

Supplementary material

Synthesis of polymers

Synthesis of poly-2-[(2E)-1-methyl-2-butene-1-yl]aniline (P1) (Fig. S1) was carried out by the following method: an oxidizer solution of 2.85 g (12.5 mmol) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was slowly added to a solution of 1.62 g (10.0 mmol) 2-(1-methylbut-1-en-1-yl)aniline M1 in 50 ml 0.2 M HCl with constant stirring $2\text{S}_2\text{O}_8$ in 50 ml 0.2 M HCl. The duration of the reaction at room temperature and constant stirring was 24 hours. The precipitate was filtered and washed with 0.2 M HCl solution. The resulting filtrate was dried under vacuum for 3 hours at 40°C. The polymer yield was 60% [47].

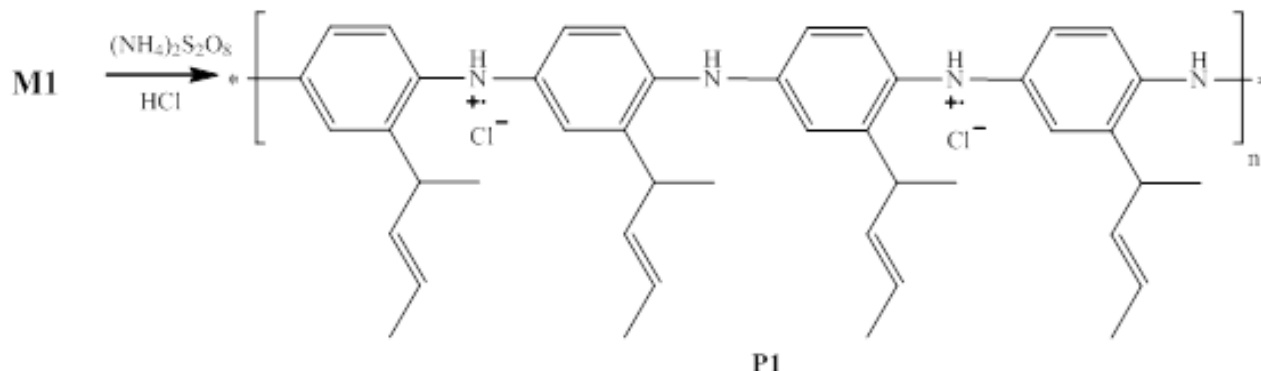


Fig. S1. Synthesis of poly-2-[(2E)-1-methyl-2-butene-1-yl]aniline.

For the synthesis of the poly-2-(cyclohex-2-en-1-yl)aniline (P2) (Fig. S2), the following technique was used: an oxidizer solution of 2.85 g (12.5 mmol) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was slowly added to a solution of 1.72 g (10.0 mmol) 2-(cyclohex-2-en-1-yl)aniline in 50 ml 0.2 M HCl with constant stirring M2 in 50 ml 0.2 M HCl. The duration of the reaction at room temperature and constant stirring was 24 hours. The precipitate was filtered and washed with 0.2 M HCl solution. The resulting filtrate was dried under vacuum for 3 hours at 40°C. The polymer yield was 61% [48].

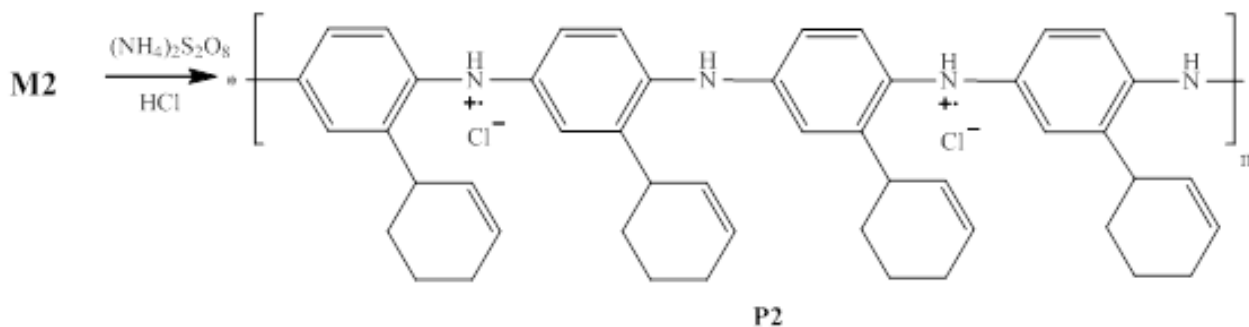


Fig. S2. Synthesis of poly-2-(cyclohex-2-en-1-yl)aniline.

Research methods

To form thin films, the obtained polymers P1 and P2 were dissolved in dimethylformamide (DMFA).

Multilayer structures of resistive sensors were obtained on the basis of thin films (Fig. S3). In resistive sensors, a sital substrate was used as a substrate. Aluminum electrodes were applied to the sital substrate from above by thermal spraying in a vacuum chamber at the VUP-5 installation with a thickness of about 400 – 500 nm, the gap was created using a shadow mask. For some samples, a film polymer P1 and for others P2 was applied to the area of the gap between the electrodes of 50 microns by centrifugation from a solution. The ohmic nature of the contacts has been proven by measuring their current-voltage nature. The uniformity of the polymer surface in the working area of resistive sensors is confirmed by AFM and SEM studies. The resulting layer was subjected to thermal annealing to remove solvent residues by heating to 150°C for 20 – 25 minutes.

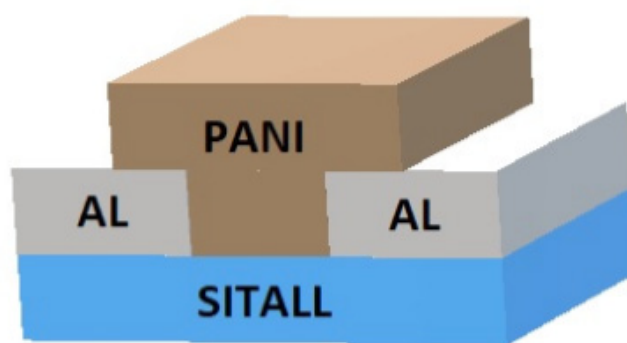


Fig. S3. (Color online) Structure of a thin-film resistive sensor.

In the experiments, the following power supplies were used for measurements: MASTESN, DS ROWER SUPPLY HYZ005D-2, universal voltmeter V7-21 as an ammeter, sealed cap, digital thermometer hygrometer RSTQ317, the thickness of thin polymer films was controlled based on the analysis of SEM images.

A sample of the humidity sensor was placed under a hood containing a control humidity sensor and a water tank (Fig. S4). The values of the input signal were taken at certain humidity values. Humidity was monitored using a DHT11 sensor. Humidity values were displayed via Arduino UNO and USB to the laptop screen. The measurements were carried out at room temperature 25°C, the voltage on the samples 30 V.

Studies of the microstructure of polymers were carried out using a Scanning Electron Microscope (SEM) TESCAN MIRA LMS.

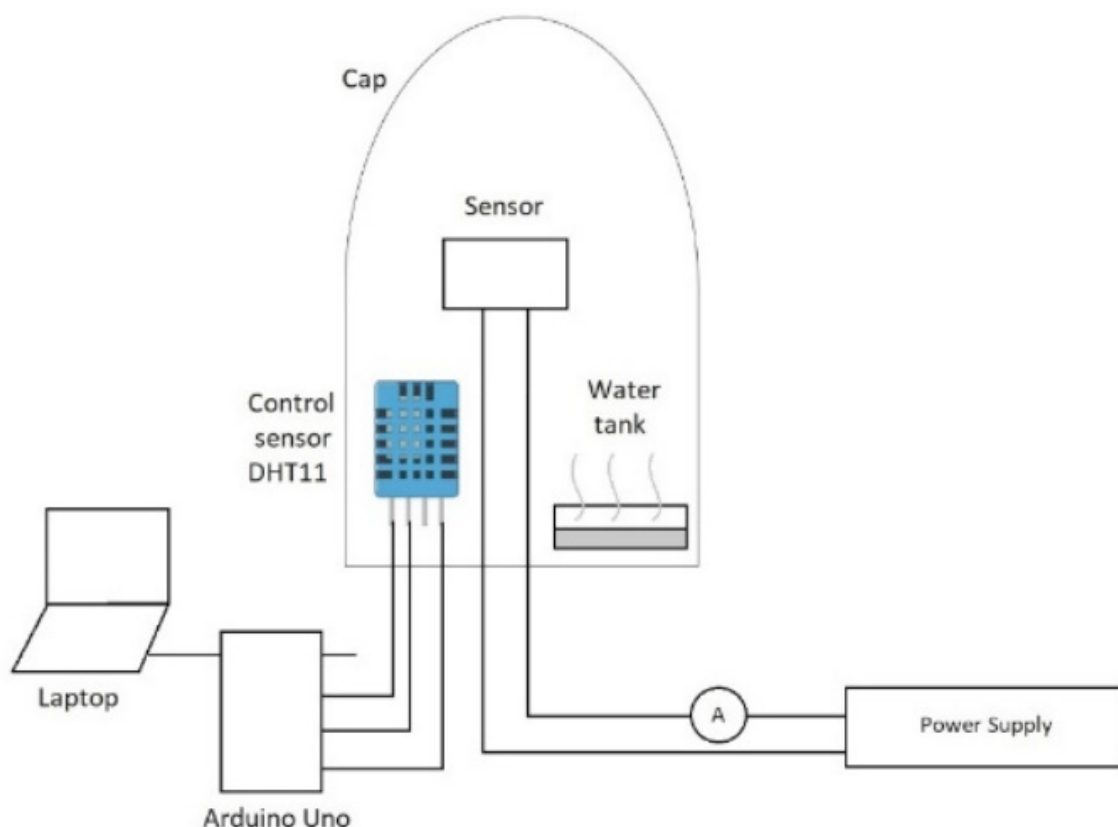


Fig. S4. (Color online) Installation for measuring the volt-ampere characteristics of sensor samples.

Optical spectroscopy of samples

The IR spectra of the synthesized samples are shown in Fig. S5a. The structure of the obtained polymers is confirmed by spectral analysis methods. All samples demonstrate absorption in the region of 3385 – 3392 cm^{-1} , which corresponds to the oscillation of the N-H bond. The absorption peak in the region of 2928 – 3000 cm^{-1} is caused by fluctuations in the C-H

bonds of the aromatic ring. Signals at 2816 cm^{-1} are characteristic of the C-H coupling in the substituent. The main peaks characteristic of the polymer structure of PANI derivatives are at 1530 and 1604 cm^{-1} . They correspond to the fluctuations of the benzoin and quinoid parts, respectively. The presence of these bands indicates partial oxidation of the macromolecular chain, since the fully oxidized state is characterized by the presence of only quinoid fragments. The maximum in the region of $1370\text{--}1383\text{ cm}^{-1}$ is characteristic of the C-N bond. The presence of a peak at 1106 cm^{-1} indicates that the polymer is in an alloyed state [49]. The absorption bands at 594 and 821 cm^{-1} correspond to deformation vibrations of the C-H bond, which indicate attachment in the para-position to the main chain.

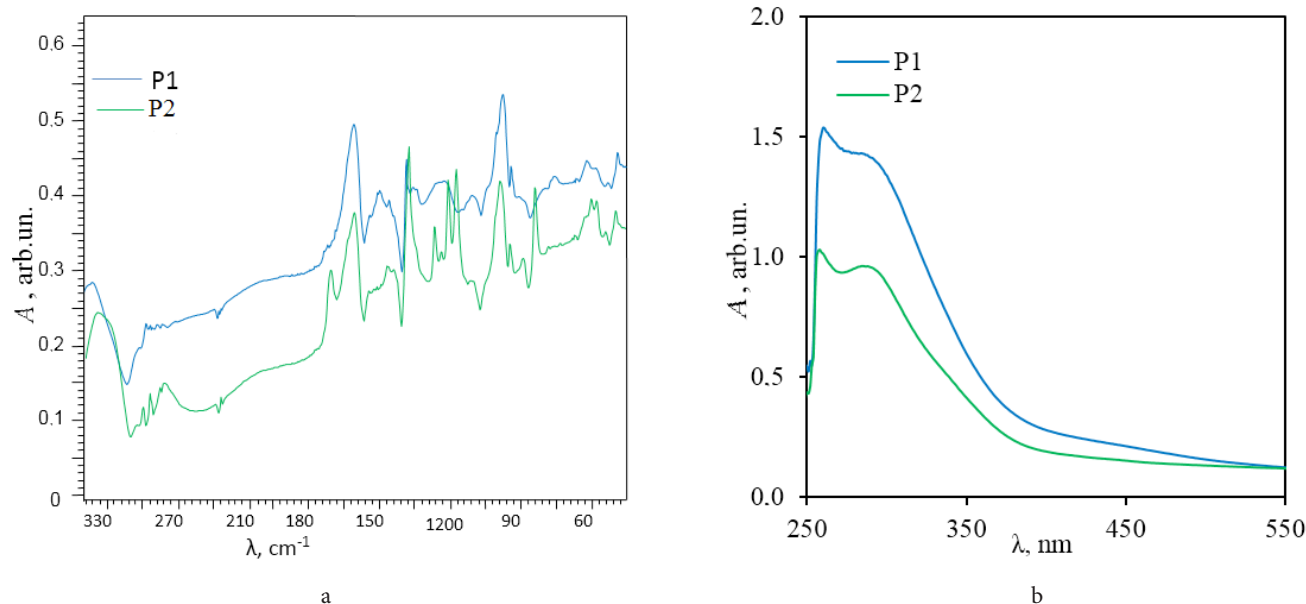


Fig. S5. (Color online) IR (a) and UV (b) spectra of synthesized samples.

The results of UV spectroscopy are shown in Fig. S5b. It is known that absorption peaks in the region of 350 and 600 nm are characteristic of unsubstituted PANI [50]. The samples of the PONY derivative considered in this paper contain an alkynyl substituent in the ortho position, a large volume of which increases the torsion angle between adjacent aromatic rings. This effect is accompanied by a hypsochromic shift of the absorption spectra (Fig. 5Sb) relative to the known spectrum of the unsubstituted PANI. The spectra of the studied polymers contain an absorption band in the region of $285\text{--}300\text{ nm}$, which corresponds to the electronic transitions of benzoid and quinoid rings [51].

Influence of particle sizes on polymerization processes

With the help of the laser analyzer SALD-7101, the measurement of polymer particle sizes during the reaction was carried out. Distilled water was used as a background solution. Fig. S6a shows the curves of the differential size distribution of P1 particles during polymerization, which shows that over the course of the reaction, the particles change their size from $5\text{--}15\text{ }\mu\text{m}$ in the first 10 minutes of synthesis, to $20\text{--}30\text{ }\mu\text{m}$ after 24 hours of reaction.

Similarly, the curves of the distribution of the size of the particles of P2 (Fig. S6b) were obtained, the size of which was $20\text{--}30\text{ }\mu\text{m}$ in the first 4 hours of synthesis, and $30\text{--}50\text{ }\mu\text{m}$ after 24 hours of reaction.

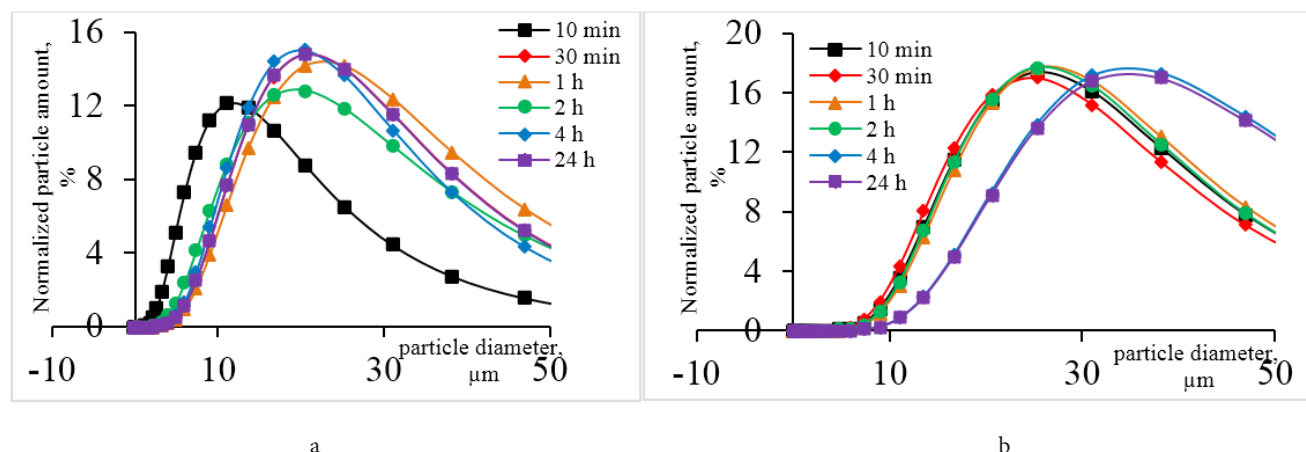


Fig. S6. (Color online) Sizes of P1 particles in the polymerization process (a), sizes of P2 particles in the polymerization process (b).