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Fluorinated phthalonitrile resins with improved thermal oxidative stability

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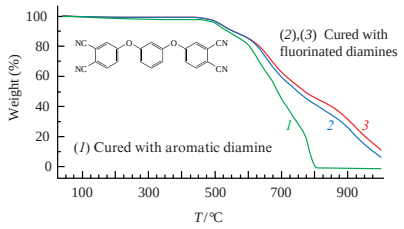
Fluorinated phthalonitrile monomers exhibit low activity in polymerization initiated by a wide range of curing agents of various nature. On the contrary, the use of fluorinated diamines as hardeners for common non-fluorinated phthalonitrile monomer allows one to obtain thermosets with high glass transition temperature (T_g > 426 °C) and improved thermal oxidation stability ($T_{5\%}$ = 520 °C in air).



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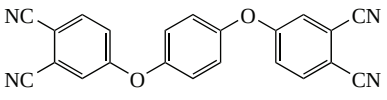
Phthalonitrile thermosets are known as the most heat resistant matrices for fiber reinforced plastics and composites. Curing of phthalonitriles in the presence of aromatic diamines,[1–4] phenols,[5–7] metals salts,[8,9] or self-promoted[10–13] results in the formation of highly heat-resistant thermosets. Glass transition temperatures over 400 °C and degradation ($T_{5\%}$) over 500 °C allow one to consider phthalonitrile matrix composites as substitutes for aluminum and titanium alloys in aerospace and automotive industries.[1,14–18] Parts made of carbon fiber reinforced plastics based on phthalonitrile matrices can be used at elevated temperatures and provide up to 90% retention of mechanical properties at 300 °C.[19–22] Despite the higher T_g and $T_{5\%}$ values the use of such composites at above 350 °C is still limited by oxidation of the matrix. A development of phosphorus-containing phthalonitrile monomers and resin formulations based on them[16,18,23,24] allows one to enhance thermal-oxidative properties, however the synthesis of such monomers is fraught with difficulties. An alternative approach for designing new resins stable against thermal oxidation can be the use of fluorinated phthalonitrile monomers or curing agents which would together form a 3D-network of thermosets. The use of fluorinated polymers as thermally and oxidation stable materials is well known,[25–31] while fluorinated phthalonitriles are rarely documented[9,32,33] when in all cases an increase in thermal-oxidation stability of the fluorinated thermosets was observed.

To perform the study, a series of structurally similar phthalonitrile monomers were synthesized. The known phthalonitrile monomer **1** was obtained according to previously published procedure.[34] Fluorinated phthalonitrile monomers **2** and **3** were prepared by nucleophilic substitution of fluorine atoms in tetrafluorophthalonitirile using hydroquinone or tetrafluorohydroquinone, respectively, in the presence of KF as a base (for details, see Online Supplementary Materials). Both monomers **2** and **3** were synthesized in lower yields than it was reported for **1**. During the reaction, byproducts of multiple replacement of fluorine by hydroxyl ions were also formed. The more fluorine atoms in the aromatic rings were involved in the reaction, the lower yield of the target product was observed. Compound **2** was obtained in 61% yield while the yield of product **3** was 21%.

The preliminary curing experiments have shown inactivity of fluorinated monomers in polymerization initiated by 1,3-bis(4-aminophenoxy)benzene (diamine APB). DSC thermograms did not contain exothermic peak referred to polymerization, whilst for monomer **1** mixed with APB curing starts immediately after monomer melts (see Online Supplementary Materials, Figure S1). No polymer formation was observed even after heating of the mixtures containing monomer **2** and the curing agent at 240 °C for 24 h. Rheology study of the mixture also did not show viscosity growth below 300 °C (Figure S2, A). At the same time, just a slight increase in viscosity up to 140 mPa·s was observed during the isothermal viscosity study at 250 °C after 6 h (Figure S2, B).



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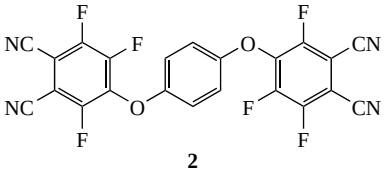

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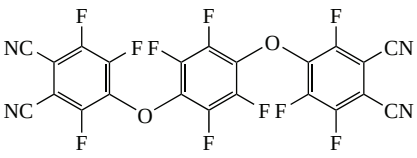

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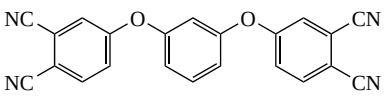

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Table 1 Thermal properties of the thermosets obtained from monomer **2**.

Curing agent	Curing agent content (mol%)	$T_{5\%}$ (mode 1)[a]/°C		$T_{5\%}$ (mode 2)[b]/°C	
		N_2	Air	N_2	Air
$SnCl_2$	10	324	316	517	504
$SnCl_2$	25	337	375	498	500
$SnCl_2$	50	339	373	428	439
TsOH	10	536	509	515	512

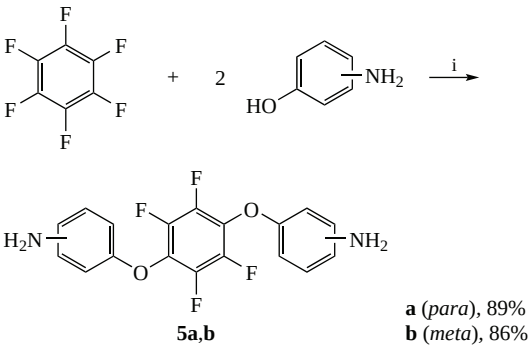
[a] 200 °C for 24 h. [b] 200 °C for 8 h, 330 °C for 3 h, 375 °C for 6 h.

Next, monomer **2** was subjected to polymerization in the presence of inorganic salts such as $ZnCl_2$, CuI, copper(II) 2-ethylhexanoate and $SnCl_2$ as the curing agents. In contrast to APB, addition of these salts resulted in an appearance of exothermal peak indicating curing reaction in all the cases except for CuI. Meantime, heat release values of these processes were 2–6 times lower than those for amine-cured phthalonitriles (see Online Supplementary Materials, Table S1, Figure S3).[35] Based on heat release value, $ZnCl_2$ was chosen as the most effective curing agent, however curing by stepwise program (starting from 180 °C with final treatment at 375 °C) did not result in thermoset formation and mass lost up to 80% was detected for the samples.

In alternative experiments, $SnCl_2$, *p*-toluenesulfonic, methanesulfonic, phosphoric, sulfuric, terephthalic, isophthalic, phenylphosphonic, 3-hydroxybenzoic acids and bisphenol A were tested as curing agents. After heating at 200 °C for 24 h blends with $SnCl_2$, TsOH, MsOH and H_2SO_4 revealed thermosets (Table 1). Therefore, subsequent curing at 375 °C was carried out for these polymers. In the obtained thermosets, a weight loss of up to 12% was observed. Use of TsOH made it possible to obtain a polymer with the smallest weight loss of 6.5%. In the case of terephthalic, isophthalic, phenylphosphonic and 3-hydroxybenzoic acids, porous elastic polymers were produced, and after post-curing up to 35% of a mass loss was detected for the samples. Phosphoric acid and bisphenol A demonstrated lower activity as curing agents and the corresponding samples remained liquid.

p-Toluenesulfonic acid (10 mol%) as the most active agent of the considered was used to cure monomer **3**. It was found that a gelation time for monomer **3** was three hours longer than that for monomer **2** under the same conditions, and the resulting thermoset lost 15 wt% during curing, was porous and brittle. Thus, it may be concluded that monomers **2** and **3** containing perfluorinated phthalonitrile rings cannot be polymerized under the conditions common for non-fluorinated ones.

The second approach comprised the use of fluorine-containing amines **5a**,**b** as the curing agents. Diamines **5a**,**b** were synthesized from hexafluorobenzene and *p*- or *m*-aminophenols, respectively (Scheme 1). The effect of agents **5a**,**b** on the thermo-oxidative stability was studied using polymers obtained from resorcinol-based phthalonitrile **4**. A mixture of compound **4** and curing



5a,**b**

a (*para*), 89%
b (*meta*), 86%

Scheme 1 *Reagents and conditions*: i, K_2CO_3, $MeC(O)NMe_2$, 110 °C.

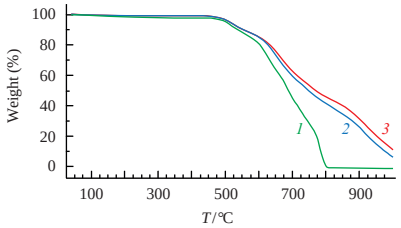


Figure 1 TGA curves for polymers obtained from phthalonitrile **4** with different curing agents: (*1*) APB, (*2*) diamine **5b**, and (*3*) diamine **5a**.

agent (10 mol%) was cured at 180 °C for 8 h, at 330 °C for 3 h and at 375 °C for 6 h. The obtained polymers had good thermo-oxidative stability and high glass transition temperatures, namely, in case of **5a** polymerized phthalonitrile **4** had T_g of 438 °C and $T_{5\%}^{air}$ of 520 °C, while for **5b** these parameters were 426 and 519 °C, respectively. Apparently, the stability of the polymer network determines the decomposition temperature which should remain unchanged regardless of the curing agent used. In our case, fluorine-containing amines decrease the oxidation rate of the sample, which is confirmed by the data of thermogravimetric analysis (Figure 1). Therefore, amines **5a**,**b** can be used to improve the thermal oxidative stability of the phthalonitrile polymer matrix.

Thus, by the example of polymerization of monomers **2** and **3**, we have shown that fluorinated phthalonitrile rings demonstrate low activity in polymerization process when the reaction is initiated by various types of known curing agents. The formation of a stable polymer network from fluorine-containing phthalonitrile monomers occurs with difficulty. In the meantime, the use of fluorinated aromatic diamines **5a**,**b** as curing agents led to an increase in the thermo-oxidative stability of the obtained polymer. An assumption that the nature of the aromatic amine makes a significant contribution to the formation of an oxidation resistant polymer network has been confirmed. As a result, the search for new curing agents is a promising approach to improve thermal oxidative stability of phthalonitrile polymer matrices *via* chemical modification of the resin components.

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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.2020.09.040.

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