



**HAL**  
open science

# Precision design of ethylene- and polar-monomer-based copolymers by organometallic-mediated radical polymerization

Anthony Kermagoret, Antoine Debuigne, Christine Jérôme, Detrembleur Christophe

## ► To cite this version:

Anthony Kermagoret, Antoine Debuigne, Christine Jérôme, Detrembleur Christophe. Precision design of ethylene- and polar-monomer-based copolymers by organometallic-mediated radical polymerization. Journée du département de chimie Université de Liège, Jul 2014, Liège, Belgium. 2014. hal-01345432

**HAL Id: hal-01345432**

**<https://hal.archives-ouvertes.fr/hal-01345432>**

Submitted on 13 Jul 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

MARCH 2014 VOL6 NO3  
www.nature.com/naturechemistry

# nature chemistry

**INELASTIC COLLISIONS**  
Observing oscillations

**MOLECULAR MACHINES**  
A light workout

**SUPRAMOLECULAR POLYMERIZATION**  
Living up to expectations

**A radical approach to copolymers**

nature  
chemistry

ARTICLES

PUBLISHED ONLINE 26 JANUARY 2014 | DOI: 10.1038/NCHEM.1850

## Precision design of ethylene- and polar-monomer-based copolymers by organometallic-mediated radical polymerization

Anthony Kermagoret, Antoine Debuigne, Christine Jérôme and Christophe Detrembleur\*

The copolymerization of ethylene with polar monomers is a major challenge when it comes to the manufacture of materials with potential for a wide range of commercial applications. In the chemical industry, free-radical polymerization is used to make a large proportion of such copolymers, but the forcing conditions result in a lack of fine control over the architecture of the products. Herein we introduce a synthetic tool, effective under mild experimental conditions, for the precision design of unprecedented ethylene- and polar-monomer-based copolymers. We demonstrate how an organocobalt species can control the growth of the copolymer chains, their composition and the monomer distribution throughout the chain. By fine tuning the ethylene pressure during polymerization and by exploiting a unique reactive mode of the end of the organometallic chain, novel block-like copolymer structures can be prepared. This highly versatile synthetic platform provides access to a diverse range of polymer materials.

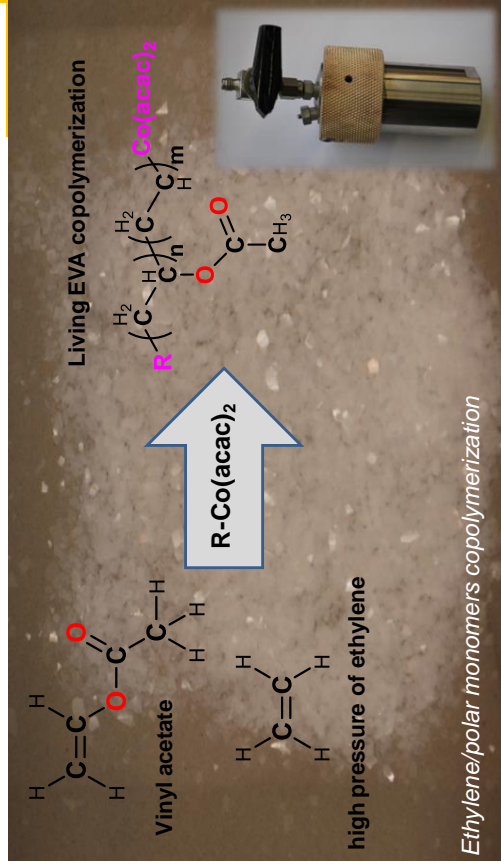


Table 1 | Statistical organometallic-mediated radical copolymerization of ethylene and polar comonomers (M<sub>2</sub>).

Entry	M	Pressure (bar)	Comonomer conversion (%) <sup>a</sup>	M <sub>n</sub> (g mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	F <sub>M</sub>		T <sub>g</sub> (°C) <sup>f</sup>
						Composition <sup>b</sup>	F <sub>M</sub> ethylene	
1	VAc	10	99	8,800 <sup>c</sup>	1.23 <sup>d</sup>	0.87 (0.85) <sup>g</sup>	0.13 (0.15) <sup>h</sup>	26.2
	VAc	25	80	11,200 <sup>c</sup>	1.37 <sup>d</sup>	0.67	0.33	7.4
	VAc	50	55	8,900 <sup>c</sup>	1.34 <sup>d</sup>	0.46 (0.49) <sup>g</sup>	0.54 (0.51) <sup>h</sup>	-7.7
2	NMVA	10	85	9,100 <sup>c</sup>	1.18 <sup>d</sup>	0.82 (0.80) <sup>g</sup>	0.18 (0.20) <sup>h</sup>	124.8
	NMVA	50	66	4,700 <sup>c</sup>	1.09 <sup>d</sup>	0.50 (0.46) <sup>g</sup>	0.50 (0.54) <sup>h</sup>	81.7
3	AN	10	95	23,700 <sup>c</sup>	1.23 <sup>d</sup>	0.95 (0.93) <sup>g</sup>	0.05 (0.07) <sup>h</sup>	-
	AN	50	95	24,900 <sup>c</sup>	1.31 <sup>d</sup>	0.87 (0.83) <sup>g</sup>	0.13 (0.17) <sup>h</sup>	-

Conditions: 40 °C, 24 hours, R-Co = 4.0 × 10<sup>-3</sup> mol, M<sub>0</sub>R-Co = 100, magnetic stirring at 500 rpm. <sup>a</sup>Determined by SEC in THF using PS calibration. <sup>b</sup>Determined by SEC in DMF containing 0.025 M LiBr using a multiangle light-scattering detector. <sup>c</sup>Determined by elemental analysis from O or N concentrations. <sup>d</sup>THF, tetrahydrofuran; <sup>e</sup>PS, polystyrene; <sup>f</sup>DSC, differential scanning calorimetry.