Microstructure of 1,4-diethynylbenzene frontal polymerization products

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Abstract. A comparative study of two processes was carried out: frontal polymerization of 1,4-diethynylbenzene, proceeding as a result of high-temperature initiation under increased nitrogen pressure ($P = 2–6$ MPa), and ammonium perchlorate burning in the same conditions. It was shown that the linear rate of thermal transformations of 1,4-diethynylbenzene is close to the linear burning rate of the energetically saturated compound. The structure of the carbon material obtained as a result of thermal transformations of 1,4-diethynylbenzene was investigated using elemental analysis, Raman spectroscopy and scanning electron microscopy.

1. Introduction

The widespread use of acetylene and its derivatives in organic chemistry and in the field of materials science is associated with their unique reactivity caused by high degree of triple bond unsaturation [1]. Alkyne-containing molecules, because of their high reactivity, provide the possibility of producing carbon materials (CMs) of various shapes and sizes, and preparation of carbon nanomaterials (CNMs) is the focus of many research groups [2-5].

Two-step methods are usually proposed [2-5] for obtaining carbon materials: preliminary synthesis of precursors or oligomers and their pyrolysis at temperatures from 400 °C to 1000 °C. Another unique property of acetylene derivatives is the high heat of their formation, what makes them capable of reactions proceeding with high heat release and even explosion-like processes. This property allows these compounds to be used as high-energy fuels [6].

The purpose of the present work is to show the possibility of carbon materials producing by self-propagating frontal polymerization of the solid 1,4-diethynylbenzene (DEB) and to analyze the microstructure of the material obtained.

2. Methods and materials

The following reagents were used: 1,4-diethylbenzene (DEB), CAS 935-14-8, $T_m = 368$ K of “chemically pure “ (reagent) grade was purified by recrystallization from hexane, the content of the main substance was 99.5%, density $\rho = 1.150$ kg/m$^3$; ammonium perchlorate (AP), CAS 7790-98-9, standard GJB617A-2003 99.5% series 1207 of 12.2017, density $\rho = 1.950$ kg/m$^3$.
A standard Crawford bomb (or a constant pressure bomb, figure 1) with a volume of $3 \cdot 10^{-3}$ m$^3$ was used to determine linear rates of thermal transformations of DEB and AP. Samples for testing were prepared by blind pressing in the form of a cylinder with a diameter of 8 mm and a height of 12 mm. The samples prepared this way were placed into the bomb in an asbestos-cement cup of the same internal size (figures 1) followed by filling of 2 or 6 MPa of nitrogen (99.999%, Logika Ltd). Thermal initiation of the process was carried out from the open side of the cup using a nichrome spiral when an alternating current with voltage of 8 V was applied to it. The initiation time was 2 sec; the temperature herewith did not exceed 1500 K. Temperature measurements were performed using a thermocouple mounted at a distance of 4 mm from the open side of a cup. The thermocouple was touching the side surface of the monomer pressed into this cup. The pressure in the system was monitored using inductive pressure sensors DD-10 and ID-21.

The average time of the process $t$ was determined from experimental dependencies of pressure on process time (figure 2) as an interval between the time of beginning of the growth and the time of pressure drop. The average linear rate of the process $U$ was defined as $U = h/t$, where $h$ is the height of the cylindrical sample. After the process, the solid residue was collected and weighed.

The morphology and microstructure of the carbon material were characterized using the JEOL JSM-6390LA scanning electron microscope operating at 25 kV and the SENTERRA Bruker Raman spectroscope with a laser wavelength of 532 nm.

3. Results and discussion

It is known that AP ignites after thermal initiation and burns due to internal oxygen with the release of gaseous products. The thermal conversion of acetylene derivative, DEB, in the bomb occurs as follows. The open upper layer of the sample is heated as a result of thermal initiation, after which a vigorous evaporation process begins, followed by fast polymerization of DEB in the gas phase. Due to high thermal effect of triple bond polymerization [1], the temperature in the reactor remains high even after the initiation heat impulse is turned off. Since DEB has low melting (95 °C) and boiling (183 °C) points and high volatility, after polymerization of the first upper layer, each subsequent layer of DEB also evaporates and polymerizes in the gas phase. This may explain the unusual result of polymerization: an insoluble crosslinked polymer “extends” from the cup in the form of a black cylindrical rod. Its diameter is equal to 8 mm, which is consistent with the internal diameter of the cup.
Figure 3 shows the photo of the carbon material obtained as a result of the DEB transformations under the conditions described above. In this process, a cylindrical rod was formed, apparently, directly in the front of the reaction wave, moving out of the reactor due to the large volume of porous carbon material. The rod length reaches 50 cm. During growth, this rod can break under the influence of its gravity, since its structure is porous and fragile.

![Carbon material obtained as a result of the DEB thermal FP in the Crawford bomb.](image)

The process described above can be attributed to the thermal frontal polymerization – an autowave, self-propagating mode of polymerization reaction. This process begins after a local heat impulse initiation and heat impulse – local initiation. It differs from other polymerization modes by the presence of a moving narrow, usually flat spatial boundary, where the reaction takes place (the reaction front) separating the initial monomer from the final product, the polymer [7]. By the formal signs (presence of the reaction front, heat generation, dynamics), this process is similar to burning and to self-propagating high temperature synthesis (SHS).

It should be noted that during the DEB polymerization under conditions of stationary propagation of the reaction front, the temperature in the reactor reached 1540 K and remained high until the end of the process. In addition, the reaction was accompanied by periodic fluctuations in temperature around the mean value of 1500 K and by appearance of weak flashes of dark red flame.

Figure 2 presents the results obtained by studying the dynamics of AP combustion and of DEB thermal transformations and demonstrates that duration of the thermal DEB transformation (the time of the pressure increase to the maximum point) coincides with the burning time of AP. In other words, the linear rate of the thermal FP of diacetylene is almost equal to the linear burning rate of the high-energy substance. The linear rate of these processes, or reaction front advance velocity, depends on the pressure of the inert gas: during the DEB polymerization, its value increases from 2.3 mm/s to 3.4 mm/s with pressure increasing from 2 to 6 MPa.

The combustion of AP is accompanied by a greater increase in pressure ($\Delta P_{\text{max}} = 0.50$ MPa, figure 2, curves 1) compared with the maximum value of the pressure increase in the case of the DEB frontal polymerization ($\Delta P_{\text{max}} = 0.16$ MPa, figure 2, curves 3). This is quite natural, since the combustion of AP is accompanied by a strong gas evolution, and the increase in pressure during the DEB polymerization is apparently due mainly to the evaporation of the monomer. In addition, it should be considered that the carbonization process involves aromatization and condensation with evolution of H$_2$, which also contributes to the pressure increase in the bomb. Besides that, the mass burning rate of AP is higher than the mass rate of the DEB transformation, since the AP density $\rho$ is 1.950 kg/m$^3$, while that of DEB is 1.150 kg/m$^3$.

A high temperature in the reactor may lead to a partial degradation (pyrolysis) of both initial and polymerizing molecules of DEB. Nevertheless, the yield of the solid residue of the process is almost 100%, and elemental analysis shows that the resulting product contains 96.49% C, 0.822% H and 0.45% N atoms by weight (nitrogen atoms are apparently absorbed by the carbon material during the
experiment in the bomb). Hence, the pressure in the system is growing mainly as a result of the vapor formation of DEB.

Figure 4 shows Raman spectrum of the carbon material obtained as a result of the DEB thermal FP. Raman spectroscopy is one of the techniques which can complement the previous analysis and contribute to better understanding of carbon materials (CMs) structure. In Raman spectra, carbon materials typically exhibit two broad bands, called D (disordered) and G (graphitic). In highly oriented pyrolytic graphite, only a G-peak appears in Raman spectra at 1582 cm$^{-1}$, while in disordered carbons, besides the G-peak, a D-peak appears at lower wavenumbers 1350 cm$^{-1}$ due to the asymmetric vibrations of the carbon bonds near defects in the structure of CMs. The information reflected in Raman spectra depends on both ordering and hybridization [8].

Figure 4. Raman spectrum of the carbon material obtained as a result of the DEB thermal FP at the initial pressure of 6 MPa.

The D- and G-peaks of the completely amorphous carbons spectra normally are distorted. The spectrum of the carbon material obtained in our experiments demonstrates the presence of well-defined $D$ (1345 cm$^{-1}$) and $G$ (1595 cm$^{-1}$) modes, which indicates that a graphite structure was developed in the carbonized DEB. In other words, the sample contains some amounts of sp$^2$ bonded carbon. Such atoms can be located on the surface layers and in nanoflakes of graphite. The height of the $D$ peak is almost equal to the intensity of the G peak, which means a high degree of structure disorder. However, since the high $D$-peak intensity directly depends on the presence of sixfold aromatic rings [8], the significant height of the peak in the Raman spectrum (Figure 4) indicates the presence of a large number of aromatic rings in the carbon material obtained.

Figure 5 shows SEM images of the carbon material obtained at the initial pressure of 6 MPa. The most significant feature of the microstructure of these samples, in our opinion, is the presence of micro spheres with a rather narrow size distribution. The average diameter of the micro spheres is 100-200 nm, and only a small fraction of the micro spheres has size of 500 nm (figure 5 c, d). Apparently, such narrow size distribution is a consequence of the frontal method of polymerization. This happens because the thermal wave of the stationary polymerization front creates uniform conditions for the formation of micro particles resulting from the polymerization. The fact that the polymerization proceeds in the gas phase creates conditions for preventing the agglomeration of the particles during the process.
4. Conclusion

The regularities of thermally initiated frontal polymerization of 1,4-diethynylbenzene proceeding under conditions of elevated pressure (2-6 MPa) of an inert gas are investigated. It was shown that the temperature in the reactor could rise during this process up to 1540 K.

The carbon material obtained consists of microspheres with a narrow size distribution. The average diameter of the particles is 100-200 nm. Frontal polymerization of 1,4-diethynylbenzene is an ecologically clean (since no solvent is used in this process), fast, and energy-saving approach to preparing structured carbon and composite materials. Moreover, it should be noted that the most advantageous factor of frontal polymerization, from the perspective of its implementation, is that the process can be performed in continuous reactors [7].

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