Synthesis and Biodegradation of Model Intermediates of Polyethylene Mineralization

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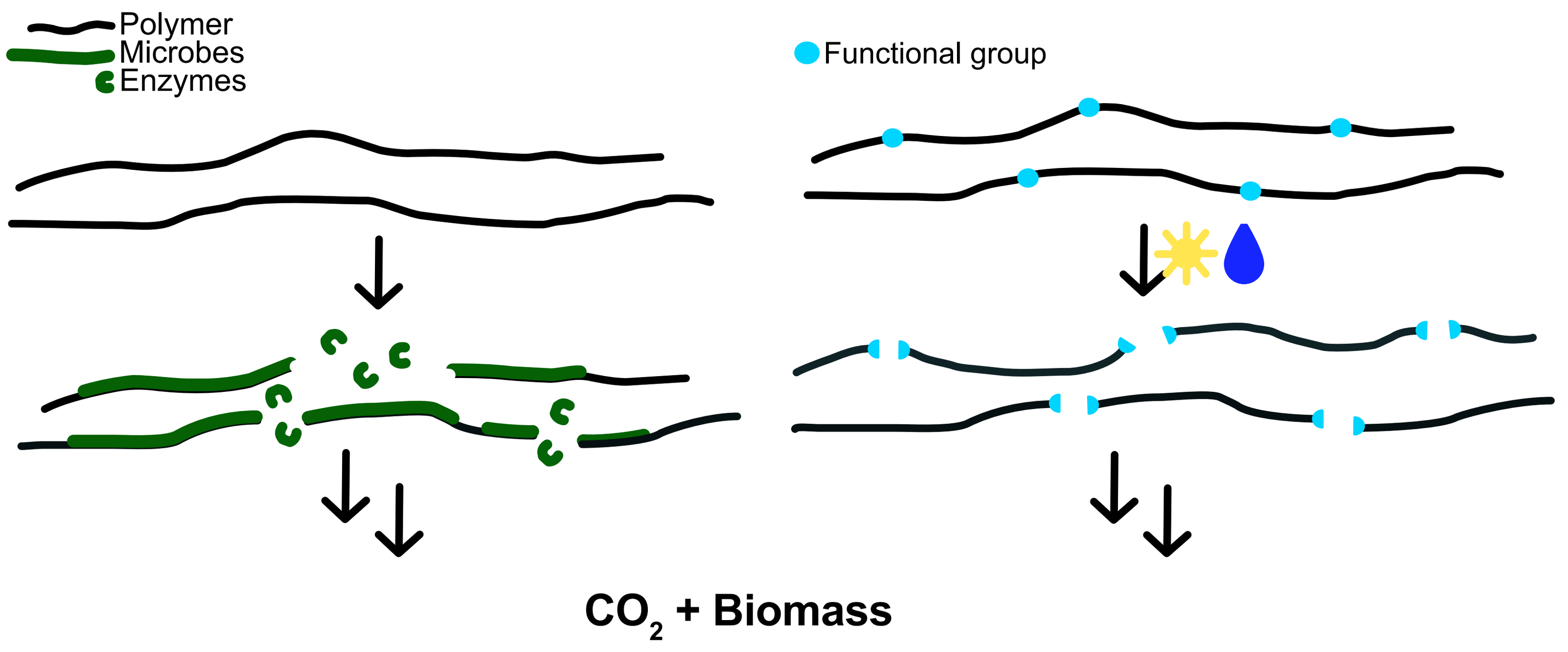
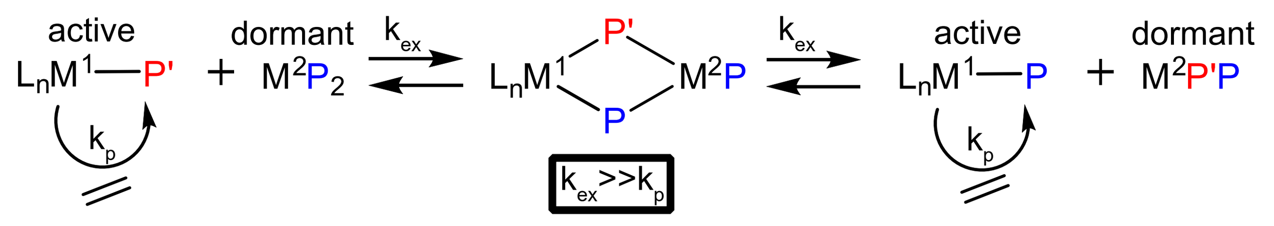
Introduction

Biotic and abiotic degradation processes can break polyethylene-like polymers down to lower molecular weight segments, consisting of long linear methylene chains with a small number of functional groups. The amenability of such compounds to ultimate mineralization is unclear to date, and subject to controversial discussions. Model degradation intermediates of polyethylene (PE) and polyethylene-like intermediates are synthesized to elucidate the biodegradability of these materials. Therefore, catalytic chain-growth systems are used to gain control over the molecular weight and distributions as well as the possibility of introducing functional groups.[1,2] These polymers are subjected to biodegradation studies in laboratory incubations with natural soil samples to determine the relationship between structure and biodegradability.

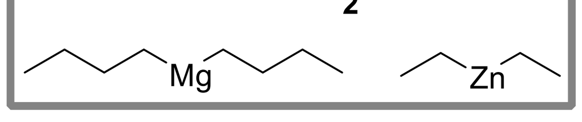


Catalyzed Chain Growth

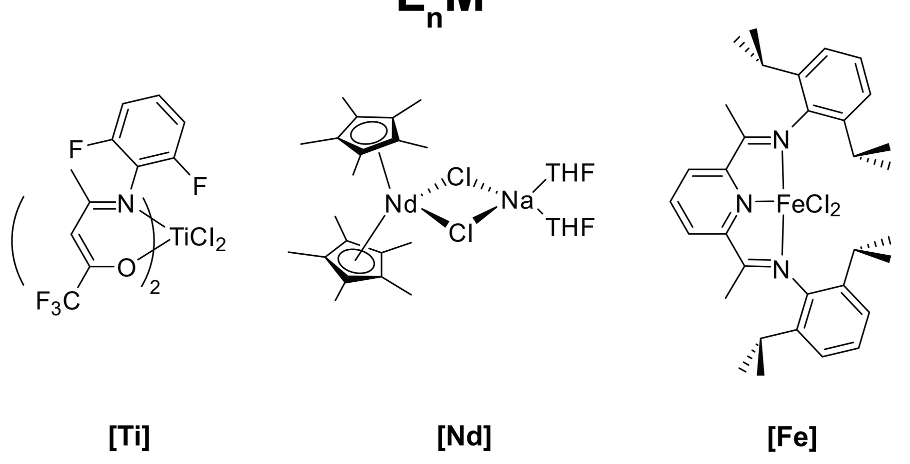


- ✓ Control over the molecular weight
- ✓ Narrow molecular weight distribution
- ✓ Possibility of introducing end groups

M^2P_2

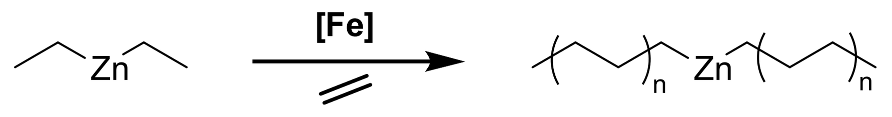


L_nM^1



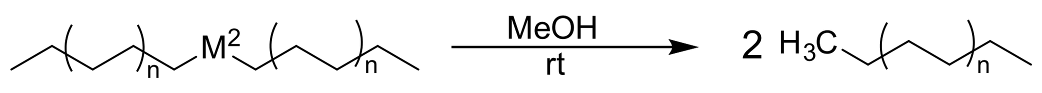
Activation of [Ti] and [Fe] with modified methylaluminoxane

Example Polymerization System



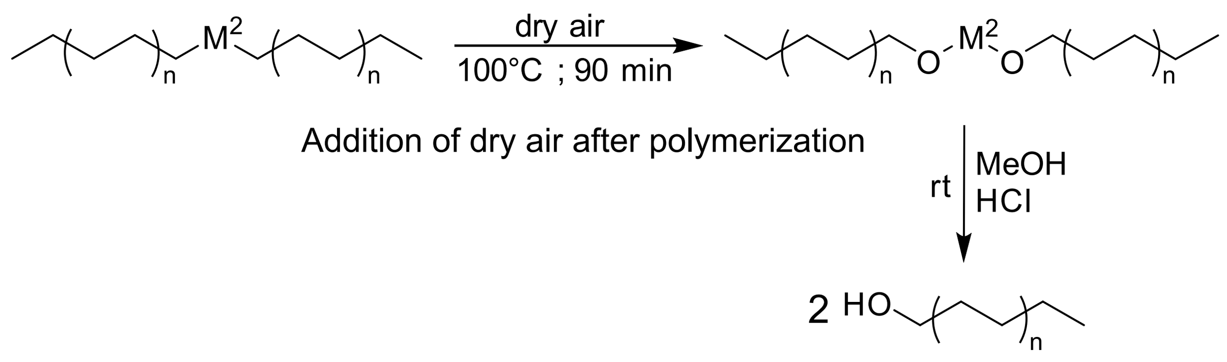
Chain End Functionalization

Introduction of methyl end groups

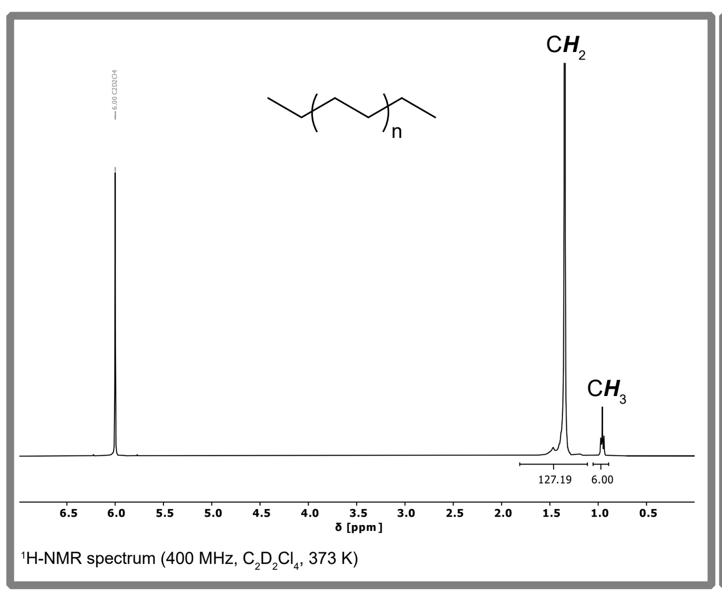


Addition of alcohol after polymerization

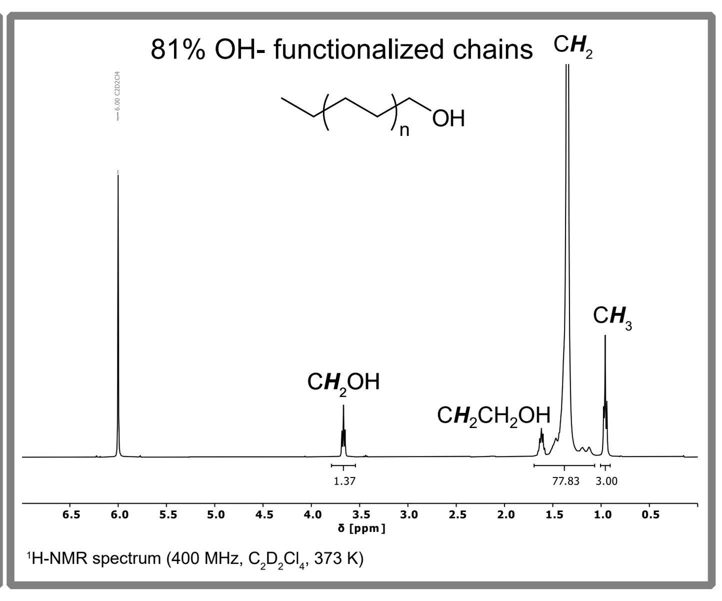
Introduction of hydroxy end groups



Addition of dry air after polymerization

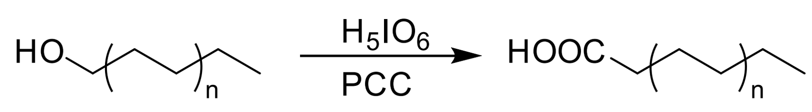


^{1}H-NMR spectrum (400 MHz, $C_2D_2Cl_4$, 373 K)



^{1}H-NMR spectrum (400 MHz, $C_2D_2Cl_4$, 373 K)

Oxidation of the hydroxy end groups to acid end groups



orthoperiodic acid (H_5IO_6)
pyridinium chlorochromate (PCC)

Characterization

Methyl end functionalized polymers

Calculation of ideal Poisson distributions

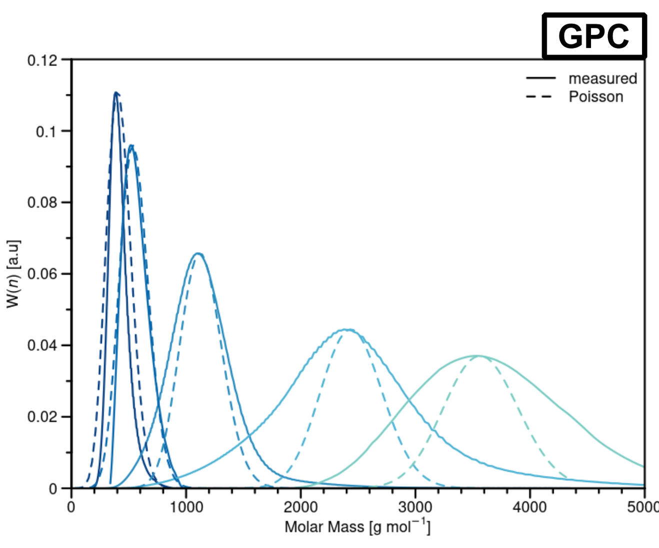
$$DP = \frac{M_p}{M_0} \qquad n = \frac{M}{M_0}$$

$$W(n) = n \cdot DP \cdot DP^n \cdot e^{-DP} / n!$$

from oligomeric to polymeric PE, varying M_n with narrow PDI

#	M_p† [g mol^{-1}]	M_n† [g mol^{-1}]	M_w/M_n †	T_m [°C] (% Cryst.)‡
1	390	380	1.04	58 (60)
2	520	520	1.04	80 (67)
3	1100	990	1.08	109 (72)
4	2400	2000	1.12	126 (73)
5	3500	3400	1.03	132 (77)

†Determined by GPC in 1,2-dichlorobenzene at 160 °C vs. polyethylene standards.
‡Determined by DSC, second heating cycle. Crystallinity determined from enthalpy of melting compared to reference PE of 100% crystallinity

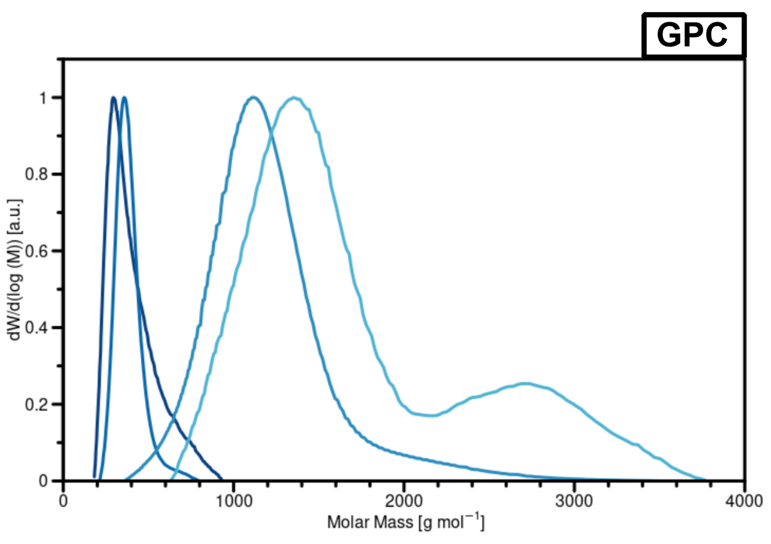


Polymerization yields a molecular weight distribution close to the Poisson model - Accuracy decreases as molecular weight increases.

Hydroxy and acid end group functionalized polymers

#	M_n† [g mol^{-1}]	M_w/M_n†	Functionalization‡ [%]
-OH	360	1.04	73
-COOH	330	1.10	78
-OH	1000	1.09	82
-COOH	1300	1.12	73

†Determined by GPC in 1,2-dichlorobenzene at 160 °C vs. polyethylene standards.
‡Percentage of chains functionalized on one end with either hydroxyl (OH) or carboxyl (COOH) groups. Determined by ^{1}H-NMR.



Molecular weight distribution unchanged by functionalization

References

[1] Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; van Meurs, M. Iron-Catalyzed Polyethylene Chain Growth on Zinc: Linear α-Olefins with a Poisson Distribution. *Angew. Chem. Int. Ed.* **2002**, *41* (3), 489–491.

[2] Mazzolini, J.; Espinosa, E.; D'Agosto, F.; Boisson, C. Catalyzed Chain Growth (CCG) on a Main Group Metal: An Efficient Tool to Functionalize Polyethylene. *Polym. Chem.* **2010**, *1* (6), 793–800.

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AG Mecking

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