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Synthesis of low molecular weight polyethylenes and polyethylene mimics with controlled chain structures

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ABSTRACT

The controlled synthesis of narrowly distributed low molecular weight polymers with functionalization possibilities is of great industrial interests. Although living polymerization allows for control over polymer architecture, the production of low molecular weight polymers with low polydispersities via living polymerization systems is challenged by the use of large amounts of catalysts and broadening in molecular weight distribution. This review addresses the synthesis of narrowly distributed, functional, low molecular weight polyethylene and polyethylene mimics. The review is structured for quick identification of relevant systems for the production of specific polymer architectures with specific cost, efficiency, and safety concerns.

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Nomenclature

Ar	2,6-(*i*-Pr)$_2$Ph
Bz	benzene
CB	chlorobenzene
CCTP	catalytic chain transfer polymerization
CGS	chain growth state
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CTA	chain transfer agent
CTM	chain transfer mediator
CTS	chain transfer state
Cy	cyclohexyl
DCB	dichlorobenzene
DCM	dichloromethane
DEE	diethyl ether
DMSO	dimethyl sulfoxide
E	ethylene
Flu	fluorenyl
H_2IMes	1,3-dimesityl-imidazolidine-2-ylidene
Ind	indenyl
o-DCB	*ortho*-dichlorobenzene
PE	polyethylene
PDI	polydispersity index
Ph	phenyl
P_M	monomer pressure (atm)
M_n	number-average molecular weight (g/mol)
NHC	*N*-heterocyclic carbenes
ROMP	ring-opening metathesis polymerization
RT	room temperature
THF	tetrahydrofuran
TOF	turnover frequency (mol mol^{-1} h^{-1} for liquid monomers; mol mol^{-1} h^{-1} atm^{-1} for gaseous monomers)
Tol	toluene
Tol-*d8*	deuterated toluene
t_p	time of polymerization reaction
T_p	temperature of polymerization reaction (°C)
vers	versatate

1. Introduction

The precise control of molecular weight and chain microstructure is critically important in the preparation of polymers with targeted chemical and physical properties and is a topic of fundamental importance to the field of polymer synthesis [1]. For the simplest polymer chain – polyethylene (PE) – polymer morphology, chemical properties, phase properties, and mechanical properties can be tuned by changing various aspects of the polymer chain structure, including the polymer molecular weight, molecular weight distribution, branching, and chain-end functionality. Specifically, the synthesis of narrowly distributed, low molecular weight, functional PEs is of great industrial interests. Low molecular weight PEs and PE mimics are used in various applications, including but not limited to lubricants, adhesives, inks, and polymer additives. The uniformity of narrowly distributed polymers enables consistent material performance and the tailored functionalization allows for polymer processing and applications in different media.

Low molecular weight PEs and PE mimics can be industrially obtained via thermal cracking processes [2]. However, these polymer products lack microstructure, polydispersity and functionalization control [3]. As a result, commercial low molecular weight polymers are not suitable for technologically advanced applications, such as printing inks, where defined chemical and physical properties, including compatibility with specific media and sharp melting temperature, are required.

Polymerization reactions can also be used to obtain low molecular weight PEs and PE mimics. There are various methods of controlling chemical and physical properties of PEs, including living or controlled alkene polymerization, implementation of chain transfer reactions, and controlled copolymerization of alkenes with functional monomers. Living or controlled polymerization is a method that allows for high degrees of control in molecular weight and chain architectures [1]. An ideal living polymerization system has the following features: the polymerization system proceeds to complete monomer conversion, one active centre is responsible for the growth of one polymer chain, the number of active centres remains constant during polymerization, chain initiation is fast and complete, there are no chain transfer or termination, the degree of polymerization (or number-average molecular weight,

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