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A Synthetic Approach to Homologous Blockcopolymers

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Summary: Blockcopolymers of 3-methyl-3-phenylcyclopropene and norbornene derivatives were synthesized via ROMP. The crossover reaction during ROMP blockcopolymerization was successfully monitored via MALDI-TOF MS in agreement with GPC and NMR-methods.

Keywords: blockcolymers; crossover reaction; cyclopropene; MALDI-TOF MS; ROMP

Introduction

ROMP has been proven as a powerful tool for generating blockcopolymers. Sequential addition of two or more monomers leads to di- and triblockpolymers. Cyclopropenes represent a highly strained class of monomers, which should make them suitable for homo- and blockcopolmers. Despite this fact their polymerization has been reported rarely.[1,2] We recently have reported on the homopolymerization of cyclopropenes via ROMP and their subsequent hydrogenation to generate linear polyolefins which differ from their vinyl counterparts by one ore more methylene units.[2] The present publication reports on the generation of blockcopolymers of cyclopropene-monomers and their study of the respective crossover-reaction via MALDI-TOF MS.

Experimental Part

Instrumentation

Nuclear-magnetic-resonance ^{1}H-NMR spectra were performed on a Varian Gemini 200 or 400 MHz FT-NMR spectrometer and MestRec (4.9.9.9) was used for data interpretation. GPC analysis was done on a Viscotek VE2001 system using THF as an eluent with a flow rate of 1 ml/min and injection volume of 100 μL. Polystyrene standards were used for conventional external calibration using a Viscotek VE3580 refractive index detector. Positive ion MALDI-TOF MS (Matrix Assisted Laser Desorption/Ionisation-Time of Flight) measurements were performed on Bruker Autoflex-III instrument equipped with smart ion beam laser. Measurements were carried out in linear mode. Samples were prepared from THF solution by mixing matrix (20 mg/mL), polymer (5 mg/mL), and salt (20 mg/ml solution) in a ratio of 100:40:1. Dithranol (1,8-dihydroxy-9(10*H*)-anthracetone, Aldrich 97%), was used as matrix. Lithium trifluoroacetate (Aldrich, 99.8%) salt were added for ion formation.

Solvents/reagents/materials Catalysts **I**, **II** and **III** were obtained from Sigma-Aldrich. Dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) were freshly distilled over CaH_2 and degassed with argon prior to use. All other reagents were purchased from Sigma Aldrich (Germany) and were used without further purification. *Endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid dimethylester (monomer **A**) and *endo*,*exo*-bicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic acid di-*tert*-butylester (monomer **B**) were prepared according to the procedure adopted from reference.[4] *Endo*,*exo*-bicyclo [2,2,1]-hept-5-ene-2,3-dicarboxylic acid-bis-O-

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2,2,6,6-tetramethyl piperidinoxyl-ester (monomer **T**) was prepared according to references.[5,6] *Exo-N*-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-10-oxa-4-azatricyclodec-8-ene-3,5-dione (monomer **D**) was prepared in a two-step procedure according to references;[7] 3-methyl-3-phenylcyclopropene (monomer **E**) was prepared according to literature procedures.[8,9]

General Synthesis Procedure of Block Copolymerization

As example for the synthesis of the various blockcopolymers the procedure for BCP-$\mathbf{A}_{20}\mathbf{E}_{20}$ is given below: monomer **A** (33.1 mg, 0.16 mmol) in 0.5 ml of CH_2Cl_2 was added to the catalyst **I** [Grubbs catalyst 1st-generation, $RuCl_2(PCy_3)_2(CHPh)$] (6.48 mg, 0.0078 mmol) dissolved in 1 ml of CH_2Cl_2 in a heated and argon-flushed glass vial equipped with a magnetic stir bar. The polymerization was carried out at RT for 1 h till all of the monomer **A** was consumed. Monomer **E** (20.8 mg, 0.16 mmol) as a solution in 0.5 ml of CH_2Cl_2 was then added to the above reaction mixture and stirred for 24 h at RT. The polymerization was quenched by adding cold ethyl vinyl ether. The produced polymer was isolated by precipitating in to cold methanol or alternatively, the polymer was isolated by column chromatography (SiO_2). Finally the product was dried under high vacuum overnight to yield 35 mg (65%) of BCP-$\mathbf{A}_{20}\mathbf{E}_{20}$.

Results

The blockcopolymerization of 3-methyl-3-phenylcyclopropene (**E**) was conducted with the norbornene and oxanorbornene derivatives **A**, **B**, **D** and **T** (Figure 1) using the Grubbs catalysts of the 1st-, 2nd- and 3rd-generation. Monomer **E** displays its best polymerization results with Grubbs catalyst 2nd-generation.[2] Polymerization of **E** with Grubbs catalyst 1st or 3rd-generation is slower than with Grubbs catalyst 2nd-generation, generating low molecular weight polymers (2000–4000 $g mol^{-1}$) with a PDI 1.5-2.1. Except for monomer **T**, the monomers **A**, **B** and **D** display their best results with Grubbs 1st or 3rd-generation catalysts. Polymerisation of these monomers with Grubbs catalyst 2nd-generation leads to high molecular weight polymers and lack of control with respect to the molecular weight. As homopolymer poly-**E** (above a molecular weight of ~ 3000 g/mol) is only poorly soluble in common solvents at room temperature (Table 1, entry 4), this is assumed as reason for the incomplete crossover-reactions and the slow-down of the propagation.

In order to circumvent this problem two strategies were applied: (a) change of solvent and reaction temperatures (Table 1. entry 5, 9) and (b) starting the polymerization with the norbornene monomers and then performing the crossover-reaction to the cyclopropene **E** (Table 1. entry 1, 3, 6).

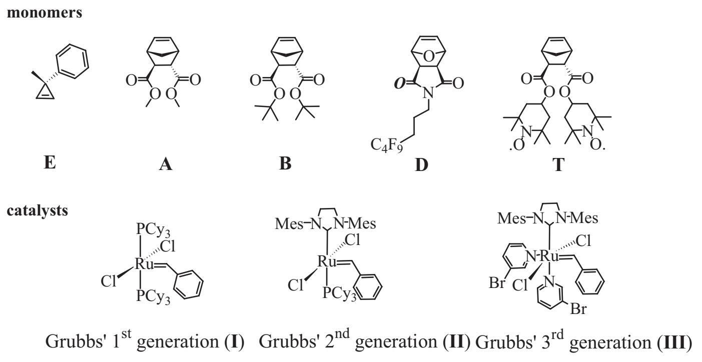

Figure 1.
Monomers and catalysts used for blockcopolymerization reactions.

Table 1.
Polymerization results.

entry	BCP	Cat.	Solvent	$M_{n,\ calc.}$	$M_{n,\ exp.}$	PDI	Yield %
1	$A_{20}E_{20}$	I	DCM	6800	4900	1.3	65
2	$A_{25}E_{25}$	II	DCM	8504	32000	1.3	33
					2800	1.5	
3	$A_{50}E_{20}$	III	DCM	13100	13500	1.1	60
4	$E_{25}A_{25}$	II	DCM	8504	108000	1.4	30
					3500	1.3	
5	$E_{40}A_{30}$	II	$CHCl_3$	11500	16100	1.7	40
6	$B_{33}E_{95}$	III	THF	27000	12100	1.7	50
7	$D_{20}E_{50}$	III	DCM	15000	9300	1.2	40
8	$E_{40}T_{8}$	II	DCM	9400	7450	1.5	50
9	$E_{40}T_{19}$	II	$CHCl_3$	14500	9200	1.8	45

The obtained molecular weights are in many cases lower than the expected values (Table 1. entry 1, 6) due to slow propagation of the cyclopropene block with isolated yields in the range of 40% to 60%.

Encouraged by the good results for blockcopolymer **A-E** with Grubbs 1st- and 3rd-generation-catalysts we investigated the crossover reaction via MALDI-TOF mass spectrometry. This was achieved by addition of 1 or 4 equivalents of **E** to a living poly-**A** and subsequent quench with ethylvinylether, using Grubbs 1st and 3rd-generation-catalyst. In the case of Grubbs 1st-generation-catalyst significant amount of homopolymer can be observed after addition of 1 equiv. of **E** (Figure 2, e). After addition of 4 equiv. of **E** the signal of the homopolymer is strongly reduced (Figure 2, f). In contrast to Grubbs 1st-generation-catalyst, Grubbs 3rd-generation-catalyst provides nearly complete crossover after addition of 1 equiv. of **E** (Figure 3, e). In both cases (Grubbs 1st and Grubbs catalyst 3rd-generation-catalyst) the $\mathbf{A_nE_1}$ series remains the major series even after addition of 4 equiv. of monomer **E** (Figure 2, f; Figure 3, f). This is most likely a result of the slow propagation of **E** or - alternatively - a result of strongly differing desorption in the ionization process, as poly-**A** desorbs well in the MALDI-process, whereas poly-**E** is poorly desorbing, presumably due to its apolar nature.

The observations made in MALDI-TOF MS are in agreement with 1H-NMR measurements for the blockcopolymerization of $\mathbf{A_{20}E_{20}}$. The initiation phase of the

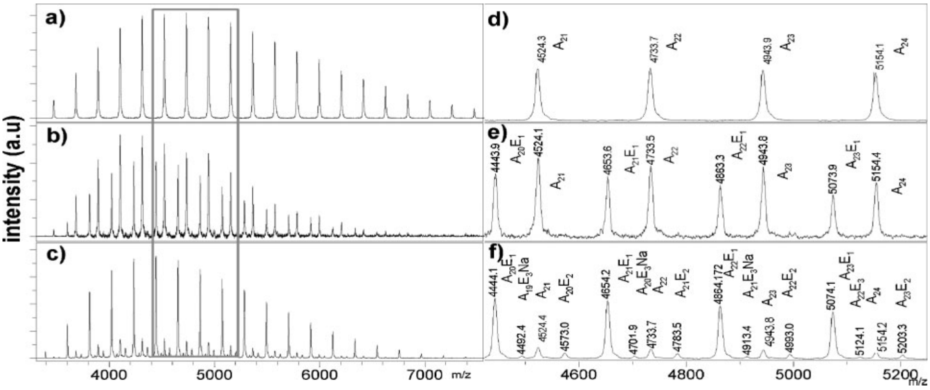

Figure 2.
MALDI-TOF mass spectra of poly ($\mathbf{A_{15}}$) (a: complete spectra, d: enlargement), BCP-$\mathbf{A_{15}E_1}$ (b: complete spectra, e: enlargement) and BCP-$\mathbf{A_{15}E_4}$ (c: complete spectra, f: enlargement) prepared with catalyst **I**. (all the chains of main series are desorbed as [m-Li +]-ions).

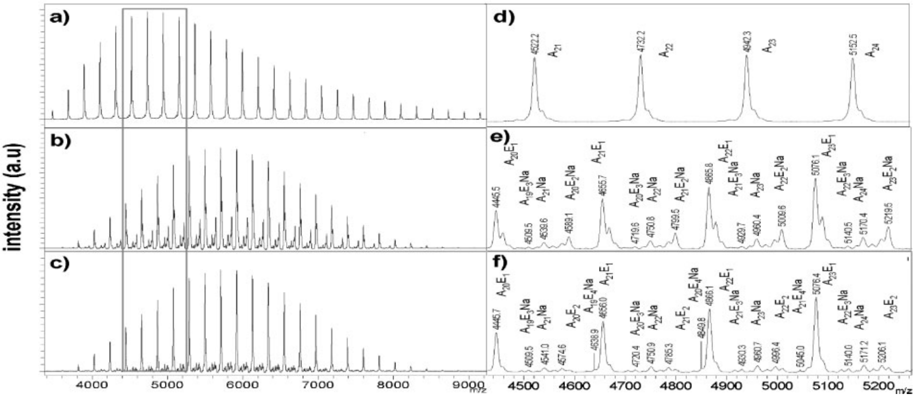

Figure 3.

MALDI-TOF mass spectra of poly (**A_{15}**) (a: complete spectra, d: enlargement), BCP-**$A_{15}E_1$** (b: complete spectra, e: enlargement) and BCP-**$A_{15}E_4$** (c: complete spectra, f: enlargement) prepared with catalyst **III**. (all the chains of main series are desorbed as [m-Li +]-ions).

macroinitiator poly-**A** during the cross-over from **A** to **E** for Grubbs catalyst 1st-generation was approximately 10 min according to ^{1}H-NMR kinetics whereas for Grubbs 3rd-generation-catalyst the formation of the new carbene-species is much faster – i.e. the carbene-species of block-**A** disappears within 30 s. The monitoring of the blockcopolymerization via GPC showed a shift towards higher molecular weights from **A_{15}** to **$A_{15}E_1$** for Grubbs catalyst 1st and 3rd-generation. However there was no significant difference in the retention volumes of the blockcopolymers **$A_{15}E_1$** and **$A_{15}E_4$**.

Conclusion

Blockcopolymers of different norbornene and oxanorbornene monomers and 3-methyl-3-phenylcyclopropene can be prepared in decent yields, achieving best results by starting with the norbornene monomers and then conducting the cross-over-reation to the cyclopropene.

The block-copolymerization reactions can be successfully monitored via MALDI-TOF MS in the case of the BCP **A-E**. The informations obtained can be useful for catalyst evaluation and the investigation of intermediate species. For the investigated system **A-E**, Grubbs catalyst 3rd-generation-catalyst provided better cross-over than Grubbs 1st-generation-catalyst.

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