ISSN 0012-5008, Doklady Chemistry, 2018, Vol. 480, Part 1, pp. 89–92. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.M. Belomoina, E.G. Bulycheva, R.S. Begunov, M.I. Buzin, I.S. Chashchin, 2018, published in Doklady Akademii Nauk, 2018, Vol. 480, No. 3, pp. 293–296.

CHEMISTRY

An Alternative Approach to the Synthesis of Poly(naphthoylenebenzimidazole)s

N. M. Belomoina[a,*], E. G. Bulycheva[a,], R. S. Begunov[b], M. I. Buzin[a], and I. S. Chashchin[a]**

Presented by Academician A.R. Khokhlov January 30, 2018

Received February 2, 2018

Abstract—An alternative approach to the synthesis of poly(naphthoylenebenzimidazole)s in supercritical carbon dioxide has been accomplished without use of hazardous chemical solvents, which resulted in preparation of high-purity polymers by a more efficient contemporary method. A series of poly(naphthoylenebenzimidazole)s has been obtained at 90°C and 15 MPa for 8 h with the use of a mixture of benzoic acid and benzimidazole as a catalyst. Certain properties of the synthesized polymers have been studied.

DOI: 10.1134/S0012500818050051

In the series of completely or partially ladder polyheteroarylenes (PHAs), poly(naphthoylenebenzimidazole)s (PNBIs) are of the most practical interest [1]. These polymers exhibit high thermal, heat, fire, and chemical resistance and can be used as materials for new equipment [2, 3].

However, in most cases, PNBI synthesis is carried out in hazardous solvents, such as polyphosphoric acid, phenolic solvents, and nitrobenzene.

PNBI preparation in a green supercritical medium, which is used for the synthesis of other classes of PHAs, seems to be more promising [4, 5].

In this work, we used an approach to the synthesis of PNBIs in a medium containing supercritical carbon dioxide (sc-CO_2), which allowed preparation of high-purity polymers.

Polyheterocyclization reaction in sc-CO_2 (Scheme 1) was carried out by reacting bis(*o*-phenylenediamine)s and bis(naphthalic anhydride)s taken in equimolar ratios at 90°C and 15 MPa for 8 h. The catalyst used was a 1 : 1 mixture of benzoic acid and benzimidazole [6], which are used in food industry and pharmacology.

Under these conditions, we obtained a series of PNBIs, including those previously unknown, whose characteristics are presented in Table 1.

All the polymers are soluble in sulfuric acid. Polymers **2**, **3**, **5**–**7** are soluble in a phenol–TCE mixture (1 : 3). Polymers **2**, **3**, **6**, and **7** are also soluble in *N*-methyl-2-pyrrolidone (N-MP).

We confirmed the PNBI structure by IR spectroscopy. The IR spectra of the prepared polymers showed absorption maxima in the range 1550–1560 cm^{-1} typical for the absorption of 1',8'-naphthoylene-1,2-benzimidazole. Maxima at 1620, 1590, and 1450 cm^{-1} were assigned to the benzimidazole ring [7].

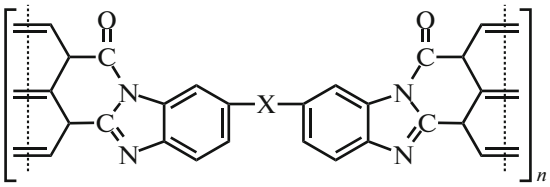
The effect of the introduction of different groups into the main chain on the thermal-oxidative stability of the polymers was studied by thermogravimetric analysis (TGA). Figure 1 displays comparison of TGA curves for PNBIs **1**, **2**, and **4** (Table 1) prepared in sc-CO_2 (curves *1*–*3*) and for PNBI obtained by high-temperature polycondensation [8] in solution (curve *4*). In the latter case, PNBIs had a structure identical to PNBI **1** (Table 1).

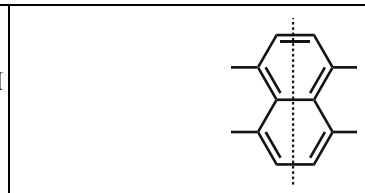
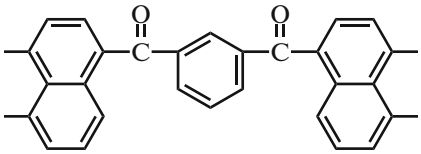
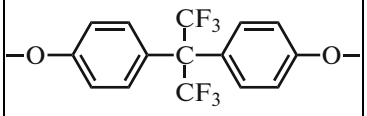
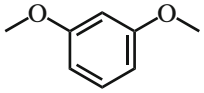
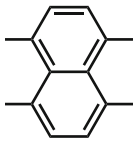
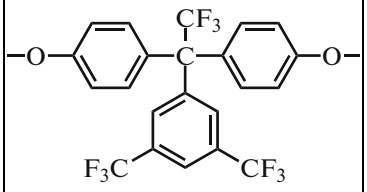
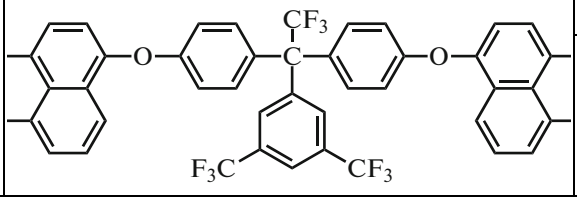
Degradation onset temperatures in air for PNBIs prepared under different reaction conditions virtually coincide, being about 470°C and little dependent on their structure, which agrees well with data in [8, 9].

The softening temperatures for the polymers determined from thermomechanical curves were in the range 250–365°C depending on the chemical structure of amine and anhydride components (Table 1). PNBI **4** has the softening temperature higher than the degradation temperature.

The introduction of fluorine in polymers is known to impart them solubility, fire resistance, improved electrophysical characteristics, etc. [10, 11].

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Demidov Yaroslavl State University, Yaroslavl, 150000 Russia*
**e-mail: bel@ineos.ac.ru*
***e-mail: bulychev@ineos.ac.ru*

Table 1. Selected characteristics of PNBIs of general formula 

PNBI no.		–X–	Yield, %	η_{red}, (25°C, H_2SO_4)	T_{dec}, °C
1		–O–	95	0.50	365
2			93	0.36	250
3			94	0.38	315
4		–O–	94	0.59	–
5			93	0.33	290
6		–O–	87	0.30	270
7		–	91	0.35	290

nescence curves are presented in Fig. 2. We observed the maxima of luminescence spectra for the polymer depending on excitation wavelength at 558, 440, and 561 nm.

We also studied the optical properties of PNBIs **6** and **7** (Table 1) by UV spectroscopy and photoluminescence in an N-MP solution. The UV spectra of PNBIs **6** and **7** displayed two absorption peaks (Table 2). The photoluminescence spectra of the PNBIs at an excitation wavelength of 400 nm exhibit light emission with one strong maximum. In other words, the study of PNBI polymers **6** and **7** revealed yellow-orange emission with a fluorescence maximum at 530 nm. These polymers are of interest for organic light-emitting diodes similarly to other polyheteroarylenes [12].

Table 2. Optical properties of PNBIs

Polymer –X–	UV absorption, λ_{abs}, nm	PL after exposure to UV, λ_{em}, nm
–O–	310, 404	530
–	300, 400	530

λ_{abs} is wavelength of absorption maximum, λ_{em} is wavelength of photoluminescence (PL) maximum.

Thus, the alternative approach to the synthesis of PNBIs by polycyclocondensation in sc-CO_2 allowed us to exclude the use of environmentally hazardous strong mineral acids or organic high-boiling solvents, decrease the reaction temperature from 160 to 90°C, and obtain high-purity thermally stable polymers by a more efficient contemporary method.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 16–03–00119).

“УТВЕРЖДАЮ”

ВРИО директора ИНЭОС РАН

д.х.н. Трифонов А.А.

№12111-6251/6

2018 г.

ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев ***статью в журнал ДАН, Беломоиной Н.М., Булычевой Е.Г., Бегунова Р. С., Бузина М.И., Чащина И. С.*** **«Альтернативный подход к синтезу полинафтоиленбензимидазолов»**

подтверждает, что в материале ***не содержатся*** сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала ***не следует*** получать разрешение ***ФАНО и/или Президиума РАН***

Заключение: ***статья может быть опубликована в открытой печати, т.к. она не содержит сведений, не подлежащих открытой публикации***

Руководитель-эксперт _____

(подпись)

Пономарев И.И., д.х.н., проф. , зав. лаб. Синтеза гетероцепных полимеров ИНЭОС РАН

(ф. и. о., должность)