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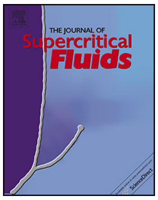

# Study of the process of poly(phenylquinoxaline)s formation in supercritical carbon dioxide

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ABSTRACT

A study of the formation of poly(phenylquinoxaline)s in supercritical carbon dioxide was performed. It was found that the reaction conditions of cyclopolycondensation had a significant impact on the formation of polymers. When using certain catalysts, soluble polymers were obtained which were cast into thin films and some of their properties were then studied.

## 1. Introduction

Polyheteroarylenes (PHA) are of special interest due to their high thermal, chemical and radiation stability [1–3] as well as their photophysical properties [4,5]. Poly(phenylquinoxaline)s (PPQ), besides the mentioned properties of PHA, possess high solubility in organic solvents and high cyclization rate of quinoxaline fragment which is very important for the formation of non-defective structures [6].

PPQ are attractive for many applications such as binder for composite materials, electro-insulating materials, high performance films and adhesives, and materials for electrooptic applications [7] and organic light emitting diodes (LED) [8].

One of the key factors hindering world spread introduction of these polymers is that toxic, environmentally hazardous solvents such as phenol, chlorinated hydrocarbons etc are used in their synthesis [9,10].

In the literature there are reports of successful attempts to synthesize some members of PHA, such as polyimides, in supercritical carbon dioxide (sc-$CO_2$) [11–13].

As an inert medium, sc-$CO_2$ is widely considered as the "green" alternative for volatile organic solvents in polymer synthesis [14]. As a solvent sc-$CO_2$ has several obvious benefits: it dissolves many organic compounds, has low viscosity (~10–100 times lower than that of a liquid) and low surface tension, it is inert towards the majority of monomers, it can be easily and completely removed from the reaction zone after synthesis is finished, it is recyclable, non-toxic, non-flammable, non-explosive, non-hazardous and cheap. Consequently, sc-$CO_2$ is widely used as a solvent and reaction medium in polymer synthesis [15,16].

In connection with the above-shown facts it seems relevant and timely to explore this approach for the synthesis of another class of polymers, in particular poly(phenylquinoxaline)s.

## 2. Experimental

We used 99.998% pure carbon dioxide (Linde Gas AGA, Balashiha, Russia) with water content no higher than $5 \times 10^{-6}$ vol.%. The general scheme of equipment used to perform PPQ synthesis is presented in Fig. 1.

FTIR spectra were recorded with KBr pellets on a Thermo-Nicolet Nexus Fourier transform IR spectrophotometer to control the completeness of the PPQ synthesis.

Thermogravimetric analysis was performed on a MOM Derivatograph-C instrument (Hungary) with ~15 mg samples at a heating rate of 10°/min in air.

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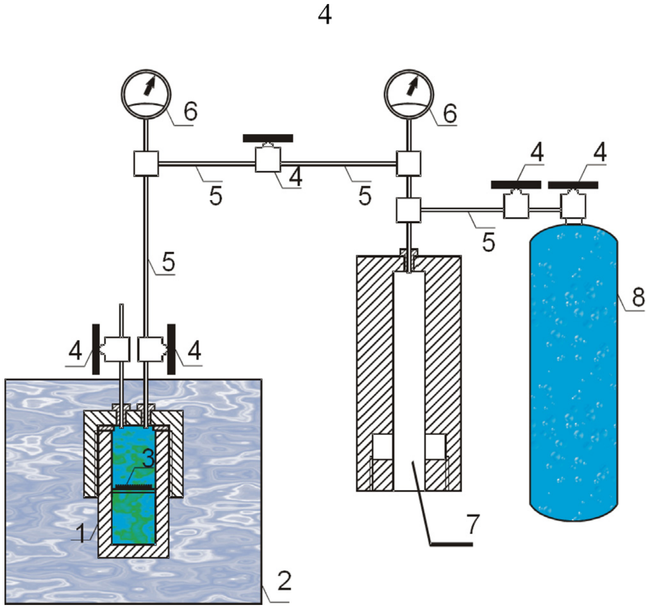


**Fig. 1.** Scheme of equipment for PPQ synthesis. (1) – high-pressure vessel; (2) – thermostat; (3) – monomers; (4) – high-pressure valves; (5) – high-pressure tubing system; (6) – manometers; (7) – high-pressure generator «Thar Technologies»; (8) – $CO_2$ tank.

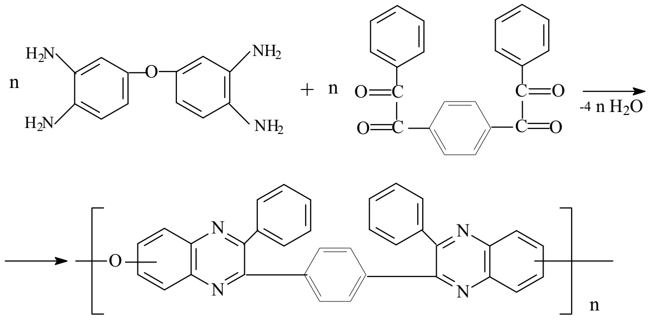
Thermomechanical studies were carried out using UIP-70 M analyzer (Russia). The heating rate was of 5°/min at the load of 0.2 MPa.

For AFM study, MultiMode$^{TM}$ Scanning Probe Microscope with NanoScope-IIIa (Digital Instruments, USA) controller was used. All images were obtained in Tapping Mode with 1 Hz scanning rate and information density of 512 × 512 points.

Mechanical properties of polymer films were evaluated on LLOYD Instruments LR5 K Plus testing machine with 50 mm/min stretching speed.

### 2.1. Polymer synthesis

A mixture of 0.342 g ($10^{-3}$ mol) 1,4-bis(phenylglyoxalyl) benzene and 0.230 g ($10^{-3}$ mol) of 3,3′,4,4′-tetraaminodiphenyl oxide was placed in the vessel with and without the catalyst (1 $cm^3$ of methanol) and with magnetic stirrer. The vessel was blown with $CO_2$ in order to eliminate any trace of aqueous vapors and than heated up to the reaction temperature (35–70 °C). The reactor was then filled with $CO_2$ from the tank and needed pressure of 7–20 MPa was created with pressure generator. After temperature and pressure were set, the reactor was exposed for several hours (Tables 1 and 2). After the reaction was completed, reactor was cooled down, decompressed and opened.



**Scheme 1.** Synthesis of polyphnylquinoxalines.

The reactor content was first dissolved in benzylic alcohol and then precipitated in ethanol with subsequent filtration. Polymer was then dried in vacuum under 100 °C for 10 h. Polymer yield was 49–96% and varied with synthesis parameters.

### 2.2. Preparation of PPQ films

Films were prepared from 10% solutions of PPQ in chloroform and dried at ambient temperature and then in vacuum at 100 °C. Films' thickness was 20–50 μm.

### 2.3. Samples preparation for atomic force microscopy (AFM)

Thin polymer films were produced on the substrate and their morphology was studied by means of atomic force microscopy (AFM). As a substrate we have chosen mica (Plano GmbH, Germany). Thin films were produced via dip-coating method using polymer solutions in acetone, of different concentrations.

## 3. Results and discussion

Here we present the study of a new approach to PPQ synthesis in liquid sc-$CO_2$. No hazardous solvents are used and the resulting polymer is free of any residues of high-boiling solvents which are difficult to eliminate by using conventional synthetic procedures.

The present approach to PPQ synthesis was studied on the reaction of 3,3′,4,4′-tetraaminodiphenyloxide with 1,4-(phenylglyoxalyl) benzene under different conditions (varying pressure, temperature and reaction time), with and without catalyst (Scheme 1).

Attempts to synthesize PPQ in liquid $CO_2$ were unsuccessful. No polymer was formed, judging from the lack of red coloring of sulfuric acid upon addition of reaction products (qualitative test for phenylquinoxaline fragment). The addition of methanol as a catalyst to the mixture did not yield any polymer in liquid $CO_2$, either. Only the use of catalyst and rise of the temperature to 35 °C

**Table 1**
Reaction parameters for PPQ synthesis with methanol as catalyst and properties of the obtained polymers.

| Experiment number | Time (h) | T (°C) | Pressure (MPa) | Yield (%) | $\eta_{red}$ (dL/g, 25 °C, in NMP) | Comments |
|---|---|---|---|---|---|---|
| 1 | 4 | 35 | 15 | 72 | 0.29 | |
| 2 | 4 | 50 | 15 | 80 | 0.43 | Robust film |
| 3 | 8 | 50 | 15 | 90 | 0.56 | Robust film |
| 4 | 25 | 50 | 15 | 92 | 0.60 | Robust film |
| 5 | 40 | 50 | 15 | 96 | 0.64 | Robust film |
| 6 | 4 | 50 | 20 | 80 | 0.48 | Robust film |
| 7 | 4 | 50 | 7 | 92 | 0.23 | |
| 8 | 4 | 70 | 15 | 96 | 0.33 | Brittle film |

$\eta_{red}$ means reduced viscosity; it was measured with an Ubbelohde viscometer by using polymer solutions of 0.5% concentration; it is given by the equation: $\eta_{red} = (t - t_o)/(c \times t_o)$, where t is flow time of polymer solution; $t_o$ is flow time of solvent; c is concentration of polymer solution. Brittle films means that they break at the first attempt to bend them; Robust films means that they resist to repeated bendings, at least 10 bendings.