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Use of a Renewable and Degradable Monomer to Study the Temperature-Dependent Olefin Isomerization during ADMET Polymerizations

Patrice A. Fokou and Michael A. R. Meier*

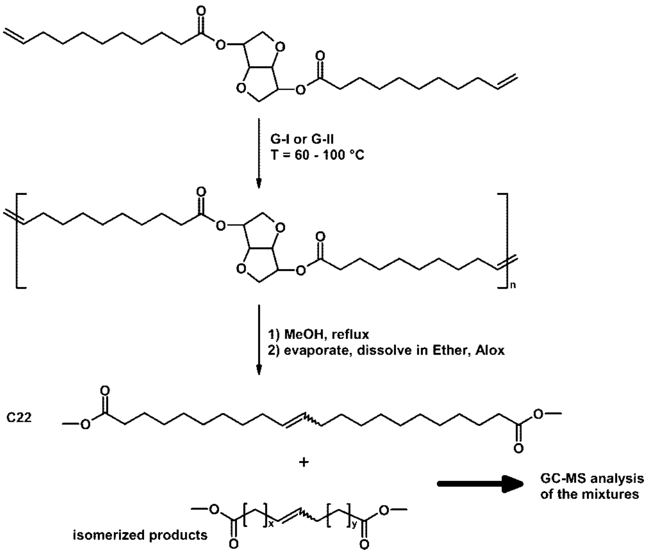
University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven, Constantiaplatz 4, 26723 Emden, Germany

Received November 5, 2008; E-mail: michael.meier@fh-oow.de

Acyclic diene metathesis (ADMET) polymerization has developed into a very versatile technique for the preparation of a variety of macromolecular architectures, including linear polymers,[1,2] polymers with a defined degree of branching,[3,4] and telechelics,[5−8] as well as block-copolymers.[6,8] Most recently, the technique was also applied to monomers with a functionality >2, thus resulting in hyperbranched macromolecules from AB_2, AB_3, and A_3 monomers with B_1 chainstoppers, respectively.[9,10] Despite this success, it is known from low molecular weight model compounds that especially second generation olefin metathesis catalysts show a temperature dependent double-bond isomerization activity.[11,12] The mechanism leading to the formation of the ruthenium-hydride species that are responsible for these isomerizations is discussed in detail in the literature.[13] Moreover, phenylphosphoric acid, benzoquinones, and other additives were shown to efficiently suppress these isomerizations.[14,15] A detailed overview of nonmetathesis side reactions of ruthenium-based olefin metathesis initiators can be found in the literature.[16] Such side-reactions were, for instance, also observed during organic synthesis procedures and studied in more detail for a ring-closing metathesis, double-bond isomerization reaction sequence.[17−19] Here, the actually undesired isomerization side reaction has been successfully exploited for the synthesis of a variety of useful cyclic building blocks in a tandem catalytic reaction. However, only a few reports studied the presence of such side-reactions during ADMET polymerizations.[20−22] MALDI-TOFMS and NMR were used for these studies having the disadvantage that only oligomers could be investigated in the case of MALDI and that the NMR investigations were only possible because of the presence of different chemical shifts of isomerized and nonisomerized structures.

Owing to the lack of knowledge of isomerization side-reactions present during ADMET polymerization conditions, we developed a new approach for the investigation of these side reactions in a systematic fashion. Therefore, we prepared the degradable monomer **1**, polymerized it under frequently applied ADMET conditions with the Grubbs first (**G-I**) and Grubbs second (**G-II**) generation catalysts, and subsequently degraded the resulting polyesters by transesterification with methanol in order to be able to investigate the nature and the amount of side-reactions that occurred during the polymerizations by GC−MS (cf. Scheme 1). This strategy does not display the disadvantages of the methods used thus far and therefore enables a straightforward and reproducible assessment of the side reactions present in a quantitative fashion. Moreover, it is worth mentioning here that the monomer used for this study, dianhydro-D-glucityl diundec-10-enoate **1**, is a yet unknown monomer that is 100% renewable and can be obtained from isosorbide and fatty acid derivatives. Isosorbide can be obtained from glucose by hydrogenation to sorbitol and subsequent double dehydration and was already used as a renewable building block for several applications,[23,24] whereas 10-undecenoic acid is obtained from castor oil and is a very promising building block for polymers from fatty acid derivatives.[25,26] Table 1 summarizes the results of all performed polymerizations. Typical ADMET polymerization conditions were applied and thus polymerizations were run for 5 h with 1% of the respective catalyst at different temperatures ranging from 60 to 100 °C. In all cases the reaction mixtures were deoxygenized with nitrogen at room temperature before the reaction was performed. Only for polymers **P3** and **P9** was continuous nitrogen purging applied throughout the polymerization to investigate the effect of this parameter on the molecular weight and isomerization side reactions of this often applied reaction parameter. Generally, moderate molecular weights were obtained for the investigated renewable monomer and no further increase in molecular weights was observed after 5 h of reaction time. It is worth mentioning that the molecular weights reported in Table 1 are relative to poly(styrene) and that our experience with similar monomers suggests that the molecular weights are most likely underrepresented by a factor of ~1.5.[8]

Scheme 1. Concept of the Synthesis of 100% Renewable Polymers, Their Subsequent Degradation, and Investigation of the Degradation Products by GC−MS in Order to Evaluate the Isomerization Side Reactions Present during the ADMET Polymerizations



Concerning the isomerization side reactions, the first generation Grubbs catalyst (**G-I**) generally showed very little isomerization, independently of the applied temperature or applied purging. Nevertheless, for **P1**−**P4** we could observe small amounts of an α,ω-diester with a chainlength of only 19-C atoms leading to the conclusion that even with **G-I** the isomerization cannot be completely avoided. Only at high temperatures of 100 °C and above were large amounts of side reactions observed by GC−MS. However, in this case the side products were not the expected α,ω-diesters and could not be identified by GC−MS. Therefore, other,

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yet unidentified, side-reactions take place and ADMET reactions with **G-I** should be performed at temperatures below 100 °C if defined polymer architectures are desired.

Table 1. Synthesis and Characterization Details of the Prepared Polymers

	C[a]	*T*[b]	N_2 purging[c]	M_n[c]	PDI[d]	% iso[e]
P1	G-I	70 °C	no	4400	1.57	3
P2	G-I	80 °C	no	4750	1.56	4
P3	G-I	80 °C	yes	6600	1.77	3
P4	G-I	90 °C	no	5450	1.69	3
P5	G-I	100 °C	no	5000	1.61	42[f]
P6	G-II	60 °C	no	5600	1.65	48
P7	G-II	70 °C	no	6000	1.71	49
P8	G-II	80 °C	no	6100	1.61	69
P9	G-II	80 °C	yes	8400	1.75	76
P10	G-II	90 °C	no	6200	1.65	66

[a] All polymerizations were performed with 1% of the respective catalyst for 5 h. [b] Temperature. [c] Continuous nitrogen purging during polymerization. [d] GPC in THF with poly(styrene) calibration. [e] The % amount of isomerized diesters observed with GC−MS after transesterification of the respective polymer. [f] Unidentified side-products.

In the case of the second generation Grubbs metathesis catalyst (**G-II**) the situation is completely different. Isomerizations were already detected at low temperatures of 60 °C and less. An increase of the temperature continuously increased the amount of isomerization reactions. Moreover, the continuous purging of nitrogen during the ADMET polymerization, as it is usually applied to remove the ethylene from the reaction mixture, did not only significantly increase the molecular weight of **P9** (if compared to **P8**) but also led to the highest amount of isomerization observed. This effect is clearly observed if the GC−MS traces of different transesterified products are compared to each other (Figure 1). Figure 1A depicts the result of **P3**, where almost only the expected α,ω-diester with a chainlength of 20-C atoms is observed. Figure 1B on the other hand depicts the result of **P7** with 5 different α,ω-diesters present (C17−C21). These are a result of double bond isomerizations of the monomer and of the polymer repeat units and subsequent secondary metathesis reactions of the isomerized double bonds (see Scheme S1, Supporting Information for further details). The situation is even more dramatic in the case of **P9** (Figure 1C), where at least 9 different α,ω-diesters with a C-chainlength ranging from 16 to 23 were identified by GC−MS.

The results shown in Figure 1 clearly visualize that a large amount of side reactions are present and that the resulting polymers are quite irregular if the second generation catalyst is utilized. This fact was further evidenced in the thermal behavior of the polymers: **P9**, the polymer with the highest degree of isomerization, showed a melting point (M_p) of 17.4 °C, whereas **P1** showed a higher M_p of 55.8 °C due to its higher regularity.

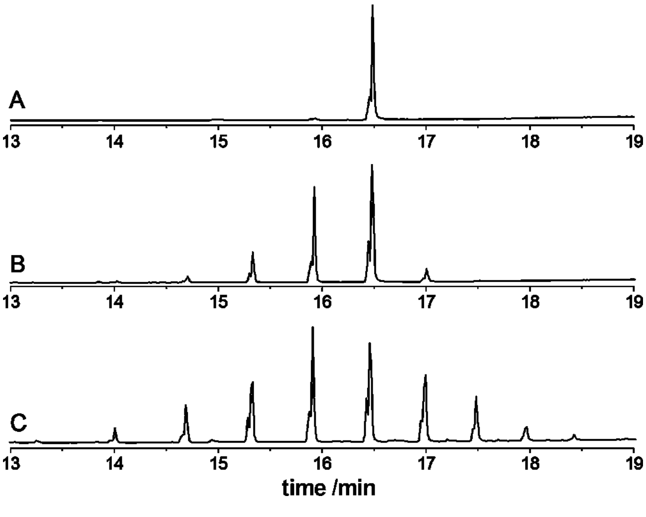

Figure 1. GC−MS investigation of the transesterification products of **P3** (A), **P6** (B), and **P9** (C).

In summary, we have described the first quantitative method to study olefin isomerization reactions during ADMET polymerizations and applied it to a monomer from renewable resources. We could show that the extent of isomerization side reactions is largely dependent on the type of catalyst, the reaction temperature as well as other reaction conditions such as a continuous nitrogen purging as it is frequently applied during ADMET polymerizations. We could also show that the amount of isomerization reactions influences polymer properties, such as melting temperatures. Thus, this knowledge might be applied in the future for the tailoring of a polymers structure and therefore also its properties. More generally, these results might be useful for the development of different kinds (e.g., RCM, CM, and others) of more selective olefin metathesis reactions.

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Supporting Information Available: Experimental procedures, analytic data, GPC traces, double bond isomerization mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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