Trifunctional thermosetting monomer with propargyl and phthalonitrile groups

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A new monomer containing thermosetting groups of two types, namely, propargyl ether and phthalonitrile, in the structure of the molecule was synthesized and studied. It was found that thermal polymerization was accompanied by the degradation of the monomer with propargyl ether decomposition. This problem can be solved using catalysts based on Cu(1) favoring the polymerization at both the propargyl group and phthalonitrile fragments. The cured monomer has a non-porous structure and high thermal properties (Vicat softening temperature 395 °C, $T_{5\%}$ 451 °C). The low viscosity of the melt (<200 mPa s at 120 °C) and low glass-transition temperature (9 °C) of the monomer make it possible to use it for the formation of composite materials by vacuum infusion or injection into a mold.

Key words: thermosetting resins, phthalonitriles, propargyl ether, self-curing monomers.

The progress in aircraft production is associated with the development of materials with high specific strength. Polymer composite materials (PCM), the role of which in the modern aircrafts is permanently increasing with the appearance of new polymers and processing technologies, correspond to these requirements. One of the limiting factors in the application of PCM is a rather low temperature at which their long-term operation is possible. Nowadays, propargyl ether, ^{1,2} bismaleimide, ^{3,4} cyanoester, ^{5,6} polyamide, ⁷ and polyimide^{8,9} resins can be used at high working temperatures but only in a range of 250–300 °C.

Phthalonitrile resins are known due to their exceptional thermo-oxidative stability, high mechanical properties at elevated temperatures, low water absorption and fire resistance.^{10–15} Thermal polymerization of the amine-containing phthalonitrile resins occurs at high temperatures (200–300 °C). A noticeable change in the monomer viscosity is observed only after several days of continuous heating¹⁶ without curing agents. Various phenols¹⁷ and aromatic amines are widely used as curing agents.^{10,18}

The resin prepared using a curing agent is at least a two-component system, the properties of which depend strongly on the uniformity of the blend, which is especially essential in the case of low concentrations of the curing agent. The method for the development of self-curing phthalonitrile resins is to introduce initiating functional groups into the structure of the monomer itself.^{19,20} Such monomers do not require the addition of a curing agent.

Phthalonitriles with a propargyl group have been studied earlier in numerous works.^{21–25} They are of interest primarily as the initial self-curing monomers that require no external curing agent and provide polymerization without release of volatiles. A possibility of altering their polymerization process using various catalysts is also noteworthy.^{25–29}

A significant problem of the use of many phthalonitriles is their high melting points (about 150–200 °C), which are extremely close to the curing onset temperature (180-220 °C).¹² For a long time, the only way to obtain composites from carbon fiber with phthalonitrile matrices was the use of a resin solution impregnated prepreg technologies.^{30–33} The synthesis of low-melting phosphate- or siloxane-bridged monomers,^{34,35} propargyl ether containing monomers²⁵, as well as the use of thermosetting plasticisers^{36,35} made it possible to apply cost-efficient injection techniques such as vacuum infusion and resin transfer molding to fabricate such composites.^{38–40}

In this work, the phthalonitrile monomer bis[3-(3,4dicyanophenoxy)phenyl]prop-2-ynyl phosphate (PPgPN) containing both the phthalonitrile group (PN) and propargyl ether fragment (Pg) was synthesized and studied. The synthesized compound possesses a sufficiently low temperature of transition to the liquid state and is capable of curing without the use of additional accelerating agents.

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Experimental

Materials and methods. All manipulations with moisture- and oxidation-sensitive compounds were carried out in an inert atmosphere using the standard Schlenk technique. All solvents were purchased from Alfa Aesar, purified according to standard procedures, and stored under an inert Ar atmosphere. Solvent THF was distilled twice: over potassium hydroxide and over metallic sodium in the presence of benzophenone in an argon atmosphere. Triethylamine was distilled over CaH₂ and stored under argon, and POCl₃ was purchased from Khimmed (Moscow, Russia) and distilled before use. Resorcinol, 4-nitrophthalonitrile, 1,3-bis(4-aminophenoxy)benzene (APB), hydrochloric acid, and potassium carbonate were purchased from Sigma Aldrich and used as received. NMR spectra were recorded on a Bruker Advance 600 instrument (600 MHz for ¹H, 151 MHz for ¹³C, and 243 MHz for ³¹P) using CDCl₃ as the solvent. Differential scanning calorimetry (DSC) data were obtained on a DSC Q20 instrument (TA Instruments) at a heating rate of 10 °C/min (Ar purge rate 50 mL min⁻¹). The thermal stability of the samples was determined by the thermogravimetric analysis (TGA) method on a Netzsch TG 209 P3 Tarsus instrument at a heating rate of 10 °C/min in a temperature range of 40-1000 °C and in an argon or air flow (50 mL min⁻¹). The heat deflection temperature (Vicat softening point) was determined by thermomechanical analysis (TMA) in the penetration mode on a Netzsch TMA 402 instrument with a load of 0.1 MPa (ASTM-D1525-09). The melt viscosity was measured in the dynamic mode on a Brookfield CAP2000 7 cone viscometer at 200 rpm with a heating rate of 2 °C min⁻¹.

Polymerization. A monomer weighed sample (total weight 3 g) in the absence or in the presence of the polymerization catalyst was heated to melting, stirred, and subjected to curing in a forced air convection oven according to the following program: heating from 25 to 180 °C at a rate of changing temperature of 2 °C min⁻¹, maintaining at 180 °C for 8 h, heating from 180 to 330 °C at a rate of 10 °C h⁻¹, and maintaining at 330 °C for 8 h. The cured samples were removed from the vial and used to determine the thermal ($T_{5\%}$) and thermo-oxidative (TOS_{5%}) stability by the TGA method and the Vicat softening temperature. 4-(3-Hydroxyphenoxy)benzene-1,2-dicarbonitrile (MPB) was synthesized according to a published procedure.³⁴

Synthesis of 3-propynyl phosphorodichloridate. Phosphorus oxychloride (45.0 g, 0.293 mol) was added to a 100-mL threenecked round-bottom flask equipped with a water trap for hydrogen chloride and cooled until freezing initiation (\sim 1 °C). Then propargyl alcohol (11.0 g, 0.195 mol) was added dropwise through the septum with stirring avoiding heating above 5 °C. The mixture was left stirring at 20 °C for 12 h. Excess of phosphorus oxychloride was distilled off at 20 °C. The target compound was isolated by distillation under reduced pressure (66 °C at 1 Torr). The yield was 63% (28.5 g). ¹H NMR (CDCl₃), δ : 2.76 (t, 1 H, J = 2.43 Hz); 4.93 (dd, 2 H, J = 14.53 Hz, J = 2.43 Hz). ¹³C NMR (CDCl₃), δ : 58.40 (d, J = 7.74 Hz); 74.81 (d, J = 8.85 Hz); 78.81. ³¹P NMR (CDCl₃), δ : 11.28.

Synthesis of bis[3-(3,4-dicyanophenoxy)phenyl] prop-2-ynyl phosphate (PPgPN). Tetrahydrofuran (125 mL), 4-(3-hydroxyphenoxy)phthalonitrile (15 g, 0.064 mol), and triethylamine (6.43 g, 0.064 mol) were added sequentially to a 250-mL roundbottom three-necked flask equipped with a reflux condenser. Then the mixture was cooled to -30 °C, and 3-propenyl phosphorodichloridate (5.54 g, 0.032 mol) was added dropwise through the septum with stirring at such a rate that the temperature did not exceed -20 °C. The reaction mixture was stirred for 12 h and filtered through a glass porous filter to remove triethylamine hydrochloride, after which the product was purified by flash chromatography on silica gel (methylene dichloride as eluent). After removal of the solvent, a yellowish-white glassy substance with $T_{o} = 9 \,^{\circ}\text{C}$ was isolated. The yield was 46% (8.32 g). ¹H NMR (DMSO-d₆), δ : 3.77 (br.s, 1 H); 5.03 (d, 2 H, J = 10.91 Hz); 7.04–7.14 (m, 4 H); 7.23 (d, 2 H, J = 6.88 Hz); 7.44 (d, 2 H, J = 8.44 Hz); 7.55 (t, 2 H, J = 7.34 Hz); 7.85 (s, 2 H); 8.11 (d, 2 H, J = 8.62 Hz). ¹³C NMR (DMSO-d₆), δ: 57.55 (d, J = 4.42 Hz); 77.89 (d, J = 6.63 Hz); 80.50, 109.37, 112.82 (d, J = 4.42 Hz); 115.77, 116.27, 117.27, 117.60 (d, J = 4.42 Hz); 117.90, 123.03, 123.68, 132.28, 136.82, 151.31 (d, J = 6.63 Hz); 155.34, 160.71. ³¹P NMR (CDCl₃), δ : -9.68. HPLC/MS (EI), m/z (I_{rel} (%)): 573 [M + H] (99).

Results and Discussion

The PPgPN monomer was synthesized by the reaction shown in Scheme 1. The purity and structure of the resulting compound were confirmed by NMR and HPLC/MS.

Rheological tests were carried out for the synthesized monomer PPgPN without addition of the curing agent. The viscosity profile in the temperature range from 50 to 300 °C is shown in Fig. 1. It is worth noting that an increase in viscosity associated with the start of polymerization is observed at ~250 °C. This was not observed in the case of phthalonitriles without curing agents.¹⁶ The melt viscosity





Fig. 1. The viscosity profile of the monomer without a curing agent in the temperature range from 50 to $300 \,^{\circ}$ C.

was 200 mPa at 120 °C, which makes it possible to consider fabrication of a composite material using this monomer by vacuum infusion or resin transfer molding processes.⁴¹

It was previously shown that the phthalonitrile monomer containing the propargyl group, 4-[3-(prop-2-yn-1yloxy)phenoxy]benzene-1,2-dicarbonitrile (PPN), does not require a curing agent to form a polymer matrix.²⁵ Therefore, primary experiments with PPgPN were carried out without initiator. The polymerization process of the studied monomer was investigated by DSC (Fig. 2).

Two peaks of heat release are observed on the DSC curve of the previously studied compound²⁵ also containing the phthalonitrile and propargyl groups: the first peak corresponds to the polymerization of the propargyl fragments, and the second peak corresponds to the polymerization of the phthalonitrile groups. An analysis of PPgPN revealed three peaks in a temperature range of 200-250 °C. To study in more detail the nature of the chemical processes preceding the interaction of propargyl ether and phthalonitrile groups, the samples of the monomer kept at 200 °C for 90 min were prepared.

The polymerization process was investigated by the NMR method. The monomer was examined before and after heating at 200 °C (Fig. 3). Samples were taken after 15, 30, 45, 60, and 90 min from the start of the experiment.



Fig. 2. DSC curve of the PPgPN monomer without curing agent.

A decrease in the intensity of the signals from the propargyl group (3.77 br.s, 5.03 d) and the appearance of new peaks in the range of signals corresponding to aromatic groups were observed in the ¹H NMR spectra. There were no signals in the range of vinyl protons corresponding to the products of triple bond polymerization.

To detect intermediate products of the polymerization process, an HPLC/MS analysis of the mixture after heating was carried out (Fig. 4).

The main substance in the mixture was compound 1, which is the starting monomer with the eliminated propargyl group. Compound 2, which is a transesterification product, was also present in a significant extent. To prevent the destruction of the monomer, it was proposed to select a catalyst for the polymerization of the propargyl group. The initiation of polymerization at a lower temperature should facilitate primary crosslinking of the monomers prior to the initiation of transesterification and degradation of phosphate ester.

It is known that Ni²⁺ salts catalyze homopolymerization and trimerization of triple bonds, ^{26,42} Co²⁺ salts catalyze cyclotrimerization, ²⁷ Cu²⁺ salts catalyze crosscoupling. ^{28,29} In addition, the Co and Cu compounds are capable of reacting with phthalonitriles at temperatures above 195 °C to form phthalocyanine complexes. ⁴³ The effects of a standard initiator of polymerization of phthalonitrile resins (1,3-bis(4-aminophenoxy)benzene (APB)) and several metal-containing catalysts (nickel(11) ethylhexanoate Ni(C₄H₉CH(C₂H₅)COO)₂, triphenylphosphine





Fig. 3. NMR spectra of the PPgPN monomer before (a) and after (b) heating at 200 °C for 90 min.

complex of cobalt chloride $Co(P(C_6H_5)_3)_2Cl_2$, copper(11) ethylhexanoate $Cu(C_4H_9CH(C_2H_5)COO)_2$, triphenylphosphine triflate complex of copper(1) CF₃SO₂OCu-(P(C₆H₅)₃)₃ on the polymerization process were studied.

Initially, experiments were carried out to study the effect of the curing agent on the polymerization rate. Vials containing mixtures of the monomer PPgPN and catalysts were kept at T = 200 °C for several hours, while the polymer was periodically tested for hardness using a metallic wire. The polymerization activity was estimated from the time required for complete polymer solidification. The polymerization time for all mixtures containing catalysts was shorter than that for the neat monomer without curing agent (more than 8 h). The most active curing agent were APB (6 h) and nickel(II) ethylhexanoate (6 h).

The polymerization of the PPgPN monomer with various catalysts was investigated by the DSC method. The thermograms are shown in Fig. 5.

In previous studies^{25,29} it was shown that the use of 1 wt.% nickel catalyst leads to the rapid polymerization at



Fig. 4. HPLC/MS chromatogram of the products of PPgPN polymerization after heating at 200 °C for 90 min.



Fig. 5. DSC curves for the polymerization of the pure monomer PPgPN (*a*) and in the presence of 4% APB (*b*), 1% Co(PPh₃)₂Cl₂ (*c*), 0.1% Ni(EtHex)₂ (*d*), 1% Cu(PPh₃)₃OTf (*e*), and 1% Cu(EtHex)₂ (*f*).





Fig. 6. DSC curves for the cured PPgPN monomer with 1 wt.% (a) and 5 wt.% Cu(P(Ph)₃)₃OTf (b).

the propargyl group immediately after melting of the mixture and, therefore, its content in our experiment was chosen to be the lowest among other metal-containing catalysts. On the contrary, the mass fraction of APB is the highest, since a content of aromatic amines used as curing agents of 3 wt.% or higher is required for a noticeable effect on polymerization. At 1 wt.% and lower, the polymerization acceleration on these catalysts will be negligible.⁴⁴

The DSC curves show that the addition of the copper(1) and copper(11) salts contributes to a decrease in the exothermic peak preceding the polymerization of the monomer. After increasing the concentration of $Cu(P(Ph)_3)_3OTf$ to 5 wt.%, no clear peak of monomer destruction was observed on the DSC curve (Fig. 6).

The overall thermal effect of the polymerization reactions was calculated for all experiments performed. The results are presented in Table 1.

The use of catalysts of all classes reduces the overall thermal effect. The highest decrease is observed in the case when 5 wt.% $Cu(P(Ph)_3)_3OTf$ are used.

To study the thermal properties of the polymers, samples of the neat PPgPN monomer and with additives of 4 wt.% APB and 5 wt.% Cu(P(Ph)₃)₃OTf were cured. The post-curing temperature was 330 °C. The thermal $(T_{5\%})$ and thermo-oxidative (TOS_{5\%}) stabilities were determined for these samples by the TGA method as the temperature of 5 wt.% mass loss. For all samples, TOS_{5%}

Table 1. Overall thermal effect of the polymerization ofPPgPN

Catalyst	Amount (wt.%)	$Q/{ m J~g^{-1}}$
_	_	608.9
APB Cu(PPh ₃) ₃ OTf Cu(PPh ₃) ₃ OTf Ni(EtHex) ₂ Co(PPh ₃) ₂ Cl ₂ Cu(EtHex)	4 1 5 0.1 1	552.5 556.5 468.9 588.7 562.4 500.4

was ~470 °C. Figure 7 shows the thermogravimetric curves of the cured resin with 5 wt.% $Cu(P(Ph)_3)_3OTf$. The plots of the samples with APB and without a catalyst nearly coincide with these curves.

The structures of the fabricated resins were analyzed using a scanning electron microscope. The micrographs of the polymer sample chips are presented in Fig. 8. Pore associated with the destruction of the monomer during polymerization are observed on the entire surface of the resin obtained without using the curing agent (see Fig. 8, a). Smooth surfaces are observed in the micrographs of the resins cured with 4 wt.% APB and 5 wt.% Cu(P(Ph)₃)₃OTf (see Figs. 8, b and c, respectively). Small areas of the crystalline fraction are observed for the resin with the copper-containing catalyst presumably associated with traces of the catalyst or its decomposition products. Using energy dispersive X-ray spectroscopy (EDX) we found that the crystalline regions contain no copper but have a high content of phosphorus and oxygen atoms. Probably, the major component of these insertions is the product of catalyst oxidation: triphenylphosphine oxide.

Heat deflection temperatures were determined by the TMA method for the cured mixtures. It was about \sim 395 °C



Fig. 7. TGA curves for the resin based on PPgPN with 5 wt.% $Cu(P(Ph)_3)_3OTf$ (solid line represents the experiment in an inert nitrogen atmosphere, and dotted line was obtained in air).



Fig. 8. Micrographs of the cured resins based on PPgPN without a curing agent (a) and using 4 wt.% APB (b) and 5 wt.% Cu(P(Ph)₃)₃OTf(c).

for the resin from the PPgPN monomer without initiator. The resins cured using APB or Cu(P(Ph)₃)₃OTf demonstrated lower thermal softening points $(380 \,^{\circ}\text{C} \text{ and } 375 \,^{\circ}\text{C}$, respectively). This difference in softening temperatures can be explained by the fact that the introduction of catalysts reduces the heat release during polymerization. As a result, the reaction mixture heats up less and the polymerization completes at a lower temperature, which is consistent with the previous data.²⁵

Thus, we synthesized earlier undescribed compound PPgPN containing phthalonitrile and propargyl groups, which requires no curing agents for polymerization, unlike the most part of phthalonitriles. During investigation of the polymerization of this compound, it was discovered that the monomer undergoes thermal degradation with the decomposition of the propargyl ether fragment. The PPgPN-based resin post-cured at 330 °C has a heat deflection temperature of ~395 °C and $T_{5\%}$ equal to 451 °C.

The use of various metal-containing catalysts accelerates the curing process, and aromatic diamine APB exhibited the highest activity. The DSC analysis showed that the use of 5 wt.% $Cu(P(Ph)_3)_3OTf$ completely suppresses the peak of heat release corresponding to the destruction of the monomer.

The resins cured with APB or Cu(P(Ph)₃)₃OTf have a lower heat deflection temperature (380 and 375 °C, respectively) than the self-cured monomer, and $T_{5\%}$ of the resulting polymers remains at the same level as the resin without using the curing agent or catalyst. The new monomer can be used to obtain non-porous meterials with high thermal properties characteristic of the phthalonitrile resins. The prepared monomer is a promising component of phthalonitrile resins for manufacturing composite materials.

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