



Short communication

Low-melting siloxane-bridged phthalonitriles for heat-resistant matrices



Alexander V. Babkin^a, Elvek B. Zodbinov^b, Boris A. Bulgakov^{a,b,*}, Alexey V. Kepman^a, Viktor V. Avdeev^b

^a Institute of new carbon materials and technology (INCMAT), 119991, Leninskie gory st, 1-11, Moscow, Russia

^b M. V. Lomonosov Moscow State University, Department of Chemistry, Division of Chemical Technology and New Materials, 119991, Leninskie gory st, 1-11, Moscow, Russia

ARTICLE INFO

Article history:

Received 19 November 2014

Received in revised form 6 March 2015

Accepted 7 March 2015

Available online 13 March 2015

Keywords:

Phthalonitrile

Heat-resistance

Low-melting thermosets

Processability

Thermal properties

ABSTRACT

New low-melting phthalonitrile monomers were obtained by introduction of different flexible siloxane bridges such as $-O-SiPh_2-O-$ and $-O-SiPhMe-O-$. In spite of the presence of the siloxane groups the considered monomers were separated as single compounds by column chromatography with good yields (up to 90%). The synthesized monomers possessed $T_g = 12-27^\circ C$ which were by a decade lower than it had been reported for phthalonitrile monomers before and even lower than the lowest $T_g = 41^\circ C$ detected for phthalonitrilic oligomers. The cured monomers demonstrated high thermal and thermooxidative stabilities at the same level as described earlier for that type of polymer matrices. Thus a significant decrease of the T_g of the suggested monomers dramatically expands the processing window for the whole class of phthalonitrile matrices for reinforced plastics.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The quick development in aerospace field in the past several decades required new light and durable materials such as reinforced plastics. Since 1950s the a considerable amount of researches dedicated to development of polymer matrices possessing high thermal stability, convenient processability and good mechanical properties had been conducted. According to these requirements several types of resins had been developed, including polyimides [1–3] and modified phenolic resins [4,5], phthalonitriles [6–10] and others.

The industrial use of phthalonitriles began with paints manufacturing, until in 1934 Dent and Linstead discovered that phthalocyanine sublimes without decomposition at

560 °C [11]. This finding had stimulated researchers to synthesize thermostable polymers based on phthalocyanine. In 1958 Marvel and Martin first attempted to introduce a phthalocyanine moiety in the polymer structure however the resulting polymer had a low molecular weight [12]. The rapid development of the phthalonitrile-based matrices began in 1980s and since they have been gradually established as one of the most prospective resins for the composite materials due to high glass transition temperature, outstanding thermal and thermo-oxidative stability, excellent mechanical properties, good moisture resistance and superior fire resistance [6–10]. Nevertheless phthalonitriles had disadvantages such as high softening points (180–250 °C) which raised and narrowed the processing window due to the start of polymerization shortly after melting (around 230 °C) which caused the viscosity growth. The development of oligomeric phthalonitrile [13–16] matrices resulted in a significant decrease of the glass transition temperatures to 41–80 °C but nevertheless

* Corresponding author at: M. V. Lomonosov Moscow State University, Department of Chemistry, Division of Chemical Technology and New Materials, 119991, Leninskie gory st, 1-11, Moscow, Russia.

E-mail address: bbulgakov@gmail.com (B.A. Bulgakov).

processing of such materials at room temperature without preheating was limited.

The present article discusses the synthesis of new silicon-containing phthalonitrile monomers, their polymerization and the properties of the resulting polymers in comparison with known materials based on phthalonitrile. The new approach to decrease melting points of phthalonitrile monomers applied in the present investigation consists of the introduction of flexible siloxane ($-\text{O}-\text{SiR}_2-\text{O}-$) bridges which presumably increase the chain mobility in the target molecule in comparison to existing phthalonitriles. Siloxane groups usually have great thermal stability but have not found wide applications in the new polymers manufacturing because of their low hydrolytic resistance [17]. On the other hand there is data confirming a good hydrolytic stability of Si–O–C bond in a polymer due to shielding of these groups by the polymer chain and the hydrophobic nature of the $-\text{SiR}_2-\text{O}-\text{C}$ group [18,19]. For these reasons the approach to introduce siloxane groups to phthalonitrile monomers to decrease their melting points seemed to be reasonable and has been successfully implemented in this work.

2. Experimental

2.1. Materials

All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. All the solvents were purchased from Alfa Aesar and purified according to the standard procedures [20] and stored under Ar. Dimethylformamide (DMF) was distilled over CaH_2 . Tetrahydrofuran (THF) was distilled twice over potassium hydroxide and then over sodium metal in the presence of benzophenone. Dichloromethane (DCM) was distilled over P_4O_{10} . Triethylamine was distilled over CaH_2 and stored under Ar. Methanol, diethyl ether and hydrochloric acid, 3-hydroxybenzaldehyde, 4-nitrophthalonitrile, 1,3-bis(4-aminophenoxy)benzene, sodium borohydride and potassium carbonate were obtained from Aldrich and used as received. Diphenyldichlorosilane and phenylmethylchlorosilane were purchased from Aldrich and were purified by distillation over quinoline and stored under inert atmosphere in the glove box. 1,3-bis(3,4-dicyanophenoxy)benzene (**5**) was synthesized according to the know procedure [21] with quantitative yield (98%).

2.2. Analytical methods

NMR spectra were run on Bruker Avance 600 at 600 MHz for ^1H and 125 MHz for ^{13}C with $\text{DMSO}-d_6$ as solvent and at 120 MHz for ^{29}Si NMR in CDCl_3 . Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix, at a heating rate of $10^\circ\text{C}/\text{min}$ and an Ar purge rate of 50 mL/min and was applied for T_g of the uncured resins determination and curing study. HPLC–UV–ESI–MS was performed with Agilent Technologies 1100 MSD Trap VL equipped with UV and Mass-detector (ESI, mass range 50–2000 in positive ions). The

chromatographic separation was performed on a Zorbax Eclipse XDB-C18 column ($3.5\ \mu\text{m}$, $4.6\ \text{mm} \times 75\ \text{mm}$) by gradient elution with methanol and 0.02 M ammonium acetate solution (0 min 20% methanol V/V, 10–20 min 100% methanol V/V) at 25°C with a flow rate of 0.6 mL/min and UV detection at 254 nm. Thermal stability was evaluated by TGA on Netzsch TG 209 P3 Tarsus, at a heating rate of $10^\circ\text{C}/\text{min}$ in range 40–980 $^\circ\text{C}$ and an Ar or air purge rate of 50 mL/min. Heat deflection temperature was measured by 3 the point bending method according to ASTM-E2092-03 on Netzsch TMA 402 with 1.82 MPa loading.

2.3. Synthesis of 4-(4-formylphenoxy)benzene-1,2-dicarbonitrile (**1**)

4-hydroxybenzaldehyde (5 g, 0.041 mol) was dissolved in 30 ml of dry DMF in a 250 ml three-neck round bottom flask equipped with a Dimroth condenser and a dropping funnel. Then potassium carbonate (5.65 g, 0.041 mol) was stirred into the solution, the reaction mixture was chilled to 0°C and 4-nitrophthalonitrile was added dropwise. The mixture was left at room temperature stirring overnight and then held at 70°C for 6 h. After that the flask content was poured into 500 ml of iced water and brown precipitate of the desired product was formed and separated by filtration. The product was then dissolved in DCM (200 ml) and washed with brine (50 ml) three times. After the solvent had been removed by a rotary evaporator 10 g of brownish powder were obtained. Yield 98%. ^1H NMR (DMSO , δ , ppm): 10.03 (s, 1H, CHO), 8.01–8.00 (m, 2H, ArH), 7.81–7.80 (d, 1H, ArH), 7.40 (d, 1H, ArH), 7.35–7.33 (dd, 1H, ArH), 7.23–7.22 (m, 2H, ArH).

^{13}C NMR (DMSO , δ , ppm): 190.31, 160.07, 158.84, 135.65, 133.88, 132.35, 122.76, 122.59, 120.31, 118.01, 115.01, 115.01, 114.60.

Anal. Calcd. ($\text{C}_{15}\text{H}_8\text{N}_2\text{O}_2$): C 72.58; H 3.25; N 11.28. Found: C 72.43; H 3.35; N 11.36%.

2.4. Synthesis of 4-[4-(hydroxymethyl)phenoxy]benzene-1,2-dicarbonitrile (**2**)

In a 500 ml three-neck round bottom flask equipped with a Dimroth condenser, a dropping funnel and a thermometer **1** (10 g, 0.04 mol) was dissolved in 40 ml of absolute THF under stirring with magnetic stirrer. The solution was chilled to 0°C and crushed NaBH_4 (2.29 g, 0.06 mol) was added. Then methyl alcohol (20 ml, 0.8 mol) was added dropwise at a rate allowing to maintain the temperature at 0°C and avoid intensive gassing. The reaction mixture was stirred for additional 30 min at 0°C . The mixture was poured into 400 ml of ice water and acidified with HCl to $\text{pH} = 3$. The desired product was extracted with diethyl ether (100 ml + 100 ml + 75 ml). The organic layer was washed with brine (100 ml + 75 ml) and dried over Na_2SO_4 . The solvent was removed by rotary evaporator and 7.81 g of a white crystalline powder were obtained. Yield 77%. $M_p = 89^\circ\text{C}$.

^1H NMR (CDCl_3 , δ , ppm): 7.75 (d, 1H, ArH), 7.50 (d, 2H, ArH), 7.28 (m, 2H, ArH), 7.10 (d, 2H, ArH), 4.77 (d, 2H, $-\text{CH}_2-$), 2.06 (t, 1H, OH).

Download English Version:

<https://daneshyari.com/en/article/7805591>

Download Persian Version:

<https://daneshyari.com/article/7805591>

[Daneshyari.com](https://daneshyari.com)