ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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RESEARCH ARTICLE

Development of the technique for quality control of 1,3-bis(3,4-dicyanophenoxy)benzene by HPLC

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Abstract

Objectives. *Determination of target products and byproducts is necessary for the quality control of phthalonitrile monomer synthesis as well as production scaling and performing related kinetic studies. High-performance liquid chromatography (HPLC) is a simple and affordable method for quantitative chemical analysis, which also verifies the quality of raw materials. The objective of this study was to develop an HPLC technique for determining the composition of the reaction mixture in the synthesis of 1,3-bis(3,4-dicyanophenoxy)benzene (DPB).*
Methods. *Reversed-phase HPLC was used to quantitatively analyze the reaction mixture.*
Results. *A simple and rapid method for the quantitative HPLC analysis of phthalonitrile monomers and their mixtures with reagents was developed. Reaction times and the accumulation of byproducts were also studied.*
Conclusions. *The successful performance of the developed technique allows us to recommend it for practical applications. The results obtained for reactors of different sizes have good convergence, and DPB synthesis was successfully scaled up to intermediate scale equipment.*

Keywords: *1,3-bis(3,4-dicyanophenoxy)benzene, high-performance liquid chromatography, quantitative analysis, scaling up, phthalonitrile resins*

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НАУЧНАЯ СТАТЬЯ

Разработка методики количественного анализа целевого и побочных продуктов синтеза 1,3-бис(3,4-дицианофенокси)бензола методом ВЭЖХ

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Аннотация

Цели. *Для аналитического контроля производства фталонитрильных мономеров, изучения масштабирования технологии их получения и проведения кинетических исследований актуальна задача по разработке способа определения концентрации целевого и побочных продуктов в присутствии реагентов. Наиболее простым и доступным методом количественного анализа рассматриваемых соединений является высокоэффективная жидкостная хроматография (ВЭЖХ), позволяющая также проводить верификацию сырья и контроль качества готовой продукции. Цель данной работы заключалась в разработке методики количественного анализа компонентов реакционной смеси при синтезе 1,3-бис(3,4-дицианофенокси)бензола (ДБФ) методом ВЭЖХ.*
Методы. *Для количественного анализа компонентов реакционной смеси использовали метод ВЭЖХ в обращенно-фазовом режиме.*
Результаты. *Разработана простая и быстрая методика количественного анализа фталонитрильных мономеров и их смесей с реагентами методом ВЭЖХ. По данным исследования конверсии компонентов реакционной смеси сделан вывод о продолжительности реакции и накоплении побочных продуктов.*
Выводы. *Успешная апробация позволяет рекомендовать разработанную методику для применения в аналитической практике. Результаты, полученные при переходе от реакции в колбе к реактору объемом 15 л, характеризуются хорошей сходимостью. Синтез ДФБ успешно масштабируется на оборудование промежуточного масштаба.*
Ключевые слова: *1,3-бис(3,4-дицианофенокси)бензол, высокоэффективная жидкостная хроматография, количественный анализ, масштабирование, фталонитрильные связующие*

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INTRODUCTION

Phthalonitriles are promising compounds to produce highly heat-resistant resins and polymer composite materials (PCMs), which are widely utilized in the space and aviation industries. Phthalonitrile matrices have good mechanical characteristics, low moisture absorption, high heat resistance, and are currently the most thermally and oxidatively stable polymers [1–7].

Along with low-melting phosphorus containing monomers [8–10], an important component of phthalonitrile resin compositions for PCMs [11–14] is 1,3-bis(3,4-dicyanophenoxy)benzene (DPB) (**3**), a product of the reaction between 4-nitrophthalonitrile (4NPN) (**1**) and resorcinol (**2**) [15]. The thermal properties of DPB and a corresponding polymer[1] are presented in Table 1 [15]. This data demonstrates the high heat-resistance of the thermoset plastic derived from DPB.

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[1] The authors used 2.4 mol % 1,3-bis(3-aminophenoxy)benzene for curing DPB. The process was conducted in a nitrogen atmosphere according to the following temperature regime: 2 h at 250°C, 2 h at 325°C, 4 h at 350°C, and 8 h at 375°C.

Table 1. Thermal properties of 1,3-bis(3,4-dicyanophenoxy)benzene (DPB) and a DPB-based polymer

Monomer	Cured matrix		
mp*, °C	T_g**, °C	$T_{5\%}$***, N_2, °C	Char yield (at 900°C), N_2, %
185–190	>400	527	70

* Melting point;
** Glass transition temperature;
*** Temperature at 5% mass loss.

DPB is synthesized in an aprotic dipolar solvent in the presence of a base (potassium carbonate), forming 4-(3-hydroxyphenoxy)phthalonitrile (HPPN) (**4**) and 3,3',4,4'-tetracyanodiphenyl ether (PN2O) (**5**) as byproducts. The reaction scheme and byproduct structures are shown in Fig. 1.

An effective way to quantify target compounds and byproducts in the presence of reagents is required for the analytical control of the phthalonitrile resins production and for performing relevant kinetic studies during production process optimization. High-performance liquid chromatography (HPLC) is the simplest and most accessible method of quantitative analysis for the compounds under consideration, and it also allows to carry out quality control of the raw materials and products.

Scaling up the synthesis of phthalonitrile monomer DPB is an important step in producing high heat resistant resins at industrial level, which also requires precise analysis of the composition of the reaction mixture for the technical control of the synthesis.

This study aimed to develop an HPLC protocol for the quantitative analysis of the target products and byproducts of DPB synthesis in order to effectively scale up the reaction from laboratory to intermediate scale equipment.

EXPERIMENTAL

Equipment and reagents

Equipment: Agilent 1260 Infinity LC with a diode array detector (*Agilent Technologies*, USA) and an ultrasonic bath.

Column: Zorbax C18 Eclipse Plus 4.6 × 100 mm, 3.5 µm phase (*Agilent Technologies*).

Reagents: Resorcinol (99%, *Sumitomo Chemical Co.*, Japan); 4NPN (99.5%, *CDH Chemicals*, India); acetonitrile (A) (used without further purification) (HPLC, *CHIMMED*, Russia); and degassed water (B) (Werner UP60B ultrafine cleaning system).

DPB for constructing calibration curves was obtained as described in [15], purified by extraction chromatography (chloroform eluent and silica gel phase), and recrystallized from dimethylacetamide.

HPPN for constructing calibration curves was obtained as described in [16] and purified by extraction chromatography (chloroform eluent and silica gel phase).

PN2O for constructing calibration curves was obtained as described in [17] and purified by recrystallization from dimethylacetamide.

HPLC analysis of the components of the reaction mixture

A test sample weighing 100 ± 3 mg was added to 10 mL of acetonitrile and left in an ultrasonic bath for 10 min. Insoluble impurities were removed using a 0.45 µm pore syringe filter. In chromatographic vials, 900 µL of acetonitrile was added to 100 µL of the filtrate solution, and HPLC analysis was carried out according to the parameters listed in Table 2.

Method for DPB synthesis in a 2-L flask

A 2 L three-necked flask, equipped with a reflux condenser and mechanical paddle stirrer, was

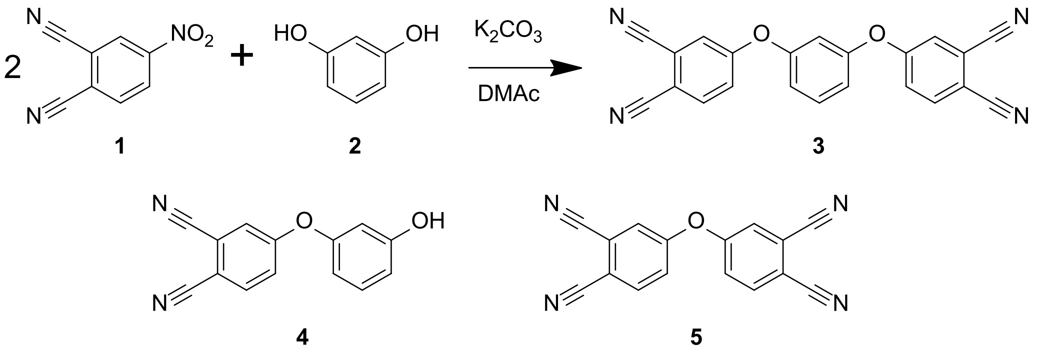

Fig. 1. 1,3-bis(3,4-dicyanophenoxy)benzene synthesis scheme.

Table 2. Parameters of the HPLC system

Chromatographic system parameters	Value
Elution mode	Isocratic
Flow rate	1.0 mL/min
Analysis time	10 min
Eluent composition	Acetonitrile and water
Solvent ratio (acetonitrile : water, v:v)	55 : 45
Injected sample volume	3 μL
Column temperature	30.0°C
Detection wavelengths	258 nm, 276 nm

loaded with 138.7 g (1.260 mol, 1 equiv) of resorcinol and 836 mL of dimethylacetamide. After degassing at 70°C with a residual pressure of 20 mbar and stirring at 300 rpm for 1 h, the system was filled with argon. To the resulting solution, 382.5 g (2.768 mol, 2.2 equiv) of powdered potassium carbonate was added and stirred, the degassing was repeated, and the system was again filled with argon. Then, 436.0 g (2.518 mol, 2 equiv) of 4NPN was added in a weak argon counterflow. The synthesis was carried out at 70°C with constant stirring for 24 h, and samples were collected at specified time intervals (Fig. 7). The reaction mass was then poured into 3010 mL of water and stirred for 1 h. The precipitate was filtered, washed on the filter three times with 93 mL of hot water for each wash, and dried at 80°C for 24 h. The obtained product was a light yellow powder with a yield of 388.1 g (85%).

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III spectrometer (*Bruker*, USA) with operating frequencies of 600 and 151 MHz, respectively.

^1H NMR (600 MHz, DMSO-d_6) δ ppm, 7.05–7.24 (m, 3 H), 7.55 (dd, J = 8.70, 2.17 Hz, 2 H), 7.60 (t, J = 7.70 Hz, 1 H), 7.92 (d, J = 2.17 Hz, 2 H), 8.13 (d, J = 8.70 Hz, 2 H).

^{13}C NMR (151 MHz, DMSO-d_6) δ ppm, 108.63 (3 C), 112.72 (4 C), 115.35 (4 C), 115.84 (5 C), 116.73 (3 C), 117.41 (7 C), 122.23–123.36 (14 C), 132.25 (4 C), 136.25 (8 C).

The NMR spectra of the target product corresponded with previously reported data [18].

Method for DPB synthesis in a 15-L reactor

A glass reactor with a 15 L volume was loaded with 1040.2 g (9.447 mol, 1 equiv) of resorcinol and 6240 mL of dimethylacetamide. The solution was stirred at 120 rpm, heated to 70°C, and degassed for around 1 h at a residual pressure of 20 mbar. The apparatus was then filled with argon.

In a weak argon countercurrent, 2872.3 g (20.782 mol, 2.2 equiv) of dry powdered potassium carbonate was added. The degassing process was repeated without stirring, and the system was refilled with argon while cooling to 20°C. In a weak argon counterflow, 3271.1 g (18.894 mol, 2 equiv) of 4NPH was added in four to five doses with periodic stirring. The synthesis was performed at 70°C with constant stirring for 24 h.[2] The suspension was poured from the reactor into an intermediate vessel, then water (22500 mL) was quickly added and stirred with a spatula until the product solidified. The suspension was then filtered using the same suction filter, keeping all of the collected filter cake solids on the filter. The reactor was then heated to 100°C and rinsed with water in portions and stirred for around 10 min. The filter cake was washed using this water at 95°C in the filter jacket by transferring it through an intermediate vessel and stirring the filter cake after each wash, requiring a total of 8300 mL of water for three washes. The substance from the suction filter was transferred onto trays and dried for 48 h at 80°C, giving a yield of 2909.6 g (85%) of the product in the form of a light yellow to yellow powder.

Reaction mixture sample preparation for HPLC analysis

Distilled water was added to approximately 3 mL of the reaction mixture and acidified at a ratio of 1.0 : 3.6 with glacial acetic acid. The resulting suspension was filtered through a glass filter, leaving a precipitate that was washed with ~12 mL of distilled water three times and then dried at 80°C.

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[2] During composition analysis, the reaction mixture was mixed for 54 h and samples were collected after predetermined periods of time.

RESULTS AND DISCUSSION

Development of a procedure for analyzing the components of the reaction mixture by HPLC

Determination of the maximum working concentration. Portions of resorcinol, 4NPN, HPPN, and DPB each weighing 100 ± 3 mg were mixed with 10 mL of acetonitrile, and the resulting solutions were placed in an ultrasonic bath for 10 min.

Reference solutions with concentrations of 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 mg/mL of each component were diluted with acetonitrile from the initial solutions in chromatographic vials.

Chromatographic separation was performed in the gradient mode, as outlined in Table 3.

A section of the resulting chromatogram containing the peaks of the test substances is shown in Fig. 2.

As can be seen from the chromatogram, at the same analyte concentrations the maximum peak height (H) is typical for HPPN. It is also clear that baseline resolution of the peaks corresponding to 4NPN and HPPN will be most critical for the success of the method. Table 4 shows the HPPN peak height *H* dependence on its concentration *C* in the model solution.

Table 4 shows that the maximum concentration with acceptable detector response is 1.25 mg/mL. Further tests were conducted at this concentration.

The substance PN2O is characterized by low solubility in acetonitrile. To prepare a reference solution, 10 ± 3 mg PN2O and 10 mL acetonitrile were kept in an ultrasonic bath for 10 min, which achieved complete solubilization.

Because the proportion of PN2O in the target product does not exceed 5%, the maximum concentration was chosen to be 0.10 mg/mL (10% of 1.00 mg/mL).

Determination of working wavelengths. Figure 3 shows the absorbance spectra of the analytes.

The substances 4NPN, HPPN, DPB, and PN2O have three characteristic absorption maxima in the UV-Vis range. Usually, they are analyzed at a wavelength of 258 nm; however, in this region of the spectrum, resorcinol has a much lower absorption and its maximum absorption is observed at 276 nm. Therefore, for the sensitive chromatographic analysis of their mixture, using two wavelengths is advisable, i.e., 258 and 276 nm.

Eluent composition. To determine the optimal composition of the eluent, analysis was conducted in isocratic mode with acetonitrile to water ratios of 40 : 60, 50 : 50, and 60 : 40.

The isocratic mode was chosen because it is more stable than the gradient mode and allows recycling of the solvent, which contributes to significant savings in acetonitrile.

When the composition of the eluent was 40 : 60 acetonitrile to water, the DPB peak was not observed for more than 40 min before the analysis was interrupted.

Table 3. Gradient mode for determining the maximum concentration with acceptable detector response

Time, min	0–26	26–31	31–34	34–38	38–40
A, %	55	55–98	98	98–55	55

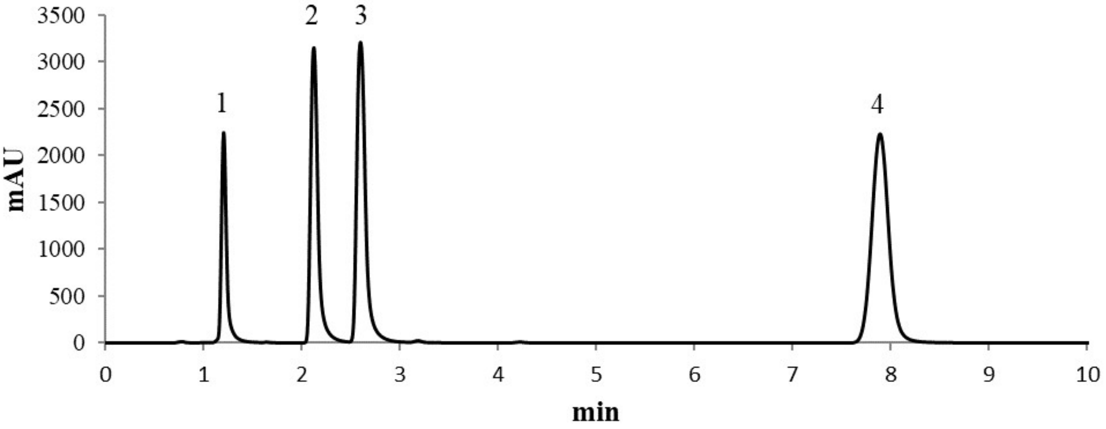


Fig. 2. Chromatogram of the reference solutions at 224 nm: (1) resorcinol, (2) 4-nitrophthalonitrile (4NPN), (3) 4-(3-hydroxyphenoxy)phthalonitrile (HPPN), and (4) 1,3-bis(3,4-dicyanophenoxy)benzene (DBP).

Table 4. HPPN peak height at different concentrations, signal recorded at 224 nm

***H*, mAU**	1112	2219	2879	3149	3250	3277	3308
***C*, mg/mL**	0.25	0.50	0.75	1.00	1.25	1.50	1.75

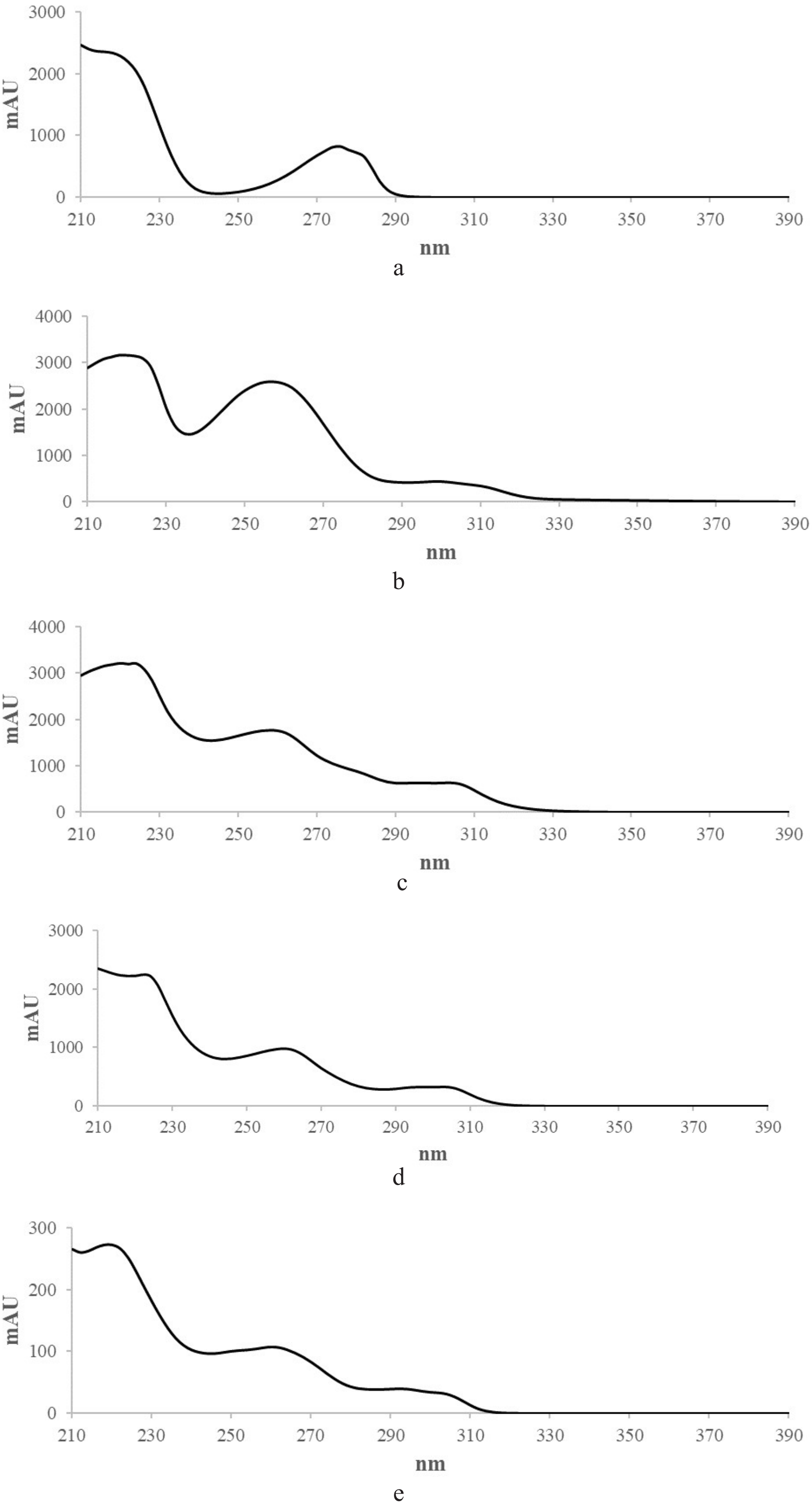


Fig. 3. Absorbance spectra of (a) resorcinol, (b) 4NPN, (c) HPPN, (d) DPB, and (e) 3,3',4,4'-tetraciano diphenyl ether (PN2O).

At a solvent ratio of 50 : 50, the separation time of the components was 15 min, and at 60 : 40, it was 7 min; however, in the latter case, the peaks were not sufficiently resolved.

Further tests were conducted at various solvent ratios ranging from 50 : 50 to 60 : 40. The results for 4NPN, the compound from the critical pair which elutes first, at a wavelength of 258 nm, are presented in Table 5.

Based on the time taken and the resolution of the critical pair, the acetonitrile to water ratio of 55 : 45 was considered optimal for the separation. Notably, the chromatogram obtained after washing the system does not show peaks of the analytes, and the change in the absorption of the baseline is only because of the contribution of the acetonitrile. The three-dimensional (3D) spectrum that demonstrates this is shown in Fig. 4.

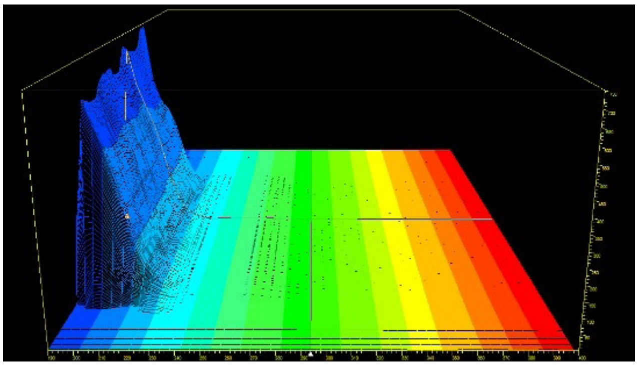


Fig. 4. 3D spectrum plotted during column washing.

Determination of the linearity range of the calibration curves. Figure 5 shows the dependence of the peak are on the concentration of the analytes.

These graphs show that the dependences are linear throughout the studied mass percent concentration range.

Conversion of reagents in the synthesis of DPB. DPB was synthesized in both a 2-L flask and a 15-L reactor (Fig. 6).

The quantity of analytes in samples of the reaction mixture was determined by the optimized HPLC protocol above, and averages were calculated from the results of two parallel analyses of each sample.

Then, the ratio of molar fractions (α) of the analytes was calculated, and the same reaction conditions were maintained in the scaled up 15-L reactor.

Figure 7 charts the conversion of the analytes, with *t* = 0 as the moment 4NPN was added.

The reaction proceeds via the intermediate HPPN that reacts with 4NPN to obtain the target product. The quantity of HPPN in the samples initially decreases gradually and then remains constant.

The DPB content reaches a plateau approximately 20 h after the start of the reaction, and the degree of 4NPN conversion reaches a maximum approximately 45.5 h.

A sharp increase in the amount of PN2O is observed in the initial section but then reaches a plateau approximately 20 h after the start of the reaction.

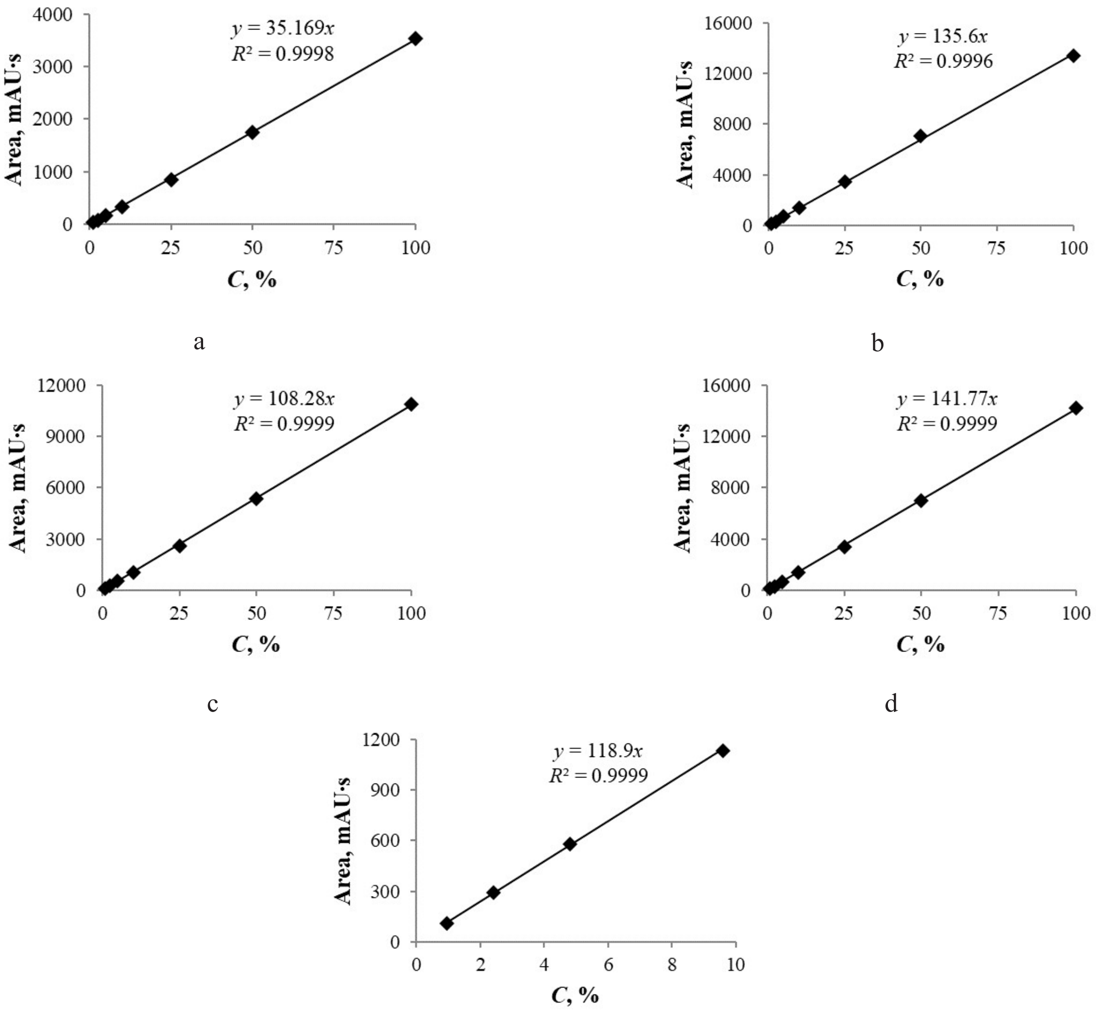
The data obtained for the 2-L and 15-L syntheses are roughly the same, indicating that the scaling up of the synthesis of DPB is achievable and effective.

CONCLUSIONS

This study developed a rapid and simple method for the quantitative analysis of phthalonitrile monomers (HPPN and DPB), resorcinol, 4NPN, and

Table 5. Chromatographic parameters of the 4NPN peak at various solvent ratios

A, %	Total run time, min	Resolution to HPPN peak	Symmetry	Efficiency
50	15	6.20	0.73	6580
52	12	5.18	0.72	6149
54	11	4.38	0.72	5726
55	10	3.88	0.71	5250
56	9	3.66	0.70	5280
58	8	3.01	0.70	5139
60	7	2.51	0.70	4640



a

b

c

d

e

Fig. 5. Calibration curves for (a) resorcinol 276 nm, (b) 4NPN 258 nm, (c) HPPN 258 nm, (d) DPB 258 nm, and (e) PN2O 258 nm. *C*, % corresponds to mass percent.

PN2O by reversed-phase HPLC. Our technique is effective for a wide range of analyte concentrations and can determine impurities as low as 0.5% of the content of each compound.

Through our analysis of the composition of the reaction mixture, we were able to determine both the reaction time and related byproducts of the synthesis. Finally, from our successful syntheses in both 2-L and 15-L reaction volumes, we conclude that phthalonitrile monomer DPB synthesis can be effectively scaled up from the laboratory scale to the intermediate scale equipment with no changes in reaction conditions.

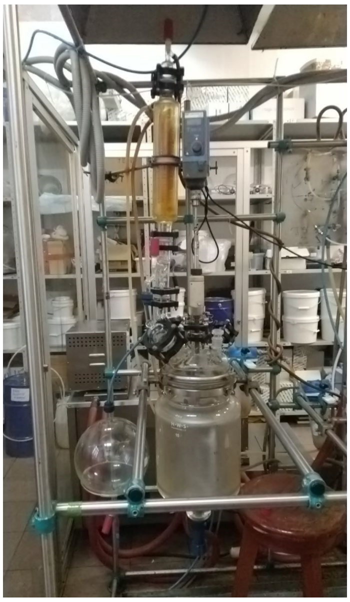


Fig. 6. 15-L reactor.

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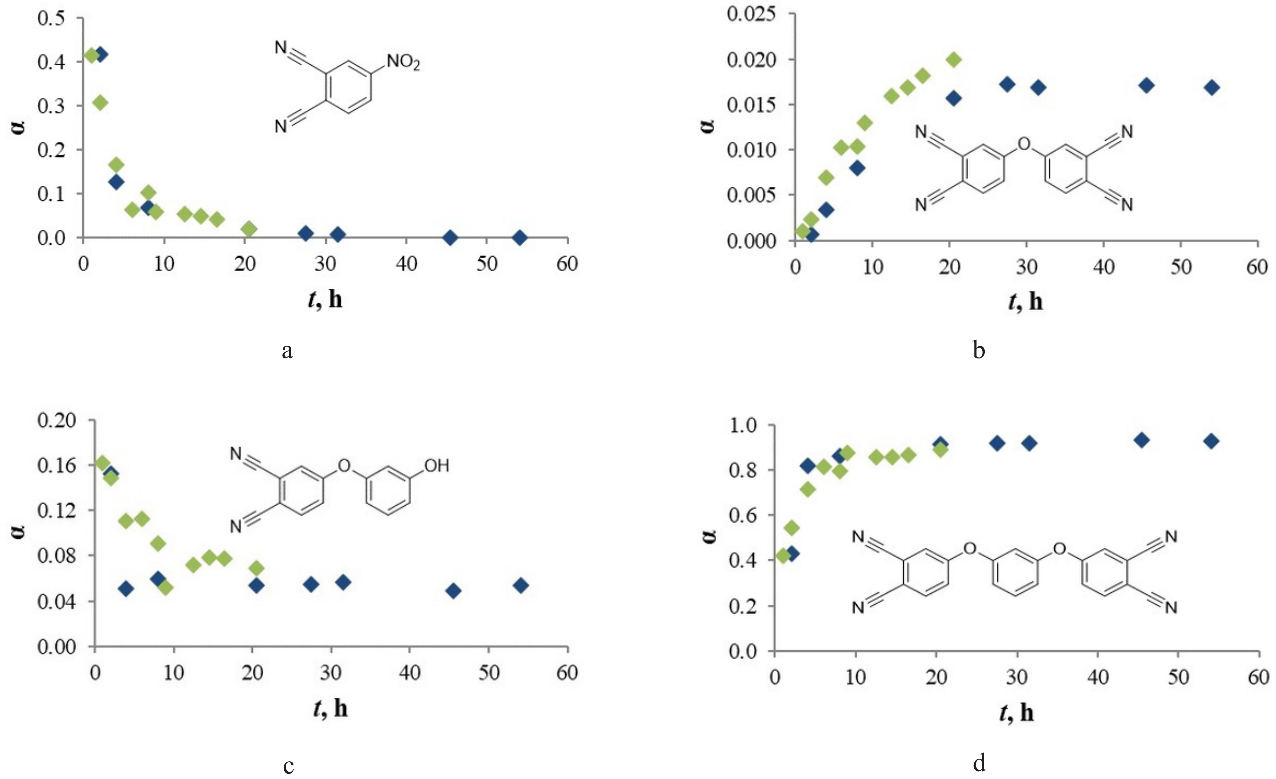

a

b

c

d

Fig. 7. Conversion of (a) 4NPN, (b) PN2O, (c) HPPN, and (d) DPB. Green is the synthesis in a 2-L flask, and blue is the synthesis in a 15-L reactor.

Authors' contribution

Z.N. Shchekoldina – synthesis in a 2-L flask, literature data collection and analysis, graphic design, and drafting a manuscript;

A.A. Bogolyubov – synthesis in a 15-L reactor and collection and systematization of experimental data on synthesis scaling;

A.Yu. Zakharov – instrumental research and collection and systematization of experimental data on the development of HPLC methods;

B.A. Bulgakov – substantiation of the research concept, planning of the main stages, experimental data analysis, formulation of conclusions, generalization of research results, and editing and revision of the manuscript;

A.V. Babkin – substantiation of the research concept, interpretation of research results, obtaining pure substances for HPLC calibration, and performing NMR;

A.V. Kepman – substantiation of the research concept, interpretation of research results, and group leadership.

The authors declare no conflicts of interest.

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