Controlled Carbene Copolymerization: Is it possible with Rhodium?

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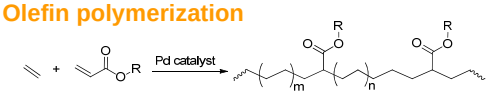
Introduction

Polymers bearing polar functionalities (e.g. esters) show beneficial properties with respect to adhesion and miscibility. To obtain these materials, copolymerization of functionalized and non-functionalized carbenes might be an alternative to traditional polymerizations based on olefins.[1-3] With this new technique we might be able to:

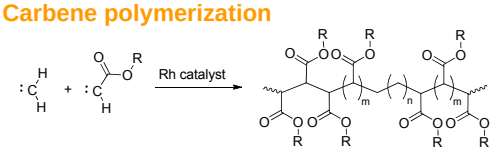
- cover a wider range of polymer composition (X_{ester}= 0-100%)
- Introduce stereoregularity
- Synthesize block copolymers

Olefin polymerization



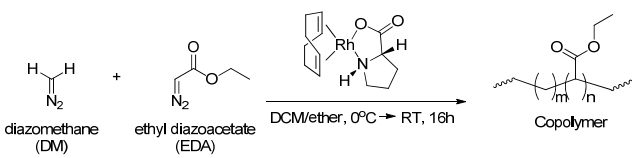
X_{ester} < 50%
Random structure

Carbene polymerization



X_{ester} 0-100%?
Block copolymer?

Diazomethane-EDA copolymerizations

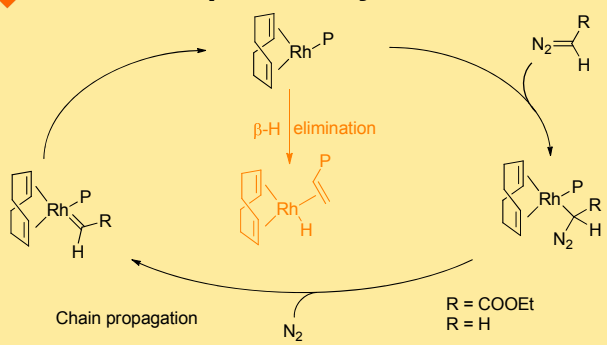


The composition of the copolymer can easily be tuned with X_{ester} of 0 - 100% by varying the monomer feed ratio and the way of addition.

Feed ratio DM:EDA	Polymer yield (%)	M_n (kDa)	X_{ester} polymer
Only EDA	30	150	100
0.2 : 0.8[a]	20	82	80
0.2 : 0.8[b]	19	65	65
0.6 : 0.4	< 5	n.d.	20
Only DM	< 5	n.d.	0

[a] Slow addition of DM; [b] Fast addition of DM.

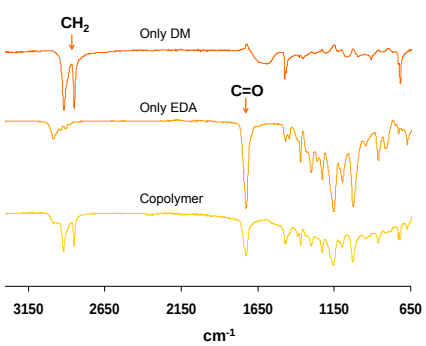
Results explained by DFT



Propagation is faster for DM than for EDA. DM polymers suffer from rapid β-H elimination since they lack stabilization via chelate formation. This explains the low yield for DM homopolymers.

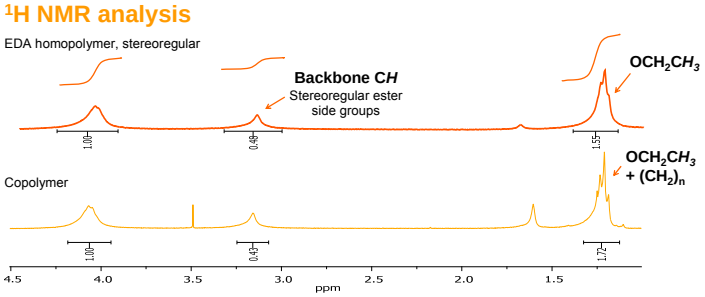
Proof of principle

IR analysis



The IR spectrum of the copolymer shows stretches of both DM and EDA, indicating incorporation of both monomers.

^{1}H NMR analysis

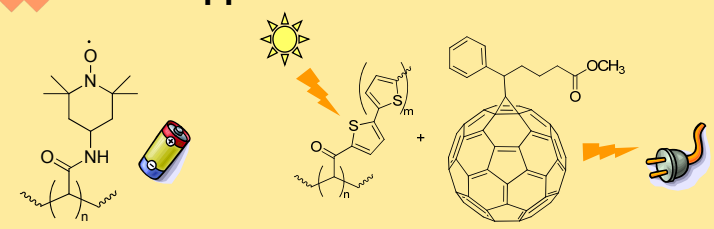


The ^{1}H NMR spectrum of the copolymer reveals incorporation of both monomers. The sharp peak at 3.2 ppm shows that the stereoregularity of sequential EDA insertions is maintained.

Yes it is…

Copolymerization of functionalized and non-functionalized carbenes is a new way to prepare high-Mw copolymers with large amounts of polar functionalities. Sequential polar monomers are inserted in a stereoregular way, although the polymer microstructure (block or random) is not yet resolved. DFT calculations confirm that DM homopolymerization suffers from rapid β-H elimination.

Future applications



Plastic batteries

Polymeric solar cells

This work is part of the Research Programme of the Dutch Polymer Institute DPI, Eindhoven, The Netherlands.

[1] de Bruin *et al.*, *J. Am. Chem. Soc.*, **2006**, *128*, 9746.
[2] de Bruin *et al.*, *J. Am. Chem. Soc.*, **2007**, *129*, 11631.
[3] de Bruin *et al.*, *Chem. Soc. Rev.*, **2010**, *39*, 1706.