



# Structurally diverse polymers from norbornene and thiolactone containing building blocks

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## ABSTRACT

A wide set of norbornene-derived polymers with a diversity in backbone and side chain structures has been prepared based on norbornene building blocks that also include a thiolactone group. For this purpose, two thiolactone monomers with differently substituted norbornene moieties were synthesized and their reactivity compared using three different polymerization strategies. First, their potential for amine-thiol-ene polymerization was evaluated using different amines, solvents and initiator concentrations in order to screen their influence on the molecular weight and glass transition temperature. Free radical (co-)polymerization and ring-opening metathesis polymerization were also applied and the obtained polymers were submitted to post-polymerization modification. The results showed that only the monomer 5-norbornenemethyl thiolactone carbamate results in polymer formation under the tested conditions. The obtained compounds were characterized by SEC, TGA, DSC and NMR.

## 1. Introduction

Norbornene and its derivatives are generally known as starting compounds for industrial olefin polymerization processes. This class of monomers can be polymerized using different approaches, i.e. ring-opening metathesis polymerization (ROMP), free radical polymerization (FRP) and transition metal catalyzed vinylogous 1,2-polymerization (Scheme 1). Norbornene is mostly used in ring-opening metathesis polymerization (ROMP), resulting in high transparency polymers with high glass transition temperature ( $T_g$ ) and good electric and resilience properties [1–3]. Applications can be found in electronics, as oil absorber and other engineering sectors [4]. On the other hand, transition metal-catalyzed 1,2-polymerization (vinyl insertion) leads to rigid polymers with exceptional thermal and physical properties [5]. Norbornene has many other properties and can also be used in polymer modification [6]. However, only lately, involvement in the formation of more complex polymer structures [7–9], e.g. bio-mimicking structures [10], has been investigated.

Substituted norbornenes are also widely applied in thiol-ene chemistry as a result of their high reaction rate in comparison to other types of double bonds [11]. However, the direct use of thiol groups has some drawbacks as they are generally prone to oxidation, lead to disulfide formation, have a low shelf-life, often have a displeasing odor

and they can react as transfer agent in radical polymerization. Therefore, we proposed a possible solution to circumvent the issues related to thiols by making use of thiolactone chemistry. This chemical approach has become more and more important in contemporary polymer research [12], combining the convenience and safety of protected thiols [13] with the advantages and multiplicity of ‘thiol-X’ chemistries [14] as well as straightforward one-pot double modification reactions (Scheme 2) [15,16].

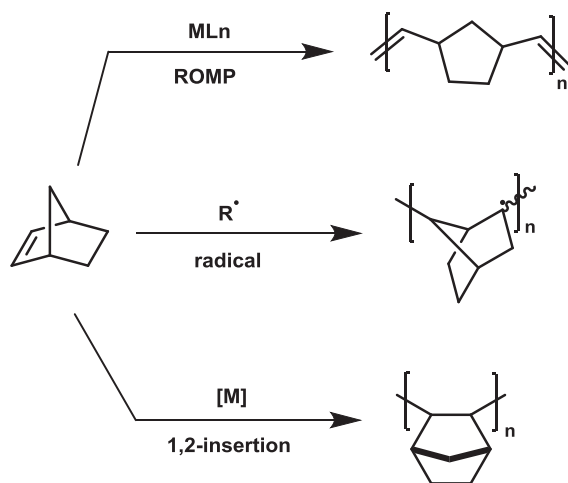
Last but not least, because of their up-scalable synthesis procedure [17], safe handling and sustainable origin, thiolactone derivatives found vast applications in sequence-controlled polymerization [18,19], end-group (double) modification [20] and the build-up of sophisticated polymer topologies [21–25]. For instance, lately, functional materials, such as coatings [26], polyampholytes [27], theranostics [28] and hydrogels [29], were prepared using the thiolactone chemistry platform.

In the present study, combination of norbornene polymerization and the versatility of thiolactone chemistry has been envisioned with the aim to provide norbornene-derived polymers with a diversity in backbone and side chain structures, which could result in novel application opportunities for norbornene-derived polymer materials.

In order to associate both norbornene resilience and thiolactone modifiability, two norbornene thiolactone derivatives were synthesized based on adapted literature protocols (Scheme 3) and tested with

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**Scheme 1.** Three polymerization methods for polymerization of norbornene and derivatives, including ring-opening metathesis polymerization (top), free radical polymerization (middle) and transition metal catalyzed vinylogous 1,2-polymerization (bottom).

regard to their ability to be polymerized using different techniques such as ROMP or thiol-ene polymerization (Fig. 1).

## 2. Results and discussion

For amine-thiol-ene (ATE) and free radical polymerization (FRP) experiments,  $M_1$  derived from pure *exo*-5-norbornene-2-methanol was used (Scheme 3) while for ROMP and comparative experiments in amine-thiol-ene polymerization,  $M_1$  based on an *endo/exo* mixture of 5-norbornene-2-methanol was used to reduce costs of the starting materials and to check macroscopic differences of the resulting polymers.

### 2.1. Amine-thiol-ene polymerization

Thiolactone-based polymers built up using amine-thiol-ene polymerization have extensively been described [18,24,26,27,32]. The choice of the amine group dominantly influences the physical properties of the polymers, such as the  $T_g$  [26,32], while it also affects molecular weight [32,33]. Following a generic procedure (*vide infra*), only 5-norbornenemethyl (2-oxotetrahydrothiophen-3-yl) carbamate ( $M_1$ ), could successfully be polymerized to result in polymer P1 (Scheme 4). LC-MS revealed that the aminolysis of  $M_2$  does not take place at the chosen conditions (see Fig. S1).

Calculations reveal a higher electron density in the double bond of  $M_2$  than in norbornene and  $M_1$  (Fig. S1). This observation is in compliance with the fact that electron-deficient olefins are more reactive in thiol-ene additions and free radical polymerizations [11], while for ROMP, only ring strain is of significance and, thus, no major influence in reaction speed should be observed.

The comparative amine-thiol-ene studies were performed in 1 M monomer solution in THF, using 1.1 eq. of the amine. Since most amine-thiol-ene reactions use high amounts of radical initiator for monomers that are less reactive than norbornene [26,32,33], 3 mol% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator was

considered as a sufficient quantity.  $T_g$ 's were measured by DSC-analysis after one completed heating/cooling cycle.

In case of the pure *exo*-substituted norbornene derivative  $M_1$ , the molecular weights ranged from 4650 to 32,600 g·mol<sup>-1</sup> (in THF) using *n*-propylamine and ethanolamine respectively. During all polymerizations, amine compounds bearing hydroxyl groups (ethanolamine and 3-propanolamine) formed a precipitate within a few minutes of irradiation, while all other polymers stayed in solution. This can be explained by a strong hydrogen bond interaction of those specific polymers. Because of the precipitation, polymerization experiments with ethanolamine and propanolamine were not further investigated. Independent of the solvent, volatile amine derivatives, such as *n*-propylamine gave irreproducible results with average molecular weights ranging between 1000 and 8600 g/mol. After a solvent study (*vide infra*), syntheses optimized for molecular weight were performed in chlorobenzene (PhCl) and the results are displayed in Table 1.

The results showed that for the *endo/exo* mixture of  $M_1$ , the molecular weights, in general, were slightly lower than those obtained for the pure *exo*- $M_1$ . A possible explanation might be the substituent position on the norbornene moiety of the molecule, which potentially increases steric hindrance of the double bond. A decreased reactivity of norbornene derivatives with polar *endo*-substituents has been reported in literature [34], however, this behavior is related to a different polymerization mechanism and is not applicable in this case.

The  $T_g$ -values (see Table 1 and Fig. S2) of P1 fluctuate between 59 °C (*n*-octylamine) and 95 °C (*n*-propylamine), which is a significant increase in comparison to other thiolactone-based polymers [26,32]. On the other hand, the unusual integration of the norbornene moiety into the backbone, which happens on the 2,5- or 2,6-position (Scheme 4), and a rather large linear segment between the norbornyl units prevent  $T_g$ -values higher than 200 °C, as reported in literature for some norbornene-derived polymers [1,5].

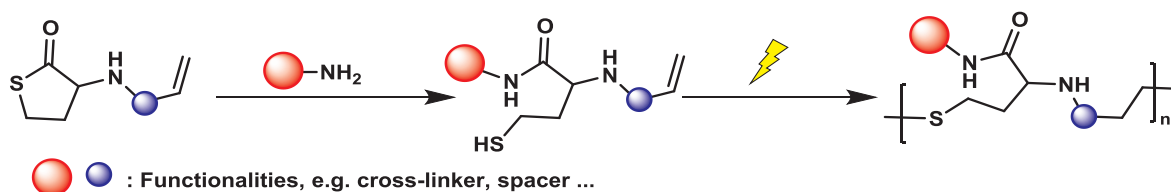
Next, a solvent study was conducted, using 0.5 and 1 M solutions in various solvents and 1.1 eq. *n*-octylamine. To increase the theoretical molecular weight and, thus, enhance the influence of the solvent, 1 mol % DMPA photoinitiator was chosen (Table 2).

The analyses showed that solvents with a medium polarity result in higher molecular weights under given conditions. Since both monomer and polymer are soluble in all investigated solvents except acetonitrile, the influence can be described to the solvation of the reactive species during the reaction, in which less polar solvent molecules favor a homolytic cleavage of the S–H bond. As mentioned before, slightly higher molecular weights can be observed when using the pure *exo*-derivative of  $M_1$ .

### 2.2. Free radical copolymerization

The copolymerization of norbornene (and derivatives) with acrylates has been reported multiple times in literature [4,36]. Thus, free radical copolymerization (FRCP) of  $M_1$  and  $M_2$  with methyl acrylate (MA) was conducted with four different ratios of norbornene derivative and comonomer (0, 50, 75, 100% of methyl acrylate) (Table 3). While the copolymerizations of  $M_1$  resulted in polymers, homopolymerizations of both norbornene thiolactone monomers as well as the copolymerization of  $M_2$  were not successful (Scheme 5).

As reported in the literature, radical polymerization of norbornene



**Scheme 2.** Amine-thiol-ene polymerization: Initial thiolactone aminolysis triggers thiol release, which subsequently is used in situ for thiol-ene polymerization.

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