Well-defined phosphonated homo- and copolymers *via* direct ring opening metathesis polymerization

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A B S T R A C T

Phosphonated polymers with a well-defined molecular weight, composition and architecture have been prepared *via* ring opening metathesis polymerization (ROMP) of phosphonated and non-phosphonated norbornene imides at room temperature for the first time. ROMP was proven to be living and versatile. This enabled preparation of a broad range of phosphonated homopolymers, statistical copolymers, AB diblock as well as ABA and BAB triblock copolymers based on poly(norbornene imide)s with low polydispersity (1.09–1.32). Complete hydrolysis of phosphonated poly(norbornene imide)s under mild conditions yielded the phosphonic acid derivatives. Thermogravimetric analysis indicated high thermal and thermo-oxidative stability of the polymers. Free standing and transparent films with good mechanical stability were obtained from the phosphonic acid functional homopolymers, diblock and triblock copolymers. Combining these basic properties with the advantages mentioned above makes ROMP a promising pathway for accessing a wide diversity of phosphonated macromolecular structures. These new phosphonated polymers will open new perspectives in advanced application areas, which require a high level of control over polymer structure.

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1. Introduction

Phosphonated polymers are interesting for various medical applications such as implant coatings [1,2] and membrane technologies such as water purification [3] and fuel cells [4–6] due to the unique combination of acidity, stability, proton conductivity and metal binding of the phosphonic acid functionality. Despite these attractive properties and potential applications, there is a current lack of direct pathways to prepare well-defined phosphonic acid functional polymers from phosphonated monomers, and thus also lack of knowledge of the fundamental properties of such materials. This is mostly due the unusual polymerization behavior of phosphonated monomers leading to difficulties during the synthesis [6–10]. Direct access to phosphonic acid functional polymers with controlled molecular properties is critical in order to obtain polymer libraries of complex macromolecular architectures for structure–property relationship studies, which will open perspectives for new applications.

Various polymerization techniques including anionic polymerization [6,8,11,12], condensation polymerization [13], free radical polymerization [7,14–19] as well as controlled radical polymerization [20,21] have been employed to prepare phosphonic acid functional polymers by direct polymerization of phosphonated monomers. Among these techniques, controlled radical and anionic polymerizations have the potential to produce polymers with well-defined structures. Still, these techniques have shown to give homopolymers, block and graft copolymers with limited conversions and degrees of polymerizations of phosphonated monomers [6,8,11,12,21]. These efforts significantly improved the ability to prepare phosphonated polymers with varying macromolecular architectures. However, they did not lead to truly living polymerization reactions, which are crucial for precise control over the polymer structure.

More recently, rare-earth metal mediated polymerization has been employed to vinyl phosphonates as an alternative [22–24]. High molecular weight ($M_w \sim 1 \times 10^6$ g/mol) homopolymers as well as diblock and statistical copolymers with low polydispersity and degree of polymerization close to the initial monomer-to-catalyst ratio were obtained at 30 °C. Diblock copolymers were prepared in nearly quantitative yields *via* sequential polymerization, where a vinyl phosphonate was added after complete polymerization of methyl methacrylate. Statistical copolymers were

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made by simultaneous addition of different dialkyl vinyl phosphonates. These results present new and exciting opportunities to synthesize macromolecular architectures directly from phosphonated monomers. Still, the rare-earth metal mediated polymerization has some distinct limitations. These limitations include the inability of the polymerization to yield diblock copolymers *via* sequential polymerization if the non-phosphonated monomer (e.g. methyl methacrylate) is added after the polymerization of the phosphonated monomer, and statistical copolymers by simultaneous addition of phosphonated and non-phosphonated vinyl monomers. This has been ascribed to the strong binding of phosphonates to the rare-earth metal center, which inhibits the coordination of an acrylic monomer at the active site [24]. These features currently limit the level of complexity of the macromolecular architectures accessible *via* rare-earth metal mediated polymerization and the flexibility in fine-tuning the polymer properties. For example, triblock copolymers having phosphonated blocks either at the end or in the middle of the polymer chain are currently inaccessible *via* rare-earth metal mediated polymerization. Moreover, the catalyst used in rare-earth metal mediated polymerization is not commercially available, which further limits the access to well-defined phosphonated polymers.

ROMP is a controlled living polymerization method that leads to a large diversity of functional polymers with precisely controlled properties without requiring protecting group chemistry because of the high functional tolerance of the olefin metathesis catalyst [25]. This is a distinct advantage over other living polymerization techniques, such as anionic polymerization and controlled radical polymerizations. The literature on ROMP of phosphonated monomers is so far very limited. The first report on the compatibility of ROMP with phosphonated monomers was published in 2009. In this study, low molecular weight amphiphilic block copolymers from a phosphonated and non-phosphonated oxa-norbornene imide were synthesized [26]. However, since then, this topic has not received further attention until a very recent publication of a study focused on the biological properties of poly(norbornene)s [27]. The analyses of molecular weight and molecular weight distribution were preformed *via* size exclusion chromatography (SEC). They indicated that the polymers obtained in both studies have low polydispersities, which hinted a living nature of the polymerization. None of these studies reported the evolution of monomer conversion or molecular weight during the polymerization, which is necessary to prove the livingness. Although previous reports briefly point out ROMP as an alternative pathway to phosphonated polymers, the advantages of ROMP were not fully identified and exploited to extent the ability to prepare phosphonated polymers that are currently inaccessible. Moreover, the basic properties of the resulting materials were not investigated. It is worth to note that unsaturated polyphosphoesters [28], fatty acid derived phosphorous-containing polyesters [29] and phosphonic acid functionalized polyolefins [30] have been prepared using step growth metathesis polycondensation technique, which allowed precise placing of phosphorous containing functionalities into the polymers. Although Grubbs-type catalysts are used in step growth metathesis polycondensation and ROMP, these techniques are different.

In the current paper, we present some advantageous features of ROMP with regard to the synthesis of phosphonated polymers with controlled molecular structures. We exploit these features to prepare phosphonated polymers in which the ionic groups are directed to certain segments of the polymer chain by using sequential polymerizations. To this end, we prepared homopolymers, statistical copolymers, AB diblock as well as ABA and BAB triblock copolymers from phosphonated and non-phosphonated norbornene imides. This is the first report on phosphonated triblock copolymers, which

are currently inaccessible *via* other polymerization methods directly from phosphonated monomers. In addition, we report on some fundamental properties of the resulting polymers. Thus, we studied the thermal stability, film forming ability and water uptake of the resulting polymers. The ability to prepare polymers with controlled spatial distribution of phosphonic acid combined with knowledge about their properties is essential to develop advanced materials based on phosphonic acid polymers with new and improved features.

2. Materials and methods

2.1. Materials

The following reagents and solvents were used as received: cis-5-norbornene-exo-2,3-carboxylic anhydride (Sigma Aldrich, 95%), urea (Acros, 98%), diethyl 2-bromoethylphosphonate (Sigma Aldrich, 97%), potassium carbonate (Sigma Aldrich, 99%), acetone (Across, 99.8%), $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (Sigma Aldrich), ethyl vinyl ether (Sigma Aldrich, 98%), lithium bromide (Sigma Aldrich), tetrahydrofuran (Sigma Aldrich, HPLC grade), N-methyl pyrrolidone (Sigma Aldrich, HPLC grade), dimethyl acetamide (Sigma Aldrich, HPLC grade), chloroform (Sigma Aldrich, HPLC grade), toluene (Sigma Aldrich, HPLC grade) and dimethyl sulfoxide (Acros, HPLC grade). N,N'-dimethyl formamide, and dichloromethane were purified by passage through solvent purification system MB SPS-800. The catalyst $([(H_2IMes)(pyr)_2(Cl)_2Ru{=}CHPh])$ [31], diethyl (2-aminoethyl)phosphonate [32], N-(butyl)-cis-5-norbornene-exo-2,3-dicarboximide [33] and diethyl (6-bromohexyl)phosphonate [34] were prepared according to literature. Moreover, cis-5-norbornene-exo-2,3-dicarboxyimide was prepared from cis-5-norbornene-exo-2,3-carboxylic anhydride using a literature procedure [35].

2.2. Methods

NMR spectra of the monomers and polymers were recorded on a Bruker 400 MHz spectrometer, while ROMP kinetics was followed on a Bruker 500 MHz spectrometer. Chemical shifts are expressed in parts per million using residual solvent protons as internal standard (5.32 ppm for CH_2Cl_2, 7.28 ppm for $CDCl_3$, 4.80 ppm and 3.30 ppm for d_4-methanol, 2.50 ppm for d_6-dimethyl sulfoxide). Coupling constants, J, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), and m (multiplet).

Conventional SEC was performed using an Agilent 1260 Infinity system equipped with an ERC refractive index detector and a set of SEC Polymer Standard Service GmbH (PSS) columns (GRAM1000, GRAM1000, GRAM100 10 μm, 8 × 300 mm with a separation range of 300 to 1×10^6 g mol^{-1}). Calibration was done using polystyrene standards. Size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) measurements were performed on an Agilent 1260 Infinity system coupled to a DAWN-EOS laser light scattering detector (Wyatt Technologies) equipped with a He–Ne laser operating at a laser wavelength of $\lambda_0 = 685$ nm and an ERC refractive index detector. Chromatographic separation was performed by using a PSS GRAM linear M 10 μm column (8 × 300 mm) with a separation range of 500 to 1×10^6 g mol^{-1}. The mobile phase for all SEC experiments was N,N-dimethyl formamide (DMF) with 1 g/L lithium bromide (LiBr). An injection volume of 100 μL and 25 μL of 0.25 wt% polymer solutions (prepared in DMF/LiBr at room temperature, stirred for 1 h) for conventional SEC and SEC-MALLS, respectively. A flow rate of 1.0 mL min^{-1} was used for all measurements. All samples were cleaned prior by filtration through PTFE membrane filters with a pore size of 0.45 μm (Millipore,