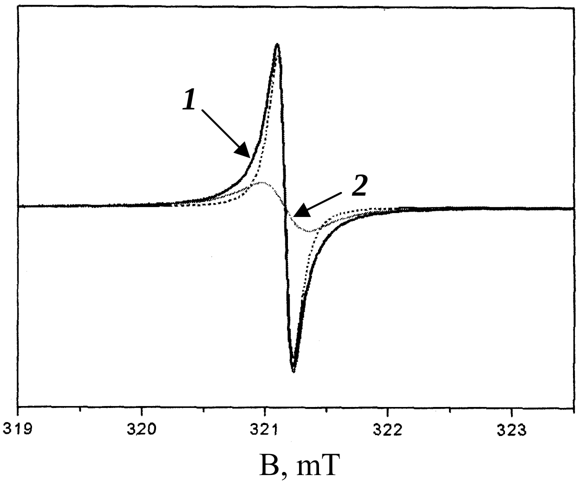

Fig. 3. A typical ESR spectrum of PPNA and its resolution on spectra of (*1*) long and (*2*) short polymer chains.

It is presumed that this spectrum is a sum of signals from radicals located on the polymer chains of different length. Fig 3 shows the resolution of PPNA spectrum on 2 spectra of (***1***) long and (***2***) short polymer chains. It is found that the spin concentration is equal to ~ 10^{19} spins/g, the line width at 300 K is equal to ΔB = 0.13 mT, and g factor is equal to 2.0020±0.0002. The data obtained confirm the presence of aromatic free radicals localized near nitrogen atoms [10].

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