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CHEMISTRY

Synthesis of Polyaniline in Supercritical Carbon Dioxide

A. M. Lopatin[a], **S. S. Bukalov**[a], **L. A. Leites**[a], **Yu. V. Korshak**[b], **L. N. Nikitin**[a], **and Academician A. R. Khokhlov**[a]

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Supercritical carbon dioxide (sc-CO_2)—an environmentally acceptable, inexpensive, nontoxic, and nonflammable medium—is widely used as a solvent in synthesis and modification of polymers based on various monomers [1, 2]. As a rule, an advantage of using sc-CO_2 is the absence of side reactions of chain termination and chain transfer to the solvent [2], which ensures the preparation of high-purity polymers.

In recent years, attention has been focused on the possibility of using sc-CO_2 in polycondensation processes [3, 4]. Of special interest is the synthesis and modification of conducting polymers polypyrrole [5], polyaniline (PANI) [6], etc., as well as design of hybrid materials based on these polymers, in an sc-CO_2 medium.

Traditional methods of production of PANI involve the oxidative polymerization of the monomer with the use of ammonium persulfate $(NH_4)_2S_2O_8$ as the oxidant or electrochemical synthesis, which is currently more popular since it offers significant advantages over the chemical synthesis [7].

In the present work, we developed for the first time the method of synthesis of PANI through oxidative polymerization of aniline in sc-CO_2 and characterized the products by spectroscopy.

The setup for synthesis by means of sc-CO_2 is shown in Fig. 1. It is equipped with a generator creating a pressure of up to 35 MPa, which is connected through a system of capillaries with a stainless steel autoclave with a working volume of 30 mL. The setup is equipped with pressure gauges for controlling the sc-CO_2 parameters. Carbon dioxide CO_2 is fed to the cell through a system of valves. The desired temperature is maintained by means of a thermostat in which the autoclave is placed. Carbon dioxide with a purity of 99.995% (State Standard GOST 8050-85) was used in the synthesis of PANI.

The following regents were used as purchased: aniline (99.8%, Aldrich) dodecylbenzenesulfonic acid (DBSA, Aldrich) with an admixture of isomers C10–C13, ammonium persulfate (98%, Aldrich), and anhydrous ethanol (96%, Khimmed, Russia).

The oxidative polymerization of aniline in sc-CO_2 was carried out in several stages.

At the first stage, the salt of DBSA and aniline was synthesized by the direct reaction of two reagents in a liquid phase at room temperature. The reaction began as soon as two liquids taken in an equimolar ratio—DBSA (6.53 g, 20 mmol) and aniline (1.86 g, 20 mmol)—contacted each other when mixed in the reactor. The mixture grew turbid within 1–2 s and then solidified within 30–40 s to form a white mass (8.31 g, 99%) of anilinium dodecybenzenesulfonate. This salt turned out to be soluble in a supercritical medium. Elemental analysis showed that the product was of high purity.

For $C_{24}H_{37}S_1N_1O_3$ anal. calcd. (%): C, 69.13; H, 9.00; N, 3.45; S, 7.57. Found (%): C, 69.31; H, 9.04; N, 3.27; S, 7.46.

At the second stage, anilinium dodecybenzenesulfonate and ammonium persulfate taken in a 1 : 1.25 molar ratio (the optimal ratio for the classical synthesis) were placed onto the bottom of the autoclave. The system was thermostated at 70°C, and CO_2 was introduced to a pressure of 35 MPa. The reaction was carried out for 2 h, and then the autoclave was cooled to room temperature. The pressure was reduced to atmospheric, and the resulting product was washed with ethanol and water. Then, PANI (insoluble black powder) was dried in air to constant weight. The reaction of formation of PANI is shown in Scheme 1.

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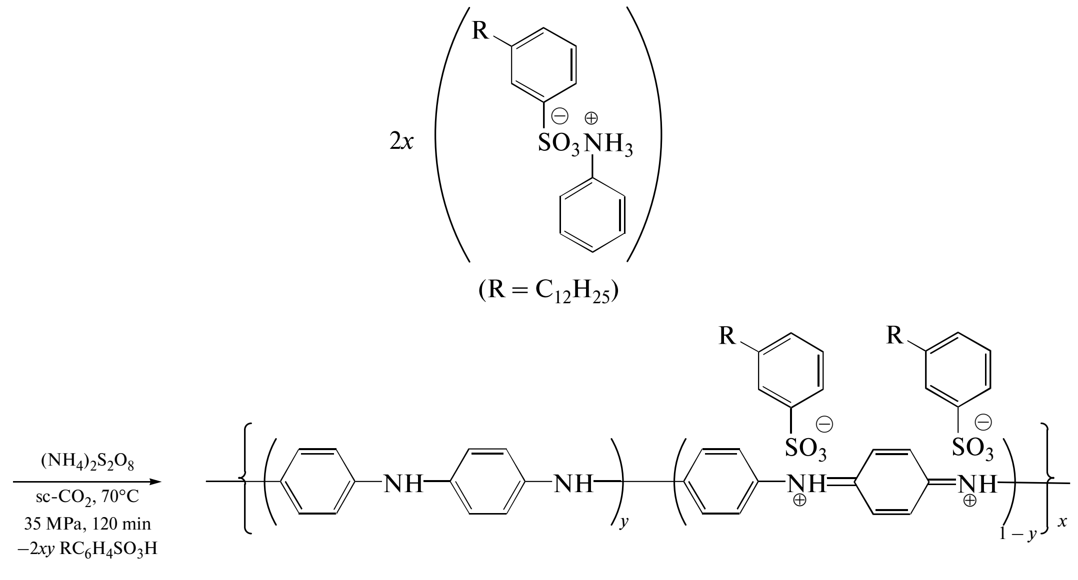
[a] *Nesmeyanov Institute of Organoelement Chemistry, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

[b] *Mendeleev Russian University of Chemistry and Technology, Miusskaya pl. 9, Moscow, 125047 Russia*



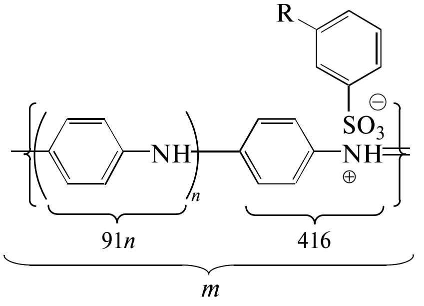
Scheme 1.

Raman spectra were recorded on a Horiba Jobin Yvon LabRAM spectrometer equipped with a cooled CCD detector and a microscope. The Raman spectra were excited with the 632.8 nm line of a He–Ne laser at a power of no more than 5 mW.

It is known that PANI contains both doped and pristine chain segments [8–10]. For PANI completely doped with DBSA (i.e., at $y = 0$, Scheme 1), anal. calcd. (%): C, 69.61; H, 8.63; N, 3.21; S, 7.41. For the product obtained in sc-CO_2, found (%): C, 64.45; H, 4.31; N, 10.54; S, 2.02. From these data, the degree of doping of the resulting polymer can be calculated using the set of equations

$$\begin{cases}416 + 91n = m,\\ 32/m = 0.0202,\end{cases}$$

where n is the number of undoped segments in the polymer unit containing one doped segment, m is the molar weight of the polymer unit containing one doped segment, 91 is the molecular weight of one undoped segment, 416 is the molar weight of one doped segment, and 0.0202 is the weight fraction of S in the polymer unit containing one doped segment.



Thus, the first equation is the expression of the molar weight of the polymer unit containing one doped segment: $416 + 91n = m$. The second equation expresses the weight fraction of sulfur in this unit and, hence, in the polymer $32/m = 0.0202$; thus, $n = 12.84$. The degree of doping of PANI can be determined from the ratio of the number of doped units to the total number of polymer units: $\{1 - [12.84/(12.84 + 1)]\} \times 100\% = 7.23\%$.

Raman spectroscopy is an informative method of studying the structures of polymers and, in particular, PANI, since various structural elements of PANI are responsible for rather different spectra [8–15]. To reveal differences in properties between PANI synthesized in sc-CO_2 and PANI obtained by the common method, we studied samples of two types.

(1) Samples of type I synthesized in an aqueous medium by the reaction of anilinium chloride and ammonium persulfate. Typical Raman spectra of such samples excited with the red line of a low-power laser (up to 0.05 mW) are shown in Fig. 2 (curves *1* and *2*). They are identical to the spectra of the conducting PANI form after primary doping, the emeraldine salt (ES) containing both the polaron (radical cations) and bipolaron (dications) lattices.

We revealed an interesting fact of significant changes of the spectra of samples of type I (Fig. 2, curves *3* and *4*): with an increase in the excitation laser radiation power from 0.005 to 0.05 mW and on further exposure, only the lines at 575, 1398, and 1645 cm^{-1} appear and build up. According to [11, 12], these lines correspond to crosslinking of polymer chains, resulting in the appearance of rings of the phenazine and

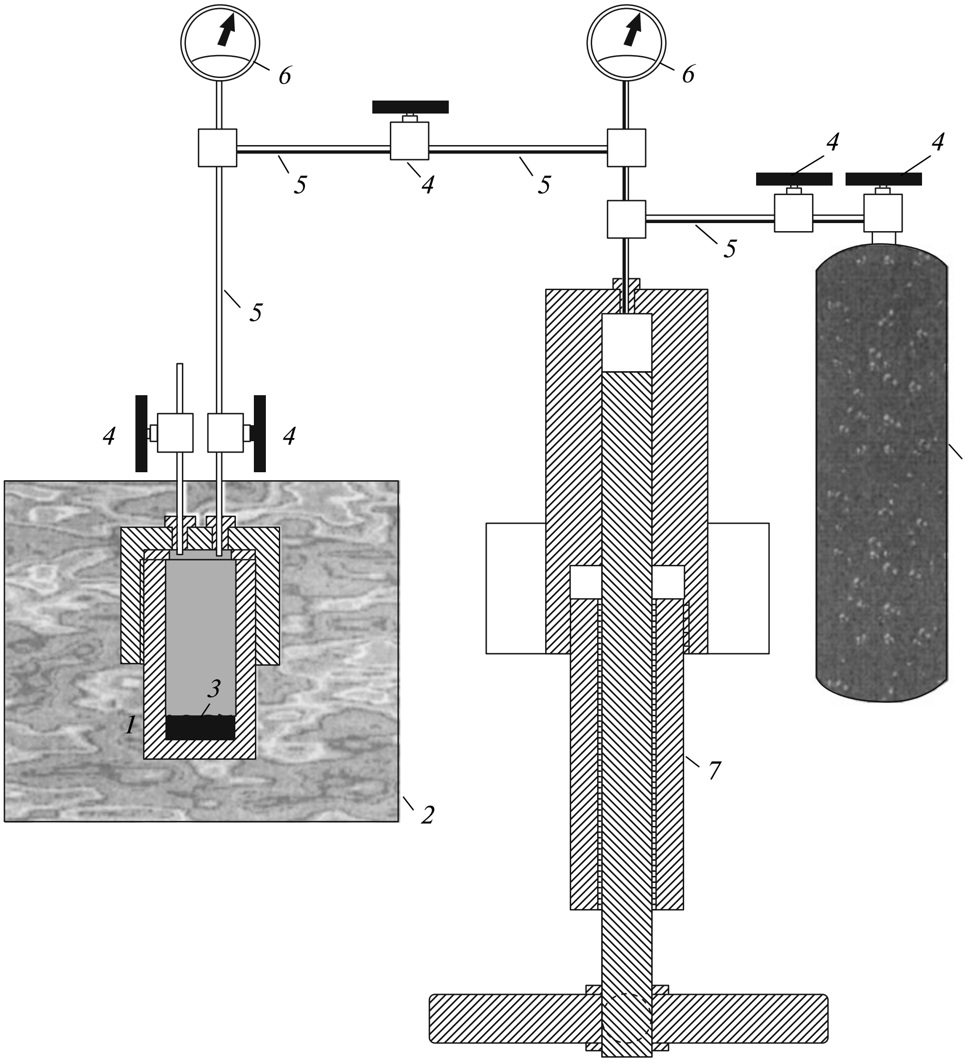


Fig. 1. Experimental setup for the synthesis of PANI in sc-CO_2: (*1*) autoclave, (*2*) liquid thermostat, (*3*) reaction mixture, (*4*) valves, (*5*) capillaries, (*6*) pressure gages, (*7*) hand pressure generator, and (*8*) CO_2 cylinder.

oxazine types [13] (in the latter case, the interaction with O_2 plays a role), which leads to a decrease in conductivity. It follows form the above results that laser radiation with λ 632.8 nm, even of relatively low power, initiates chemical transformations of the PANI structure. A similar phenomenon has been described in [11] where it was a result of heating ES samples to 100°C. In our case, photochemical activation of PANI samples presumably takes place, which is observed for the first time.

(2) PANI samples of type II were synthesized in sc-CO_2 by the reaction of anilinium dodecylbenzenesulfonate and ammonium persulfate according to Scheme 1. The Raman spectra of these samples (Fig. 3a) coincide with the spectra of PANI after its second doping [11–13]. The latter, according to [14], leads to an increase in the content of semiquinone radical cation units (polarons) at the expense of quinoid rings, as well as to extension of the polymer chain; i.e., the chain conformation changes from the coil to extended one, which facilitates delocalization of polarons and, hence, results in an increase in polymer conductivity. However, it is worth noting that, the spectra of type II samples sometimes also show lines indicating the existence of crosslinks (see, e.g., Fig. 3, curve *2*), which can somewhat decrease the conductivity.

Thus, PANI was synthesized in a sc-CO_2 medium for the first time. Raman spectroscopy showed that the synthesis in sc-CO_2 results in samples with a larger amount of radical cation units as compared with the traditional chemical synthesis. This leads to an increase in conductivity, which is promising for synthesis of high-purity conducting polymers.

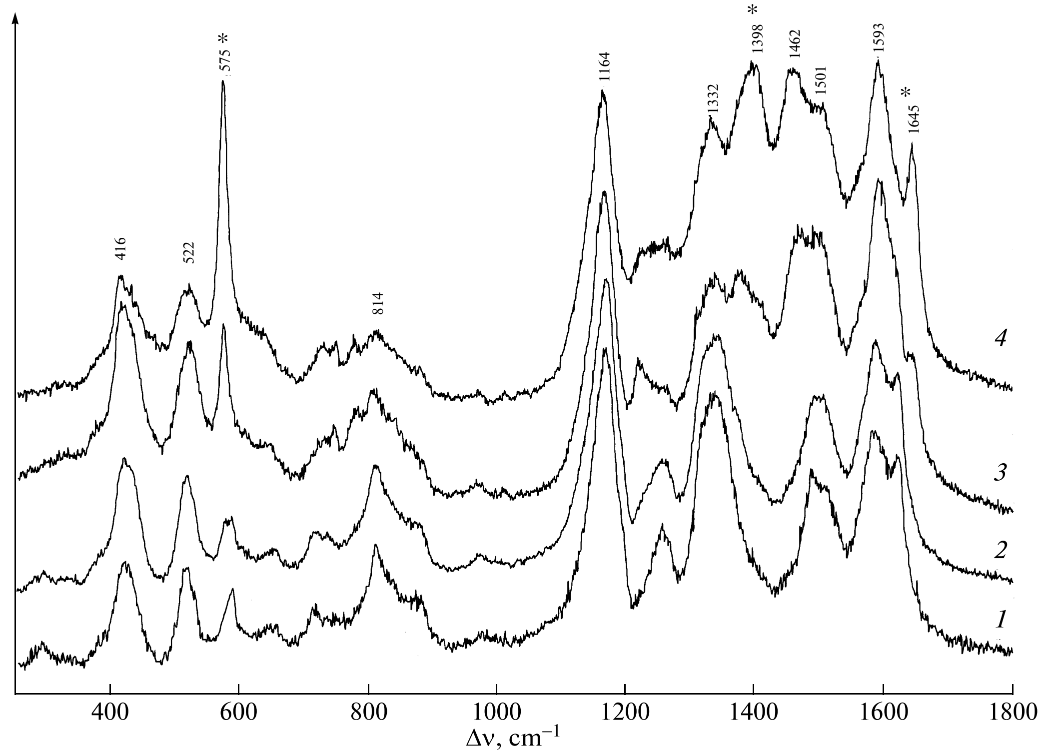


Fig. 2. Representative Raman spectra (λ_{exc} 632.8 nm) of PANI samples obtained by the routine chemical method. The excitation laser radiation power was (*1*) 0.0005, (*2*) 0.005, and (*3*) 0.05 mW, and (*4*) 0.005 mW (was obtained within 30 min after the beginning of recording the spectrum). New lines characterizing the appearance of crosslinks are asterisked (see text).

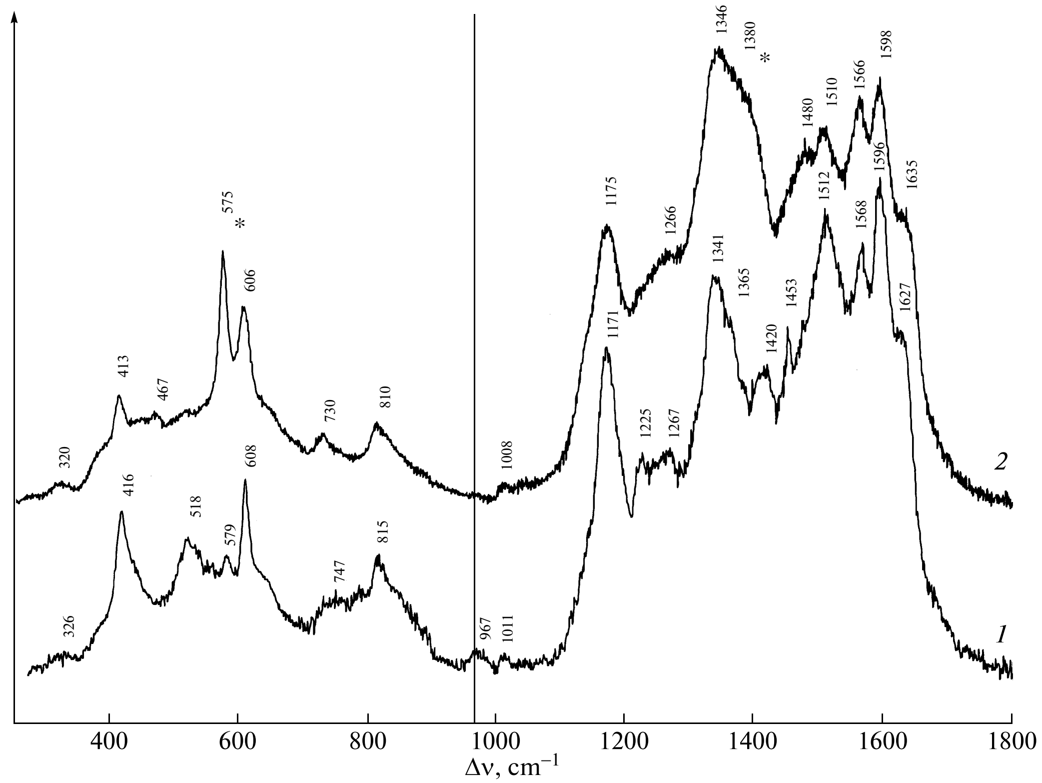


Fig. 3. Representative Raman spectra if PANI samples obtained in sc-CO_2 (λ_{exc} 632.8 nm). The excitation laser radiation power was 0.005 mW.

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