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Synthesis and polymerization of disiloxane Si–O–Si-linked phthalonitrile monomer

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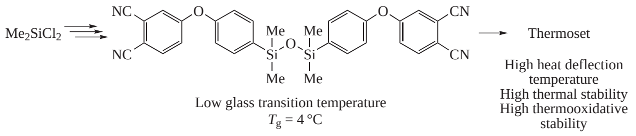
A novel low melting highly hydrolytically stable phthalonitrile monomer containing Ar–Si–O–Si–Ar bonds with T_g = 4 °C exhibits good rheological properties. Its cured resin possesses high heat deflection temperature (T_{hd} = 471 °C) and demonstrates high thermal and thermooxidative stabilities ($T_{5\%}$ = 503 °C, $\mathrm{TOS}_{5\%}$ = 495 °C, Y_c = 76%) that are typical of phthalonitrile matrices.

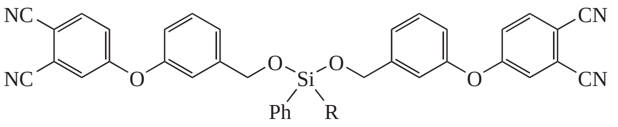


Phthalonitrile resins are a unique class of high-temperature (up to 400 °C) materials which find applications in aerospace, marine and microelectronic industry and can be used as matrices for high-temperature composite tooling for carbon fiber-reinforced plastics production.[1–7] In addition, cure mechanism of formation of these systems ensures that no volatiles evolve during the polymerization resulting in a highly cross-linked, void-free network polymers. Due to this, they should have good mechanical properties, outstanding thermo-oxidative stability at elevated temperatures, high fire resistance, and low water absorption.[8–10] Composite applications require resin systems which are liquid or have a rather low melting point, show a large processing window which is defined as the interval between the melting point and a temperature of polymerization, and possess low viscosity for manufacturing composite components by cost effective methods such as resin transfer molding (RTM) and vacuum infusion molding (VIM).

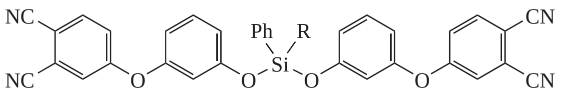
The crucial factor for the development of polymers with high oxidative stability is the incorporation of thermostable structural units such as siloxane linkage between the terminal phthalonitrile units.[6,11,12] Hydrolytically unstable polysiloxanes derived from the corresponding diphenol and dichlorosilane containing Si–O–C bonds have been described.[13,14] Noshay[15] claims that some of the polymers and block copolymers containing Si–O–C-linkers are hydrolytically stable and points out that care should be exercised when extrapolating the characteristic properties of a given chemical bond from polymers of one architectural type to those of a different type.[15] For example, polynorbornenes with pendant Si–O–C groups are steady, while the monomer is moisture-sensitive.[16] Low-melting siloxane-based phthalonitrile monomers containing O–Si–O-bridge were synthesized by our research group recently.[17] The phthalonitriles possessed the lowest glass transition temperature of 12 °C. Both the monomers and the polymers synthesized exhibit high hydrolytic stability.

Herein, we describe synthesis of low-melting hydrolytically stable Si-bridged phthalonitrile monomer and estimate its properties as high temperature thermosetting matrix for fiber reinforced plastics.

We attempted to extrapolate the data on the preparation and curing of the low-melting siloxane-bridged phthalonitriles based on benzyl alcohol derivatives **1**, **2** and synthesized phenol-based siloxane-bridged phthalonitriles **3**, **4** to estimate whether the methylene group or siloxane linker reduced T_g of the monomers reported.[17]



1 R = Ph T_g = 27 °C
2 R = Me T_g = 12 °C

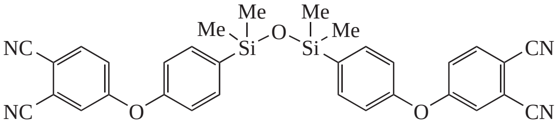
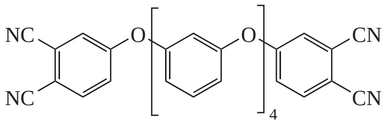
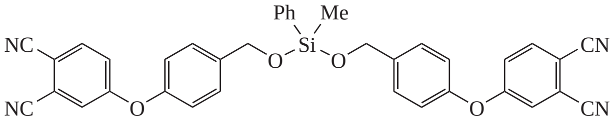
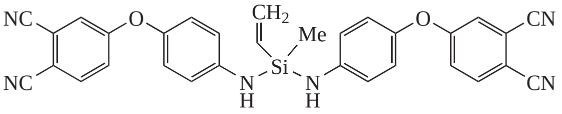
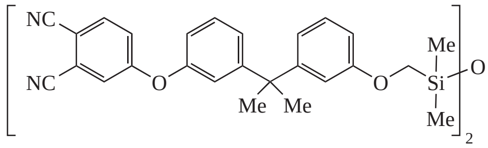


3 R = Ph T_g = 29 °C
4 R = Me T_g = 28 °C

It was found that the obtained phenolic monomers containing disiloxane Si–O–Si linkages indeed possessed T_g slightly higher than those of benzyl alcohol derivatives, however these monomers turned out to be hydrolytically unstable in the air and decomposed into the initial diphenol and a mixture of unidentifiable substances if kept outside of glovebox for several days in solid state or for several hours in a solution.[18] By this reason it was impossible to cure these monomers without foaming indicating decomposition of the monomers during polymerization.

We assumed that the bond Si–O–Si should be as flexible as O–Si–O bond, and being used as a linker should provide flexibility to the monomer structure. At the same time, Si–C and Si–O bonds are resistant to moisture and other chemical treatments so it was expected to obtain low-melting and stable phthalonitrile monomer.

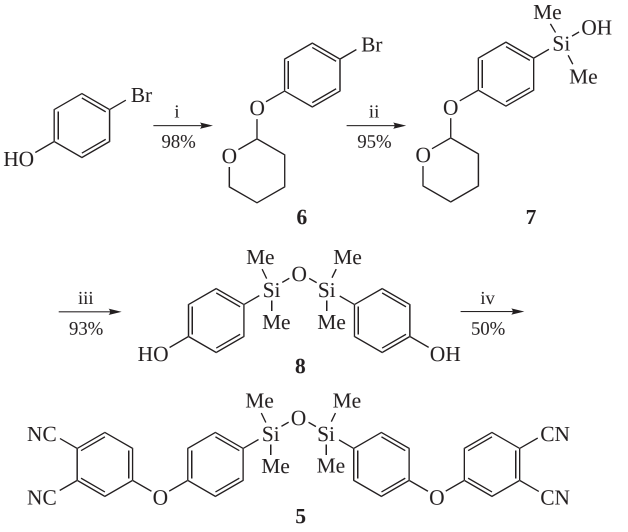
Table 1 Thermal characteristics of the cured monomers.

Monomer		Polymer (cured monomer)					
Structure	T_g/°C	Atmosphere	T_{hd}/°C	$T_{5\%}$/°C	$T_{10\%}$/°C	Y_c (%)	Reference
	4	Inert Air	471	503 495	538 579	76 22	This article
	42	Inert Air	441	493 486	– –	62 (1000 °C) –	12
	12	Inert Air	428	537 520	– –	79 (900 °C) 12 (1000 °C)	17
	40	Inert Air	428	541 543	627 597	82.4 (1000 °C) 11.3 (1000 °C)	23
	35	Inert Air	210[a]	420[a] 420[a]	– –	58 –	24

[a] Cured at a maximum temperature of 300 °C (8 h) with 10% bis[4-(3-aminophenoxy)phenyl]sulfone.

To check the validity of the judgments, we synthesized the desired monomer **5** and investigated the effect of disiloxane linker on thermal properties of this monomer and cured polymer matrix.

Several methods of disiloxane group formation are known. Disiloxanes can be successfully prepared from the corresponding trisubstituted silane and formamide using carbonyl complexes of transition metal as a catalyst.[19] Alkoxysilanes react with methylallylsilanes in the presence of scandium(III) trifluoromethanesulfonate to yield disiloxanes and isobutene.[20] Also synthesis of Si–O–Si linkage is possible by acidic catalytic dimerization of silanols.[21] The latter method was considered as the most convenient one due to availability of starting material. It made possible to synthesize product **5** in four steps without using transition metal complexes (Scheme 1).† The THP-protected 4-bromophenol[6] was used as a starting material.[22] It was converted into the Grignard reagent which was then coupled with Me_2SiCl_2 to give silanol **7** after aqueous treatment. Self-condensation of silanol **7** occurred with simultaneous deprotection and yielded disiloxane **8** with free phenolic groups. The final step was nucleophilic substitution of nitro group in 4-nitrophthalonitrile with alkali salt of compound **8** in DMA to yield the desired product.



Scheme 1 *Reagents and conditions*: i, dihydropyran, HCl; ii, Mg, THF, then Me_2SiCl_2–Et_3N, then H_2O; iii, 5% HCl, EtOH; iv, 4-nitrophthalonitrile, K_2CO_3, DMA, 70 °C.

The glass transition temperature T_g = 4 °C of the monomer prepared, determined by differential scanning calorimetry (DSC) (Figure 1), is lower than that for any reported phthalonitrile monomers (Table 1). Obviously, the Si–O bond is more mobile with a less sterically hindering substituent at the Si atom.

The rheometric analysis of the monomer during its polymerization was performed in the temperature range of 80–300 °C. The results showed that the viscosity of the monomer gradually decreased with temperature up until wide plateau from 120 °C to 220 °C where the viscosity was not above 100 mPa s. A slow gradual rising of the complex viscosity begins from 220 °C. It is known[25] that phthalonitrile resins in the absence of curing agent polymerize slowly at relatively low temperature.

Rheometric study of curing process of monomer **5** in the presence of 4 wt% 1,3-bis(4-aminophenoxy)benzene (APB) was carried out isothermally at 120 °C, which revealed that the pot life of the resin was up to 48 h and viscosity was in the range of 100–300 mPa s.

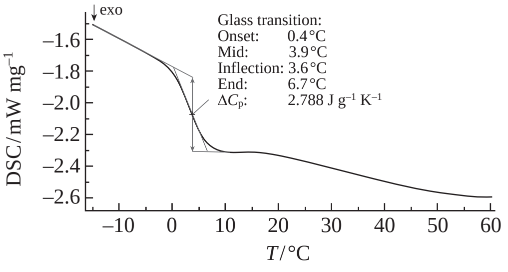


Figure 1 The DSC thermogram of the monomer.

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† For procedures and characteristics of compounds **5**–**8**, see Online Supplementary Materials.

After two days the reaction mixture was heated up to 200 °C and then isothermal study was held at a given temperature. After 120 min, the viscosity of the reaction mixture started to rise and after 140 min, we believe, polymer was gelled so that further viscosity measurement was impossible. Thus, there is 2 h period for degassing sample at reduced pressure and filling tool before the sample starts cure.

The monomer containing Si–O–Si-bridge demonstrated excellent rheological properties, namely, a wide processing window with low viscosities in the temperature range of 80–220 °C and had an increased lifetime at processing temperatures. This makes it perfectly suitable for composite manufacturing by the RTM and VIM methods.

Phthalonitrile curing occurs in the presence of amines or phenols as initiators to yield 3D-network consisting of isoindoline, triazine and phthalocyanine structures.[26,27] Monomer curing was performed by heating at 200 °C for 24 h followed by slow heating (2 K h^{-1}) up to 375 °C with 8 h hold at final temperature.[‡] Such slow program was applied to keep the external temperature lower than current T_g of the sample, which is necessary to lower shrinkage and solid samples formation. Due to the presence of highly flexible Si–O–Si-bridges in the polymer matrix one could expect lowering of heat deflection temperature of the cured samples. However, the resulting cured resin demonstrated excellent value of T_{hd} = = 471 °C featured to phthalonitrile resins, which is higher than those for reported phthalonitriles (Table 1). This can be explained by different measurement method, namely TMA in penetration mode, which usually gives uprated values.

Thermal stability of the obtained polymer, evaluated by TGA in air and argon atmosphere, are at the same high level as those of reported phthalonitriles. According to TGA curves (Figure 2) and the data in Table 1, in an inert atmosphere the polymer possessed high thermal stability (curve *1*) and did not loose weight up to 470 °C. Apparently, at this temperature the thermal degradation of the polymer occurred. At 900 °C, the char yield was 76% which was unexpectedly somewhat less than for described matrices based on reported monomers[17,24] with lower silicon content. In agreement with a 30–40 °C difference in degradation temperatures, this could mean that $Si(Me_2)–O–Si(Me_2)$ fragment probably draw some steric hindrance while the network formation resulting in insufficiently less durable 3D-structure. In the air (curve *2*), even at low temperatures (slightly higher than 200 °C) a slow weight loss was observed due to the gradual oxidative degradation of the weakest places in the matrix that were supposedly methyl substituents on the silicon atoms. Weight loss process was not very conspicuous in accordance with TGA curve, as during the oxidation process two methyl groups with the weight about 30 units are replaced by oxygen atom with the mass of 16 units. As a result, the process continues until 640 °C, which does not correlate with the TGA data obtained in inert atmosphere where abrupt degradation proceeds at 470 °C. The phenomenon can be related to the oxygen saturation of the polymer matrix. The saturation stabilizes the matrix further prior to starting the degradation process of Si–C and sterically hindered Ph–O–Ph bonds. At the temperatures > 640 °C, fast oxidation of the polymer occurred. A sharp weight loss of up to 21.8% at 1000 °C is in good agreement with theoretical amount of SiO_2 (21.1%) which should be formed after complete oxidation of the matrix.

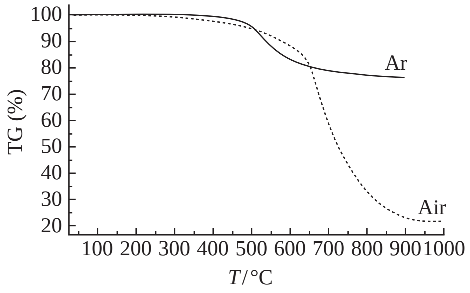

Figure 2 TGA thermogram of the cured resin **5** in Ar and air.

In conclusion, a new low-melting highly hydrolytically stable silicon-containing phthalonitrile monomer was prepared. The pure monomer demonstrates excellent rheological properties due to very low for phthalonitriles T_g = 4 °C and could be used for FRP production by RTM or VIM techniques. The study of the curing process in the presence of 4 wt% of APB by rheometric analysis showed that the considered thermosetting resin possessed excessively long pot-life at 120 °C and at 200 °C gel time was ~2 h. These facts are very promising for high temperature polymer matrix for composite applications. The flexible disiloxane linkage enhances processability without compromising thermal and oxidative stability. The cured resin possesses high heat deflection temperature T_{hd} of 471°C. In argon atmosphere 5% weight loss of the cured polymer occurs at 503 °C, and with 76% residual mass at 900 °C.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.11.023.

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[‡] For more detail, see Online Supplementary Materials.