

## Synthesis of Poly(naphthoylenebenzimidazole)s in a Green Supercritical Fluid

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Poly(heteroarylene)s (PHAs) are of special interest as materials for thermo-, heat-, fire-, and chemical-resistant systems, films, and matrices used for immobilization of catalysts, coatings, fibers, etc. [1]. Poly(naphthoylenebenzimidazole)s (PNBIs) are one of the promising classes of PHAs. PNBIs based on six-membered dianhydrides of tetracarboxylic acids are known to be considerably superior in hydrolytic, thermal, and thermal-oxidative stability to analogues derived from five-membered dianhydrides of tetracarboxylic acids [2, 3].

At the same time, due to the ease of formation of six-membered naphthylimide rings, it is impossible to accomplish a two-stage process of their preparation, with the first stage being the formation of organosoluble poly(amidoacid)s. The fact that PNBIs form immediately in a cyclic form determines the difficulty of their processing into goods without imparting them with a special structure (bulky substituents, flexible bridging groups, etc.) that makes them more soluble [2–5]. In most cases, the saturation of PNBI molecules with bridging groups or

introduction of side substituents improves the solubility of these polymers [2, 3].

In recent time, successful attempts have been made to introduce trifluoromethyl substituents in PNBI structures [6]. This enables the preparation of polymers soluble in organic solvents, such as N-methylpyrrolidone, DMF, DMA, and DMSO.

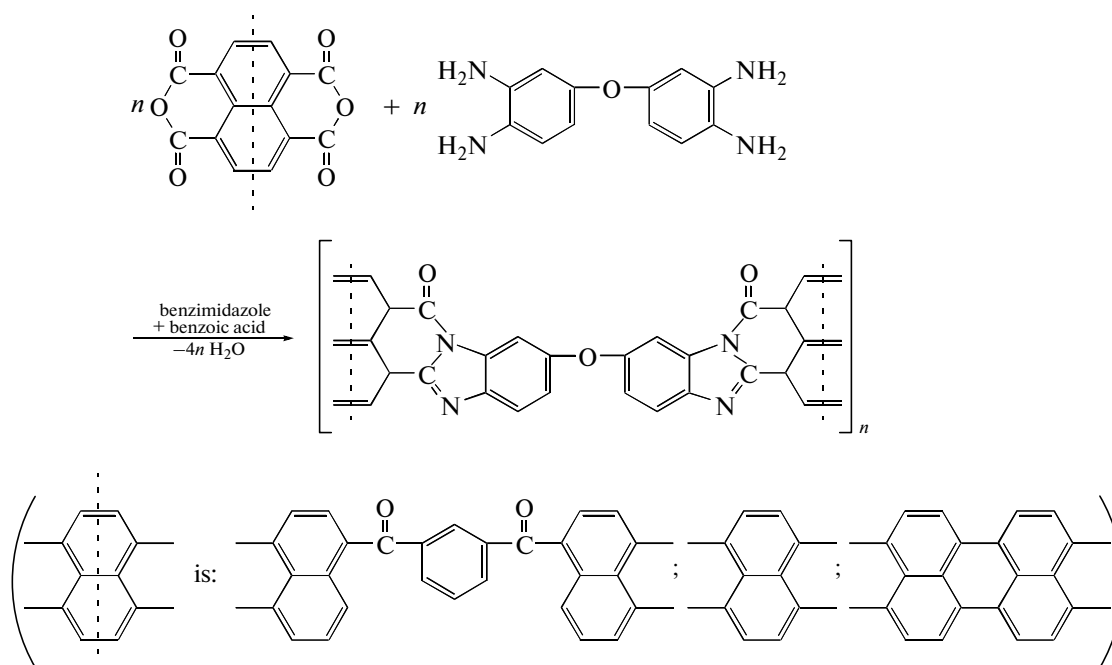
To avoid the use of phenolic solvents commonly employed in the synthesis of PNBIs and poorly removable from the target polymer, it seemed to be expedient to study PNBI formation in a green supercritical fluid successfully used in the synthesis of other PHA classes [7–9]. The wide application of supercritical carbon dioxide (sc-CO<sub>2</sub>) is due to its special physicochemical properties, such as availability, low cost, incombustibility, low toxicity, and relative inertness in chemical reactions [10].

The aim of this work is to search for fundamentally new approach to the synthesis of PNBIs in a green supercritical fluid sc-CO<sub>2</sub>.

PNBIs were obtained by the reaction of equimolar amounts of bis(naphthalic anhydride)s of different structure and 3,3',4,4'-tetraaminodiphenyloxide in sc-CO<sub>2</sub>:

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Initially, the features of PNBI formation in  $sc\text{-CO}_2$  were studied by the example of the reaction of 1,3-phenylenebis(4-naphthoyl-1,8-dicarboxylic) dianhydride, containing two bridging carbonyl groups favorable for solubility, and 3,3',4,4'-tetraaminodiphenyl ether at different temperatures and reaction times.

The change in polycondensation reaction parameters (temperature, pressure, reaction time, presence of catalyst) considerably affects the process of polymer formation. Initially, the reaction was carried out without a catalyst for 4 h at  $50^\circ\text{C}$ . The pressure in all experiments was the same, 15 MPa. The data of the table (run 1) show that the attempted preparation of PNBI was failed under these conditions and gave probably only an oligomer with  $\eta_{\text{red}} = 0.03 \text{ dL/g}$  in 53% yield.

To achieve the aim, it seems to be expedient to use an equimolar mixture of benzimidazole and benzoic acid as a catalyst [11]. The use of the catalyst under above conditions provided no opportunity to obtain higher molecular weight compounds, but the yield of the oligomeric product enlarged to 80% (run 2). An increase in reaction temperature to  $70^\circ\text{C}$  (run 3) or reaction time to 6 h (run 4) also did not lead to significant changes. Only at  $90^\circ\text{C}$  and 6 h exposure, we prepared PNBI with  $\eta_{\text{red}} = 0.48 \text{ dL/g}$  in 95% yield (run 5). Polymers soluble in amide solvents were isolated in all cases. Further elevation of reaction temperature to  $120^\circ\text{C}$  gave rise to cross-linked polymer insoluble even in sulfuric acid.

The synthesis of PNBI in  $sc\text{-CO}_2$  from more reactive naphthalene-1,4,5,8-tetracarboxylic dianhydride at  $70^\circ\text{C}$  for 4 h leads to a high-molecular-weight poly-

mer in high yield (run 7). An increase in reaction time and temperature has no considerable effect on the yield and viscosity characteristics of the resultant polymer (run 8).

The use of perylene-3,4,9,10-tetracarboxylic dianhydride under conditions suitable for the synthesis of other PNBI led to only low-molecular-weight products (runs 9 and 10).

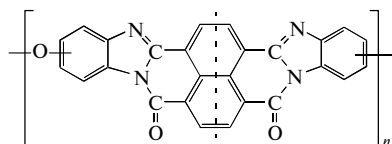
The IR spectra of all obtained polymers show absorption maxima in the range  $1550\text{--}1560 \text{ cm}^{-1}$  typical for 1',8'-naphthoylene-1,2-benzimidazole: absorption bands at  $1620$ ,  $1590$ , and  $1450 \text{ cm}^{-1}$  assigned to benzimidazole ring, and at  $1695 \text{ cm}^{-1}$  assigned to the carbonyl group of 1',8'-naphthoylene-1,2-benzimidazole [12].

Thus, we established the formation of naphthoylenebenzimidazole ring from bis(naphthalic anhydride)s and tetraamine in  $sc\text{-CO}_2$  fluid. The nature of the used bis(naphthalic anhydride) markedly affects the features of PNBI formation, and particular optimal synthesis conditions seem to exist for each monomer pair.

All obtained PNBI are soluble in sulfuric acid, while polymers 2–5 (table) are also soluble in amide solvents. According to TGA in air, the 10% weight loss temperature of these polymers is  $480\text{--}520^\circ\text{C}$ .

Our new approach to the synthesis of PNBI in  $sc\text{-CO}_2$  excludes the use of environmentally hazardous phenolic solvents in the polycondensation process and enables the preparation of high-purity polymers.

Conditions of synthesis in sc-CO<sub>2</sub> and viscosity of PNBI of general formula



Experiment		Time, h	<i>T</i> , °C	Catalyst	Yield, %	$\eta_{\text{red}}$ , dL/g
1		4	50	—	53	0.03
2		4	50	+	80	0.08
3		4	70	+	88	0.11
4		6	70	+	85	0.18
5		6	90	+	95	0.48
6		6	120	+	95	See. *
7		4	70	+	83	0.55
8		6	90	+	78	0.58
9		4	70	+	69	0.17
10		6	90	+	57	0.18

At 15 MPa.

\* Polymer is insoluble.

## EXPERIMENTAL

An experimental setup for PNBI synthesis was described in [9]. Carbon dioxide corresponded to State Standard GOST 8050-85, purity of 99.998% (Linde Gas AGA Corporation, Balashikha, Russia). According to the certificate of analysis, the water volume content was no higher than  $5 \times 10^{-6}$  vol %.

IR absorption spectra were recorded on a Nicolet Magna-IR 750 Fourier-transform spectrophotometer in the range 4000–400 cm<sup>-1</sup> as KBr pellets.

TGA was performed in dynamic mode at a temperature growth rate of 5 K/min in air on a Paulik–Paulik–Erdey C-type derivatograph.

The melting points of monomers were determined on a Melt-Temp II apparatus.

The viscosity of polymer solutions was determined with an Ubbelohde capillary viscometer at 25°C at a polymer concentration of 0.5 g/dL. Reduced viscosity was calculated by the formula

$$\eta_{\text{red}} = \frac{\tau_{\text{solution}} - \tau_{\text{solvent}}}{c\tau_{\text{solvent}}}.$$

**Synthesis of initial compounds.** Synthesis and purification of 3,3',4,4'-tetraaminodiphenyl oxide was carried out according to procedure [13].

**Synthesis of PNBI.** A 22-mL high-pressure stainless-steel reactor was charged with a carefully stirred mixture of an appropriate dianhydride, 3,3',4,4'-tetraaminodiphenyl oxide, benzimidazole, and benzoic acid,  $10^{-3}$  mol of each, (table, runs 2–10) or a mixture of monomers,  $10^{-3}$  mol of each, without the catalyst (run 1). The reactor was purged with carbon dioxide before synthesis to remove water vapors and then heated to required temperature (50–120°C) in a thermostat with programmable temperature controller. A mixture in the reactor was stirred with a magnetic stirrer. Carbon dioxide was supplied into the reactor to provide a necessary pressure of 15 MPa using a piston generator (High Pressure Equipment Company, USA). The reactor was kept under prescribed conditions for 4 or 6 h. After completion of the reaction and cooling, stirring of reaction mixture was terminated and the pressure was lowered. The resulting polymer was dissolved in *N*-methylpyrrolidone or sulfuric acid, precipitated

with water, separated by filtration, washed with ethanol, and dried in a vacuum at 100°C for 10 h.

#### ACKNOWLEDGMENTS

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