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Imidazole end-functionalized polycyclooctenes from chain-transfer ring-opening metathesis polymerization and aminolysis reactions

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ABSTRACT

Imidazole end-functionalized polycyclooctene derivatives were synthesized using a two-step procedure; combining ring-opening metathesis polymerization (ROMP)/cross-metathesis (CM) and aminolysis reaction. ROMP/CM of cyclooctene (COE) in the presence of methyl-10-undecenoate (MU) as a chain transfer agent in the presence of Grubbs first generation catalyst (G1) at 40 °C afforded mono ester end-functionalized (MF) as the major and bis ester end-functionalized (DF) polycyclooctene as the minor product. No isomerized mono ester end-functionalized (IMF) polycyclooctene was formed during G1 catalyzed ROMP/CM reactions. The post-polymerization modification of MF in the presence of 1-(3-aminopropyl) imidazole and different catalysts ($Sn(Oct)_2$, $Ti(OiPr)_4$ and triazabicyclodecene (TBD) in THF at 70 °C afforded imidazole end-functionalized polyolefins in excellent yields. All polymers were characterized by means of MALDI ToF-MS, ^1H and ^{13}C NMR spectrometry and Size Exclusion Chromatography (SEC) analyses. The solvent selectivity and catalyst screening experiments were carried out for both ROMP/CM and aminolysis reactions to determine the optimum reaction conditions.

1. Introduction

Precise end-labeling of polymers is of great importance for the development of functional materials as biosensors, ligands and for surface coating applications [1]. Tremendous progress in Ru and W, Mo-catalyzed ROMP reactions extended the application of ROMP in the development of end-functionalized polymers [2]. As ruthenium carbenes only react with olefins in a metathesis catalyst, functional symmetrical or unsymmetrical olefins can be used as chain transfer agents (CTA) in ROMP reactions [3]. As it has been reported in several mechanistic studies, a transition metal alkylidene complex is formed during propagation step in ROMP reactions [4]. The cross-metathesis between the chain-transfer agent and propagating metal alkylidene complex results in mono or di-functionalized ROMP polymers [5,6]. Hydroxy end-capped telechelic ROMP polymers were synthesized through ROMP of 1,5-cyclooctadiene (COD), COE and 1,5-dimethyl-1,5-cyclooctadiene in the presence of cis-1,4-bis(acetoxy)-2-butene as the chain-transfer agent followed by removal of acetoxy end-groups to yield hydroxy end-groups [7–11]. Following this strategy, cis-1,4-bis(2-tert-butoxycarbonyl)-2-butene and cis-1,4-di-tert-butyl-2-butene-1,4,-dicarbamate were used as a chain-transfer agent in ROMP of COD, yielding diamino and dicarboxy telechelic poly(butadiene) [12]. Mono telechelic silyl end-capped glycopolymers were synthesized using a successful strategy that combines ROMP and azide-alkyne cycloaddition reactions [13]. Maleic acid was used as the chain-transfer agent to synthesize functional linear polyethylene using ROMP/hydrogenation in the presence of Grubbs 2nd generation catalyst [14]. 1,4-dicyano-2-butene, 1,8-dicyano-4-octene, and 1,4-dichloro-2-butene were used as the chain-transfer agent to form dicyano and dichloro telechelic polybutadiene (PBD) derivatives, extending the portfolio of end-functionalized polymers [4,5].

Amine functionalized olefins are challenging substrates in end-functionalized ROMP polymer chemistry due to their ability to coordinate to the ruthenium catalyst [15,16]. Kilbinger et al. developed a novel strategy to form amine end-capped ROMP polymers utilizing a cyclic olefin, 1-phenoxy-2,3,4,7-tetrahydro-1H-1,3,2-diazaphosphepine 2-oxide which acted both as a protecting agent for the amino groups and as a chain-transfer agent [17]. Mono-telechelic poly(oxa)norbornene derivatives with a variety of end-functional groups; such as alcohols, acetates, bromides, α-bromoesters, thioacetates, bromides, amines, fluorescein and biotin, were successfully synthesized via two different routes; 1) direct end-capping of polymers by chain-transfer agent and 2) cross-metathesis between methylene end-capped

Abbreviations: ADMET, Acyclic diene metathesis polymerization; COD, Cyclooctadiene; COE, Cyclooctene; CM, Cross-metathesis; CNF, Cyclic non-functional polycyclooctene; CTA, Chain-transfer agent; DF, Bis ester-functionalized polycyclooctene; G1, Grubbs first generation catalyst; G2, Grubbs second generation catalyst.; G3, Grubbs third generation catalyst; HG2, Hoveyda-Grubbs second generation catalyst; IMF, Isomerized mono ester-functionalized polycyclooctene; ILNF, Isomerized non-functional polycyclooctene; MF, Mono ester-functionalized polycyclooctene; Mod-MF, Mono imidazole-functionalized polycyclooctene; Mod-DF, Bis imidazole-functionalized polycyclooctene; MU, Methyl-10-undecenoate

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polyoxanorbornene and cis-chain-transfer agent [18].

A sacrificial synthesis method was developed using vinylene carbonate and 3H-furanone to obtain carboxylic acid and aldehyde terminated ROMP polymers in one step reaction [19]. In addition to homo telechelic ROMP polymers, synthesis of hetero telechelic ROMP polymers utilizing lactones as the chain-transfer agent was reported by Kilbinger et al. [20]. Functional COE derivatives were also used in tandem ROMP/CM. Silyl functionalized chain-transfer agents such as vinyl trimethoxysilane, allyl trimethoxysilane and 3-(trimethoxysilyl) propyl acrylate were used to synthesize mono-end functionalized ROMP polymers for various applications [21]. Following this study, the nature of the chain-transfer agents and catalyst influence on the formation of α,ω-bis(trialkoxysilyl) difunctionalized polycyclooctene was investigated in details [22]. Guillaume et al. showed that vinyl or acryloyl glycerol carbonates could be used as chain-transfer agents in ROMP/CM, extending the portfolio of chain-transfer agent agents in ROMP/CM reactions [23]. The modification of telechelic epoxy end-functional polycyclooctene with dithiocarbonatation and aminolysis afforded non-isocyanate polyurethanes derivatives [24]. This versatile method offers an environmentally friendly approach towards the synthesis of polyurethane based materials.

In addition to ROMP/CM reactions to end-functionalize polymers, acyclic diene metathesis polymerization (ADMET)/CM reactions are frequently used as an alternative to tandem ROMP/CM reactions [25]. The degradation of 1,4-PBD in the presence of allylsilanes and Mo- or W- based alkylidene catalysts afforded corresponding telechelic low molecular weight PBDs [26–28]. Nomura et al. reported a one-pot procedure to synthesize poly(9, 9′-di-n-octylfluorenevinylene)s by ADMET polymerization in the presence of di-substituted olefins as chain-transfer agent [29].

Although a wide range of functional end groups were integrated into unsaturated polymers using ROMP and ADMET reactions, imidazole end-capped ROMP polymers haven't been reported up to date. Imidazole groups are of great importance as they can be used as *N*-heterocyclic carbene ligand precursors in catalytic chemistry applications and ionomer precursors to enhance the physical & chemical properties of non-polar polymers [30]. In addition to these features, the biocompatibility of imidazolium ring provides a scaffold for biomimetic applications such as gene expression and DNA alkylation studies [31]. Imidazolium salts can be used as coating agents to tune the hydrophobic/hydrophilic nature of nanoparticle surfaces [32]. Also, imidazolium salts have an important role as metal scavengers in aqueous solutions in environmental chemistry applications [32]. In addition to these features, imidazole functionalized macromolecules can be used as latent initiators for polymerization reactions in self-healing systems [33]. As mentioned above, the extensive applications range of imidazole groups encouraged us to synthesize imidazole end-functionalized polycyclooctene via ROMP/CM reactions. Imidazole groups are known as inhibitors (suppressing the activity of the catalyst) for Grubbs type complexes [34]. As a result of inhibition effect, the direct integration of imidazole groups through ROMP/CM reactions is not possible. For this reason, we have designed a two-step procedure combining ROMP/CM and aminolysis reaction as the post-polymerization modification reaction. Methyl-10-undecenoate (MU); an olefin obtained from renewable sources was chosen as the chain-transfer agent since MU is known to be a good cross-metathesis partner and a green platform chemical [35,36]. ROMP/CM reactions of cyclooctene in the presence of MU yielded MF and DF polycyclooctenes. Subsequent modification of MU end-capped polycyclooctenes with 1-(3-aminopropyl)imidazole in the presence of TBD afforded imidazole end-functionalized poly(COE)s. The effect of COE/CTA, solvent selectivity, catalyst ratio on the formation of mono imidazole end-functionalized (mod-MF) polycyclooctene was investigated in details. To the best of our knowledge, this is the first study that reports the synthesis of poly(COE) bearing imidazole end groups.

2. Experimental section

2.1. Materials

Unless otherwise noted all chemicals were purchased from Sigma-Aldrich and used as received. Grubbs 1st generation catalyst was purchased from Sigma-Aldrich. Chloroform and dichloromethane were dried over P_2O_5 and distilled prior to use. Toluene and THF were dried over Na wire/benzophenone and distilled prior to use. All solvents were stored under a nitrogen atmosphere. All reactions were performed under an inert atmosphere of nitrogen, using Schlenk techniques.

2.2. Instrumentation and measurements

Number average molar masses (M_n) were determined by a size exclusion chromatography (SEC) System LC-20A from Shimadzu equipped with a SIL-20A auto-sampler, RID-10A and a refractive index detector. The analysis was performed on the following column system operating on THF (flow rate 1 mL/min) at 40 °C: main-column PSS SDV analytical (5 μm, 300 mm × 8.0 mm, 10,000 Å) and a PSS SDV analytical pre-column (5 μm, 50 mm × 8.0 mm). The calibration was created using narrow linear poly(methylmethacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981,000 Da. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker GmbH 400-MHz high performance digital FT-NMR spectrometer using $CDCl_3$ as the solvent. A relaxation delay of 1 s was used during the acquisition to afford ^{1}H NMR spectra. MF and DF polycyclooctene amounts were determined by ^{1}H NMR analysis. The integration value of methyl-ester end group signal (−OCH_3, 3.66 ppm) was arbitrarily set to 1. The integration value of vinylidene proton signal of MF, appearing at 5.82 ppm, was used in the following formula to determine the MF % content of the polymer assuming that polymer mixture only consists of only MF, DF and IMF.

$$\mathrm{MF\%} = [\mathit{Integration}(5.82) \times 3] \times 100$$

IMF amount was determined using following formula:

$$\mathrm{IMF\%} = [\mathit{Integration}\ (1.66)] \times 100$$

DF amount was calculated by the formula: DF % = 100-(MF + IMF)% assuming that polymer only consists of IMF, MF and DF. M_n values were determined using integration values of olefinic proton signal (5.33 ppm) and methyl-ester end group signal (-OCH_3, 3.66 ppm) in the formula, assuming that all the polymer only consists of MF and DF poly(COE).

$$\mathrm{Mn(NMR)} = \left[\left[\left(\frac{\mathit{Integration}(5.33)}{2}\right) \div \left(\frac{\mathit{Integration}(3.66)}{3}\right)\right] \times \mathrm{MWCOE} + \mathit{MW}\mathrm{MU}\right] \times (\mathit{MF} + \mathit{IMF})\% + \left[\left[\left(\frac{\mathit{Integration}(5.33)}{2}\right) \div \left(\frac{\mathit{Integration}(3.66)}{6}\right)\right] \times \mathrm{MWCOE} + 2\mathit{MW}\mathrm{MU}\right] \times \mathit{DF}\%$$

$$\mathrm{Mn(Theo.\ )} = \left[\frac{[\mathrm{DF\%} \times \mathrm{ConversionCOE} \times \mathrm{MCOE} \times [\mathrm{COE}]0]}{\frac{1}{2}[\mathrm{MU}]0 \times \mathrm{ConversionMU}} + \frac{[(\mathrm{MF} + \mathrm{IMF})\% \times \mathrm{ConversionCOE} \times \mathrm{MCOE} \times [\mathrm{COE}]0]}{[\mathrm{MU}]0 \times \mathrm{ConversionMU}}\right]$$

MALDI ToF mass spectra were recorded by a Voyager-DE Pro MALDI-TOF mass spectrometer (Applied Biosystems, USA). Sample desorption and ionization were carried out using the 337 nm output from a pulsed nitrogen laser (Spectra-Physics, USA) at ca.