Nanostructures of n-Type Organic Semiconductor in a p-Type Matrix via Self-Assembly of Block Copolymers

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There has been an increasing interest in the morphology of organic semiconductors[1−3] in film because of its strong influence on the performance of devices using these materials. Especially for electrooptical applications like light-emitting diodes and solar cells, an increase in the interface area between the electron (ETM) and the hole transport material (HTM) could enhance the performance since the interface is the active area for charge recombination or separation. This phenomenon was studied experimentally[4] and by numerical simulations.[5] In photovoltaic devices the light is absorbed by the dye, and the generated exciton (electron−hole pair) has to diffuse to the interface between ETM and HTM where they are separated. The exciton diffusion length is only on the order of a few nanometers, which is at least 10 times smaller than the optical absorption depth. This limits the efficiency for simple two-layer devices.[6] To overcome this problem, the active organic layer has to be structured on a nanometer scale. Such microphase separation can be realized using block copolymers. Synthetic attempts for obtaining functionalized block copolymers have been successfully tried out by Hadziioannou et al.[7] using *p*-phenylenevinylene and a partially fullerene functionalized block, by Zentel et al.[8] using triphenylamines and NLO-functionalized triphenylamines, by Stupp et al.[9] using functional triblock copolymers, and in our group by using metal-centered bifunctional polymers.[10] In this work, we use poly(vinyltriphenylamine) as HTM, which is known to be a stable and good hole conductor. The other block is made up of perylene bisimide[11] acrylate, which has high electron mobility and high light fastness so that it can also be used as a dye as it strongly absorbs light between 400 and 600 nm. The perylene-3,4:9,10-tetracarboxylic bisimide monomer **5** (PerAcr) was designed unsymmetrically with a swallow-tail substituent[12] for good solubility and an acrylate group at the other end for the polymerization. Thus, in this concept, all the three functions of light absorption, hole transport, and electron transport are taken care of in a self-assembling system with the challenging task of creating nanostructures with large amount of interface suitable for solar cell applications.

To get well-defined block copolymers, we used the nitroxide-mediated living radical polymerization.[13] This controlled radical polymerization technique tolerates a wide range of functional groups and is a metal-free method. The initiator **1** is a second-generation initiator which was first reported by Hawker et al.[14] With this initiator styrene and acrylate derivates could be polymerized. As a first step, 4-vinyltriphenylamine (**2**) was polymerized via nitroxide-mediated controlled radical polymerization (Scheme 1). In Figure 1a the linear dependence between the reaction time and the conversion for conversions up to 50% is shown, which is consistent with the controlled nature of the polymerization. The polydispersities are in the range 1.20−1.26. With longer reaction time the polydispersity increases to 1.43 for 80% conversion. A small excess (5 mol %) of the free nitroxide **3** was added to optimize the control of the polymerization. The free nitroxide is necessary so that it can act as an artificial persistent radical functioning similar to the persistent radical effect.[15] Initial experiments without the free nitroxide resulted in poorer control of the reaction and therefore higher polydispersities. Two macroinitiators, PvTPA1 **4A** and PvTPA2 **4B**, were synthesized using the same technique. The polymer properties are listed in Table 1. Even for high molecular weights the polydispersities are low. These homopolymers are amorphous with glass transition temperatures of about 144−145 °C and are thermally stable.

The perylene bisimide monomer **5** was also homopolymerized to get the polymer PPerAcr **7**. This perylene containing homopolymer **7** has a melting point of 190 °C, but no glass transition temperature could be detected down to −50 °C. For the polymerization of the perylene bisimide substituted acrylates longer reaction times were necessary, and the polydispersity of the homopolymer **7** was higher than those of the homopolymers **4**. This may be due to the dilution of the acrylate group in the monomer **5**, which mainly consists of the substituted perylene core. Similar effects for the dilution with solvent were previously reported.[16] If polymer **7** was used as a macroinitiator for the polymerization of 4-vinyltriphenylamine (**2**), the polydispersities were about 2 with a low molecular weight shoulder in the GPC eluogram, which can be attributed to the macroinitiator. This result suggests that the solubility of the macroinitiator may limit this synthetic pathway, and therefore, the synthetic route starting from PvTPA macroinitiator was used (Scheme 1).

The macroinitiator PvTPA1 **4A** was used to synthesize the block copolymers PvTPA1-bl-PPerAcr **6A**−**6C**. All the block copolymerizations were performed in 1,2-dichlorobenzene with a 5 mol % excess of the free nitroxide **3**. The polymers exhibited polydispersities below 1.5 for dye contents up to 40 wt %. The compositions of the block copolymers were determined by NMR spectroscopy. The UV/vis spectra of this series of block copolymers **6A**−**6C** prepared from the same macroinitiator **4A** show the expected increase in perylene absorption proportional to the incorporation of perylene bisimide block, as seen in Figure 1b. Additionally, the dye content in **6A**−**6C** was also determined using UV/vis spectroscopy making use of the extinction coefficient of PPerAcr **7**. The dye contents were 13.0, 40.8, and 73.2 wt % for **6A**, **6B**, and **6C**, respectively. These values are in close agreement with the compositions calculated from NMR spectroscopy. The block copolymers **6A**−**6C** are thermally stable with T_{onsets} obtained from TGA well above 300 °C. DSC measurements showed that the glass transition temperatures and the melting points of the block copolymers **6A**−**6C** are in the same range as those of the corresponding homopolymers **4** and **7**. These

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Scheme 1. Living Radical Polymerization and Block Copolymerization of vTPA and PerAcr Monomers via Nitroxide-Mediated Polymerization (NMP)

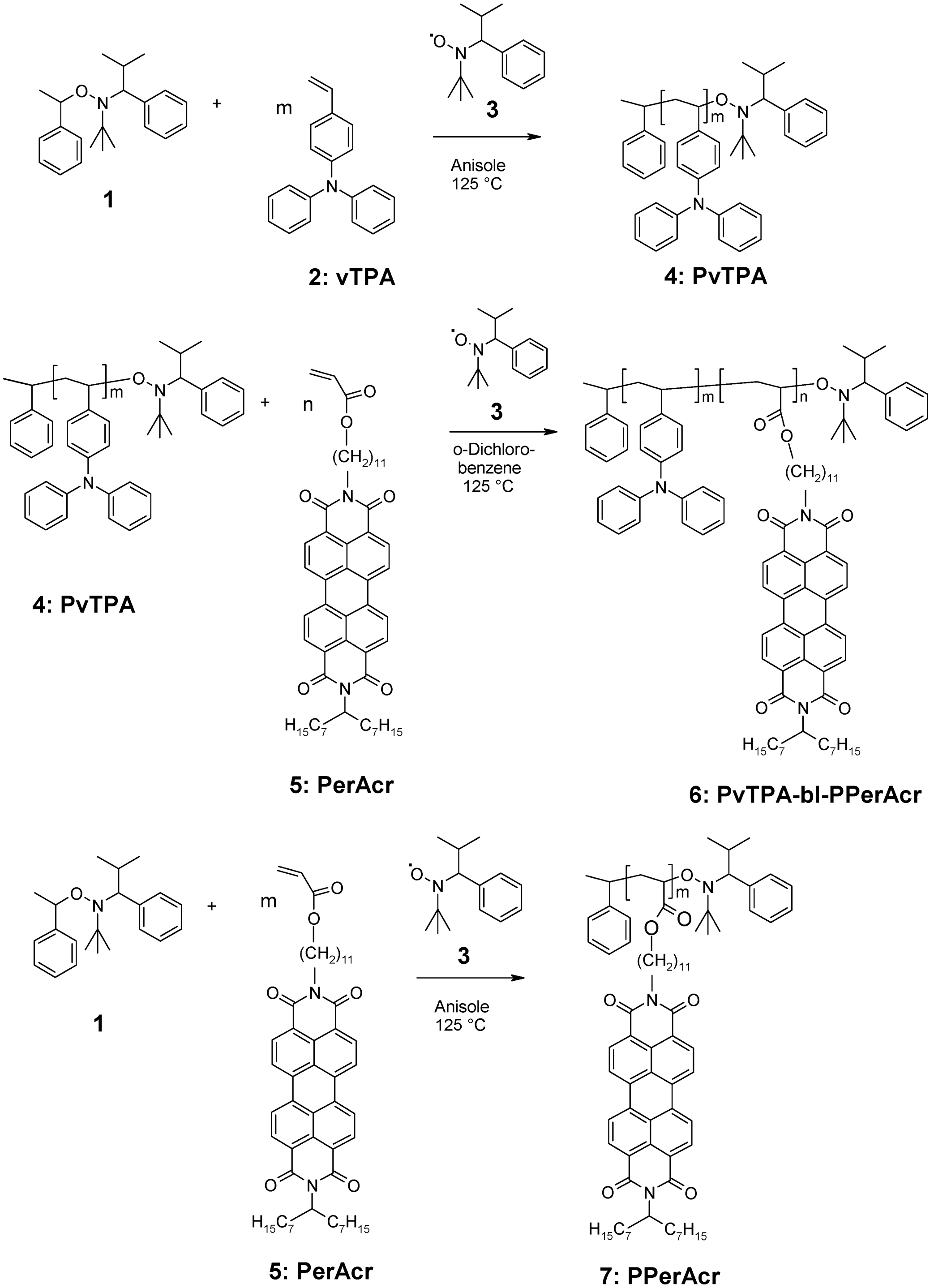

Table 1. Overview of Molecular Weight and Thermal Properties of the Homopolymers and Block Copolymers

	M_n [g/mol][a]	PDI[a]	wt % of PerAcr[b]	T_g [°C][c]	T_m [°C][c]	TGA$_{-5\%}$ [°C]
4A: PvTPA1	15 830	1.22		143.6		378
4B: PvTPA2	23 210	1.19		145.3		376
6A: PvTPA1-bl-PperAcr1	17 610	1.37	13.7	141.9	181.3	380
6B: PvTPA1-bl-PperAcr2	24 170	1.47	40.3	137.7	187.7	391
6C: PvTPA1-bl-PperAcr3	37 710	1.97	78.9	149.5	198.0	396
7: PPerAcr	19 900	1.65	100	*d*	189.8	404

[a] Measured against polystyrene standards via GPC. [b] Calculated from ^{1}H NMR spectra. [c] Heating rate 10 K/min; values taken from second heating curve. [d] T_g could not be observed down to −50 °C.

thermal properties and the fact that all block copolymers give optically clear films indicate a microphase separation. The final proof for microphase separation was achieved with transmission electron microscopy. TEM

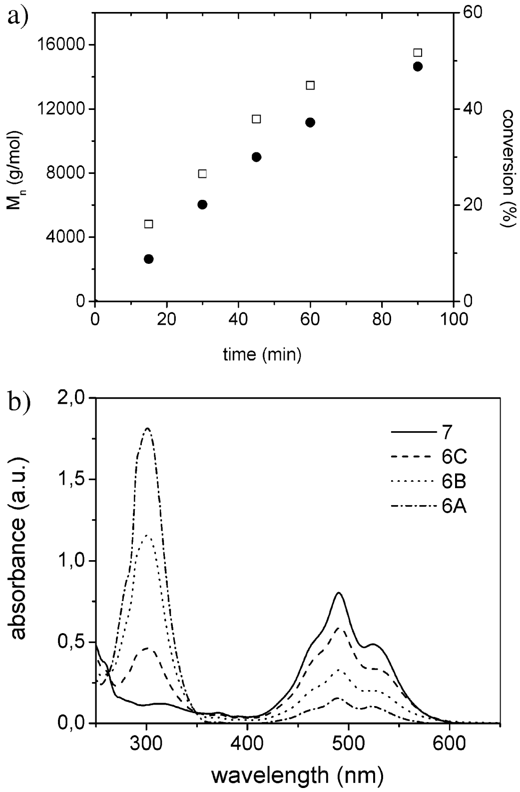

Figure 1. (a) Evolution of molecular weight and conversion with time for nitroxide-mediated living polymerization of vTPA to PvTPA. Composition: 6 mmol of **2**, 0.03 mmol of **1**, 0.0015 mmol of **3**, 600 μL of anisole; $T = 125$ °C. (b) UV–vis spectra of **6A**–**6C** measured in THF (concentration: 0.02 mg/mL).

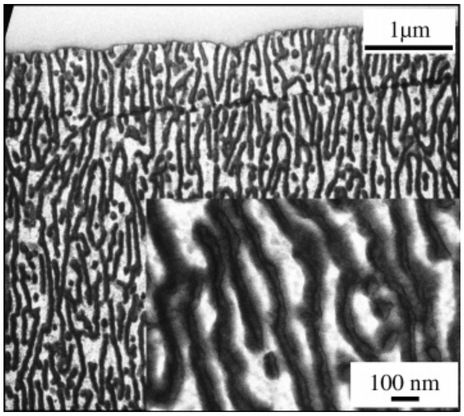

Figure 2. TEM of cross section of **6C** from relatively thick films (5–6 μm) obtained by melting down the polymers onto a glass substrate and subsequently tempering them at 200 °C for 1 h.

measurements were carried out on thin cross sections of relatively thick films (5–6 μm) obtained by melting down the polymer onto a glass substrate and subsequently tempering them at 200 °C for 1 h. The TEM of **6A**–**6C** show phase separation on nanometer scale. As the amount of dye block in copolymer increases, the perylene moieties in **6C** aggregate together to form nanowires, which are embedded into the PvTPA matrix (Figure 2). The nanostructures are about 40–60 nm thick and 1–2 μm long, thus exhibiting high aspect ratios which favor a better percolation of charge transport. Moreover, the tempering process favors a vertical orientation of these nanowires on glass substrates, as can be seen from Figure 2. We assume that the strong π–π interaction and crystallization of perylene moieties are the driving forces for the buildup of nanowires in block copolymer **6C** with high perylene dye content. The situation here may be very similar to that in rod–coil polymers in which the stiff rodlike segments cause the nanostructures.[17]

Evidence for photoinduced charge transfer is provided by quenching of photoluminescence (see Supporting Information). After excitation at a wavelength of 492 nm, the homopolymer **7** shows an intense red fluorescence at 632 nm arising from perylene core. Using the same excitation wavelength, block copolymers **6A**–**6C** exhibit a quenching of this fluorescence with an efficiency of more than 95%, which can be ascribed to an electron transfer from the excited state of perylene to PvTPA domains. The chance of energy transfer from perylene to TPA moieties is almost negligible due to the unfavorable HOMO/LUMO energy levels of the two species, TPA having a higher band gap energy than the perylene unit. Further studies of phase separation in thin films (<500 nm) and the application of such a nanostructured self-assembled film for photoinduced charge separation are underway, and the results will be published later.

In summary, we have shown for the first time that the block copolymerization of 4-vinyltriphenylamine and a perylene bisimide acrylate could be achieved by nitroxide-mediated living radical polymerization with control of molecular weight and low PDI. These fully functionalized block copolymers consist of one block with a hole transport moiety and a second block with an electron transport moiety having light absorption properties. In films these polymers show phase separation on a nanometer scale, and with increasing amounts of dye they build up nanostructures of perylene bisimide in a PvTPA matrix over a large area. Initial experiments show that charge transfer between the domains occurs, which is essential for the use in photovoltaic devices. The formation of oriented nanowires of an n-type organic semiconductor in a polymer matrix opens up new concepts not only in the field of existing electrooptics but also in nanoscience and molecular electronics.

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Supporting Information Available: Experimental procedures, characterization of materials, TEM cross sections of **6A** and **6B**, and photoluminescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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