

Phase-separated block molecules for next generation functional materials

PhD article

The Macro-organic chemistry group of Prof. Bert Meijer and Dr. Ghislaine Vantomme aims to investigate the fascinating properties of supramolecular materials. My research is focused on functional supramolecular materials, where we strive both to gain a fundamental insight of the design principles of functional materials. Next to that, we try to develop new materials for applications in the fields of energy and information.

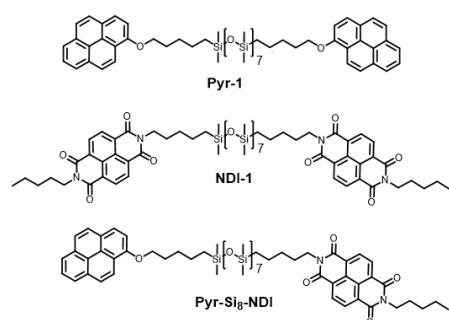


Figure 1: Chemical structures of **Pyr-Si8-Pyr**, **NDI-Si8-NDI** and **Pyr-Si8-NDI**.

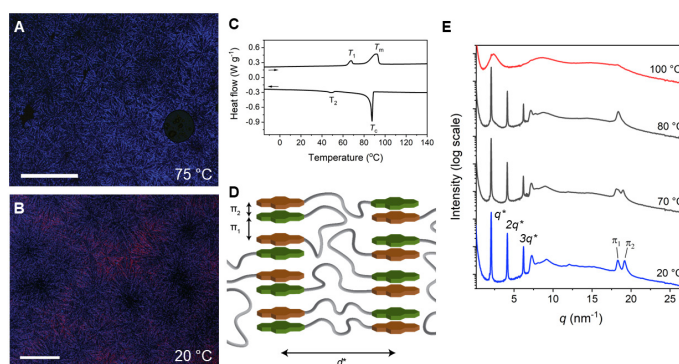
As you are reading this article, the chance is pretty high that you are doing that on your phone, or you will pick it up soon after. However, your phone is only one of many so-called “Internet-Of-Things” devices that people own on average. Since our demand for smart devices is increasing, so will our energy demand, even though we know that our current sources of energy are limited. It is therefore of utmost importance to develop new, more efficient devices, to keep up with everyone’s wishes. We believe that self-assembled materials are essential to create a paradigm shift in electronic and responsive materials and nanolithography applications. We explore new nanomaterials with highly ordered 1D- or 2D-morphologies with domain sizes < 10 nm. To achieve this, we have developed a protocol to

obtain well-defined oligomers of CPT-track), the working principal

Figure 2: (A-B) Polarized optical microscope (crossed polarizers) images of **Pyr-Si8-NDI** at (A) 75 °C and (B) room temperature, rate was 5 K min⁻¹. Scale bar represents 250 μm. (C) DSC trace (second heating and cooling run) of **Pyr-Si8-NDI**. Endothermic heat flows have a positive value, the rate was 10 K min⁻¹. (D) Schematic representation of the room temperature packing of **Pyr-Si8-NDI**. (E) Variable temperature 1D transmission scattering profile of **Pyr-Si8-NDI** upon heating.

oligodimethylsiloxanes (oDMS) with an extremely low dispersity ($\mathcal{D} < 1.0001$).[1] By attaching the flexible spacers with functional, crystalline units we obtain phase-separated block molecules that exhibit properties that are in-between the behavior of classic liquid crystals and block-copolymers. Recently we worked on new block molecules (Figure 1) that were equipped with a combination of both electron-rich pyrene (Pyr) and electron-poor naphthalenediimide (NDI).[2] Although the names might seem a bit scary (especially for the readers that are more interested in the

is relatively straightforward. Since one of the molecules is electron-rich and the other is electron-poor, they can form so-called donor-acceptor assemblies via charge-transfer (CT) interactions. This typically results in highly ordered nanomaterials with great electronic properties.[3] Another benefit of such CT-driven assemblies is that the CT-interaction changes the absorption spectra of the materials. This change means that you can see the formation of the complex by eye, as the color changes (in this case the co-assembly is very bright purple). Below, I will briefly



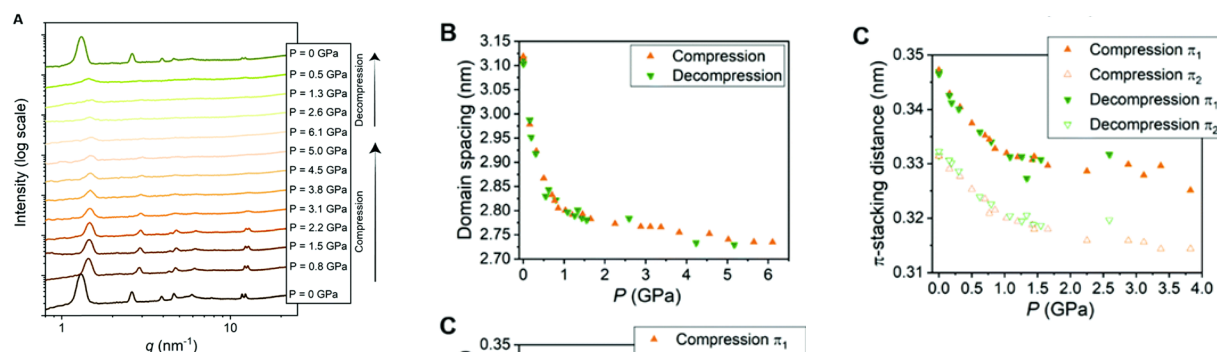


Figure 3: (A) 1D transmission scattering profiles of **Pyr-Si8-NDI** at room temperature under compression and decompression. (B) Domain spacing of the lamellar structure changes as a function of pressure. (C) π_1 - and π_2 -stacking distance changes as a function of pressure.

explain the main results on the heterotelechelic block molecule **Pyr-Si8-NDI**, where both Pyr and NDI are attached to the same siloxane spacer.

First, we start by designing and synthesizing the block molecules. Although the aforementioned concept sounds pretty easy, complex molecules like **Pyr-Si8-NDI** are not commercially available. Therefore, we have to develop a synthetic protocol to yield the block molecule, which is often not trivial. Herein we developed a robust and reproducible synthetic protocol to obtain the block molecule in five steps. After assessing the purity using a combination of MALDI-ToF-MS and ^1H - and ^{13}C -NMR, we characterized the nano-morphologies of the materials. We typically do this by measuring Polarized Optical Microscopy (POM), Dynamic Scanning Calorimetry (DSC) and Small Angle X-Ray Scattering (SAXS). The results of these studies are shown in Figure 2. With POM, we found that large birefringent domains are formed upon controlled cooling from an isotropic melt. This tells us that we go from a disordered state at elevated temperatures, to more ordered aggregates at room temperature. Since these aggregates have a certain orientation in different directions, they break the incident light anisotropically which results in bright birefringent structures. Next up is the DSC analysis, which reveals the thermal transitions that are present in a material. This is especially important for the processing of functional materials because it will determine the operating window

wherein the materials show their desired properties. In this case, we found that the material was completely molten above $T_m = 95$ °C, and crystallized below $T_c = 88$ °C. Moreover, we saw liquid crystalline behavior between T_l and T_m which gives us an additional operation window. Finally, we discovered the exact nanomorphology using SAXS. Depending on the relative positions of the peaks in a SAXS spectrum, the type of morphology can be determined. Typically, we strive to obtain lamellar morphologies, where domains of functional moieties are separated by channels of oDMS. Using Bragg's law, we can derive that peaks that are spaced at perfect integers from each other (q^* , $2q^*$, $3q^*$, ...) are indicative of a lamellar ordering and that their spacing follows from $d_{lam} = 2\pi/q^*$. Thereby we concluded that this heterotelechelic block molecule is indeed phase separated into lamellae with a domain spacing of 3.1 nm. Surprisingly, we could even distinguish the 0.01 nm difference between the inter- and intramolecular π -stacking.

To summarize, we have shown that the NDIs and pyrenes form a highly ordered lamellar nanostructure stacks, characterized by crystalline dimers of NDI and Pyr. Our collaborators in Japan even discovered that the crystalline material is very robust and can withstand pressures up to 6.1 GPa at room temperature without losing their morphology (Figure 3). The NDI- and Pyr-cores are brought in closer proximity by pressure, resulting in charge delocalization which makes this **Pyr-Si8-NDI** system a promising

material for semi-conducting purposes. We envision that this type of fundamental knowledge will be the first step towards new and more efficient devices.

Even though I was asked to write a PhD research article, I want to spend my final few words on a more personal note why I like my research in the Meijer/Vantomme-group. On a daily basis, I work on both the synthesis of new block molecules, as well as their in-depth characterization. This means that I have very varied days, which makes time pass really quickly. One of the biggest benefits of the group is that we have very well-equipped labs and huge expertise on the subject, which means we can do the majority of all experiments in Eindhoven which would not be possible anywhere else. Interested in learning more about our research or the possibilities to do your BEP or Graduation Project on the fourth floor? Check our website (meijerlab.nl) or walk by for a talk!

WRITTEN BY:

Bart van den Besselaar

Bart was very excited to share the work of his PhD in the Meijer/Vantomme group.

[1] Lamers, B.A.G. et al., *J Polym Sci.* **2021**, 59: 1142–1150.

[2] Lamers, B.A.G. et al., *Mater. Horiz.*, **2022**, 9, 294–302.

[3] Paxton W.F. et al., *Nature*, **2012**, 488, 485.