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## PREPARATION OF PHTHALONITRILE MONOMER WITH LOW MELTING POINT

**Abstract.** This article presents the results of the synthesis of para – and meta-hydroxyphenoxyphthalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus and 4-(3-propargyloxyphenoxy) phthalonitrile, the introduction of which into the binder, allowed to achieve the necessary viscosity indicators without loss of heat resistance. At the first stage, it was proposed to obtain a monomer with a phenoxy group in phosphorus. For this purpose, we proposed the use of dimethylacetamide (DMAA) with  $K_2CO_3$ , but the product was hydrolytically unstable in the main medium, so it was impossible to isolate the desired monomer. To solve this problem, we conducted a number of experiments on the selection of synthesis conditions using various solvents. Comparing the  $T_{gt}$  of the obtained monomers, we found higher values for para-oriented phthalonitriles, which is probably due to higher structure symmetry, as well as an increase in glass transition temperature ( $T_{gt}$ ) for phosphonate-based monomers. Due to the equally high thermal properties of the cured matrices, we decided to use 4-(3-hydroxyphenoxy) phthalonitrile as the main precursor, as well as phosphate chlorangidrides. Based on the calculated data, a pattern was identified that consists in a decrease in the  $T_{gt}$  of phosphorus-containing phthalonitriles when switching to aliphatic substituents in phosphorus. A decrease in the  $T_{gt}$  of monomers was found with an increase in the size of the aliphatic substituent. As a result of the experiment, we obtained 9 new phosphorus-containing phthalonitrile monomers with high yield that are resistant to hydrolysis, which is confirmed by the fact that the products were isolated by flash chromatography on silica gel, as well as two-dimensional TLC. The synthesized substances were glassy masses with  $T_{gt} = - 5-58$  °C. The consistency of the approach involving the introduction of phosphate bridges into the structure of phthalonitriles was shown.

**Key words:** thermosetting polymers, temperature-time-transformation diagrams, isothermal transformation diagrams, thermal stability, thermal analysis, polymer composite materials (PCM).

**Introduction.** Intensive industrial development is impossible without progress in the field of materials science [1,2]. Recently, significant progress in its development has been achieved due to the use of qualitatively new special-purpose materials for the manufacture of machine parts and mechanisms that operate at a high level of loads, temperatures and sliding speeds, in aggressive and abrasive environments when using lubricants and cooling liquids and without them [3,4].

The most promising special-purpose materials are polymers and PCM based on them [3]. The presence of a wide range of polymer matrices, fillers and modifying systems allows us to obtain materials with the necessary level of properties, which vary in a wide range depending on the composition and technology of their production. Modern polymers and PCM based on them approach such structural materials as metals and their alloys by their physical and mechanical properties, while having a number of significant advantages: low cost of manufacturing products, a high level of chemical resistance, low weight, the ability to work in friction units without lubrication, and so on [4,5].

The paper considers a literature review on the scientific basis of obtaining composite materials in Kazakhstan, which shows the principal possibility of creating new composite films from alicyclic polyimide and polyethylene glycol with improved physical and mechanical properties [6]. For example, the authors point out that the resulting nanocomposites are tin dioxide nanoparticles immobilized in an inorganic polymer mesh of silicon dioxide and deposited carbon. At the same time, silicon dioxide provides high adhesive properties and prevents crystallization of the composite, while nano- and microparticles of tin and carbon dioxide determine gas-sensitive properties. The film-forming solutions obtained by Sol-gel technology contain tetraethoxysilane, tin salts ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), silicic acid ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) and sodium silicic acid ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ). The resulting solutions were applied to metal substrates with subsequent heat treatment. Additional introduction of tetraethoxysilane into Sol solutions as a source of  $\text{SiO}_2$  allowed to obtain xerogels of oxide compositions of 5% wt.  $\text{SnO}_2$ -95% wt.  $\text{SiO}_2$ , 30% wt.  $\text{SnO}_2$ -70 % wt.  $\text{SiO}_2$ . The change in the content of elements shows that the microstructure of the obtained compounds changes as carbon nanoparticles build up [7].

The synthesis of phthalonitrile monomers is well studied and described in the literature and includes the stages of nucleophilic aromatic substitution between 4-nitrophthalonitrile and aromatic amides. To obtain a phthalonitrile monomer with a low melting point, it was proposed to introduce phosphate fragments into the structure of the monomer [8-10].

**Experimental part and results.** To obtain a phthalonitrile monomer with a low melting point, it was proposed to introduce phosphate fragments into the structure of the monomer [11-13]. For this purpose, we synthesized para- and meta-hydroxyphenoxyphthalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus, and 4-(3-propargyloxyphenoxy) phthalonitrile, the introduction of which into the binder, presumably, would allow to achieve the necessary viscosity indicators without loss of heat resistance. The scheme of synthesis proposed in this paper is shown in figure 1 [14].

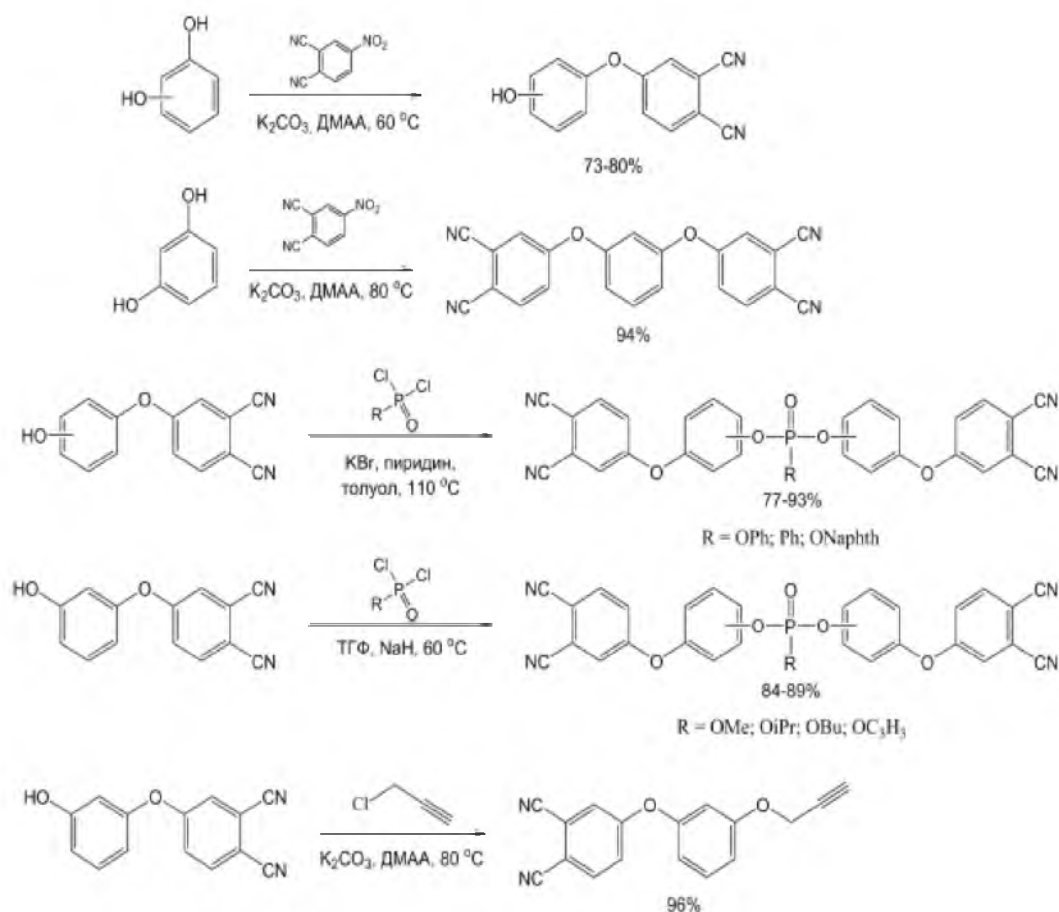


Figure 1 – Scheme of synthesis of phthalonitrile monomers

At the first stage, it was proposed to obtain monomer 1 with a phenoxy group in phosphorus. For this purpose, we proposed the use of dimethylacetamide (DMAA) with  $K_2CO_3$ , but the product was hydrolytically unstable in the main medium, so it was impossible to isolate the desired monomer. To solve this problem, we conducted a number of experiments on the selection of synthesis conditions using various solvents (table 1) [15].

Table 1 - Selection of optimal synthesis conditions

Solvent	Synthesis Condition	Result
DMA	$K_2CO_3$ , 70 °C	Monomer hydrolysis
Toluene	$\Delta^\circ C$	The desired monomer (yield 81%)
Dichloroethane	$\Delta^\circ C$	4- (3-hydroxyphenoxy) phthalonitrile, insoluble
Bu <sub>2</sub> O	$\Delta^\circ C$	A large number of by-products
	Addition of acid chloride to the precursor melt	A large number of by-products
Pyridine	$\Delta^\circ C$	The desired monomer (yield 67%)
THF (Tetrahydrofuran)	$\Delta^\circ C$	A large number of by-products

Thus, the desired monomer was obtained only when using toluene and pyridine as solvents, but the main disadvantage of pyridine is its high toxicity ( $LD_{50} = 500$  mg / kg), whereas when using toluene, the reaction time is about a week. Since it is necessary to remove the released HCl to shift the equilibrium of the reaction, we proposed using toluene as a solvent with an equimolar amount of pyridine acid. Thus, it was possible to reduce the amount of pyridine used and reduce the reaction time to 24 hours.

Comparing the  $T_{gt}$  of the obtained monomers 1-4 (table 2), we found higher values for para-oriented phthalonitriles, which is probably due to higher structure symmetry, as well as an increase in  $T_{gt}$  for phosphonate-based monomers. Due to the equally high thermal properties of the cured matrices, we decided to use 4-(3-hydroxyphenoxy) phthalonitrile as the main precursor, as well as phosphate chlorangidrides.

To study the General regularities, researchers from the laboratory of A. R. Khokhlov performed calculations that allow predicting the glass transition temperature of phosphorus-containing phthalonitriles [16]. Based on the calculated data, the expected pattern was revealed, which consists in a decrease in the  $T_{gt}$  of phosphorus-containing phthalonitriles when switching to aliphatic substituents in phosphorus. In addition, a decrease in the  $T_{gt}$  of monomers was found with an increase in the size of the aliphatic substituent.

In order to confirm the calculated model, as well as to study the changes in the properties of monomers and cured matrices depending on the size of the substituent in phosphorus, we attempted to obtain monomers 5-9 (table 2), using a similar scheme, but only monomer 5 (table 2) was obtained in this way. In other cases, after the addition of pyridine, a resin began to form in the reaction mixture, which makes it impossible to isolate the desired product. To solve this problem, we have tested batch addition of pyridine to the reaction mixture (10%), but the ultimate is the addition of 50% of a given amount of pyridine, then is quite fast (~ 10 minutes) formation of resin; in addition, the selection of the desired monomer difficult (yield ~5%). We also proposed the use of Et<sub>3</sub>N (triethylamine) instead of pyridine and THF as a solvent, as well as various combinations, but it was not possible to isolate the desired monomer in any of the cases. As a result, to obtain monomers 6-9(table 2), and study them, THF with NaH was used as a base with further isolation by flash chromatography. After studying the properties of monomers 6-9(table 2), it can be found that the lowest glass transition temperature is monomer 8(table 2), with a butyl group at phosphorus ( $T_{gt} = -5$  °C), while monomer 6 (table 2), turns out to be crystalline, having a melting point of  $T_{mp} = 116$  °C.

**Discussion of results.** As a result of the experiment, we obtained 9 new phosphorus-containing phthalonitrile monomers with a high yield, which are shown in table 6. they are resistant to hydrolysis, which is confirmed by the fact that the products were isolated by flash chromatography on silica gel, as well as two-dimensional Thin layer chromatography (TLC). The synthesized substances were glassy masses with  $T_{gt} = - 5-58$  °C, which is significantly lower than for classical phthalonitriles[17,18] and

lower than for oligomers [19,20]. In addition, monomer 6 was a crystalline substance with a  $T_{mp} = 116\text{ }^{\circ}\text{C}$ , so the developed calculation method is not applicable. Thus, the consistency of the approach involving the introduction of phosphate bridges into the structure of phthalonitriles was shown. The thermal properties of the resulting monomers are shown in table 2.

Table 2 - Thermal properties of the obtained phthalonitrile monomers

№	Structure	$T_{gl}/T_{mp}$ (exp.), $^{\circ}\text{C}$	$T_{gl}/T_{mp}$ (calculated value), $^{\circ}\text{C}$	$\Delta T$ , $^{\circ}\text{C}$
1		22	49±11	27
2		42	48±7	6
3		20	-	-
4		46	-	-
5		58	61±7	3
6		116	43±8	73
7		5	33±5	28
8		-5	-	-
9		12	32±6	20
10		118	-	-
11		185		

**Conclusion.** The introduction of phosphate fragments into the structure of the monomer is proposed to obtain a phthalonitrile monomer with a low melting point. Para - and meta-hydroxyphenoxyphthalonitrile, phosphorus-containing chlorangidrides with various substituents in phosphorus and 4-(3-propargyloxyphenoxy) phthalonitrile were synthesized, the introduction of which into the binder allowed to achieve the necessary viscosity indices without loss of heat resistance. 9 new

phosphorus-containing phthalonitrile monomers resistant to hydrolysis were obtained. The synthesized substances were glassy masses with  $T_{gt} = -5-58$  °C. In addition, monomer 6 was a crystalline substance with  $T_{mp} = 116$  °C, in connection with which the developed calculation method is not applicable. Thus, the consistency of the approach implying the introduction of phosphate bridges into the structure of phthalonitriles was shown.

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### **БАЛҚУ ТЕМПЕРАТУРАСЫ ТӨМЕН ФТАЛОНИТРИЛЬДІ МОНОМЕР АЛУ**

**Аннотация.** Өнеркәсіп дамуындағы жоғары табысқа жоғары деңгейде жүктемемен қызмет атқаратын машина мен механизм бөлшектерін дайындау барысында арнайы мақсатта сапалы жаңа материалдарды пайдалану негізінде қол жеткізілді. Оның қатарына полимер және соның негізінде жасалған ПКМ жатқызуға болады.

Полимерлік матрица, толтырғыш және түрлендіргіш жүйелердің кең спектрі болуы тиіс қасиетке ие материалды алуға мүмкіндік береді. Олар құрамы мен дайындалу технологиясына орай түрліше келеді. Қазіргі заманғы полимерлер мен ПКМ физикалық-механикалық қасиетіне сәйкес, металл мен қорытпа сияқты конструкциялық материалдарға жақын келеді, бұл ретте өндіріс өнімінің төмен құны, химиялық төзімділіктің жоғары деңгейі, аз салмақ, майланбаған үйкеліс қондырғыларында жұмыс атқару мүмкіндігі сынды елеулі артықшылығы бар.

Фталонитрильді мономерлер синтезі зерттеген әдебиеттерде жете түсіндірілген әрі сипатталған және құрамында 4-нитрофталонитрилді және хош иісті диолдар арасындағы нуклеофильді хош иісті алмастыру сатылары бар. Балқу температурасы төмен фталонитрилді мономер алу үшін мономер құрылымына фосфатты фрагмент енгізу ұсынылды. Бұл үшін пара және мета-гидроксифеноксифталонитрилді, фосфор мен 4- (3-пропаргиллоксифеноксид) фталонитрилдегі түрлі алмастырғышы бар фосфорлы қышқыл хлоридтер синтезделді және оны байланыстырушы құрамға енгізу жылуга төзімділікті жоғалтпастан тұтқырлыққа қол жеткізуге мүмкіндік береді.

Бірінші кезеңде фосфордағы фенокси тобы бар мономер алу туралы ұсыным жасалды. Ол үшін біз  $K_2CO_3$  бар диметилацетамид (ДМАА) пайдалануды ұсындық, алайда өнім негізгі ортада гидролитикалық тұрақсыз болғандықтан, біз іздеген мономердің бөлінуі мүмкін емес еді. Осы мәселені шешу үшін түрлі еріткіштерді пайдалана отырып, синтездеу шарттарын таңдау бойынша бірқатар тәжірибе жүргіздік.

Алынған мономердің Тст-ін салыстыра отырып, пара-бағытталған фталонитрилге арналған жоғары мәнді айқындадық. Бұл құрылымның жоғары симметриясымен, сондай-ақ фосфонат негізіндегі мономерге арналған Тst-нің жоғарылауына байланысты болуы ықтимал. Қатырылған матрицаның термиялық қасиетінің бірдей жоғарылығын ескере отырып, негізгі прекурсор және фосфат хлориді ретінде 4- (3-гидроксифеноксид) фталонитрилді қолданған жөн деп таптық.

Есептелген мәліметтер негізінде фосфор құрамындағы алифатты алмастырғыштарға өтуде құрамында фосфоры бар фталонитрилдердің Тst азаю үдерісін көрсететін заңдылық анықталды. Сонымен қатар, алифатты алмастырғыш мөлшері ұлғайғанда Тst мономердің төмендейтіні анықталды.

Тәжірибе нәтижесінде гидролизге төзімді 9 жаңа фосфорлы фталонитрилді мономерлер алынды, аталған өнімдер силикагельде флеш-хроматография әдісімен, сондай-ақ екіөлшемді ТСХ негізінде анықталды. Синтезделген заттар – Тst =  $-5-58$  °C болатын әйнек массалар, бұл классикалық фталонитрилге, олигомерге қарағанда айтарлықтай төмен. Сонымен қатар, мономер  $T_{пл} = 116$  °C кристалды зат болғандықтан есептік әдіс қолданылмайды. Фталонитрил құрылымына фосфат көпірін енгізуді білдіретін тәсілдің ауқымдылығы көрсетілді.

**Түйін сөздер:** термореактивті полимер, «температура-айналу уақыты» диаграммасы, изотермиялық түрлену диаграммасы, термиялық тұрақтылық, термиялық талдау, полимерлік композициялық материал (ПКМ).

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### **ПОЛУЧЕНИЯ ФТАЛОНИТРИЛЬНОГО МОНОМЕРА С НИЗКОЙ ТЕМПЕРАТУРОЙ ПЛАВЛЕНИЯ**

**Аннотация.** Значительные успехи в развитии промышленности достигнуты за счет использования качественно новых материалов специального назначения для изготовления деталей машин и механизмов, работающих при высоком уровне нагрузок, в число которых можно отнести полимеры и ПКМ на их основе.

Наличие широкого спектра полимерных матриц, наполнителей и модифицирующих систем позволяет получать материалы с необходимым уровнем свойств, которые изменяются в широком интервале в зависимости от состава и технологии их получения. Современные полимеры и ПКМ на их основе по физико-механическим свойствам приближаются к таким конструкционным материалам, как металлы и их сплавы, имея при этом ряд существенных преимуществ: невысокая себестоимость изготовления изделий, высокий уровень химической стойкости, невысокая масса, возможность работы в узлах трения без смазывания.

Синтез фталонитрильных мономеров достаточно хорошо изучен и описан в литературе и включает в себя стадии нуклеофильного ароматического замещения между 4-нитрофталонитрилом и ароматическими диолами. Для получения фталонитрильного мономера с низкой температурой плавления было предложено введение фосфатных фрагментов в структуру мономера. Для этого были синтезированы пара- и мета-гидроксифеноксифталонитрил, фосфорсодержащие хлорангидриды с различными заместителями при фосфоре и 4-(3-пропаргиллоксифенокси) фталонитрил, введение которого в состав связующего, предположительно, позволило бы достичь необходимых показателей вязкости без потери термостойкости.

На первом этапе было предложено получение мономера с фенокси-группой при фосфоре. Для этого нами было предложено использование диметилацетамида (ДМАА) с  $K_2CO_3$ , однако продукт оказался гидролитически нестабилен в основной среде, в связи с чем выделение искомого мономера было невозможно. Для решения этой проблемы нами был проведен ряд экспериментов по подбору условий синтеза с использованием различных растворителей.

Сравнив  $T_{ст}$  полученных мономеров, мы обнаружили более высокие значения для пара-ориентированных фталонитрилов, что, вероятно, связано с более высокой симметрией структуры, а также возрастание  $T_{ст}$  для мономеров на основе фосфонатов. Ввиду одинаково высоких термических свойств отвержденных матриц, нами было решено использовать 4-(3-гидроксифенокси) фталонитрил в качестве основного прекурсора, а также фосфатные хлорангидриды.

На основе расчетных данных была выявлена закономерность, заключающаяся в снижении  $T_{ст}$  фосфорсодержащих фталонитрилов при переходе к алифатическим заместителям при фосфоре. Кроме того, было обнаружено снижение  $T_{ст}$  мономеров при увеличении размера алифатического заместителя.

В результате эксперимента нами были получены с высоким выходом 9 новых, фосфорсодержащих фталонитрильных мономеров, устойчивых к гидролизу, что подтверждено тем, что продукты были выделены методом флеш-хроматографии на силикагеле, а также двумерной ТСХ. Синтезированные вещества представляли собой стеклообразные массы с  $T_{ст} = -5-58$  °С, что значительно ниже, чем для классических фталонитрилов и ниже, чем для олигомеров. Кроме того, мономер представлял собой кристаллическое вещество с  $T_{пл} = 116$  °С, в связи с чем разработанный расчетный метод неприменим. Таким образом была показана состоятельность подхода, подразумевающего введение фосфатных мостиков в структуру фталонитрилов.

**Ключевые слова:** термореактивные полимеры, диаграммы «температура-время-превращения», диаграммы изотермических превращений, термическая стабильность, термический анализ, полимерные композиционные материалы (ПКМ).

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