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Synthesis of a Conjugated Macromolecular Initiator for Nitroxide-Mediated Free Radical Polymerization**

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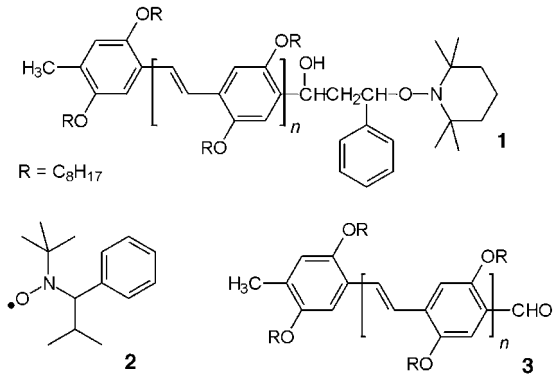
Recent years have seen the increased use of organic materials for opto – electronic applications, such as light-emitting diodes (LEDs) and photovoltaic cells. Such applications require a combination of material properties, for example, good conductivities for holes as well as for electrons, or both electron-donating and electron-accepting capabilities. Since this combination is not likely to be found in a single component, a range of multicomponent systems have been evaluated for use in devices and some have clearly shown beneficial effects.[1] However, simple mixtures containing a polymer component may exhibit macrophase separation. Macrophase separation occurs on a length scale of micrometers (or coarser), which is too large for optimum performance. This is especially true when essential processes rely on the diffusion of excited species to the interface between the components. The diffusion length of a neutral exciton, for example, is of the order of a few nanometers.[2] Hence, in a simple blend, most of the excitons will be lost to some decay channel before having a chance to interact with the second component.

When it comes to the combination of desirable properties in a single chemical compound, block copolymers may be the materials of choice. They might show the phenomenon of microphase separation (if the product of molecular weight (N) and interaction parameter (χ) is large enough) into various ordered structures on a nanometer scale, while the blocks of one macromolecule can have different functionalities.[3] These properties comply well with the requirements for performance enhancements of optoelectronic devices, and our research therefore focuses on the preparation and evaluation of appropriately functionalized block copolymers.

Our goal is to obtain block copolymers suitable for photonic applications such as LEDs or photovoltaic cells. We chose one of the blocks as poly(2,5-dioctyloxy-1,4-phenylene vinylene) (PPV), a polymer frequently used in opto – electronic applications serving as the hole-transporting and luminescent material in an LED or as the light absorber and electron donor in a photovoltaic cell.[1] The second block should contain the complementary functionality required for the specific application: an electron-conducting material to achieve balanced charge transport in LEDs (e.g. an oxadiazole) or an electron acceptor (e.g. C_{60}) for photovoltaic cells. To achieve microphase separation, the second block should also be incompatible (high value of the interaction parameter) with the PPV block.

Recently, we published our approach to synthesizing this kind of molecule, which involves the attachment of an alkoxyamine to the PPV block.[4] This yields a macroinitiator **1**, which is suitable for nitroxide-mediated free radical



polymerization (NMRP), one of several controlled radical polymerization techniques.[5] The nitroxide we used was the commercially available 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO). While a number of publications on conjugated rod – coil block copolymers have appeared in the literature,[6] only a few deal with the use of controlled radical polymerization techniques to construct the coil block.[7] These rather new methods allow the synthesis of block copolymers and tolerate a wide range of substituents.

The aim of our work, controlling optoelectronic properties by synthesizing appropriate block copolymers, can be achieved by varying two parameters: the length of the blocks (degree of polymerization N) or their degree of incompatibility (described by the χ-parameter).[8] The control over the block length is achieved by using a "living" polymerization method (the NMRP method), in which the block length increases linearly with polymerization time. One of the major drawbacks of the use of TEMPO in this controlled radical polymerization is that control can only be established for

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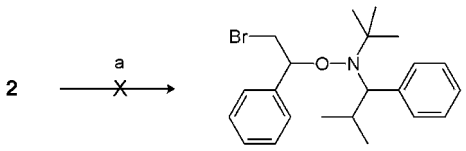
styrene and some of its derivatives. To achieve microphase separated systems, it might be desirable to use chemically different monomers for the coil block, such as (meth)acrylates. These would have the additional advantage of being easily derivatized through esterification.

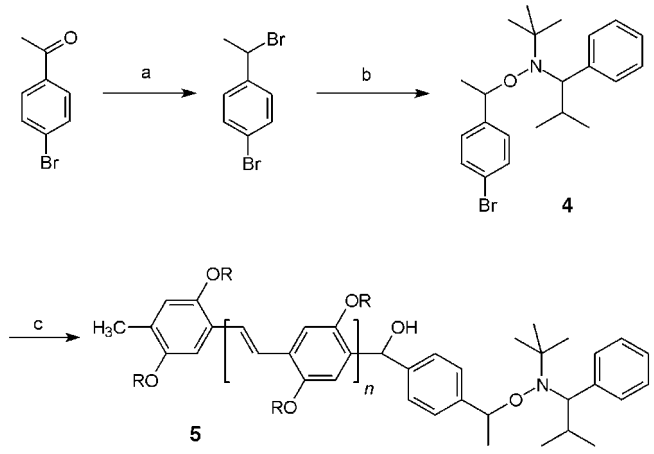
Recently, Benoit et al.[9] synthesized a whole library of alkoxyamines and investigated their usefulness in the NMRP of styrene as well as other monomers, such as acrylates, and acrylonitrile[9] or 1,3-dienes.[10] They found that acyclic nitroxides such as **2**, yield polymers with very low polydispersities for a wide variety of monomers. Hence, we decided to pick up this strategy for our synthesis of rod–coil block copolymers containing a rodlike PPV block. Herein we describe the synthesis of a new macroinitiator for this strategy.

After synthesizing nitroxide **2** (TIPNO) according to reference [9], we first tried to utilize the reaction sequence that we had used successfully for the TEMPO-containing macroinitiator **1**. However, it turned out that the method of Kobatake et al.[11] could not be employed for the synthesis of a brominated alkoxyamine by a route analogous to that used for TEMPO (Scheme 1). Most probably, the intermediate salt of bromine and the nitroxide is formed readily (the reaction mixture became cloudy), but does not add styrene in the following step.



Scheme 1. Reagents: a) 1) Br_2, CCl_4, RT; 2) styrene, 50 °C.

Consequently, a different strategy had to be devised for the synthesis of an alkoxyamine, from **2** (TIPNO), that is substituted with a halogen atom for the subsequent coupling of the initiator to the conjugated polymer. This approach is illustrated in (Scheme 2) for the synthesis of the macroinitiator **5**. The first step is the reduction of 4-bromoacetophenone with $LiAlH_4$ and its subsequent conversion to the



Scheme 2. Reagents: a) 1) $LiAlH_4$, diethyl ether, RT, 3 h; 2) PBr_3, toluene, pyridine, RT, 12 h; b) **2**, CuBr, Cu, bipy, toluene, 75 °C, 12 h; c) 1) *n*-BuLi, diethyl ether, −40 °C→RT; 2) **3**, THF, 60 °C, 2 h. Full details in the Supporting Information. RT = room temperature, bipy = 2,2′-bipyridine.

bromide by treatment with PBr_3. The alkoxyamine **4** was synthesized by the procedure of Matyjaszewski et al.[12] from 1-(4-bromophenyl)ethylbromide and nitroxide **2**. The coupling to the PPV-aldehyde **3**, obtained by Siegrist polycondensation as described by Kretzschmann and Meier,[13] is accomplished by first lithiating the alkoxyamine with equimolar amounts of *n*-butyllithium, followed by addition to a solution of **3** in THF.

As a first test we polymerized *n*-butylacrylate (BA) from the new macroinitiator to form PPV-*b*-PBA. Samples were withdrawn after 4 and 7 hours and precipitated into methanol (see Supporting Information).

As a control experiment, BA was polymerized with alkoxyamine **4** under the same conditions as for the block copolymers. The resulting polymer was still soluble in methanol. Therefore, the presence of *n*-butylacrylate homopolymer in the block copolymer samples can be excluded.

The molecular weights of the two block copolymers are shown in Table 1. The weight fractions were obtained from NMR spectroscopic data by comparing the resonance signals in the aromatic part (PPV) with those centered at $\delta = 4.1$ (OCH_2 of PPV and BA). The length of the PPV block was

Table 1. Molecular weights of PPV-*b*-PBA determined from ^{1}H NMR spectroscopy after polymerization for 4 and 7 hours (with the PPV-block taken as 3.9×10^3 g mol^{-1}).

Sample	w_{PPV}[a]	M_n [10^3 g mol^{-1}]
PPV-TIPNO	1.00	3.9
PPV-*b*-PBA 4 h	0.61	6.4
PPV-*b*-PBA 7 h	0.40	9.7

[a] Weight fraction of PPV block as calculated from ^{1}H NMR spectroscopy.

estimated through UV/Vis absorption spectroscopy by comparing the absorption maximum with those of monodisperse alkoxy-substituted oligo(*p*-phenylene vinylene)s.[14] The λ_{max} value of 477 nm obtained for the macroinitiator **5** (PPV–TIPNO) would correspond to an oligomer with nine repeating units. Therefore, the average molecular weight of the PPV block was taken as 3.9×10^3 g mol^{-1}; based on this number, the number average total molecular weights were calculated from the NMR spectroscopic data (Table 1). To verify the values, we also measured the absorption spectra of **5** and of the two block copolymers, and normalized the signals on weight (Figure 1). Taking **5** as a reference, the absorption of the two block copolymers is reduced to 68% and 48%, respectively. These values are somewhat higher than the values calculated from NMR spectroscopy, but show the same trend.

Values obtained from gel permeation chromatography (GPC) measurements in THF are at least one order of magnitude higher than the values from NMR spectroscopy. Aggregation might be the reason for the overestimated molecular weights determined by GPC. That compounds **3** and **5** are also strongly overestimated in GPC measurements, indicates that the rodlike structure of the PPV is responsible for this overestimation. Nevertheless, these measurements show the increase of molecular weight with polymerization time, indicating the formation of block copolymers in a "living" manner. The ratios between the molecular weight

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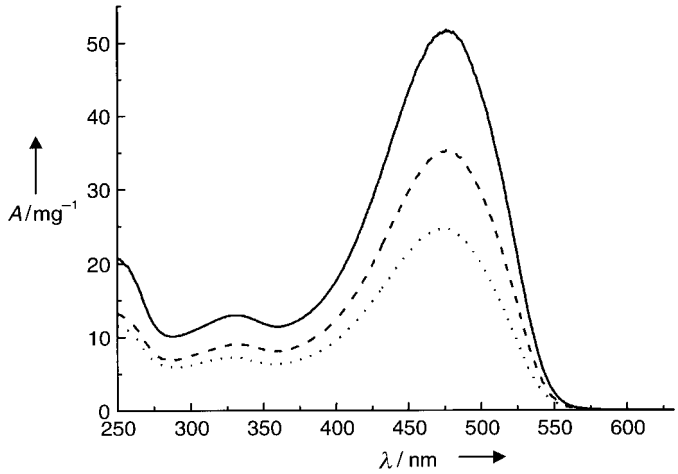

Figure 1. Mass-normalized UV/Vis absorption spectra in $CHCl_3$ of macroinitiator **5** (——) and block copolymers PPV-*b*-PBA after polymerization for 4 h (- - - -) and PPV-*b*-PBA after polymerization for 7 h (····).

data obtained from NMR spectroscopy and GPC are roughly the same for **3**, **5**, and the block copolymers, providing evidence for similar aggregation numbers for all samples.

The glass transition temperature (T_g) of the PBA block in the block copolymer PPV-*b*-PBA (7 h polymerization) is $-43\,^{\circ}C$ and the melting temperature of the PPV block is $180\,^{\circ}C$ as determined by differential scanning calorimetry (DSC). The corresponding homopolymers of PBA and (dioctyloxy)PPV show a T_g of $-61\,^{\circ}C$ and a melting temperature of $185\,^{\circ}C$, respectively. Thermogravimetric analysis (TGA) shows a decomposition temperature of the block copolymer of $340\,^{\circ}C$ (5% weight loss).

Transmission electron microscopy (TEM) studies on a drop-cast film revealed elongated domains of a fairly uniform thickness of approximately 10 nm (Figure 2). This size is

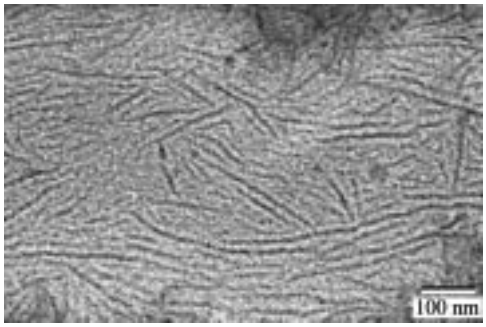

Figure 2. Bright field electron micrograph of PPV-*b*-PBA (polymerization for 7 h) revealing the microphase separated morphology.

compatible with a double-layer of the PPV blocks. The bright field electron micrograph does not resemble traditional images of highly ordered phase-separated coil–coil block copolymers. Firstly, this is probably because of the rodlike character of the PPV block. Rod–coil polymers have been found to exhibit morphologies quite different from coil–coil polymers.[15] Secondly, because of the low molecular weight of our block copolymers, the system may be in the weak segregation regime of the phase diagram. The presence of PPV block in the material between the domains is very well supported by the increase of T_g.

To conclude, we have synthesized a new PPV-containing macroinitiator suitable for nitroxide-mediated free radical polymerization (NMRP) and have used it successfully to obtain rod–coil block copolymers comprising a PPV (rod) and an *n*-butylacrylate (coil) block. The block length increased with polymerization time, as indicated by UV/Vis absorption and NMR spectroscopy. Transmission electron microscopy studies revealed a microphase separated morphology. As acrylates can easily be functionalized, this method offers a promising way to synthesize block copolymers for optoelectronic applications.

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