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Blue emitting side-chain pendant 4-hydroxy-1,3-thiazoles in polystyrenes synthesized by RAFT polymerization

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ABSTRACT

Blue emitting dyes bearing a luciferin analogous chromophore were attached to a polystyrene backbone. For this purpose, 4-hydroxy-1,3-thiazoles were functionalized with a styrene unit and polymerized using the reversible addition–fragmentation chain transfer (RAFT) polymerization technique. Two different chain transfer agents were investigated and one monomer was studied in terms of its kinetic behavior. The polymerization kinetics are presented and discussed in detail, showing a controlled polymerization behavior, resulting in well-defined copolymers with polydispersity indices below 1.2. The obtained polymers were characterized by size exclusion chromatography (SEC), ^{1}H NMR, MALDI-TOF MS and UV–vis absorption and fluorescence spectroscopy. In addition, the UV–vis absorption and emission behavior was investigated in thin films.

1. Introduction

Fluorescent polymers derived from luminescent monomers are in the focus of intense research today [1–3]. A variety of different chromophores attracted high interest due to potential applications in various fields, for instance, their successful application in organic light emitting diodes (OLEDs) [2,4,5], as one emitting species in white polymer light emitting diodes (WPLEDs) [2,6–8], as sensor molecules in biochemical and environmental applications [3,9–11], and dye sensitized solar cells [2,12–14]. Moreover, blue emitting monomers carry the potential of mimicking photosynthetic proteins in plants by incorporating the chromophores into polymers as donor molecules for Förster resonant energy transfer (FRET) process [15–21]. Main chain π-conjugated polymers are not attractive for this application due to the synthetic complexity and the dependence of the optical properties from the number of repeating units and, therefore, the distance between the chromophores [22]. In contrast, polymers which are functionalized with dye units in the side chain feature defined and predictable optical properties, independent from the degree of polymerization (DP) [23–26]. A homogeneous distribution of the dye in the polymer can be achieved by

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direct polymerization of functional monomers. Moreover, the degree of functionalization can be adjusted by the concentration of the labeled monomer in the overall monomer feed of the polymerization. Such polymers are of potential interest for a wide range of applications, *e.g.*, in fluorescent nanoparticles for the investigation of biological substrates, in particular of living cells [27]. In contrast to common postpolymerization conjugations of dyes onto preformed particles, the direct polymerization leads to uniformly distributed dyes, resulting in an enhanced fluorescence of the particles, which are not vulnerable to dye-leakage [28].

Despite the large number of blue emitting molecules, *e.g.*, coumarins [29], naphthalimides [30], pyrenes [31], and nile blue [32], only a small part of them were incorporated into polymers so far. Moreover, many of these "conventional" dyes feature drawbacks, which have to be overcome; for instance, low quantum yields, strong solvent dependency of the electronic properties, excimer formation [33], and a low photostability [34]. A promising class of blue-emitting dyes are 1,3-thiazoles. These dyes generally feature very high room-temperature fluorescence, with quantum yields ranging from 0.7 up to unity, in combination with an unusually large Stokes shift [35,36]. Furthermore, the choice of different types of substituents strongly influences absorption and emission behavior in the UV and visible region of the electromagnetic spectrum [37]. In addition, the introduction of hydroxyl functionalities (*i.e.* 4-hydroxy-1,3-thiadiazoles) offers the possibility of an easy functionalization, in particular, alkylation as well as acylation, *i.e.* with styrene and methacrylate derivates, respectively. The ease in synthetic access and functionalization combined with high fluorescence quantum yields, improved photostability compared to other chromophores (*e.g.*, rhodamines, fluoresceins) as well as chemical stability made 4-hydroxy-1,3-thiazoles suitable for the fabrication of luminescent polymeric materials. Previously, it was demonstrated that 4-hydroxy-1,3-thiazoles can be successfully incorporated into poly (methyl methacylate) (PMMA) backbones [23] by reversible addition–fragmentation chain transfer polymerization (RAFT) [38,39]. The advantage of RAFT is the good tolerance to functional groups (*e.g.*, incorporation of dyes) [40,41] and the possibility to construct a wide range of different architectures, *e.g.*, combs, blocks, and star copolymers [42–44]. A control over the molar mass and the polydispersity index (PDI) can be obtained by this type of controlled radical polymerization technique.

In comparison to methacrylates, styrene derivatives feature a better chemical stability, in particular, a better resistance towards hydrolysis.

In this contribution the synthesis and characterization of statistical thiazole-functionalized styrene copolymers are described. Two different chain transfer agents, 2-cyano-2-propyl dithiobenzoate (CPDB) and a trithiocarbonate (2-(butylthiocarbonothioylthio)propanoic acid, BTTCP) were investigated. Additionally, the copolymerization kinetics with styrene and one thiazole functionalized monomer were studied. Furthermore, absolute emission quantum yields and fluorescence lifetimes of the functionalized monomers and copolymers are determined using stationary UV–vis and time correlated single photon counting measurements. Finally, the optical properties between a selected copolymer and its corresponding monomer unit in solution were compared to its behavior in thin films.

2. Experimental

2.1. Materials and instrumentation

All reagents were purchased from commercial sources (Biosolve, Fluka, Aldrich, Alfa Aesar and Acros Organics) and were used directly without further purification. All solvents were of reagent grade, purified using common methods and distilled prior to use. Styrene was passed over a short neutral aluminum oxide column directly before use to remove the stabilizer. 2,2′-Azobis(*iso*-butyronitrile) (AIBN) was recrystallized from methanol prior to use. **1a** [45] and **2a** [23] were synthesized according to literature methods. 2-Cyano-2-propyl dithiobenzoate (CPDB) was purchased from Sigma–Aldrich and 2-(butylthiocarbonothioylthio)propanoic acid (BTTCP) was kindly provided by BASF SE. All reactions were performed under an argon atmosphere in glassware equipped with a Teflon® coated magnetic stirring bar. Size exclusion chromatograms were recorded using a SEC Shimadzu SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector and a PL gel 5 μm mixed-D column at 40 °C (eluent $CHCl_3$:TEA:*i*-PrOH 94:4:2; flow rate 1 mL/min) applying linear polystyrene standards. GC measurements were performed on an Interscience Trace GC with a Trace Column RTX-5 connected to a PAL autosampler. A spin coater from Laurell Technologies Corporation (North Wales, USA) was used for the preparation of the films. The surface topography and thickness of the polymer films was measured by an optical interferometric profiler Wyko NT9100 (Veeco, Mannheim, Germany). For this purpose, each film was scratched with a scalpel in a controlled manner. At five different positions of the film, the center and the four edges, the depth of the scratch was measured with the optical profiler. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 250 (250 MHz), 300 (300 MHz) and 400 (400 MHz) spectrometers at 298 K, respectively. The chemical shifts are reported in parts per million (ppm, δ scale) relative to signals from the NMR solvents, coupling constants are given in Hz. The melting points were measured with a Galen III apparatus (Boëtius system). Reactions were monitored by TLC on 0.2 mm Merck silica gel plates (60 F254). The mass spectra were measured either with a Finnigan MAT SSQ 710 (EI) or a MAZ 95 XL (FAB) system. Elemental analyses were carried out on a CHN-932 Automat Leco instrument.

The UV–vis absorption and PL emission spectra were recorded on an Analytik Jena SPECORD 250 and a Jasco FP-6500 spectrometer, respectively, at 298 K. UV–vis and fluorescence spectra of the films were measured with a modified Hitachi F-4500. For this purpose, dilute solutions (10^{-6}–10^{-5} M, 1 cm quartz cuvette) in $CHCl_3$ were used. As reference, a quartz cuvette filled with the pristine solvent was utilized. Fluorescence lifetimes were obtained by streak camera measurements in the time-correlated