

**SYNTHESIS AND PROCESSING OF POLYMERS
AND POLYMERIC COMPOSITES**

**СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ
И КОМПОЗИТОВ НА ИХ ОСНОВЕ**

ISSN 2686-7575 (Online)

<https://doi.org/10.32362/2410-6593-2022-17-5-410-426>



UDC 678.7; 678.764.43; 678.01

RESEARCH ARTICLE

Synthesis of new photo-cured phosphorus-containing oligoestermethacrylates with a spacer in the structure ¹

Boris A. Buravov[✉], **Ali Al-Khamzawi**, **Eugene S. Bochkarev**,
Nazmiya Kh. Grichishkina, **Sergey V. Borisov**, **Nina V. Sidorenko**,
Oleg I. Tuzhikov, **Oleg O. Tuzhikov**

Volgograd State Technical University, Volgograd, 400005 Russia

[✉]Corresponding author, e-mail: buravov@ya.ru

Abstract

Objectives. To synthesize phosphorus-containing oligoestermethacrylates spatially separated by spacers of aliphatic or aromatic structure and evaluate their effect on photocuring kinetics.

Methods. For determining the qualitative and quantitative composition of the synthesized compounds, the following methods were used: thin layer chromatography; chromatographic and mass spectrometry; infrared spectroscopy; ¹H, ¹³C, ³¹P nuclear magnetic resonance spectroscopy; differential scanning calorimetry. The dielectric loss tangent was determined on a specially designed optical cell with an ultraviolet (UV) light source to an immittance meter. Elemental analysis was performed on an energy dispersive X-ray fluorescence spectrometer.

Results. Spatially separated oligoestermethacrylates based on phosphorus trichloride containing aliphatic or aromatic spacers in the structure were synthesized. During the interaction of glycidyl methacrylate with phosphorus trichloride in the mass of the latter, reaction products were shown to be formed both according to the Krasusky rule from the side of the α -carbon atom, as well as against this rule with the formation of isomeric products. Obtaining these compounds in bulk is possible only in the presence of a homopolymerization inhibitor. The influence of the spacer

¹ This paper is an updated and translated from Russian version of the original article in Russian published in *Izvestiya VolgGTU*, 2020. Original Russian Text © Buravov B.A., Bochkarev E.S., Al-Khamzawi A., Sidorenko N.V., Tuzhikov O.O., Tuzhikov O.I. Study of the influence of spacer on features of UV curing of phosphorus-containing methacrylates of various functionality. *Izvestiya VolgGTU*. 2020;12(247):136–143. <https://doi.org/10.35211/1990-5297-2020-12-247-136-143>

structure on the curing rate of oligoestermethacrylates under the action of UV radiation has been established. It has been shown that the introduction of a spacer into the oligomer structure is accompanied by an increase in the induction period by a factor of 39 compared to a sample without a spacer.

Conclusions. The results obtained indicate the possibility of obtaining new oligoestermethacrylates with aliphatic and aromatic spacers in the structure. The influence of the structure of the spacer on the kinetics of photocuring is determined.

Keywords: synthesis, oligoestermethacrylates, polymerization, phosphorus-containing flame retardants, kinetics, photocuring, DSC

For citation: Buravov B.A., Al-Khamzawi A., Bochkarev E.S., Grichishkina N.Kh., Borisov S.V., Sidorenko N.V., Tuzhikov O.I., Tuzhikov O.O. Synthesis of new photo-cured phosphorus-containing oligoestermethacrylates with a spacer in the structure. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(5):410–426. <https://doi.org/10.32362/2410-6593-2022-17-5-410-426>

НАУЧНАЯ СТАТЬЯ

Синтез новых фотоотверждаемых фосфорсодержащих олигоэфирметакрилатов со спейсером в структуре

Б.А. Буравов[✉], А. Аль-Хамзави, Е.С. Бочкарев, Н.Х. Гричишкина, С.В. Борисов, Н.В. Сидоренко, О.И. Тужиков, О.О. Тужиков

Волгоградский государственный технический университет, Волгоград, 400005 Россия

[✉]Автор для переписки, e-mail: buravov@ua.ru

Аннотация

Цели. Синтез фосфорсодержащих олигоэфирметакрилатов, пространственно-разделенных спейсерами алифатического или ароматического строения, и оценка их влияния на кинетику фотоотверждения.

Методы. Для определения качественного и количественного состава синтезированных соединений использованы: тонкослойная хроматография; хромато-масс-спектрометрия; инфракрасная спектроскопия; ^1H , ^{13}C , ^{31}P спектроскопия ядерного магнитного резонанса; дифференциальная сканирующая калориметрия. Тангенс диэлектрических потерь определяли на специально разработанной оптической ячейке с УФ-источником света к измерителю иммитанса. Элементный анализ проводили на энергодисперсионном рентгенофлуоресцентном спектрометре.

Результаты. Синтезированы пространственно разделенные олигоэфирметакрилаты на основе трихлорида фосфора, содержащие в структуре алифатический или ароматический спейсеры. Установлено, что при взаимодействии глицидилметакрилата с трихлоридом фосфора в массе последнего, образуются продукты реакции как по правилу Красуского со стороны α -углеродного атома, так и против правила с образованием изомерных продуктов. Получение данных соединений в массе возможно только в присутствии ингибитора гомополимеризации. Установлено влияние структуры спейсера на скорость отверждения олигоэфирметакрилатов под действием УФ-излучения. Показано, что введение спейсера в структуру олигомера сопровождается увеличением индукционного периода в 39 раз по сравнению с образцом, не содержащим спейсера.

Выводы. Достигнутые результаты свидетельствуют о возможности получения новых олигоэфирметакрилатов со спейсерами алифатического и ароматического строения в структуре. Установлено влияние строения спейсера на кинетику фотоотверждения.

Ключевые слова: синтез, олигоэфирметакрилаты, полимеризация, фосфорсодержащие антипирены, кинетика, фотоотверждение, ДСК

Для цитирования: Buravov B.A., Al-Khamzawi A., Bochkarev E.S., Grichishkina N.Kh., Borisov S.V., Sidorenko N.V., Tuzhikov O.I., Tuzhikov O.O. Synthesis of new photo-cured phosphorus-containing oligoestermethacrylates with a spacer in the structure. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(5):410–426. <https://doi.org/10.32362/2410-6593-2022-17-5-410-426>

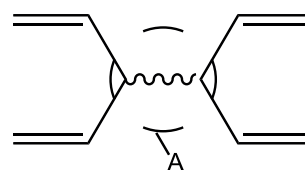
INTRODUCTION

To solve the problem of combustibility of composite materials based on oligomeric binders, fire retardants of various nature are added to them. Some of these do not react with the main polymer during processing and operation, while others act as a reactive additive, for example, integrating into the structure of the cured binder [1, 2]. However, it should be noted that it is not always possible to balance the set of required performance characteristics necessary to obtain desired final products. For example, some flame retardants are able to transfer materials to the class of low combustibility, while worsening the physical-mechanical, dielectric, technological and operational properties [3]. The production of polymeric binders that reduce flammability while simultaneously improving physical and mechanical properties solves a number of the above problems, which are related, among other things, to the thermodynamic incompatibility of the binder and flame retardant.

In order to ensure the required level of properties in terms of resistance to combustion, phosphorus-containing polymeric materials and fillers based on organophosphorus, organophosphorus-element compounds are widely used. A promising method involves the synthesis and use of reactive compounds containing fragments of different sizes and structures (spacers) between reactive centers in a single molecule. However, the works describing such methods either present spacers that are located in the side chain of the resulting

polymer, or compounds having different spacer structures as co-reagents in the preparation of the cured material [4–6].

From our point of view, a more promising approach sets out to obtain bi-, tri-, and tetra-functional compounds of the (meth)acrylate series in which the spacer is located between the functional polymerizable centers. For obtaining compounds with spacers, three reagents of different functionalities can be used. As a result of their sequential interaction, it is possible to obtain an oligomeric structure (Scheme 1).



Scheme 1. Structure of oligoestermethacrylate with spacers of various structures;

A is a spacer of different structure and molecular weight.

Subsequently, in the process of polymerization at double bonds, the structures of a rigid-chain polymer are formed, in the mass of which there is a movable or limitedly movable spacer.

It is known that chemically bound phosphorus in the structure of (meth)acrylate compounds makes it possible to obtain polymers with reduced flammability. For example, the use of phosphorus-containing monomers and oligomers of the (meth)

acrylate series [7, 8] or phosphorus-containing epoxy resins [9] makes it possible to obtain materials with a satisfactory balance of physico-mechanical and heat-resistant properties with reduced flammability.

EXPERIMENTAL

For the synthesis of phosphorus-containing compounds capable of polymerization under the action of ultraviolet (UV) radiation, we used freshly distilled phosphorus trichloride (98%, analytical grade, TU 2152-380-0763441-2002), glycidyl methacrylate (GMA) (no less than 97%, purity, analytical grade, *Sigma-Aldrich*, USA), active diluent for epoxy resins grade E-181 (mass fraction of epoxy groups $\geq 25\%$, *Chimex Limited*, Russia, TU 2225-606-11131395-2003) and epoxy resin grade ED-20 (mass fraction of epoxy groups, 20.0–22.5%, *Chimex Limited*, GOST 10587-84²). Prior to synthesis, the exact content of epoxy groups in epoxy resins was analytically determined. To obtain the polymers, a photoinitiator comprising bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPhO) (no more than 100%, chemically pure, *Sigma-Aldrich*, USA) was used. For thin layer chromatography (TLC), benzene (99.8%, chemically pure, *Ekos-I*, Russia) and freshly distilled ethanol (96.3%, *Ferein*, Russia) were used as the eluent.

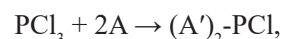
Chromatographic and mass spectrometry were carried out on a GC/MS Saturn 2100T instrument (*Varian*, USA) with a VF-1ms quartz capillary column (100% methylpolysiloxane, 30 M \times 0.25 mm, ID = 0.25 mm, DF = 0.25 μ m, helium was used as a carrier gas) using a prepared 0.2% solution of the substance in acetone (99.8%, chemically pure, *Ekos-I*, Russia). Nuclear magnetic resonance (NMR) ¹H, ¹³C, and ³¹P spectroscopy was performed on a Mercury 300 plus instrument (*Varian*, USA) with operating frequencies of 300, 75, and 121 MHz, respectively; here, CDCl₃ was used as a solvent. Chemical shifts are given on a scale of δ (ppm) relative to tetramethylsilane (TMS) as an internal standard. Spin-spin coupling constants (*J*) are given in Hz. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 204 F1 instrument with a compressor cooling system and an OmniCure S2000 UV irradiation unit in an inert gas flow (argon, 90 mL/min) (*Netzsch*, Germany). The sample was placed in a standard open aluminum crucible. Controlled irradiation was carried out according to a temperature program

(20°C, 4 min) comprising two identical isothermal segments using the full spectrum of the radiation source (power 1 W/cm²). The resulting curve was obtained by subtracting the second segment from the first in the NETZSCH Proteus software environment³. To determine the dielectric loss tangent, we used a specially designed optical cell with a UV light source connected to an E7-25 immittance meter (*MNIPI*, Belarus). Infrared (IR) spectra were recorded on an FT-801 spectrometer (*SIMEX*, Russia). Elemental analysis was performed on an EDX-8000 energy dispersive X-ray fluorescence spectrometer (*Shimadzu*, Japan).

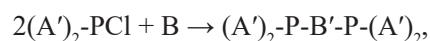
For the study, several phosphorus-containing polymerizable compounds (PPC) were synthesized:

- (PPC-1) is the reactive monomer without spacer;
- (PPC-2) is the spacer is introduced with E-181 epoxy resin;
- (PPC-3) is the spacer is inserted with epoxy resin ED-20.

The synthesis of phosphorus-containing polymerizable compounds was carried out in two stages. At the first stage, the reaction was carried out in a molar ratio of 1:2 according to the scheme:



where A is one of unsaturated alpha oxides; A' is the structure of addition of unsaturated alpha oxides. At the second stage, the interaction of the bifunctional epoxide with residual chlorine in a ratio of 2:1 was carried out, leading to the preparation of a compound with a spacer, according to the scheme:



where B is one of diepoxy oligomers, B' is the structure formed as a result of addition of diepoxy oligomers.

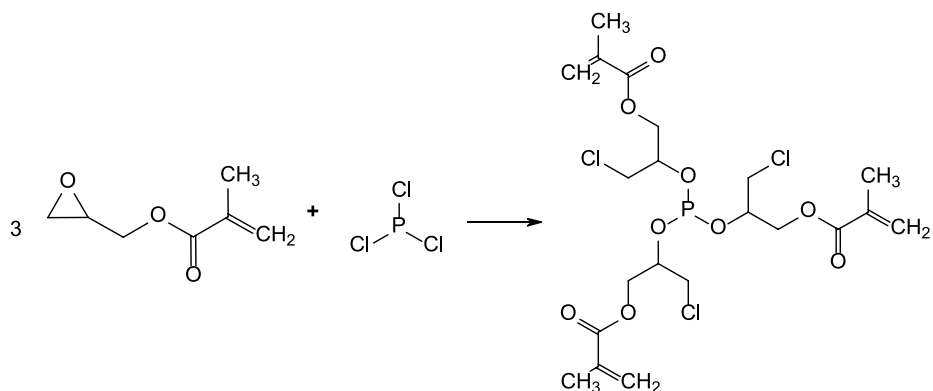
As an object of comparison, a PPC-1 product was synthesized that did not contain a spacer. The reaction was carried out in excess of PCl₃ in one stage in a ratio of 1:3 with GMA (Scheme 2).

The synthesis of substances with spacers was carried out in two stages. At the first stage, a disubstituted intermediate was obtained (Scheme 3).

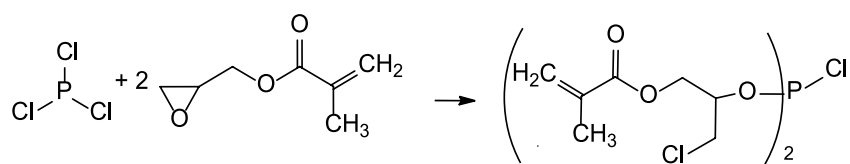
At the second stage, the disubstituted intermediate was added to epoxy resins (epoxy resin E-181 was used for PPC-2, ED-20 was used for PPC-3), the reactions were carried out in bulk (Schemes 4 and 5).

² GOST 10587-84. USSR State Standard. Uncured epoxy resins. Specifications. Moscow: Izd. Standartov; 1989.

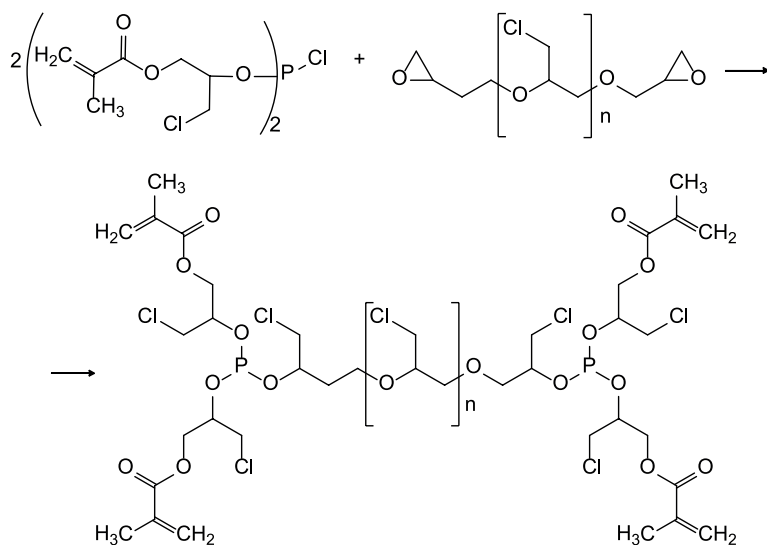
³ <https://analyzing-testing.netzsch.com/ru/pribory-resheniya/differencialnaya-skaniruyushhaya-kalorimetriya-dsk-differencialnyj-termicheskij-analiz-dta/dsc-204-f1-phoenix>, accessed April 15, 2022.



Scheme 2. Reaction of glycidyl methacrylate with phosphorus trichloride to produce the PPC-1 product.



Scheme 3. Reaction of phosphorus trichloride with glycidyl methacrylate to produce an intermediate.



Scheme 4. Reaction of the intermediate with epoxy resin E-181 to obtain the product PPC-2.

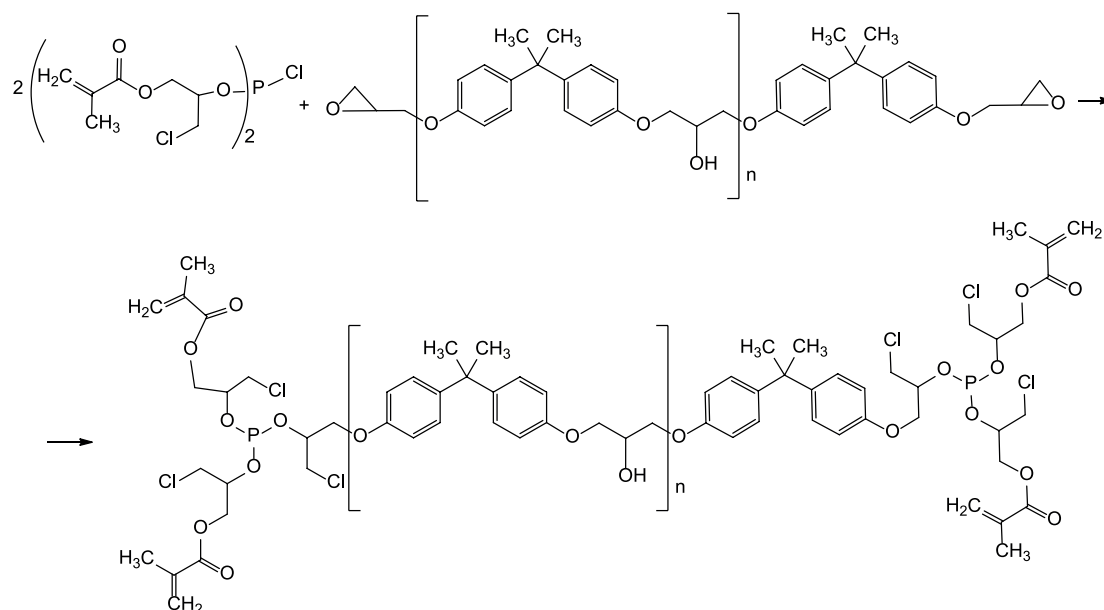
The composition and structure of the synthesized products were confirmed by IR and NMR spectral studies.

PPC-1, PPC-2, and PPC-3 products were used to prepare photocurable compositions in order to evaluate the effect of the spacer on the properties of the cured material.

PPC-1. Tris-[(1-chloromethyl-2-methacryloxy)-ethoxy]phosphine (RF Pat. No. 2697721 [10])

A four-necked reactor equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer,

which had been preliminarily purged with dry argon for 30 min (purging with argon was subsequently carried out throughout the entire process), was loaded with 5 g (0.036 mol) of phosphorus trichloride. A mixture of 15.49 g (0.11 mol) of glycidyl methacrylate (GMA) and 0.155 g (1 wt % of the mass of GMA) *N*-nitrosodiphenylamine was fed to it with constant stirring through a dropping funnel at such a rate that the temperature of the reaction mass did not exceed 15°C, the reactor cooled with a mixture of salt and ice. After the addition of the mixture, the resulting reaction mass was kept for 2 h at 45°C. Then, following evacuation for 60 min at a residual pressure



Scheme 5. Reaction of the intermediate with the epoxy resin ED-20 to obtain the product PPC-3.

of 5 mm Hg, the reaction mass was filtered on a Schott filter from the precipitated crystalline *N*-nitrosodiphenylamine. The yield of PPC-1 was 20.49 g (99.0%).

The product is a mobile liquid of light-yellow color, readily soluble in acetone and chloroform. Analysis for the content of epoxy groups showed their almost complete absence. Epoxy value (E.V.) = 0.066%, n_D^{20} = 1.4935; acid number (A.N.) = 11.58 mg KOH/g; bromine number (B.N.) = 85.3 g/100 g of organic substance.

The identification of the obtained product was carried out using NMR spectroscopy:

^1H NMR spectrum (300 MHz, CDCl_3) δ , ppm: 1.85 (s, 9H), 3.51 (m, 6H), 3.72 (m, 6H), 4.20 (m, 6H), 4.42 (m, 6H), 5.55 (s, 6H), 6.6 (s, 6H), 4.62 (m, 3H) (d, J = 1.7 Hz, 1H).

^{13}C NMR spectrum (75 MHz, CDCl_3 , TMC) δ , ppm: 17.9 (3C); 41.5; 62.4; 69.9; 124.3; 134.5; 164.5.

^{31}P NMR spectrum (121 MHz, CDCl_3) δ , ppm: 140.54 P(OR)₃.

In order to determine the elemental composition, a sample of the test material was placed in a cuvette for measuring liquid samples equipped with a thin film window. The material of the cuvette bottom was polypropylene; the medium was vacuum. The study was conducted according to the standard procedure for the energy dispersive X-ray fluorescence spectrometer EDX-8000. Detection limits of P and Cl ~10 ppm. Found (%): P 6.14; Cl 18.44. Calculated (%): P 5.49; Cl 18.86.

PPC-2. (((4-((1-(2-((bis((1-chloro-3-(methacryloyloxy)propan-2-yl)oxy)phosphine)oxy)-3-chlorophenoxy)-3-chloropropan-2-yl)oxy)-1-chlorobutan-2-yl)oxy)phosphindiy)bis(oxy))-bis(3-chloropropan-2,1-diy)bis(2-methacrylate) (RF Pat. No. 2712107 [11])

A four-necked reactor equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer, preliminarily purged with dry argon for 30 min (purging with argon was subsequently carried out throughout the entire process), was loaded with 5 g (0.036 mol) of phosphorus trichloride. A mixture of 10.33 g (0.073 mol) of HMA and 0.1 g (1 wt % of the mass of HMA) *N*-nitrosodiphenylamine was added to it, with constant stirring, from a dropping funnel at such a rate that the temperature of the reaction mass did not exceed 15°C, the reactor was cooled a mixture of salt and ice. After the mixture was added, the resulting reaction mass was kept for 2 h at 45°C. Then, the resulting intermediate was loaded into a dropping funnel and dosed into another four-necked reactor equipped with a stirrer, a thermometer, and a reflux condenser with E-181 diepoxide in the amount of 5.73 g (0.033 mol, based on the actual amount of epoxy groups). Upon completion of the addition of the mixture, the resulting reaction mass was kept for 2 h at 45°C.

The reaction mass was additionally evacuated for 60 min at a residual pressure of 5 mm Hg and filtered on a Schott filter from the precipitated

crystalline *N*-nitrosodiphenylamine. The yield of PPC-2 was 21.06 g (99.0%).

The product is a mobile liquid of light-yellow color, readily soluble in acetone and chloroform. Analysis for the content of epoxy groups showed their almost complete absence. E.V. = 0.04%; n_D^{20} = 1.4951; A.N. = 12.19 mg KOH/g; B.N. = 72.6 g/100 g of organic substance.

The product obtained was identified by NMR spectroscopy:

^1H NMR spectrum (300 MHz, CDCl_3) δ , ppm: 1.66, 3.63, 3.65, 4.42 (17 CH_2), 3.48, 3.53, 3.86, 4.13 (7 CH), 2.01 (4 CH_3), 6.40, 6.48 (8 H).

^{13}C NMR spectrum (75 MHz, CDCl_3 , TMC) δ , ppm: 43.7, 46.9, 47, 50.7 (7 CH_2), 167.2 (4 C); 70.6, 71.6, 67.2, 86.2 (7 CH); 62.7, 67.9, 74.8, 73.4 (7 CH_2), 136 (4 C), 34.3, 125.2 (6 CH_2), 17.9 (4 CH_3).

^{31}P NMR spectrum (121 MHz, CDCl_3) δ , ppm: 141 P(OR)₃.

Found (%): P 5.02; Cl 22.41. Calculated (%): P 5.74; Cl 22.98.

PPC-3. (((((((((2-hydroxypropane-1,3-diyl)-bis(oxy))bis(4,1-phenylene))bis(propan-2,2-diyl))-bis(4,1-phenylene))bis(hydroxy))-bis(1-chloropropane-3,2-diyl))bis(oxy))-bis(phosphintriyl)tetrakis(oxy)tetrakis(3-chloropropane-2,1-diyl)tetrakis(2-methyl acrylate) (RF Pat. No. 2712116 [12])

A four-necked reactor equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer, which had been preliminarily purged with dry argon for 30 min (purging with argon was subsequently carried out throughout the entire process), was loaded with 5 g (0.036 mol) of phosphorus trichloride. With constant stirring, a mixture of 10.33 g (0.073 mol) of HMA and 0.1 g (1 wt % of the mass of HMA) *N*-nitrosodiphenylamine was added from a dropping funnel at a rate such that the temperature of the reaction mixture did not exceed 15°C; the reactor was cooled with a mixture of salt and ice. After the mixture was added, the resulting reaction mass was kept for 2 h at 45°C. Then, the resulting intermediate product was loaded into a dropping funnel and dosed into another four-necked reactor equipped with a stirrer, a thermometer, and a reflux condenser with ED-20 epoxy resin in the amount of 7.66 g (0.035 mol, based on the actual amount of epoxy groups). Upon completion of the addition of the mixture, the reaction mixture was kept for 2 h at 45°C.

Before unloading the product, the reaction mass was evacuated for 60 min at a residual pressure of 5 mm Hg, filtered on a Schott filter from the

precipitated crystalline *N*-nitrosodiphenylamine. The yield of PPC-3 was 22.99 g (99.0%).

The product is a mobile liquid of light-yellow color, readily soluble in acetone and chloroform. Analysis carried out to identify the content of epoxy groups revealed their almost complete absence. E.V. = 0.09%; n_D^{20} = 1.5210; A.N. = 13.46 mg KOH/g; B.N. = 74.62 g/100 g of organic substance.

The IR spectra of the synthesized compounds PPC-1, PPC-2, PPC-3 contain characteristic absorption bands of stretching vibrations of the C=O (1720 cm^{-1}), C=C (1640 cm^{-1}), C-Hal (760–770 cm^{-1}). There are no absorption bands corresponding to vibrations of the epoxy cycle (860 and 910 cm^{-1}) and P=O (1280–1300 cm^{-1}). Chemical analysis for the content of epoxy groups also showed their absence.

The product obtained was identified by NMR spectroscopy:

^1H NMR spectrum (300 MHz, CDCl_3) δ , ppm: 1.66, 3.63, 3.65, 4.09, 4.21, 4.42 (14 CH_2); 4.04, 4.23, 4.13, 6.91, 7.19 (22 CH); 1.72, 2.01 (8 CH_3), 6.40, 6.48 (8 H); 3.58 (OH).

^{13}C NMR spectrum (75 MHz, CDCl_3 , TMC) δ , ppm: 46.9, 47, 67.9, 70.1, 125.2 (7 CH_2); 69, 70.6, 71.2, 86.2, 114.9, 127.7 (23 CH); 42.4, 136, 146.3, 156.9, 167.2 (18 C); 17.9, 30.9 (8 CH_3).

^{31}P NMR spectrum (121 MHz, CDCl_3) δ , ppm: 141 P(OR)₃.

Found (%): P 4.98; Cl 14.71. Calculated (%): P 5.23; Cl 17.97.

The obtained samples were studied by TLC (GOST 28366-89⁴) with subsequent determination of retention factor R_f values according to formula (1), sorbent: Sorbfil TLCP-AF-A plates (SORBFIL, Russia), eluents—benzene and ethanol in a ratio of 95:5, respectively. A chamber filled with iodine vapor was used to detect substances.

$$R_f = \frac{a}{b}, \quad (1)$$

where a is the distance from the center of the spot to the starting line, mm; b is the distance from the solvent front to the starting line, mm.

RESULTS AND DISCUSSION

While it was not possible to obtain any monomeric products of the addition of GMA to PCl_3 in the absence of an inhibitor of GMA polymerization, whether in excess or in deficiency

⁴ GOST 28366-89. Interstate Standard. Reagents. Method of thin-layer chromatography. Moscow: Standartinform; 2008.

of phosphorus trichloride, the stabilizer (hydroquinone monomethyl ether) contained in the original monomer in the amount of 150 ppm did not prevent the polymerization process, which led to crosslinking of the product in the reactor.

Taking into account the data of [13–15], we used *N*-nitrosodiphenylamine dissolved in the monomer to prevent the polymerization of GMA in the reaction with phosphorus trichloride. The resulting product, according to the data of the authors of [16], can be a mixture of isomers **a**, **b**, and **c** (Fig. 1).

Characteristic peaks in the ^1H NMR spectra of PPC-1 were present in the following regions, ppm: 1.85 (s, 9H, ($\text{H}_3\text{C}-\text{C}=\text{}$)); 3.51 and 3.72 (m, 6H, $-\text{CH}_2-\text{Cl}$); 4.20 and 4.42 (m, 6 H, $=\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$); 5.55 and 6.6 (s, 6 H, $-\text{CH}=\text{CH}_2$); 4.62 (m, 3H, $>\text{P}-\text{O}-\text{CH}$).

The ^{13}C NMR spectra of PPC-1 contain the following peaks: at 17.9 ppm—assigned to the CH_3 groups at the carbon atom at the double bond; at 41.5 ppm—assigned to the groups ($-\text{CH}_2-\text{Cl}$) formed during the opening of the epoxy ring; at 62.4 ppm—referred to ester acrylate groups ($-\text{CH}_2-\text{O}-$); line at 69.9 ppm—assigned to groups ($>\text{CH}-\text{O}-\text{P}<$); at 124.3 ppm—referred to the disubstituted carbon atom groups at the double bond ($-\text{CH}=\text{CH}_2$); at 134.5 ppm—referred to the trisubstituted carbon atom of the double bond ($-\text{CH}=\text{CH}_2$); at 164.5 ppm—referred to the carbon of the ether group ($-\text{O}-\text{C}(\text{O})-$).

The ^{31}P NMR spectra of PPC-1 contain characteristic peaks at 140.54 ppm assigned to the $\text{P}(\text{OR})_3$ group; the absence of peaks at 3.3 ppm characteristic of $\text{P}=\text{O}$ groups also indicates the absence of pentavalent phosphorus in the products.

The IR spectrum of PPC-1 contains characteristic absorption bands in the range of $\text{C}=\text{O}$ (1720 cm^{-1}), $\text{C}=\text{C}$ (1640 cm^{-1}), and $\text{C}-\text{Hal}$ ($760\text{--}770\text{ cm}^{-1}$)

stretching vibrations. The bands at 1340 cm^{-1} and 1500 cm^{-1} are attributed to the vibrations of NO groups and the aromatic ring of the stabilizer *N*-nitrosodiphenylamine, respectively. The absorption band in the region of 1160 cm^{-1} is assigned to bending vibrations of the $\text{C}=\text{O}$ group. The absence of characteristic bands at 860 and 910 cm^{-1} corresponding to vibrations of the epoxy cycle indicates their complete opening upon interaction with phosphorus trichloride. The absence of epoxy groups in the reaction product was also confirmed by chemical analysis. The absence of bands in the region of $1100\text{--}1200\text{ cm}^{-1}$ characteristic of $\text{P}=\text{O}$ groups indicates that pentavalent phosphorus is not formed during the synthesis of PPC-1.

The route of interaction is also confirmed by a decrease in the acid number of the synthesized products from 335.7 to 9.75 mg KOH/g and the absence of epoxy groups in them (see above), which is in agreement with the results of earlier studies [17].

Thus, the performed spectral studies confirm the formation of products of addition of GMA to phosphorus trichloride in the presence of nitrosodiphenylamine at three chlorine atoms.

The R_f value for PPC-1 was determined as the ratio of the distance from the spot center to the start to the distance from the mobile phase front to the start. The following results were obtained: $R_f(\text{A}) = 0.124$; $R_f(\text{B}) = 0.299$; $R_f(\text{C}) = 0.39$.

According to the results of TLC studies, the PPC-1 product is characterized by three separating spots, which were assigned to isomeric products **a**, **b**, and **c** (Fig. 1) formed during the synthesis of PPC-1. This is confirmed by studies [16, 18], which describe the possibility of forming compounds both according to the Krasusky rule and against this rule.

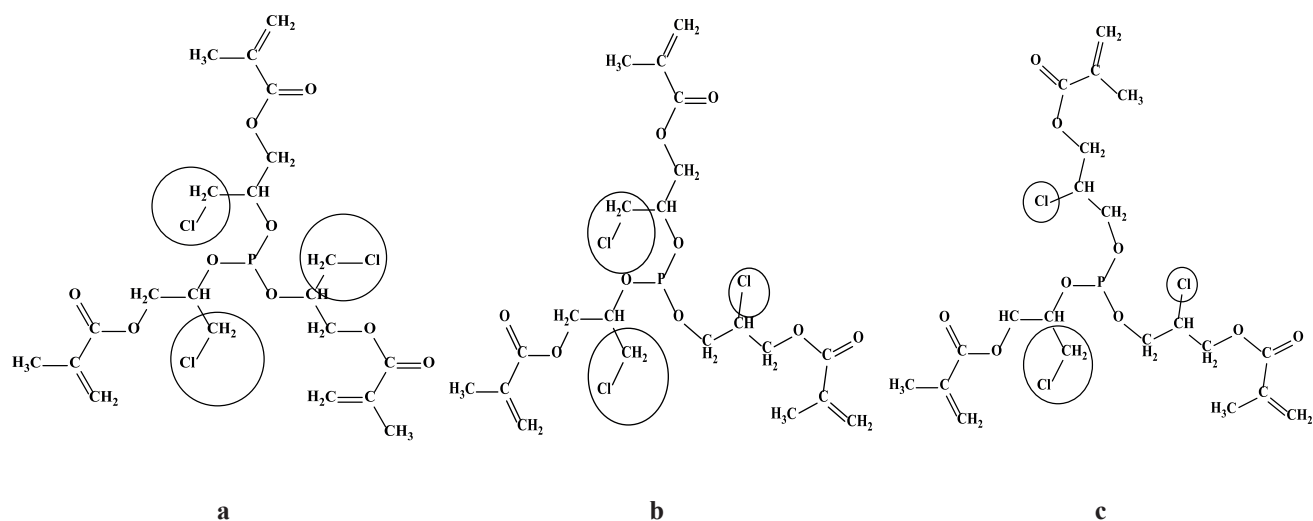


Fig. 1. Structures of PPC-1 isomers.

Any violation of the Krasusky rule as a result of an excess of PCl_3 can subsequently lead to the formation of a mixture of products. The rule can be violated under the influence of functional groups at the oxirane ring [19]. In view of the above, the formation of three spots during TLC studies is determined by the presence of three compounds in the mixture: a product in which the addition of the GMA oxirane ring occurs only according to the Krasusky rule; only against Krasusky rule; the simultaneous presence of the attached GMA, both under the rule and against the Krasusky rule. This can occur during the interaction of phosphorus trichloride at different depths of its transformation.

Chromatographic and mass spectral studies have shown that PPC-1 isomers are capable of producing several fragment ions (Figs. 2 and 3).

Along with the results of IR and NMR analyses of the primary TLC data, chromatographic and mass spectral studies confirmed that a mixture of isomers was formed during the synthesis. Thus, the obtained results confirm the formation of putative PPC-1 isomeric compounds **a**, **b**, and **c** (Fig. 1).

The synthesis of spatially separated bis-[phosphorus-di-etheracrylates] with spacers of various structures was carried out using intermediate products by partial replacement of chlorine atoms in phosphorus trichloride with glycidyl methacrylate. The resulting reaction mass was added to a bifunctional epoxide, for example, E-181 or ED-20 taken in a ratio of 2:1, respectively. Under such conditions, the diepoxide is inserted between two phosphorus atoms along the chlorine atoms. The

basis for the conditions for the synthesis of substances with spacers (PPC-2 and PPC-3) was the experimental data obtained during the synthesis of PPC-1.

The ultimate goal of the research was to evaluate the effect of the spacer structure on the properties of crosslinked polymeric materials, which were determined by the structure of the bifunctional epoxide. Products of total chlorine substitution obtained by the interaction of phosphorus trichloride with GMA in a ratio of 1:3 were used as the basic object of comparison.

Figure 4 shows the IR spectra of GMA and end products that do not contain (PPC-1) and contain spacers (PPC-2, PPC-3). The insignificant difference seen in the spectra of the presented data is associated with the similar structure in the structure of the compounds.

The oxirane ring in glycidyl methacrylate has two transmission bands. The first band in the middle range of deformation of the C–O bond of the terminal oxirane group is centered at 906 cm^{-1} , while the second band observed at 3052 cm^{-1} is related to the C–H vibration of the methylene group of the epoxy ring. As well as being quite low, the intensity of this band is also very close to the transmission of the hydroxyl group; however, in epoxy monomers possessing a low degree of polymerization, it can be used to assess the qualitative presence of epoxy groups [20]. Here, it can be seen that a similar band is present in glycidyl methacrylate and absent in samples PPC-1, PPC-2, and PPC-3. The absence of vibrations of the C–O–C bonds

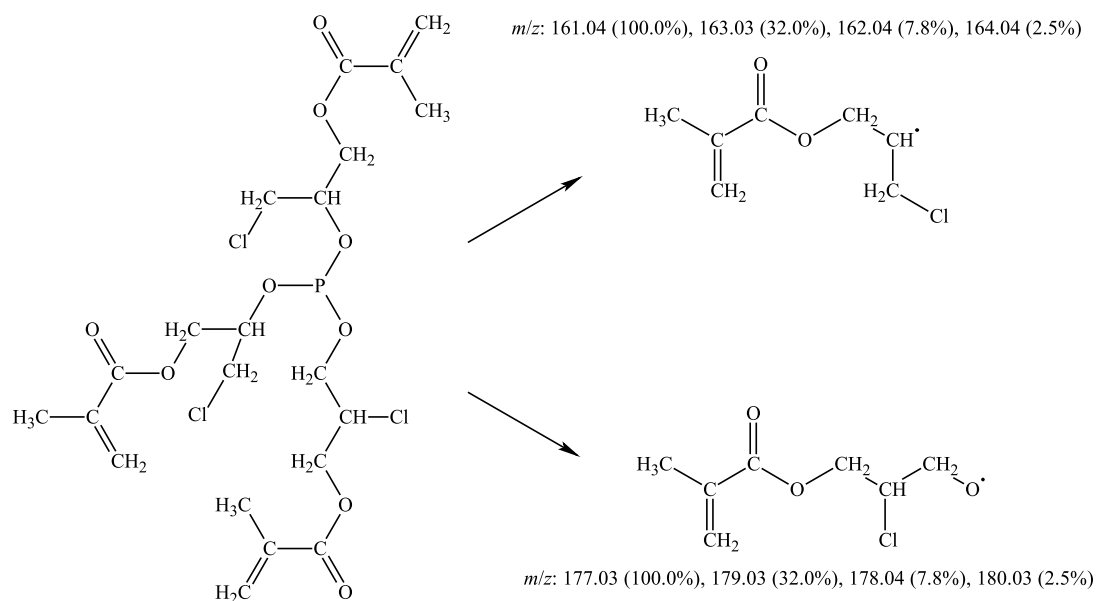


Fig. 2. PPC-1b fragment ion formation scheme (3-chloropropyl methacrylate fragment and 2-chloro-3-oxypropyl methacrylate fragment).

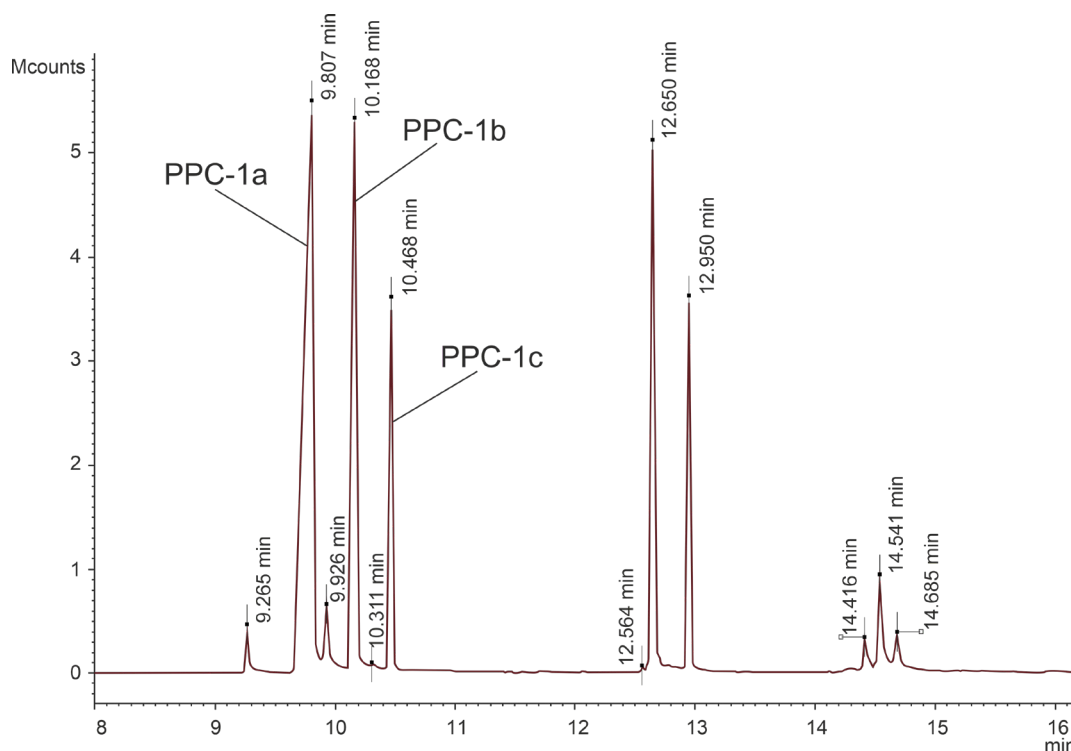


Fig. 3. Fragment of the chromatogram of a 0.2% solution of PPC-1 in acetone.

of the oxirane group in the region of $810\text{--}840\text{ cm}^{-1}$ and $-\text{CH}_2$ in the region of $760\text{--}770\text{ cm}^{-1}$ in the samples indicates the complete opening of oxirane rings.

Phosphorus containing samples contain bands corresponding to the carbonyl group $>\text{C}=\text{O}$ in the region of 1719 cm^{-1} , $>\text{C}=\text{CH}_2$ in the region of $880\text{--}900\text{ cm}^{-1}$, ether bond in the region of $1100\text{--}1200\text{ cm}^{-1}$, $\text{C}=\text{C}$ vibrations in the region of 1635 cm^{-1} , $\text{P}\text{--}\text{OR}$ in the region of $940\text{--}945\text{ cm}^{-1}$, $\text{R}\text{--}\text{Cl}$ in the region of $760\text{--}770\text{ cm}^{-1}$. The addition

of a spacer between two reaction centers binding the phosphorus atoms is not accompanied by a significant difference in the spectra of PPC-2 and PPC-1. The band in the region of about 1500 cm^{-1} in the IR spectrum of PPC-3 is assigned to vibrations of the aromatic ring; the band in the region of about 3000 cm^{-1} can be attributed to the hydroxyl group contained in the structure of ED-20.

Synthesized products PPC-1, PPC-2, and PPC-3 were used to obtain photocurable compositions.

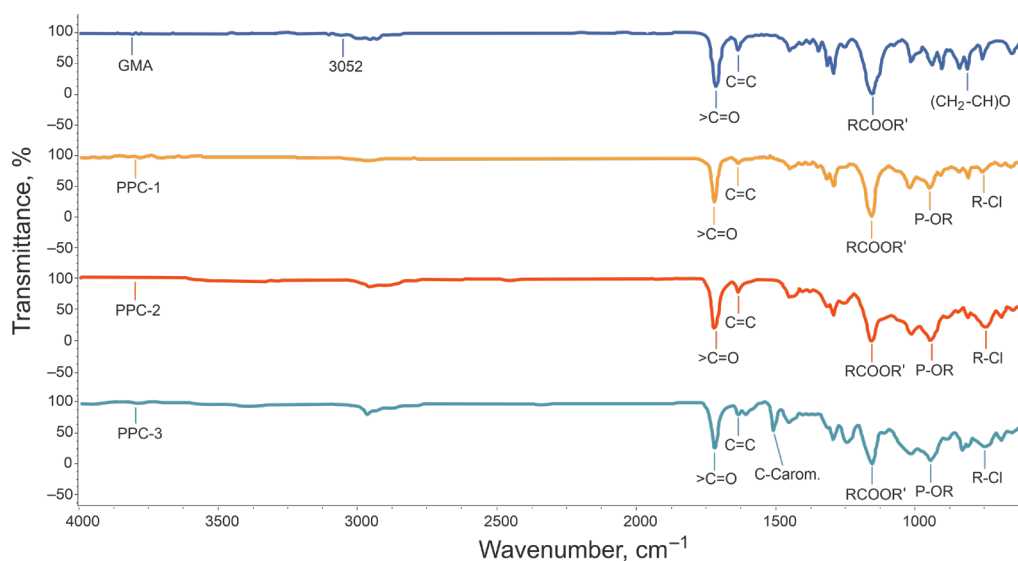


Fig. 4. IR spectra of PPC-1, PPC-2, PPC-3, and GMA products.

Investigation of the processes of curing synthesized compounds

The curing of the compositions with peroxide initiators (benzoyl peroxide, dicumyl peroxide) did not lead to a positive result, which is probably due to the presence of trivalent phosphorus in the structure of the oligoether methacrylate, which deactivates peroxides. In this regard, curing was carried out under the action of UV radiation in the presence of a photoinitiator.

Phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPhO), which is effective in a wide range of the UV spectrum with acceptable initiation parameters, was chosen as the initiator of the UV curing process, as recommended by a number of authors [21–23].

Determination of the degree of completion of the processes of photocuring of the synthesized products was carried out using DSC.

The presented data (Fig. 5 and Table) demonstrates the influence of the spacer on the thermal effects of the photocuring process. Although the introduction of an aliphatic spacer (PPC-2) has little effect on both the maximum heat release and the time taken to achieve it, an aromatic moiety (PPC-3) has a greater effect on photocuring processes, increasing the time taken to reach maximum heat release to 0.6 min, probably as a result of steric hindrances.

The introduction of a spacer with an increase in the overall functionality of the resulting compound reduces the number of polymerizable groups due to the steric factor, which is also accompanied by a decrease in the thermal effect of photocuring. According to DSC data, the contribution of one methacrylic group to the total thermal effect of the gross curing process of the

synthesized products was estimated, which was 0.09376, 0.03113, 0.01822 J/(mol·eq) for PPC-1, PPC-2, PPC-3, respectively. In the case of the PPC-3 sample, which has a more massive rigid spacer as compared to PPC-2, a lower density of the spatial structure is formed. This is probably due to the steric factor, which limits polymerization to a greater extent to groups in the side chain.

This fact was substantiated in [24] when calculating the quadratic critical conversion, whose physical meaning is the necessity to carry out at least two reactions of functional groups sequentially in order to ensure the formation of a crosslink. As a result of the first reaction, the polyfunctional oligomer must be integrated into the polymer chain and, therefore, suspended functional groups X must appear. Due to the second reaction of the interaction of the X group, the crosslink itself is formed. The authors conclude that the main reason for the deviation of the experimental gel point from the calculated one is the cyclization reaction, which limits the mobility of the polymerizing units, ultimately leading to a decrease in the thermal effect, which is also observed in our case.

Of additional interest was the determination of the degree of completion of the mass photocuring processes. For this purpose, an E7-25 immittance meter was used as part of a device with a photocell equipped with LEDs with a total luminous flux of 0.0172 mW/cm² and a wavelength of 397 nm, which made it possible to evaluate the change in the dielectric properties of the material with time. The use of the developed measuring system was based on the well-known fact [24] that cured polymers have increased dielectric

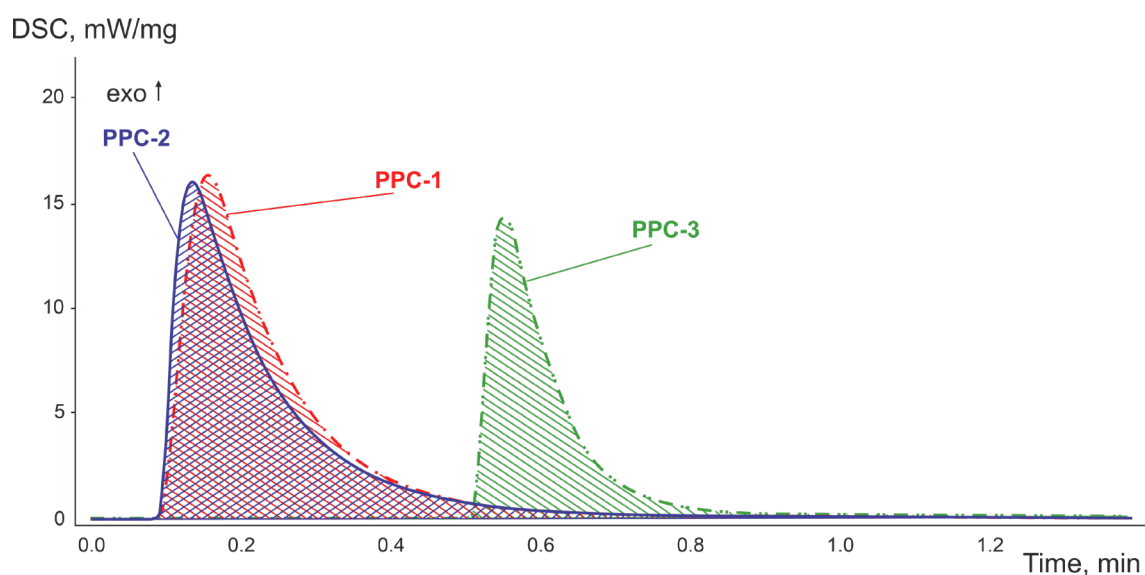


Fig. 5. Time dependences of thermal effects of photo-curing PPC-1, PPC-2, and PPC-3.

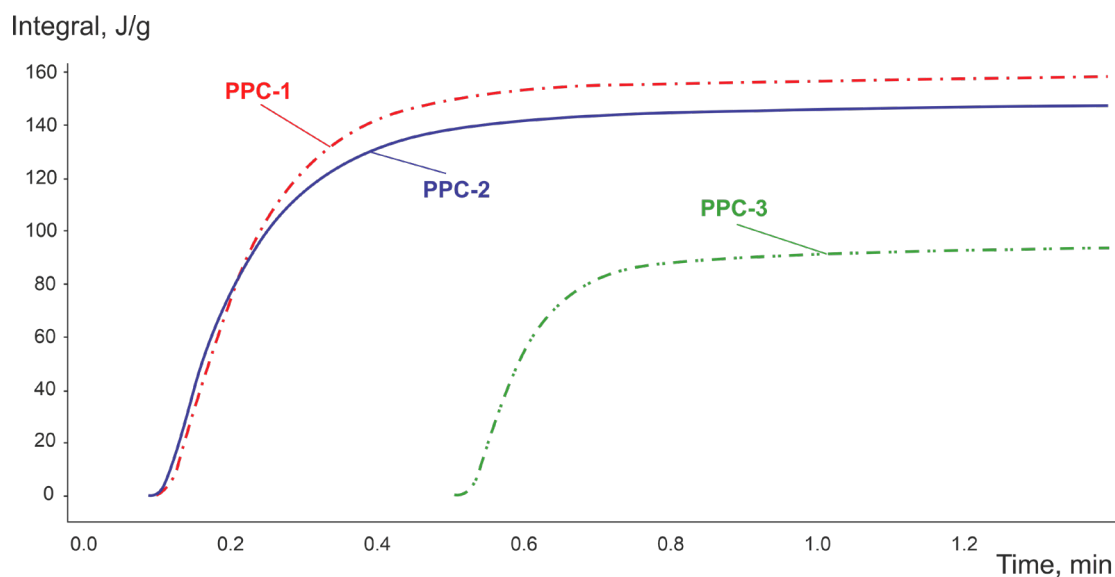


Fig. 6. Integral dependences of thermal effects of photo-curing PPC-1, PPC-2, and PPC-3.

Table. Experimental data of the photo-curing process

Method	Parameters	PPC-1	PPC-2	PPC-3
DSC	Q_{\max} , mW/mg	16.36	15.99	14.43
	Q_{sum} , J/g	158.5	147.8	93.4
	Q_{sum} , J/mol	0.2813	0.1245	0.0729
	Q_{sum} , J/(mol·eq)	0.09376	0.03113	0.01822
	Time at Q_{\max} , min	0.2	0.1	0.6
DEA	τ_{ind}	50	1650	150
	$\tau_{0.9}$	1100	2050	1430
	$a = \tau_{0.9} - \tau_{\text{ind}}$	1050	400	1280
	$1/a$, s ⁻¹	$9.52 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	$7.81 \cdot 10^{-4}$

Note: DEA is dielectric analysis. Q_{\max} is the maximum heat flow; Q_{sum} is the sum heat effect; τ_{ind} is the induction period; $\tau_{0.9}$ is 90% process completion time; a is the time of the initiated photo-curing process; $1/a$ is the photo-curing process rate.

properties due to the limitation of molecular mobility as a result of the formation of intermolecular chemical bonds.

For oligomers, the inductive effect turned out to be significant, the influence of which quickly leveled off as the chain length increased, and the reactivity of the group depended on the number of

atoms located next to it [25]. In molecules with spacers, steric hindrances become of great importance, which determine the decrease in the reactivity of side functional groups.

The obtained measurement results were processed mathematically using the calculation method given below according to formula (2) [26].

$$\beta = \frac{C_{a_{\max}} - C_a}{C_{a_{\max}} - C_{a_{\min}}}, \quad (2)$$

where C_a is the current value of the cell dielectric property index; $C_{a_{\max}}$ and $C_{a_{\min}}$ are the maximum and minimum value of the dielectric property index of the cell. The results are presented in Fig. 7.

The presented results indicate the effect of the spacer in the synthesized compounds on the curing process.

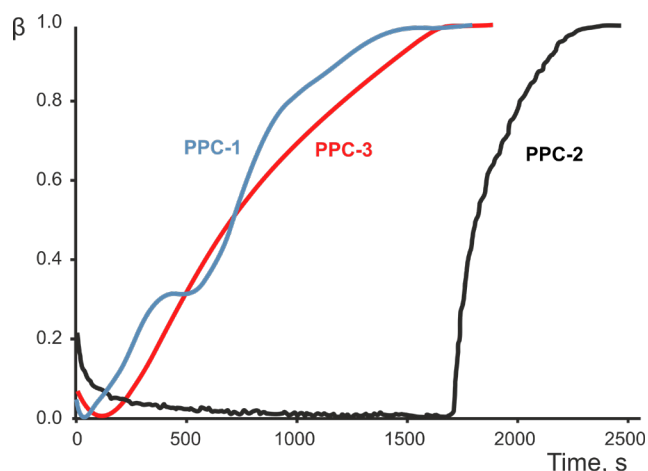


Fig. 7. Conversion degree of the photo-curing process PPC-1, PPC-2, and PPC-3 in the presence of the photoinitiator BAPhO 0.5 wt %.

Phosphorus-containing oligoether methacrylates cure relatively quickly without a spacer (PPC-1, Fig. 7). The pronounced inflection of the change curve of the dielectric properties of the studied oligomer can be used to characterize the time interval for the end of the gelation process, following which the rate of change in the dielectric properties increases and the polymerization process passes into the final phase of formation of the crosslinked polymer structure. The dynamics of photocuring of oligoether methacrylates with a spacer of different structure differs significantly from the one under consideration, including due to the absence of a pronounced gel formation area. The formation of a cross-linked PPC-2 polymer matrix proceeds with a significant induction period, which can be explained by the relatively higher mobility of ions not only of the oligomer, but also of the forming linear polymer, due to the presence of a flexible aliphatic space in its hinged part.

CONCLUSIONS

The possibility of obtaining new oligoether methacrylates with spacers in the chemical structure based on phosphorus trichloride, glycidyl methacrylate, and E-181 and ED-20 epoxy resins is confirmed. It is shown that the process of addition of the oxirane ring to phosphorus trichloride occurs both according to the Krasusky rule from the side of the α -carbon atom, and against this rule, with the formation of isomeric products.

The influence of the structure of the spacer on the rate of curing of oligomers under the action of UV radiation is determined.

According to dielectric analysis, photocuring in the bulk of oligoether methacrylates containing an aliphatic spacer is accompanied by an increase in the induction period of curing by a factor of 39, and an aromatic spacer by a factor of 4 compared to a sample without a spacer.

DSC studies established that the maximum thermal effect of UV curing (158.5 J/g) has an oligomer that does not contain a spacer. Meanwhile, the introduction of aliphatic and aromatic spacers leads to a decrease in the total thermal effect of the curing process to 147.8 and 93.4 J/g, respectively.

Acknowledgments

The work was supported by the Ministry of Science and Higher Education of the Russian Federation as a part of the state assignment (project code FZUS-2021-0013).

Authors' contributions

B.A. Buravov – carrying out syntheses, processing experimental data, and writing the text of the article;

A. Al-Hamzawi – conducting the experiment, data processing, and analysis of the results;

E.S. Bochkarev – analysis of research results, data processing;

N.Kh. Grichishkina – literature analysis, formalization of the list of references and interpretation of IR spectra;

S.V. Borisov – conducting IR research;

N.V. Sidorenko – conducting DSC research;

O.I. Tuzhikov – consultation on the chemistry of phosphorus-containing compounds, as well as planning, methodology, and implementation of the study;

O.O. Tuzhikov – the idea of the study, consultation on conducting experiments, writing the text of the article.

The authors declare no conflicts of interest.

REFERENCES

1. Levchik S.V. Introduction to Flame Retardancy and Polymer Flammability. In: Morgan A.B., Wilkie C.A. (Eds.). *Flame Retardant Polymer Nanocomposites*. John Wiley & Sons, Inc.; 2006. P. 1–29. <https://doi.org/10.1002/9780470109038.ch1>
2. Tuzhikov O.I., Khokhlova T.V., Bondarenko S.N., et al. *Elastomery i plastiki s ponizhennoi goryuchest'yu: monografiya (Elastomers and plastics with reduced flammability: monograph)*. Volgograd: Politekhnik; 2005. 214 p. (in Russ.). ISBN 5-230-04464-0
3. Berlin A.I. Combustion of polymers and polymer materials of reduced flammability. *Sorosovskii obrazovatel'nyi zhurnal = Soros Educational Journal*. 1996;2(9):57–63 (in Russ.).
4. Wang Z., Liang B. Synthesis and properties of phosphorus and nitrogen containing intumescent flame-retardant curing agent for epoxy resin. *Plast. Rubber Compos.* 2018;47(7):306–314. <https://doi.org/10.1080/14658011.2018.1491702>
5. Bier F., Six J.-L., Durand A. DOPO-Based Phosphorus-Containing Methacrylic (Co)Polymers: Glass Transition Temperature Investigation. *Macromol. Mater. Eng.* 2019;304(4). <https://doi.org/10.1002/mame.201800645>
6. Harada M., Hirotsu M., Ochi M. Synthesis and improved mechanical properties of twin-mesogenic epoxy thermosets using siloxane spacers with different lengths. *J. Appl. Polym. Sci.* 2019;136(34):47891. <https://doi.org/10.1002/app.47891>
7. Luo C., Zuo J., Wang F., Lin F., Zhao J., Xu Z. Click chemistry-assisted preparation and properties of phosphorus and nitrogen synergistic flame retardant optical resin with a high refractive index. *J. Appl. Polym. Sci.* 2018;135(38):46648. <https://doi.org/10.1002/app.46648>
8. Yang X., Chen S., Chen S., Xu H. Influencing factors on liquid crystalline properties of cholesterol side-chain liquid crystalline polymers without spacer: molecular weight and copolymerisation. *Liq. Cryst.* 2019;46(12):1827–1842. <https://doi.org/10.1080/02678292.2019.1606352>
9. Brigadnov K.A., Bilichenko Y.V., Polyakov V.A., Borisov R.S., Gusev K.I., Rudakova T.A., et al. Epoxy oligomers modified with epoxyphosphazenes. *Polym. Sci. Ser. B.* 2016;58(5):549–555. <https://doi.org/10.1134/S1560090416050018>
[Original Russian Text: Brigadnov K.A., Bilichenko Y.V., Polyakov V.A., Borisov R.S., Gusev K.I., Rudakova T.A., Filatov S.N., Kireev V.V. Epoxy oligomers modified with epoxyphosphazenes. *Vysokomolekulyarnye Soedineniya. Seriya B.* 2016;58(5):387–393 (in Russ.). <https://doi.org/10.7868/S2308113916050016>]
10. Tuzhikov O.I., Tuzhikov O.O., Buravov B.A., et al. Method for obtaining thermo- and heat-resistant polymers based on tris-[(1-chloromethyl-2-methacryloxy)ethoxy]-phosphines. RF Pat. 2697721, MPK C07F9/141, C08G 79/04. Volgograd: VolgGTU; 18.08.2019.
11. Tuzhikov O.I., Tuzhikov O.O., Buravov B.A., et al. Application of oligoesteracrylate (((4-((1-(2-((bis(1-chloro-3-(methacryloyloxy)propan-2-yl)oxy)phosphine)-oxy)-3-chlorophenoxy)-3-chloropropan-2-yl)oxy)-1-chlorobutan-2-yl)oxy)phosphindiy)bis(oxy))bis(3-chloropropan-2,1-diyl)-bis(2-methacrylate) as a monomer for the production of thermo- and heat-resistant polymers with reduced flammability. RF Pat. 2712107. MPK C08G 79/04, C08F 279/06, C07F 9/00. Volgograd: VolgGTU; 24.01.2020.

СПИСОК ЛИТЕРАТУРЫ

1. Levchik S.V. Introduction to Flame Retardancy and Polymer Flammability. In: Morgan, A.B., Wilkie C.A. (Eds.). *Flame Retardant Polymer Nanocomposites*. John Wiley & Sons, Inc.; 2006. P. 1–29. <https://doi.org/10.1002/9780470109038.ch1>
2. Тужиков О.И., Хохлова Т.В., Бондаренко С.Н. и др. *Эластомеры и пластики с пониженной горючестью: монография*. Волгоград: Политехник; 2005. 214 с. ISBN 5-230-04464-0
3. Берлин А.И. Горение полимеров и полимерные материалы пониженной горючести. *Соросовский образовательный журнал*. 1996;2(9):57–63.
4. Wang Z., Liang B. Synthesis and properties of phosphorus and nitrogen containing intumescent flame-retardant curing agent for epoxy resin. *Plast. Rubber Compos.* 2018;47(7):306–314. <https://doi.org/10.1080/14658011.2018.1491702>
5. Bier F., Six J.-L., Durand A. DOPO-Based Phosphorus-Containing Methacrylic (Co)Polymers: Glass Transition Temperature Investigation. *Macromol. Mater. Eng.* 2019;304(4). <https://doi.org/10.1002/mame.201800645>
6. Harada M., Hirotsu M., Ochi M. Synthesis and improved mechanical properties of twin-mesogenic epoxy thermosets using siloxane spacers with different lengths. *J. Appl. Polym. Sci.* 2019;136(34):47891. <https://doi.org/10.1002/app.47891>
7. Luo C., Zuo J., Wang F., Lin F., Zhao J., Xu Z. Click chemistry-assisted preparation and properties of phosphorus and nitrogen synergistic flame retardant optical resin with a high refractive index. *J. Appl. Polym. Sci.* 2018;135(38):46648. <https://doi.org/10.1002/app.46648>
8. Yang X., Chen S., Chen S., Xu H. Influencing factors on liquid crystalline properties of cholesterol side-chain liquid crystalline polymers without spacer: molecular weight and copolymerisation. *Liq. Cryst.* 2019;46(12):1827–1842. <https://doi.org/10.1080/02678292.2019.1606352>
9. Бригаднов К.А., Биличенко Ю.В., Поляков В.А., Борисов Р.С., Гусев К.И., Рудакова Т.А., Филатов С.Н., Киреев В.В. Эпоксидные олигомеры, модифицированные эпоксифосфазенами. *Высокомолекулярные соединения. Серия Б.* 2016;58(5):387–393. <https://doi.org/10.7868/S2308113916050016>
10. Тужиков О.И., Тужиков О.О., Буравов Б.А. и др. Способ получения термо- и термостойких полимеров на основе трис-[(1-галогенметил-2-метакрилокси)-этоксифосфинов. Пат. 2697721 РФ. МПК C07F9/141, C08G 79/04. Заявитель патентообладатель ВолГТУ (RU). № 2019117090, заявл. 03.06.2019. опубл. 18.08.2019.
11. Тужиков О.И., Тужиков О.О., Буравов Б.А., Бочкарев Е.С., Солодовникова К.В., Хохлова Т.В., Сидоренко Н.В., Аль-Хамзави А.Х.Д. Применение олигоэфиракрилата (((4-((1-(2-((бис(1-галоген-3-(метакрилокси)-пропан-2-ил)окси)фосфин)окси)-3-галогенпропокси)3-хлорпропан-2-ил)окси)-1-галогенбутан-2-ил)окси)фосфинди)л)бис(окси))бис(3-галогенпропан-2,1-ди)л)бис(2-метакрилата) в качестве мономера для получения термо- и термостойких полимеров с пониженной горючестью. Пат. 2712107 РФ. МПК C08G79/04, C08F279/06, C07F9/00. Волгоград: ВолГТУ; 2020.

12. Tuzhikov O.I., Tuzhikov O.O., Buravov B.A., *et al.* Application of oligoesteracrylate (((((((((2-гидроксипропан-1,3-диил)бис(окси))бис(4,1-фенилен))бис(пропан-2,2-диил))-бис(4,1-фенилен))бис(гидрокси))-бис(1-хлоропропан-3,2-диил))бис(окси))-бис(фосфинтриил))тетракис(окси))-тетракис(3-хлоропропан-2,1-диил)тетракис(2-метил акрилате) as a monomer for the production of thermo- and heat-resistant polymers with reduced flammability. RF Pat. 2712116. МПК C08G 79/04, C07F 9/141. Volgograd: VolgGTU; 24.01.2020.
13. Dogadkin B.A., Dontsov A.A., Shershnev V.A. *Khimiya elastomerov (Chemistry of elastomers)*. Moscow: Khimiya; 1981. 376 p. (in Russ.).
14. Efros L.S., Gorelik M.V. *Khimiya i tekhnologiya promezhutochnykh produktov (Chemistry and technology of intermediate products)*. Leningrad: Khimiya; 1979. 544 p. (in Russ.).
15. Gorbunov B.N., Gurvich Ya.A., Maslova I.P. *Khimiya i tekhnologiya stabilizatorov polimernykh materialov (Chemistry and technology of stabilizers of polymer materials)*. Moscow: Khimiya; 1981. 368 p. (in Russ.).
16. Khardin A.P., Tuzhikov O.I., V'yunov K.A., Khokhlova T.V. Kinetics of the reaction of phenoxymethylphosphonic acid chloride with glycidyl methacrylate. *Zhurnal Obshchei Khimii*. 1979;49(5):1031–1035 (in Russ.). URL: <https://www.elibrary.ru/item.asp?id=22974331>
17. Tuzhikov O.I., Khokhlova T.V., Bondarenko S.N., Dkhaibe M., Orlova S.A. Modification of epoxy-4,4'-isopropylidenediphenol resins with phosphorylated methacrylates for preparing compounds of the interpenetrating polymer network type. *Russ. J. Appl. Chem.* 2009;82(11):2034–2040. <https://doi.org/10.1134/S107042720911024X>
[Original Russian Text: Tuzhikov O.I., Khokhlova T.V., Bondarenko S.N., Dkhaibe M., Orlova S.A. Modification of epoxy-4,4'-isopropylidenediphenol resins with phosphorylated methacrylates for preparing compounds of the interpenetrating polymer network type. *Zhurnal Prikladnoi Khimii*. 2009;82(11):1887–1893 (in Russ.). URL: <https://www.elibrary.ru/item.asp?id=44517526>]
18. Khardin A.P., Tuzhikov O.I., V'yunov K.A., Khokhlova T.V., Rygalov L.N. Kinetics of reactions of phenoxymethylphosphonic acid chloride with unsymmetrical alpha-oxides. *Zhurnal Obshchei Khimii*. 1980;50(8):1733–1738 (in Russ.). URL: <https://elibrary.ru/item.asp?id=21264731>
19. Malinovskii M.S. *Okisi olefinov i ikh proizvodnye (Oxides of olefins and their derivatives)*. Moscow: Goskhimtekhnizdat; 1961. 553p. (in Russ.).
20. Chike K.E., Myrick M.L., Lyon R.E., Angel S.M. Raman and near-infrared studies of an epoxy resin. *Appl. Spectrosc.* 1993;47(10):1631–1635. <https://doi.org/10.1366/0003702934334714>
21. Guerra A.J., Lammel-Lindemann J., Katko A., Kleinfehn A., Rodriguez C.A., Catalani L.H., *et al.* Optimization of photocrosslinkable resin components and 3D printing process parameters. *Acta Biomater.* 2019;97:154–161. <https://doi.org/10.1016/j.actbio.2019.07.045>
22. Lima A.F., Salvador M.V.O., Dressano D., Saraceni C.H.C., Gonçalves L.S., Hadis M., *et al.* Increased rates of photopolymerisation by ternary type II photoinitiator systems in dental resins. *J. Mech. Behav. Biomed. Mater.* 2019;98:71–78. <https://doi.org/10.1016/j.jmbbm.2019.06.005>
23. Salgado V.E., Albuquerque P.P.A.C., Cavalcante L.M., Pfeifer C.S., Moraes R.R., Schneider L.F.J. Influence of photoinitiator system and nanofiller size on the optical properties and cure efficiency of model composites. *Dent. Mater.* 2014;30(10):e264–e271. <https://doi.org/10.1016/j.dental.2014.05.019>
24. Иржак В.И., Межиковский С.М. Кинетика отверждения олигомеров. *Успехи химии*. 2008;77(1):78–104. URL: <https://elibrary.ru/item.asp?id=9933186>
25. Иржак В.И., Межиковский С.М. *Химическая физика отверждения олигомеров*: монография. М.: Издательство Юрайт; 2020. 276 с.
12. Тужиков О.И., Тужиков О.О., Буравов Б.А. и др. Применение олигоэфиракрилата (((((((((2-гидроксипропан-1,3-диил) бис (окси)) бис (4,1-фенилен)) бис (пропан-2,2-диил)) бис (4,1-фенилен)) бис(окси)) бис (1-галогенпропан-3,2-диил)) бис (окси)) бис(фосфинтриил)) тетракис (окси)) тетракис (3-галогенпропан-2,1-диил) тетракис (2-метилакрилата) в качестве мономера для получения термо- и теплостойких полимеров с пониженной горючестью. Пат. 2712116 РФ. МПК C08G79/04, C07F 9/141. Заявитель патентообладатель ВолГТУ (RU). № 2019126186, заявл. 20.08.2019. опубл. 24.01.2020. Бюл. № 3.
13. Догадкин Б.А., Донцов А.А., Шершнева В.А. *Химия эластомеров*. 2-е изд., перераб. и доп. М.: Химия; 1981. 376 с.
14. Эфрос Л.С., Горелик М.В. *Химия и технология промежуточных продуктов*. Л.: Химия; 1979. 544 с.
15. Горбунов Б.Н., Гурвич Я.А., Маслова И.П. *Химия и технология стабилизаторов полимерных материалов*. М.: Химия; 1981. 368 с.
16. Хардин А.П., Тужиков О.И., Вьюнов К.А., Хохлова Т.В. Кинетика реакции хлорангидрида феноксиметилфосфоновой кислоты с глицидилметакрилатом. *Журн. общей химии*. 1979;49(5):1031–1035. URL: <https://www.elibrary.ru/item.asp?id=22974331>
17. Тужиков О.И., Хохлова Т.В., Бондаренко С.Н., Дхайбе М., Орлова С.А. Модификация эпоксиано-вых смол фосфорсодержащими метакрилатами для получения компаундов типа взаимопроницающих полимерных сеток. *Журн. прикладной химии*. 2009;82(11):1887–1893. URL: <https://www.elibrary.ru/item.asp?id=44517526>
18. Хардин А.П., Тужиков О.И., Вьюнов К.А., Хохлова Т.В., Рыгалов Л.Н. Кинетика реакций хлорангидрида феноксиметилфосфоновой кислоты с несимметричными альфа-оксидами. *Журн. общей химии*. 1980;50(8):1733–1738. URL: <https://elibrary.ru/item.asp?id=21264731>
19. Малиновский М.С. *Окиси олефинов и их производные*. М.: Госхимтехиздат; 1961. 553 с.
20. Chike K.E., Myrick M.L., Lyon R.E., Angel S.M. Raman and near-infrared studies of an epoxy resin. *Appl. Spectrosc.* 1993;47(10):1631–1635. <https://doi.org/10.1366/0003702934334714>
21. Guerra A.J., Lammel-Lindemann J., Katko A., Kleinfehn A., Rodriguez C.A., Catalani L.H., *et al.* Optimization of photocrosslinkable resin components and 3D printing process parameters. *Acta Biomater.* 2019;97:154–161. <https://doi.org/10.1016/j.actbio.2019.07.045>
22. Lima A.F., Salvador M.V.O., Dressano D., Saraceni C.H.C., Gonçalves L.S., Hadis M., *et al.* Increased rates of photopolymerisation by ternary type II photoinitiator systems in dental resins. *J. Mech. Behav. Biomed. Mater.* 2019;98:71–78. <https://doi.org/10.1016/j.jmbbm.2019.06.005>
23. Salgado V.E., Albuquerque P.P.A.C., Cavalcante L.M., Pfeifer C.S., Moraes R.R., Schneider L.F.J. Influence of photoinitiator system and nanofiller size on the optical properties and cure efficiency of model composites. *Dent. Mater.* 2014;30(10):e264–e271. <https://doi.org/10.1016/j.dental.2014.05.019>
24. Иржак В.И., Межиковский С.М. Кинетика отверждения олигомеров. *Успехи химии*. 2008;77(1):78–104. URL: <https://elibrary.ru/item.asp?id=9933186>
25. Иржак В.И., Межиковский С.М. *Химическая физика отверждения олигомеров*: монография. М.: Издательство Юрайт; 2020. 276 с.

24. Irzhak V.I., Mezhevikskii S.M. Kinetics of Oligomer Curing. *Russ. Chem. Rev.* 2008;77(1):77–103. <https://doi.org/10.1070/RC2008v077n01ABEH003752>

[Original Russian Text: Irzhak V.I., Mezhevikskii S.M. Kinetics of Oligomer Curing. *Uspekhi Khimii.* 2008;77(1):78–104 (in Russ.). URL: <https://elibrary.ru/item.asp?id=9933186>]

25. Irzhak V.I., Mezhevikskii S.M. *Khimicheskaya fizika otverzhdeniya oligomerov: monografiya (Chemical physics of curing oligomers: monograph)*. Moscow: Yurait; 2020. 276 p. (in Russ.).

26. Tuzhikov O.O., Buravov B.A., Bochkarev E.S., Avvakumov V.E., Sidorenko N.V., et al. Effect of soluble PVC and copolymer A-15-O in epoxy resin on physical-mechanical properties of hydroxosilicated polymerized systems and their fire retardant effect. *Izvestiya VolgGTU = Izvestia VSTU.* 2018;12(222):106–113 (in Russ.).

26. Тужиков О.О., Буравов Б.А., Бочкарев Е.С., Аввакумов В.Е., Сидоренко Н.В. и др. Влияние растворенных ПВХ и сополимера А-15-О в эпоксидном связующем на физико-механические свойства и огнестойкость наполненных гидроксисиликатами отвержденных полимерных систем. *Известия ВолгГТУ.* 2018;12(222):106–113.

About the authors:

Boris A. Buravov, Cand. Sci. (Chem.), Associate Professor, Department of General and Inorganic Chemistry; Senior Researcher, Laboratory of Polymer, Composite and Hybrid Functional Materials, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: byravov@ya.ru. ResearcherID AAH-5810-2021, RSCI SPIN-code 6730-5763, <https://orcid.org/0000-0001-9039-571X>

Ali Al-Khamzawi, Postgraduate Student, Department of General and Inorganic Chemistry, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: ali.alhamzawi80@gmail.com. ResearcherID M-2885-2017, RSCI SPIN-code 6024-6675, <https://orcid.org/0000-0003-4491-494X>

Eugene S. Bochkarev, Junior Researcher, Laboratory of Polymer, Composite and Hybrid Functional Materials, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: w_tovn@mail.ru. Scopus Author ID 57222574440, RSCI SPIN-code 6024-6675, <https://orcid.org/0000-0002-2343-1562>

Nazmiya Kh. Grichishkina, Senior Lecturer, Department of General and Inorganic Chemistry, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: nazmija3545@mail.ru. RSCI SPIN-code 5661-4527, <https://orcid.org/0000-0002-2208-4992>

Sergey V. Borisov, Cand. Sci. (Eng.), Associate Professor, Department of Chemistry and Processing Technology of Elastomers; Senior Researcher, Laboratory of Polymer, Composite and Hybrid Functional Materials, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: borisov.volgograd@yandex.ru. Researcher ID AAF-1221-2021, Scopus Author ID 57193435253, RSCI SPIN-code 4774-4238, <https://orcid.org/0000-0003-4400-0822>

Nina V. Sidorenko, Cand. Sci. (Eng.), Associate Professor, Department of Chemistry and Processing Technology of Elastomers, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: nvsidorenko@vstu.ru. ResearcherID A-9544-2014, Scopus Author ID 16308435400, RSCI SPIN-code 5155-3692, <https://orcid.org/0000-0002-6113-290X>

Oleg I. Tuzhikov, Dr. Sci. (Chem.), Professor, Department of Technology of Macromolecular and Fibrous Materials, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: tuzhikov_oi@vstu.ru. Scopus Author ID 6507272270, RSCI SPIN-code 7255-0330, <https://orcid.org/0000-0003-1893-2861>

Oleg O. Tuzhikov, Dr. Sci. (Eng.), Associate Professor, Head of the Department of General and Inorganic Chemistry, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: cand@vstu.ru. Scopus Author ID 12645529200, RSCI SPIN-code 8142-5915, <https://orcid.org/0000-0001-6316-8896>

Об авторах:

Буравов Борис Андреевич, к.х.н., доцент кафедры общей и неорганической химии; старший научный сотрудник лаборатории полимерных, композитных и гибридных функциональных материалов ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: byravov@ya.ru. ResearcherID AAH-5810-2021, SPIN-код РИНЦ 6730-5763, <https://orcid.org/0000-0001-9039-571X>

Аль-Хамзави Али, аспирант кафедры общей и неорганической химии ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: ali.alhamzawi80@gmail.com. ResearcherID M-2885-2017, SPIN-код РИНЦ 2551-0018, <https://orcid.org/0000-0003-4491-494X>

Бочкарев Евгений Сергеевич, младший научный сотрудник лаборатории полимерных, композитных и гибридных функциональных материалов ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: w_tovn@mail.ru. Scopus Author ID 57222574440, SPIN-код РИНЦ 6024-6675, <https://orcid.org/0000-0002-2343-1562>

Гричишкина Назмия Хуриид-кызы, старший преподаватель кафедры общей и неорганической химии ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: nazmija3545@mail.ru. SPIN-код РИНЦ 5661-4527, <https://orcid.org/0000-0002-2208-4992>

Борисов Сергей Владимирович, к.т.н., доцент кафедры химии и технологии переработки эластомеров; старший научный сотрудник лаборатории полимерных, композитных и гибридных функциональных материалов ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: borisov.volgograd@yandex.ru. Researcher ID AAF-1221-2021, Scopus Author ID 57193435253, SPIN-код РИНЦ 4774-4238, <https://orcid.org/0000-0003-4400-0822>

Сидоренко Нина Владимировна, к.т.н., доцент кафедры химии и технологии переработки эластомеров ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: nvsidorenko@vstu.ru. ResearcherID A-9544-2014, Scopus Author ID 16308435400, SPIN-код РИНЦ 5155-3692, <https://orcid.org/0000-0002-6113-290X>

Тужиков Олег Иванович, д.х.н., профессор кафедры технологии высокомолекулярных и волокнистых материалов ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: tuzhikov_oi@vstu.ru. Scopus Author ID 6507272270, SPIN-код РИНЦ 7255-0330, <https://orcid.org/0000-0003-1893-2861>

Тужиков Олег Олегович, д.т.н., доцент, заведующий кафедрой общей и неорганической химии ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: cand@vstu.ru. Scopus Author ID 12645529200, SPIN-код РИНЦ 8142-5915, <https://orcid.org/0000-0001-6316-8896>

The article was submitted: July 04, 2022; approved after reviewing: July 14, 2022; accepted for publication: October 04, 2022.

*Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Thomas Beavitt*