Polymerization of 1-Naphthylamine by DC discharge

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Abstract. Thin polymer films from 1-naphthylamine have been obtained for the first time by polymerization at the cathode and anode in DC discharge. The morphology of the films synthesized at the cathode was examined by SEM and AFM. The elemental composition, chemical structure, and thermal stability of the polymer have been studied by pyrolysis chromatography, IR and UV spectroscopy, and thermogravimetry, respectively. The surface contact properties of the films and their thickness have been determined with a microinterferometer. Polymer was also investigated by ESR method.

1. Introduction

It is well known that 1-naphthylamine holds promise for organic luminescent devices [1], and the plasma polymerization method 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 only chemical [4-6] and electrochemical [7-9] methods known for producing a polymer from 1-naphthylamine. For example, polymer from 1-naphthylamine (PNA) was synthesized chemically in methanol with CuCl2⋅2H2O as initiator in the presence of the surfactant N–cetyl–N,N,N–triethylammonium bromide [4]. This PNA was soluble in organic solvents, such as ethanol, methanol, DMSO, DMF, MP, and tetrahydrofuran. The IR and UV studies of the polymer structure showed that it contained benzenoid and quinonoid moieties, and the polymer was a mixture of naphthylamine structures linked in the 1,4- and 1,5-positions one another. By the thermogravimetric technique, it has been shown that the polymer is quite stable up to ~ 180°C and its 50% mass loss is observed at ~ 420°C. It has also been reported [7] that electrochemical synthesis in a standard three-electrode cell using a saturated aqueous solution of 1-naphthylamine hydrochloride in the presence of KCl (at a potential of 0.9 V and an initial current of 0.08–0.1 mA, with a decrease to 0.01 mA) yields coloured films of oligomers. The structure of these oligomers was investigated by IR and UV spectroscopy, and 1,4-amine/imine bonds were found in the resulting oligomer products.
In this work we performed for the first time a plasma-chemical synthesis of a polymer from 1-naphthylamine in DC discharge and studied its structure and properties.

2. Experimental

1-Naphthylamine (NA) was purified by recrystallization from ethanol prior to use; its purity was checked by measuring the melting temperature ($T_m=50^\circ$C) using differential scanning calorimetry.

The setup and procedure for DC discharge polymerization of compounds that are solid at room temperature are described by us elsewhere [10]. The process conditions were as follows: a temperature in the reaction chamber of 40$^\circ$, an NA vapour pressure of 40 Pa, a discharge current of 5 mA, and a reaction time from 60 s to 420 s. A polymer from NA (PPNA) was obtained by DC discharge in the form of thin film on an aluminium foil, conducting single-crystalline silicon, or fused silica substrate.

The film thickness was measured by interferometry in white light using a Linnik microinterferometer.

The SEM images were taken with a Zeiss EVO 40 scanning electron microscope with SDD. The AFM study of the film was conducted with a Solver P47 microscope (NT-MDT, Russia) and software Gwyddion [11].

The elemental composition of PPNA was studied by pyrolysis chromatography using a Carlo-Erba IA 1108 CHNS analyzer.

To characterize the surface contact properties, the values of contact angle ($\theta$) determined with a goniometer (error $\pm1^\circ$) using two test liquids, doubly distilled water and glycerol, were used. From the results, the work of adhesion, the total surface energy, and its polar and dispersion terms were calculated [12].

The chemical structure of the polymer was investigated by Fourier-transform IR and UV spectroscopy. The IR spectra were recorded with Bruker Equinox 50S FTIR spectrometer in CsI disks. The assignment of bands was carried out according to [13]. Electronic absorption spectra were obtained on a Shimadzu UV-2501 PC spectrometer, and luminescence and excitation spectra were recorded with scanning spectrofluorimeter ALS-1 (Russia).

The thermal stability of the polymer was studied by TGA in air and argon using a NETZSCH TG-209-F instrument and software package NETZSCH Proteus-Thermal Analysis, ver.4.8.4.

Polymer synthesized by the DC discharge was investigated by ESR method using spectrometer RADIOPAN SX (Poland) with cryostat Oxford CF935.

3. Results and discussion

The PPNA films neither dissolved nor swelled in ethanol, acetone, heptane, at all, but the films obtained at the cathode were easy detached from the aluminium foil substrate with ethanol.

Kinetics of the formation of polymer films obtained at the cathode has been investigated, and the data obtained are presented in Figure 1. It is seen that the growth rate of polymer films increases from 3 nm/s to 6 nm/s with the film thickness from 100 nm to 0.5–1 $\mu$m; then, the growth rate becomes constant.

The morphology of polymer films was examined by SEM and AFM, the results obtained by SEM are given in Figure 2. It was shown that the films have granular structure and a size of these granules is about 50 nm (Fig. 2a). The presence of micron-size agglomerates composed from granules was also established (Fig. 2b). The value of the surface roughness calculated from roughness profile obtained by AFM (Fig. 3) 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 $\mu$m. It is probably owing to the enhancement of the quantity of the agglomerates of globular particles in the structure of PPNA films.

Data on the elemental composition of PPNA films obtained at the cathode are shown in Table. 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 these results of empirical formula for C$_{10}$ shows that the amount of nitrogen in PPNA is reduced to 0.7 as compared to 1.0 in the initial NA.
Fig. 1. Dependence of PPNA film thickness (L) on the time of polymerization (t).

Fig. 2. SEM images of (a) globular particles and (b) the agglomerate of globular particles of a PPNA film synthesized at the cathode.

Fig. 3. AFM image of a PPNA film synthesized at the cathode.
Table. The elemental composition of 1-naphthylamine and the polymer (PPNA) synthesized at the cathode in DC discharge. Chemical formula of 1-naphthylamine is C_{10}H_{7}NH_{2}.

| Sample                       | C, %    | H, %    | N, %    | O, % (by difference) | Calculation in terms of C_{10}   |
|------------------------------|---------|---------|---------|----------------------|---------------------------------|
| 1-naphthylamine (calculation)| 83.9    | 6.8     | 9.8     | –                    | C_{10}H_{9}N                     |
| PPNA                         | 81.6    | 3.5     | 6.8     | 8.1                  | C_{10}H_{5.15}N_{0.71}O_{0.74}   |

The results of the goniometric measurements of the contact angles ($\theta$) on the surface of PPNA films deposited on an aluminium foil substrate at the cathode and anode are shown that the both films have the same values of $\theta$ by water (65°), the work of adhesion (103.6 mJ/m$^2$), the surface energy (38.7 mJ/m$^2$), and its polar (20 mJ/m$^2$) and dispersion (18.7 mJ/m$^2$) components.

The chemical structure of PPNA films was investigated by FTIR and UV spectroscopy. Figure 4 shows the IR absorption spectra of (1) the monomer and (2) the polymer synthesized at the cathode by DC discharge.

![Fig. 4. IR absorption spectra of (1) parent 1-naphthylamine and (2) the polymer, synthesized at the cathode.](image)

The broad band at 3370 cm$^{-1}$ is associated with stretching vibrations of secondary amines [4]. The absorption bands at 1445 and 1520 cm$^{-1}$ correspond to C=C skeletal vibrations of the aromatic rings, whereas the band at 1630 cm$^{-1}$ is apparently due to the stretching vibrations of the imino groups [7]. The absorption bands at 1378 and 1260 cm$^{-1}$ are associated with C=N stretching [14], and the absorption band peaked at 1141 cm$^{-1}$ (C=N) indicates the presence of the imine and secondary amine groups, i.e. benzenoid and quinonoid structures [15]. Absorption in the region 700-900 cm$^{-1}$ is attributed to CH bending vibrations for different kinds of attachment of the aromatic rings. The absorption bands at 720 and 879 cm$^{-1}$ apparently indicate attachment in the 1,4-position [15].
However, the weak intensity of other absorption bands in this area and their low resolution do not permit accurate assignment concerning the addition position.

The luminescence spectra of (1) NA in ethanol and (2) PPNA obtained at the cathode are shown in Figure 5, as well as the NA (3) and polymer (4) UV absorption spectra. 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.

![Graph showing luminescence spectra](image)

Fig. 5. Matching the (1, 2) luminescence and (3, 4) absorption spectra of (1, 3) parent 1-naphthylamine and (2, 4) the polymer, synthesized at the cathode.

A comparison of the absorption spectra of NA and PPNA leads to the conclusion that this may be naphthylamine nuclei luminescence strongly attenuated by the 440-nm polymer absorption band (inner filter effect). These data are shown, that the PPNA chain is apparently made of units with two different structures. In one case, the NA units are linked to one another by a spacer with broken \( \pi \) conjugation, as indicated by the presence of both the short-wavelength absorption, which coincides with the monomer absorption, and luminescence. In the other case, NA units are joined together without breaking the double bonds, as confirmed by the long-wavelength absorption (maximums at 440 and 615 nm) and the absence of luminescence.

Figure 6 shows TGA curves measured in (1) argon and (2) air atmosphere for the PPNA synthesized by DC discharge at the cathode. It is seen that PPNA loses less than 20\% of mass in an argon atmosphere when heated to 400\(^\circ\)C, whereas the polymer undergoes oxidative degradation in air: a 50\% mass loss is observed upon heating to \(~410\)^\(\circ\)C and further heating leads to a rapid loss (up to 90\% at \(~470\)^\(\circ\)C) and then slowly to the gradual complete degradation of the sample at 800\(^\circ\)C. These data resemble those reported in [4] for the polymer synthesized by chemical method.
Polymer synthesized by DC discharge was investigated by ESR method. It was found that the spin concentration is equal to $\sim 10^{19}$ spins/g, the line width at 300 K to $\Delta B = 0.13$ mT, and g-factor to $2.0020 \pm 0.0002$, respectively. The (1) experimental ESR spectrum of PPNA and its resolution (2, 3) are shown in Figure 7.

The data obtained confirm the presence of aromatic radicals localized near nitrogen atoms [16]. Previously it was shown that benzenoid-quinonoid moieties in PPNA polymer chain were also found by means of FTIR an UV spectroscopy.

4. Conclusion
Thus, polymer was obtained from 1-naphthylamine for the first time by plasmachemical polymerization at the cathode in DC discharge. Based on the elemental analysis, IR and UV spectroscopy and ESR data, we can conclude that the polymer structure is composed of benzenoid-quinonoid moieties to a considerable extent.

Acknowledgments

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