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Mendeleev Commun., 2020, **30**, 796–798

Mendeleev Communications

High-temperature phthalonitrile matrix containing silane fragments

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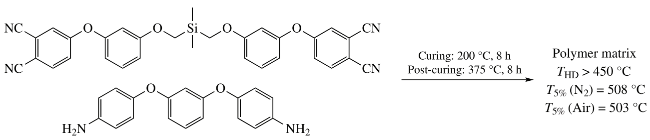
DOI: 10.1016/j.mencom.2020.11.036

A new low melting highly hydrolytically stable phthalonitrile monomer containing silane fragment was synthesized by a three-step procedure and cured to obtain a highly heat-resistant thermoset. The polymer demonstrated the glass transition temperature of 485 °C and the decomposition onset temperature over 500 °C. Stiffness of the obtained thermoset appeared to be the highest among those of the reported silicon-containing phthalonitrile thermosets.

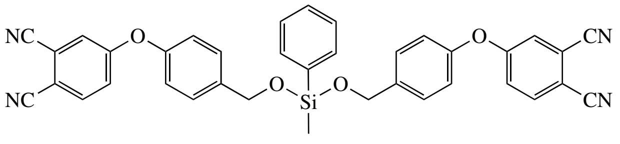


Keywords: heat-resistance, processability, phthalonitriles, thermoset, resins.

Current trends in materials science are aimed at improving the operational characteristics of materials and searching for cost-effective methods of obtaining such materials. Therefore, polymer composite materials are gradually replacing metals and alloys from their common application in aerospace industry where specific strength is particularly important. However, the use of composites becomes limited at elevated temperatures. The type of polymer matrix determines its resistance to elevated temperatures and therefore limits the operational temperature range for composites. Phthalonitrile-based thermosets are known to be the most heat-resistant polymers and have been considered as matrices for carbon fiber reinforced plastics (CFRPs) since the 1980s.[1–8] Unfortunately, for a long time the use of these resins was limited by a narrow technological window, and phthalonitrile-based CFRPs were possible to obtain by solution impregnation technique only.[9–12] Processability can be improved by the synthesis of oligomers[13,14] and the introduction of flexible segments in the structure of monomer, reducing the melting points of resins. Previously, the use of silicon-containing segments was implemented to improve the processability of phthalonitrile polymers.[12,15,16] Nonetheless, other disadvantages limit the use of these resins. A polymer, which has been prepared from an oligomer with flexible silicon-containing fragments, showed the lower Young's modulus[15] than those of phthalonitrile polymers. High melting point and high viscosity of melt for another oligomer[12] prevent from the use of cost-effective injection methods for composite moulding. The introduction of a flexible silazane fragment into the structure of monomer[16] improved the processability of resin. Yet, the difficult synthesis of such monomers complicates their use on industrial scale.

In our previous works, we have already obtained a series of low-melting siloxane-linked phthalonitrile monomers.[17–21] The use of monomer **1**[16,18,21] made it possible for the first time to obtain a carbon fiber reinforced polymer composite with a phthalonitrile matrix *via* cost-effective resin transfer molding.[22] After curing with 1,3-bis(4-aminophenoxy)benzene (APB), the resulting polymer possesses moderate mechanical properties and the higher thermal stability than common phthalonitrile resins. Compared with polymers obtained from *para*-substituted monomers, the *meta*-substituted ones exhibited the lower glass transition temperature (T_g), most probably because of a slightly less molecular symmetry.[21] Monomer **2**[20] with the lowest T_g is promising in the preparation of prepregs for room temperature layup and in cost-effective injection techniques for composite fabrication. However, the monomer with siloxane fragment is sensitive to hydrolysis and unsuitable for long-term storage. Therefore, the development of new low-melting and long-term stable monomers is of great interest.

In this work, silane fragment-containing monomer **3** (Scheme 1) was synthesized (see Online Supplementary Materials) to explore the scope of phthalonitriles with silicon-containing linkers. Unlike to monomers with siloxane linkers, monomer **3** is stable against hydrolysis and supposedly provides high Young's modulus of the derived thermoset which is typical for phthalonitriles. Initially, the synthesis of monomer **3** was attempted in *N*,*N*-dimethylacetamide (DMAA) by nucleophilic substitution of chlorine in bis(chloromethyl)dimethylsilane, resulting in only 30% conversion by NMR after 5 days.



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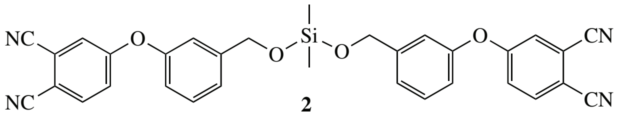

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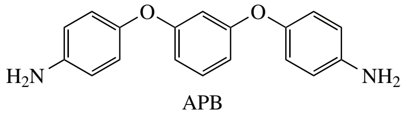
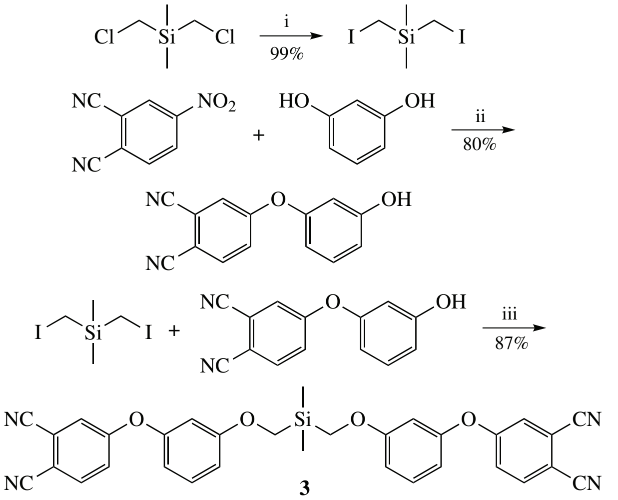


APB



Scheme 1 *Reagents and conditions*: i, KI, acetone, reflux; ii, K_2CO_3, DMAA; iii, K_2CO_3, DMAA, 80 °C.

To increase the reactivity, bis(chloromethyl)dimethylsilane was successfully converted into bis(iodomethyl)dimethylsilane by Finkelstein reaction in near quantitative yield (see Scheme 1). Despite the high electron donation effect of dimethylsilanediyl group, iodide ion is the much better leaving group than chloride ion, which should facilitate nucleophilic substitution. Thus, monomer **3** was obtained after 24 h in DMAA in 87% yield.

The structure and purity of monomer **3** were confirmed by ^{1}H, ^{13}C and ^{29}Si NMR (Figures S3–S5, see Online Supplementary Materials) and CHN elemental analysis. The resulting monomer, like monomer **2**, is an amorphous compound by DSC (Figure S6, see Online Supplementary Materials). $T_g = 26.5$ °C of monomer **3** was higher than that of its isomer **2** ($T_g = -1$ °C)[21] but still remains lower than T_g of the most known phthalonitriles, including those containing flexible silicon-based segments, such as oligomers.[15,16] The difference between T_g of the isomers may be caused by lower flexibility of the silane linker between aromatic fragments compared to the siloxane linker. Despite this, the obtained monomer **3** is low-melting and in combination with APB has a wide processing window (about 100 °C), which is also confirmed by rheological tests (Figure 1).

The viscosity (η)–temperature profile of the resin consisting of the mixture of monomer **3** with 4 mol% of APB is presented in Figure 1. The viscosity of the resin starts to increase at 210 °C with a sharp growth above 250 °C. Thus, the temperature of 210 °C can be considered as the upper boundary of processing window, which is determined by the difference between gelation onset temperature and melting temperature of resin.[23] In the case of amorphous resins, the temperature at which the melt viscosity is less than 500 mPa s determines the lower boundary. According to this rule, the processing temperature of this composition is in the range from 111 to 210 °C. The T_g and viscosity values of monomer **3** and previously reported silicon-containing phthalonitriles **1**, **2**, **4**–**7** are given in Table 1.

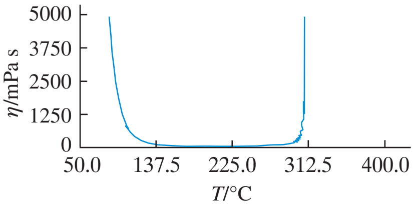


Figure 1 Temperature dependence of viscosity η for the resin consisting of monomer **3** and APB.

To evaluate thermal and mechanical properties of the polymer prepared from monomer **3**, a mixture of monomer **3** and 4 mol% APB was cured under the same conditions as for monomer **1** with the maximum temperature of 375 °C (see Online Supplementary Materials).

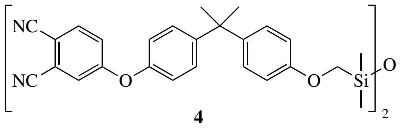
According to dynamic mechanical analysis (DMA) of the obtained polymer, there is no clear transition on the storage modulus (E) curve. However, T_g can be determined from the maximum on the curve of loss factor (tanδ) (Figure 2). The initial E at 100 °C is 3.6 GPa which is the highest among all the previously reported values for silicon-containing phthalonitrile resins (Table 2). It should be noted that even after devitrification, E exceeds 1 GPa.

Thermogravimetric analysis (TGA) of the obtained polymer was carried out (Figure 3) to estimate the stability of the thermoset at elevated temperatures. The temperatures of 5% mass loss in an inert atmosphere [$T_{5\%}$ (N_2)] and in an oxidizing one [$T_{5\%}$ (Air)] turned out to be approximately the same and amounted to 508 and 503 °C, respectively. Moreover, the obtained values are lower than those for monomer **2** [$T_{5\%}$ (N_2) = 545 °C, $T_{5\%}$ (Air) = 527 °C], which may be due to

Table 1 Properties of silicon-containing phthalonitrile monomers.

Monomer	T_g/°C	Viscosity at 150 °C/mPa s	Ref.
1	12	600	21
2	−1	287	21
3	27	72	Present work
4	33	120	15
5	59[a]	–	16
6	4	100	18
7	147	$>3\times10^6$	12

[a] Melting point.



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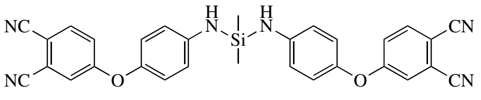

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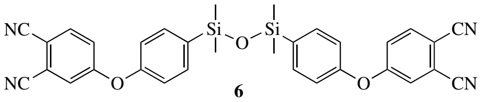

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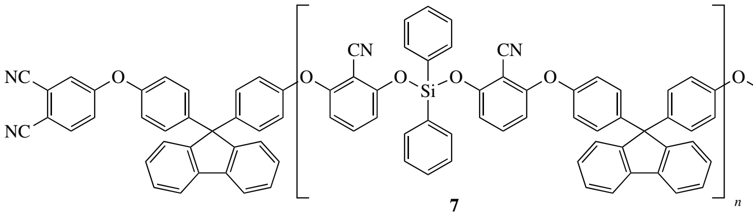

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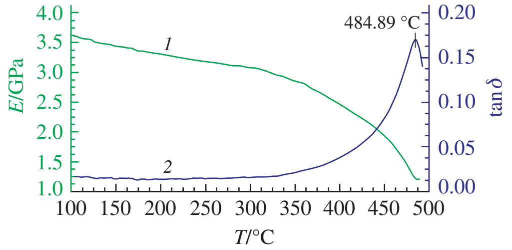

Figure 2 Temperature dependence of (*1*) storage modulus *E* and (*2*) loss factor tan*δ* for the polymer prepared from monomer **3** as measured by DMA.

the lower thermal resistance of the silane fragments. It is also worth noting that when monomer **3** is combusted in an oxidizing atmosphere, silicon oxide is formed, which determines the ash yield of 9.4%. The ash yield values for the polymers prepared from monomers **2** and **3** differ, which can be explained by the different shape of the samples, as well as the possible inclusion of unburned particles in the silicon oxide shell.

In Table 2, the experimental results for the polymer obtained from monomer **3** are compared with the characteristics of the polymer obtained from isomeric monomer **2** and the other silicon-containing phthalonitrile polymers.

In conclusion, the polymer, obtained in this work from monomer **3**, showed the outstanding value of T_g while having the high decomposition temperatures in both inert and oxidizing atmospheres. According to DMA, the initial *E* value at 100 °C is the highest among all the previously reported ones for silicon-containing phthalonitrile resins. In its turn, monomer **3** has the low value of T_g and, accordingly, the wide processing window, which allow one to use it in cost-effective methods of CFRP moulding. The presence of silane fragments, as opposed to siloxane, excludes the possibility of hydrolysis. Therefore, the polymer produced from monomer **3** is suitable for operation for a long time in humid environment.

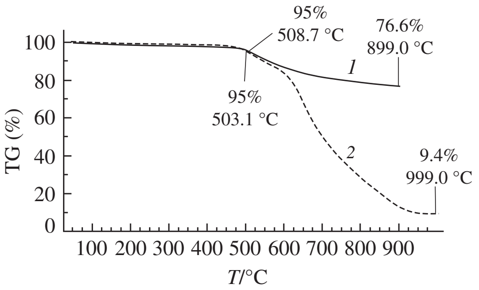

Figure 3 TGA curves for the polymer obtained from monomer **3** in the atmosphere of (*1*) N_2 and (*2*) air.

Table 2 Thermal and mechanical properties of cured phthalonitrile monomers.

Monomer	T_g/°C	*E* (25 °C) /GPa	$T_{5\%}$ (N_2) /°C	$T_{5\%}$ (Air) /°C	Y_c^b (900 °C) (%)	Y_a^c (1000 °C) (%)	Ref.
1	420^a	2.6	537	520	79	12	17, 19, 21
2	413^a	–	545	527	81	13	21
3	485	3.6	508	503	77	9.4	Present work
4	210	1.2	420	420	58	12	15
5	>450	3.1	535	558	80	13	16
6	471	–	503	495	76	22	18

^{a}Heat deflection temperature (T_{HD}) obtained by TMA (3-point bending). ^{b}Y_c is char yield. ^{c}Y_a is ash yield.

The introduction of flexible silicon-containing fragments into the structure of monomer makes it possible to create a wide range of substances with low melting/glass transition temperatures and to solve the problem of the narrow processing window of phthalonitrile resins. However, such chemical modification is usually accompanied by a decrease in performance. The use of monomer **3** avoids losses in mechanical properties and resistance to external influences, such as moisture or heat.

This study was carried out within the framework of the State Task ‘New technologies and multifunctional materials for safety, reliability and energy efficiency’ (contract no. AAAA-A16-116053110012-5).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.11.036.

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Received: 21st May 2020; Com. 20/6222