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ADMET-Polymerization of Dienes based on Sustainable Chemicals

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Summary: Eugenol and isoeugenol were used as natural based starting materials to prepare unsaturated polyethers and polycarbonates. The polymerization was achieved in a two step procedure exploiting the orthogonal phenol and ene functionalities. Thus diene terminated ethers and organic carbonates were obtained from eugenol and isoeugenol, and subjected to ADMET polymerisation using Grubbs 2nd generation catalyst[1]. The obtained unsaturated polymers have molecular weights ranging from 2.700 to 32.000 g/mol. Molecular weight build up was partly restricted by the low solubility of the products.

Keywords: Eugenol; Isoeugenol; macromonomers; metathesis; polymerization; Sustainable Chemicals

Introduction

We recently started a program with the objective to use natural based molecules with two orthogonal functionalities to prepare polymers through a condensation or addition polymerization. The interest in the topic is also driven by the fact that exploiting non simple chemicals from natural sustainable resources may become market competitive with fossil sources that are in a negative discussion and held responsible for climate change and are associated with pollution. Typical example is vanillin that has an aldehyde and phenolic group.[2] Further examples are eugenol and isoeugenol, which are the subject of this study. *Cloves* and *Petunia* are two widespread plants – clove extracts consist of 85% eugenol – containing the chemicals.[3] Eugenol can be transformed by strong alkaline solutions or metal catalysts to isoeugenol.[4,5] This availability and the perfect bifunctionality make them to interesting candidates for a route to sustainable polymers.

We thus synthesized dimeric dienes from the compounds involving the phenolic moiety. The required high purity monomers could be obtained through reactions that are cheap and with standard reactants in high yields. Polymer formation was achieved by using the step growing Acyclic-Diene-Metathesis (ADMET).[6,7] Metathesis reaction of dienes is central part of the polymerization and an attractive route to unsaturated polymers: it does not need - in contrast to condensation polymerization - consideration of an exact 1:1 stoichiometry. Desired polymer properties are high molecular mass (M_n) – up to 20 000 g/mol – and a polydispersity index (PDI) between 2 and 3.

Monomer Synthesis

Eugenol and isoeugenol were transformed into dienes through optimized, simple, large scale syntheses. The linkage of two molecules of eugenol and isoeugenol with an alkyl chain, carbonate or diethylene glycol was reached a straightforward approach using electrophilic compounds to obtain monomers suitable for an ADMET-polymerization (Table 1). The syntheses are readily performed on a 100 g scale. The dienes **1-4** can generally be recrystallized from ethyl acetate to high

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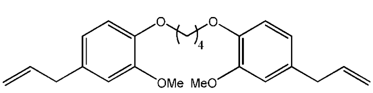
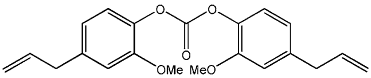
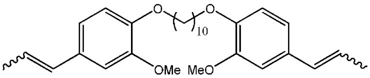
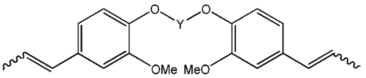
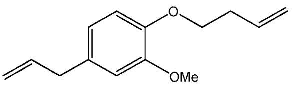
Table 1.
Synthesis of dienes using isoeugenol and eugenol as starting material.

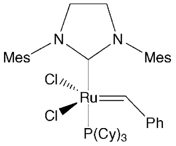
Monomer	Reactant	Mp. [°C]	Purity [%]	Yield [%]
 **1**	Dibromobutane[a)]	102	>99.5	90
 **2**	Triphosgene[b)]	83	>99.5	88
 **3**	Dibromodecane[a)]	115	>99.5	76
 **4** Y – $(CH_2)_2O(CH_2)_2$	Diethyleneglycol ditosylate[c)]	93	99.3	64
 **5**	1-Bromo-3-butene[a)]	−12	>99.5	80

[a)] 1 eq. Isoeugenol/eugenol and the electrophile were dissolved in mixture of acetone/water (2:1), 1.2 eq. KOH (33% water solution) added dropwise and followed by refluxing for 16 h.
[b)] Eugenol added dropwise to 12 eq. pyridine and 0.3 eq. triphosgene at 0 °C, stirred 2 h at 0 °C.[8]
[c)] Isoeugenol, Diethyleneglycol ditosylate and 1.2 eq. K_2CO_3 were suspended/dissolved in acetone and the mixture heated at reflux for 16 h.

purities in high yields. In addition, a diene was prepared from 4–bromobutene and eugenol and purified by column chromatography.

ADMET Polymerizations

Grubbs 2nd generation metathesis catalyst **6** was used for the ADMET reactions in concentrations from 0.2 mol% up to 3.0 mol%. ADMET polymerizations with **1-4** were first performed in a melt under solvent free conditions with reduced pressure to dynamically remove the olefin byproducts (in majority ethylene).[9] Due to the high melting points of the monomers the reaction temperatures of the melt were incompatible with the thermal stability of the catalyst. Additionally, with increasing conversion the mixture became highly viscous and solids were formed. Therefore these reactions did not lead to polymers with high molecular masses.



Cy = Cyclohexyl
Mes = Mesityl

6

Bulk polymerizations of **5** (melting point of −12 °C) were achieved to high conversions. Offline NMR spectroscopy was used to follow the reaction. It was observed that the reaction rate was temperature–dependent (Figure 1). A conversion of more than 95% could be obtained in about 10 h at 100 °C, whereas at lower temperatures the conversion subsides probably because of slow deactivation of the catalyst. Thus, a faster initial reaction at 100 °C with a faster deactivation yields better results than a slower reaction at lower temperature with a slower catalyst deactivation. Conversions

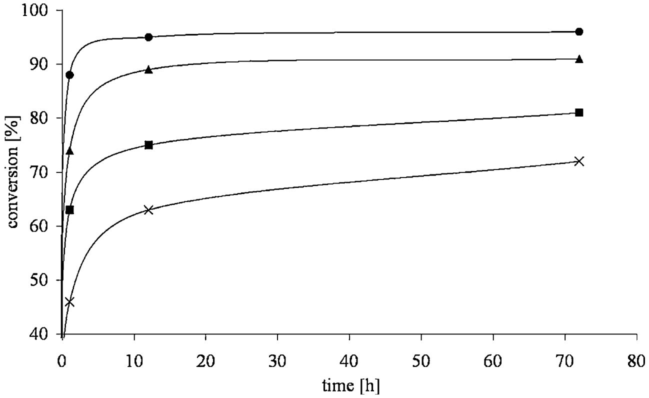


Figure 1.
Bulk reaction of monomer **5** at various temperatures (0.2 mol% catalyst, reaction at 10 mbar dynamic vacuum); ● = 100 °C, ▲ = 80 °C, ■ = 60 °C, × = 40 °C.

exceeding approx. 95% could not be achieved easily because of the high viscosity of the resulting reaction mixture.

In order to induce the transformation of **1-4** into unsaturated polymers, solution polymerizations were carried out in toluene at 80 °C and in dichlormethane and chloroform under reflux. The catalyst concentration was between 0.2 and 3.0 mol%. It was observed that isoeugenol derivatives with smaller alkyl-chains - butyl and hexyl - gave insolvable stilbene oligomeres (di and trimers) that precipitated from the solution and were protected from further conversion. Oligomers derived from longer alkyl chains and diethylene glycol bridged isoeugenol had a substantial higher solubility and could be polymerized to higher molecular masses. The results of the polymerizations are summarized in Table 2.

Isomerization

In ADMET reactions of eugenol based monomers **1**–**2** and **5** with Grubbs 2nd generation catalyst **6**, a partially isomerization of the phenyl allyl group was readily observed by NMR spectroscopy (Figure 2). The concentration of isomeric products increased with increasing reaction time (Figure 3). A reversal back to an allyl group did not occur, which is probably due to the thermodynamical stability of the resulting styrene derivative and the

Table 2.
Results of the ADMET-Polymerizations.

monomer	solvent	Catalyst conc. [mol%]	mol mass[c] (M_n) [g/mol]	Conversion[d] [%]	PDI[c]
3	DCM	0.5[a]	17600	99.9	3.0
3	chloroform	1.0[a]	4800	98.1	2.1
4	DCM	0.5[a]	32100	99.8	3.0
4	chloroform	1.2[a]	4200	96.7	1.7
5	chloroform	3.0[d]	20164	99.9	3.5
6	chloroform	3.0[d]	7300	99.8	2.7
7	neat	0.2[a]	6200	96.0	1.6

1.0 g monomer with catalyst **6** in 20 mL solvent heated reflux for 72 h.
[a] addition of the catalyst in one batch.
[b] dropwise addition of 0.75 mol% catalyst at t = 0 h respectively at 8 h, 16 h and 24 h.
[c] characterization by GPC (polystyrene calibration in chloroform), not corrected.
[d] determined by NMR spectroscopy.

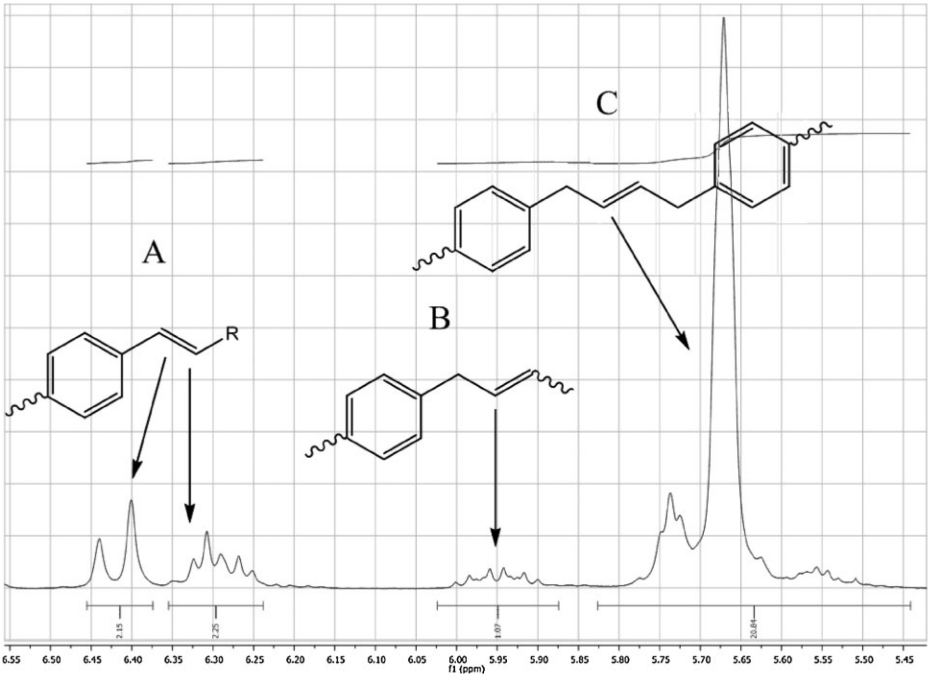


Figure 2.
NMR-spectrum of a typical ADMET mixture. A: Signals of isomerized converted allyl-groups, B: non-isomerized allyl-groups of the monomer and oligomers, C: direct ADMET products.

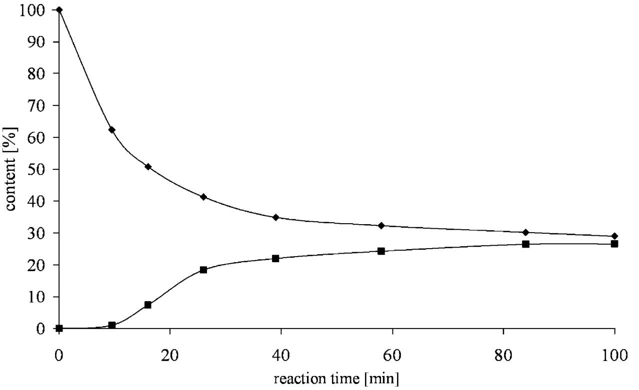


Figure 3.
Isomerization of eugenol; Conditions: 1.0 g eugenol with 0.05 mol% Grubbs 2nd generation catalyst **6**. Analyzed by gas chromatography; ◆ = content eugenol monomers, ■ = content isoeugenol monomers.

kinetically faster subsequent metathesis to stilbene and styrene oligomers. The resulting unsaturated, amorphous and transparent polymer did not crystallize and started to decompose at 220 °C.

Conclusions

It is shown that the ADMET polymerization of dienes derived from natural products is possible. The syntheses of the diene monomers were achieved in high yields and the products could be purified up to a necessary level for a step polymerization without much effort. ADMET polymerizations were performed in bulk and in solution with Grubbs 2nd generation catalyst. Polymerizations of isoeugenol derivates were possible with long alkyl- and ethylene–glycol chain bridges to high molecular mass. Also due to the observed isomerization of the allyl group, eugenol containing monomers gave amorphous transparent and soluble polymers. Notable, bulk reactions with compound **5** were possible at high temperatures with high activities and good conversions. Thus new interesting pathways for sustainable polymer products were found.

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