



Synthesis of PPV-*b*-PEG block copolymers via CuAAC conjugation

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ARTICLE INFO

Article history:

Received 5 March 2014

Received in revised form 12 March 2014

Accepted 13 March 2014

Available online 28 March 2014

Keywords:

Poly(*p*-phenylene vinylene) (PPV)

Anionic polymerization

CuAAC conjugation

Block copolymers

ABSTRACT

The synthesis of amphiphilic rod-coil block copolymers with a poly(*p*-phenylene vinylene) (PPV) rod-like block using a *Click* chemistry approach is investigated and a facile reaction pathway towards poly(*p*-phenylene vinylene)-*block*-poly(ethylene glycol) (PPV-*b*-PEG) block copolymers is presented. To reach this aim, an alkyne-functionalized PPV block (synthesized from anionic sulfinyl precursor route polymerization) was synthesized and subsequently coupled to azide-functionalized poly(ethylene glycol) of different lengths. Self-assembly of these materials in aqueous solution demonstrate successful micelle formation with core-shell morphology and different sizes for these PPV-*b*-PEG block copolymers as is confirmed by TEM and DLS measurements respectively.

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1. Introduction

In the recent years, significant advances have been made regarding the anionic polymerization pathway to produce tailor-made PPV materials [1] via the sulfinyl precursor route (see Scheme 1). With lithium hexamethyldisilazide (LHMDS) as base, specific anionic initiators and THF as the solvent [2], well-controlled anionic polymerizations can be performed and PPVs with preselected molecular weight and dispersity are obtained [3]. The base, LHMDS, has thereby a dual role in the anionic polymerization pathway: It acts as the anion-forming species by deprotonating the anionic initiator. Concomitantly, it triggers as well the formation of the actively propagating *p*-quinodimethane from the pre-monomer and thus enables polymerization

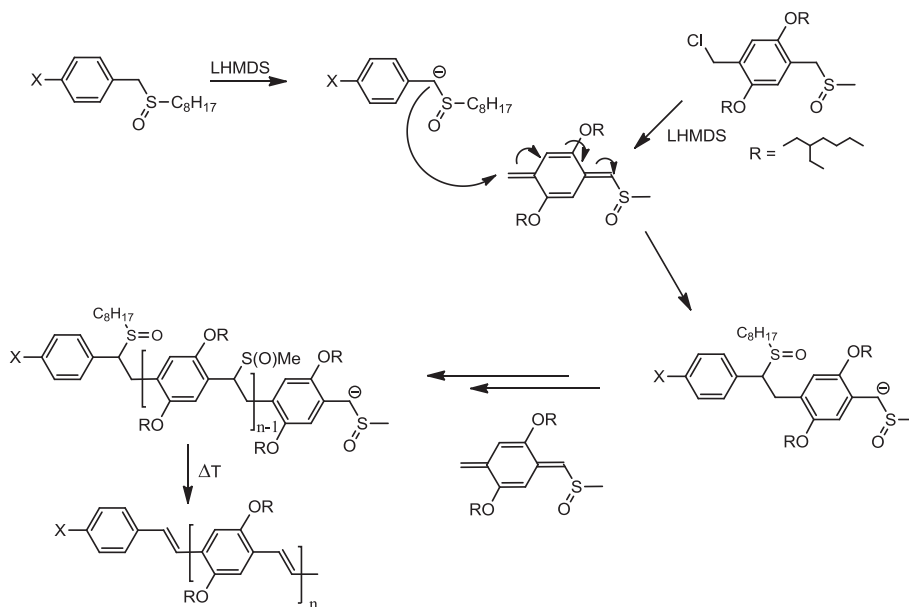
in the first place (see Scheme 1). The mechanism of precursor route PPV polymerizations can be complex and the reader is referred to literature for details [1].

High endgroup fidelity in α -position of the chain was confirmed using electrospray ionization mass spectrometry (ESI-MS) measurements for different anionic initiators before [4], thus opening up possibilities to approach sophisticated architectures and to construct more complex polymer materials.

Block copolymers (or more complex structures) containing PPV segments are attractive materials. While the demand for classical (homopolymer) PPV materials is declining in the classical field of organic electronics – especially in photovoltaics – due to limitations in the light harvesting capability of PPVs, new applications can be targeted when polymerizations can be controlled as described above. Block structures allow for self-assembly of materials and thus nanostructuring of the PPV segments, which might find new applications in organic transistors or light emitting diodes. Moreover, biomedical applications can

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Scheme 1. General scheme for the anionic sulfanyl polymerization route using an anionic initiator.

be targeted where the superior fluorescence properties of PPV can be exploited for the introduction of specific biomarkers. Ligation of PPV to nanoparticles for cell uptake has thereby very high potential. Also in this case, highly functional materials with precisely defined microstructure are required.

For PPV materials, synthesis of rod-coil block copolymers were already reported, however, these were only produced starting from a PPV block synthesized *via* the Siegrist polycondensation method and hence low molecular weight material [5,6]. In this approach an aldehyde endgroup functionality is available which can be coupled with a suitable linker in a post-polymerization functionalization process. Block copolymers synthesized *via* this method combined with *Click* chemistry were PPV-*b*-POM (polyoxometalate) [7] and PPV-*b*-PMMA (poly(methyl methacrylate)) [8]. Polycondensation reactions are often used to make PPVs, but suffer however from low efficiencies and severe limitations in molecular weight. Additionally, post-polymerization modifications are in these cases required to introduce the required functional groups to the chain end. Sulfanyl precursor polymerizations as in our approach follow chain growth mechanisms and – at least in principle – give facile access to higher molecular weight materials as well [1]. It should be noted though that we also targeted lower molecular weights for the sake of characterization and to demonstrate success of our synthesis route unambiguously.

To produce block copolymers containing a PPV block from sequential polymerization, different strategies were already described in our previous work. The PPV used in these studies was the symmetrically 2-ethylhexyloxy substituted poly[2,5-bis(2-ethylhexyloxy)*p*-phenylene vinylene] (BEH-PPV). By chain extension in consecutive anionic polymerization, a *tert*-butyl acrylate (*t*-BuA) block

could be attached to the BEH-PPV. The efficiency of the method was, however, limited, leaving significant amounts of homopolymer PPV in the product mixture behind. The block copolymer could only be isolated using preparative recycling GPC [9]. More successful was the incorporation of a bromine-functionality on the anionic initiator end, which could in a second step be used to reinitiate the polymerization of a vinyl monomer in a single electron transfer – living radical polymerization (SET-LRP) reaction [10,11]. By using this technique, BEH-PPV-*b*-P(*t*-BuA) block copolymers with different *t*-BuA chain lengths could successfully be synthesized in a robust manner. After hydrolysis of the acrylate block, amphiphilic polymers were obtained that displayed micelle formation and which featured pH-responsive morphologies [4].

While the SET-LRP approach was very successful, it still limits the choice of the second block to vinyl monomers that can undergo radical polymerization. Thus, the development of a modular approach that allows for *any* combination of building blocks is highly attractive. Modular ligation also gives access to grafting-to approaches for surface modifications. Generally, for the aim of polymer ligation, the well-known copper catalyzed azide-alkyne cycloaddition (CuAAC) can be employed [12–14], in which a polymer block containing an alkyne functionality is coupled with a polymer block containing an azide functionality.

In this paper, the synthesis of BEH-PPV-*b*-PEG block copolymers with different PEG block lengths is presented using such *Click* chemistry approach (see Scheme 2). The PPV block is synthesized using the anionic sulfanyl precursor route with an alkyne functional anionic initiator. Thus, no post-polymerization modification is required in order to create the desired *Click* functionality. *Via* this approach an easy handle is created to access coupling with an

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