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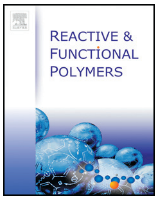

Imidazole-substituted ROMP polymers: Post-modification of poly(norbornenediester) derivatives with aminolysis reactions

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ABSTRACT

In this study, ring-opening metathesis polymerization (ROMP) polymers bearing imidazole and morpholine functionalities were synthesized using an efficient and inexpensive post-modification procedure. First, dimethyl-5-norbornene-2,3-dicarboxylate was polymerized (M_n: 130 kDa, Đ: 1.23) in the presence of Grubbs third-generation catalysts through ROMP reactions. Second, these ROMP polymers were modified using octylamine, 1-(3-aminopropyl)imidazole, and 1-(3-aminopropyl)morpholine in the presence of catalytic amounts of tin(II)hexanoate; $Sn(Oct)_2$, titanium(IV)isopropoxide; $Ti(O\text{-}i\text{-}Pr)_4$; and 1,5,7-triazabicyclo[4.4.0]dec-5-ene. Modified polymers were characterized by ^1H, ^{13}C NMR, FT-IR, differential scanning calorimetry, thermogravimetric analysis, and gel permeation chromatography. Quantitative conversions were achieved using 1-(3-aminopropyl)imidazole as a modification agent in the presence of 10% $Sn(Oct)_2$.

1. Introduction

Ring-opening metathesis polymerization (ROMP) is an efficient polymerization process to produce macromolecular structures with advanced functionalities and structural properties [1]. With the development of Grubbs first-, second-, and third-generation catalyst, the applications of ROMP reactions were extended to multidisciplinary fields, and ROMP was applied to high-tech applications such as self-healing materials [2–7]. One of the advantages of ROMP polymerization method is the polymerization of highly strained cyclic monomers with functional groups [8]. Although esters, carboxylic acids, tertiary amines, and such functional group containing monomers can be efficiently polymerized using Grubbs-type initiators, ROMP of monomers bearing primary or secondary amine functional groups is very limited [9,10]. Oxo-norbornene derivatives bearing piperazine derivatives with secondary amine groups were polymerized with a maximum yield of 37% using Grubbs second-generation catalyst [11]. One of the strategies to synthesize functional polymeric materials is the post-modification of ROMP polymers instead of using modified monomers with complex structures [12–15]. These methods offer an alternative solution, and several functionalities can be integrated to the polymer backbone. "Click" strategies including thio–bromo [12], Alder-ene [13], Diels–Alder [14], and thiol-yne coupled with Cu-catalyzed azide–alkyne [15] reactions were utilized in post-modification of ROMP polymers. ROMP polymers bearing amino functionality (such as morpholine group) can be used to synthesize novel thermo-, pH-, and salt-responsive polymeric materials [16]. As an alternative post-functionalization method, dithiocarbonate-substituted poly(norbornene) derivatives can be modified using primary amines to produce thiourethane moiety for further functionalization processes [17]. Recently, acyclic diene metathesis polymers (ADMET)-bearing pendant perfluorophenyl ester groups were modified using benzyl, octyl, allyl, propargyl, and furfuryl amines [18]. More recently, a novel post-polymerization process was developed for the modification of norbornene side-groups with functional amines in the presence of guanidine as promoter [19]. Apart from the poly(norbornene) post-modification procedures, different polymeric materials were modified using Michael's reaction [20–21], ring-opening reaction of epoxy groups [22], amide formation reactions [23], and click-reactions [24]. As observed from the literature, the common method for integrating amide functionality into polymer chains is to use pendant perfluorophenyl ester groups [18,23]. The disadvantage of this strategy is to use monomers bearing perfluorophenyl functionality. A straightforward modification procedure to transform ester groups into corresponding amide groups may extend the applications of ester-substituted polymers. In this study, an alternative post-modification procedure was developed for poly(norbornene) derivatives with ester functionalities. The motivation of this work is to develop a novel strategy to integrate imidazole functionalities on ROMP polymers to extend the applications of ROMP polymers. The integration of imidazole moiety on polymer structure is especially important because these materials are used in design and synthesis of ion exchange membranes [25], luminescence materials [26], coordination polymers [27], and anti-tumor agents [28]. The developed strategy utilizes aminolysis reactions between pendant ester group of poly(norbornene) moiety with functional

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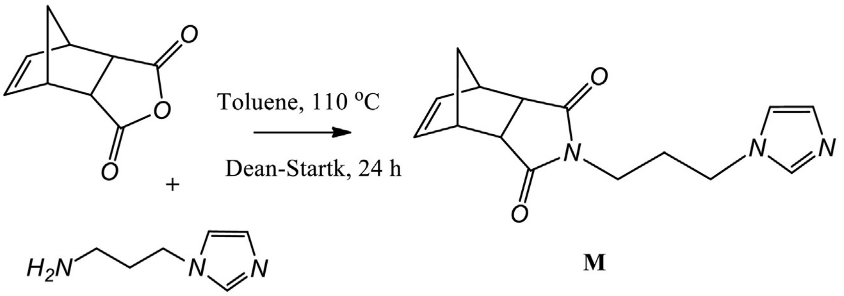


Scheme 1. Synthesis of imidazole-substituted 5-norbornene-2,3-dicarboximide derivative (M).

primary amines in the presence of $Sn(Oct)_2$, $Ti(O\text{-}i\text{-}Pr)_4$, and TBD catalysts. With this method, functional ROMP polymers bearing imidazole (P2), morpholine (P3), and octyl (P4)-substituted amide groups were synthesized efficiently.

2. Experimental

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. Grubbs first- (G1), second- (G2), and third-generation (G3) catalysts and Hoveyda-Grubbs second-generation analog (HG2); dichloro[1,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene](2isopropoxyphenylmethylene)ruthenium(II) were purchased from Sigma-Aldrich. 1-(3-aminopropyl)imidazole (denoted as A1), 1-(3-aminopropyl)morpholine (denoted as A2), 1-octylamine (denoted as A3) and diallylamine (denoted as A4) were purchased from Sigma-Aldrich and used as received. THF was dried under Na wire/benzophenone and stored under an inert atmosphere of nitrogen. ^1H 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. GC–MS analyses were performed with a Shimadzu GC–MS 2010Plus using a Restek Rxi-5Sil column (30 m × 0.25 mm × 0.25 μm) and temperature range of 50–320 °C. Molecular weights were determined with a gel permeation chromatography (GPC) 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.

2.1. Synthesis of N-(3-aminopropyl)imidazole-5-norbornene-2,3-dicarboximide (M)

A three-necked 250-ml flask was charged with endo-5-norbornene-2,3-dicarboxylicanhydride (5 g, 30.50 mmol) in 40-ml dried toluene. To this solution, 1-(3-aminopropyl)imidazole (37.0 mmol, 4.42 ml) was added in one portion, and Dean-Stark apparatus was connected to flask and reaction mixture was stirred at 110 °C for 24 h. After 24 h, the reaction mixture was cooled and poured to cold pentane. Resulting suspension was filtrated and washed several times with methanol/hexane to remove unreacted starting materials. White solid was dried under vacuum and characterized by ^1H, ^{13}C NMR, and GC–MS.

^{1}H NMR (**400 MHz, CDCl$_3$**) δ 7.46 (s, 1H), 7.02 (s, 1H), 6.91 (s, 1H), 6.08 (s, 2H), 3.86 (t, $J = 4.2$ Hz, 2H), 3.36 (t, $J = 4.6$ Hz, 2H), 3.27–3.16 (m, 2H), 2.02–1.82 (m, 2H), 1.72 (d, $J = 10.2$ Hz, 1H), 1.52 (d, $J = 10.2$ Hz, 1H).

^{13}C NMR (**101 MHz, CDCl$_3$**) δ 177.68, 137.15, 134.49, 129.69, 118.67, 52.36, 45.78, 44.91, 44.54, 35.57, 29.25

MS (EI, *m/z*): $[M^+] = 271$.

2.2. Synthesis of 2,3-dimethyl-5-norbornene-2,3-dicarboxylate (M1)

A three-necked 250-ml flask was charged with endo-5-norbornene-2,3-dicarboxylicanhydride (5 g, 30.50 mmol) and excess methanol (50 ml, 1.23 mol). After stirring the mixture for 5 min at room temperature, concentrated H_2SO_4 (1 ml) was added dropwise, and the reaction mixture was taken to an oil bath and stirred at 70 °C under reflux for 24 h. Methanol was evaporated under high vacuum, and the resulting liquid product was diluted with diethyl ether and passed through a plug of basic alumina. The mixture was then extracted with a saturated $NaHCO_3$ solution (100 ml) and then with water (50 ml × 3). After evaporation of diethyl ether, M1 was isolated in 90% yield as colorless liquid and characterized by ^1H, ^{13}C NMR, and GC–MS.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.24 (s, 2H), 3.59 (s, 6H), 3.35–3.24 (m, 2H), 3.16 (m, 2H), 1.45 (d, $J = 10.2$ Hz, 1H), 1.35 (d, $J = 8.6$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.82, 134.81, 51.40, 48.58, 47.93, 46.17.

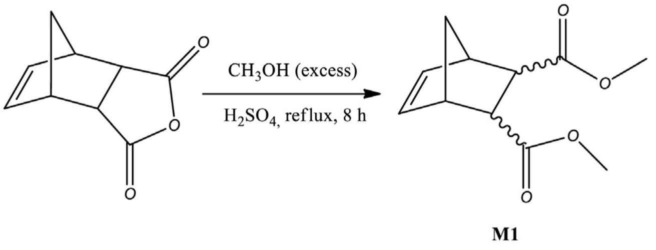
MS (EI, *m/z*): $[M^+] = 210$.

2.3. Synthesis of poly(M1) by ROMP reactions

A reactor was charged with M1 (4.76 mmol, 1 g) and Grubbs third-generation catalyst (0.0476 mmol, 0.042 g), and stirred at room temperature for 1 h. After 1 h, the reaction was terminated by the addition of ethylvinyl ether (1.90 mmol) in 5-ml THF and stirred for 30 min. **P1** was isolated by pouring the resulting solution to cold methanol. (M_n: 130 kDa, Đ = 1.23). Polymer was isolated in 95% yield.

2.4. Representative procedure for post-modification of poly(M1) with primary amines (A1–3)

Poly(M1) (0.20 g, M_n: 130 kDa, Đ = 1.23) was dissolved in 2-ml THF in a Schlenk reactor. Primary amine A1–3 (2.30 mmol) in 1-ml THF was added (1.2 mol equivalent amine was used per ester group) to reactor



Scheme 2. Synthesis of M1.