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Macromolecular architectures through organocatalysis

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ABSTRACT

In virtue of the rising demand for metal-free polymeric materials, organocatalytic polymerization has emerged and blossomed unprecedentedly in the past 15 years into an appealing research area and a powerful arsenal for polymer synthesis. In addition to the inherent merits as being metal-free, small-molecule organocatalysts have also provided opportunities to develop alternative and, in many cases, more expedient synthetic approaches toward macromolecular architectures, that play a crucial role in shaping the properties of the obtained polymers. A majority of preliminary studies exploring for new catalysts, catalytic mechanisms and optimized polymerization conditions are extended to application of the catalytic systems on rational design and controlled synthesis of various macromolecular architectures. Such endeavors are described in this review, categorized by the architectural elements including chain structure (types, sequence and composition of monomeric units constituting the polymer chains), topological structure (the fashion different polymer chains are covalently attached to each other within the macromolecule) and functionality (position and amount of functional groups that endow the entire macromolecule with specific chemical, physico-chemical or biological properties).

Contents

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Nomenclature

AOMEC 2-Allyloxymethyl-2-ethyl-trimethylene carbonate
ATRP Atom-transfer radical polymerization
*n*BA *n*-Butyl acrylate
BEMP 2-*Tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
$B(C_6F_5)_3$ Tris(pentafluorophenyl)borane
*β*BL *β*-Butyrolactone
BNPH 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate
BNPP Bis(4-nitrophenyl)phosphate
BO 1,2-Butylene oxide
t-BuP_2 1-*Tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-$2\lambda^5,4\lambda^5$-catenadi(phosphazene)
t-BuP_4 1-*Tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-$2\lambda^5,4^{\lambda}5$-catenadi(phosphazene)
$C_6F_5CHTf_2$ Pentafluorophenylbis(triflyl)methane
*ε*CL *ε*-Caprolactone
CTA Chain-transfer agent
$Đ_M$ Molar mass distribution
DBU 1,8-Diazabicyclo[5.4.0]undec-7-ene
DHC 3,4-Dihydrocoumarin
DLA (3*R*,6*R*)-3,6-Dimethyl-1,4-dioxane-2,5-dione (D-lactide)
DMAEMA 2-(Dimethylamino)ethyl methacrylate
DMAP 4-(Dimethylamino)pyridine
DMSO Dimethyl sulfoxide
DNBA 2,4-Dinitrobenzenesulfonic acid
*D*p Degree of polymerization
DPP Diphenyl phosphate
EO Ethylene oxide
GPE Glycidyl phenyl ether
GTP Group transfer polymerization
HEMA 2-Hydroxyethyl methacrylate
$HNTf_2$ Trifluoromethanesulfonimide
IMes 1,3-Dimesitylimidazol-2-ylidene
LA Lactide (general)
*rac*LA 3,6-Dimethyl-1,4-dioxane-2,5-dione (*rac*-lactide)
LCRP Living/controlled radical polymerization
LLA (3*S*,6*S*)-(−)-3,6-Dimethyl-1,4-dioxane-2,5-dione (L-lactide)
MALDI-TOF MS Matrix assisted laser desorption/ionization time of flight mass spectrometry
Me_2IMe 1,3,4,5-Tetramethylimidazol-2-ylidene
Me_2IPr 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene
Me_3SiNTf_2 *N*-(Trimethylsilyl)bis-(trifluoromethanesulfonyl)imide
MMA Methyl methacrylate
bis-MPA 2,2-Bis(methylol)propionic acid
MSA Methanesulfonic acid
MTBD 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
MTC 5-Methyl-5-carboxytrimethylene carbonate
MTC-OC_6F_5 MTC pentafluorophenyl ester
M_n Number-average molar mass
M_w Weight-average molar mass
NCA *α*-Amino acid *N*-carboxyanhydride
NHC *N*-Heterocyclic carbene
NMP Nitroxide-mediated polymerization
OCP Organocatalytic polymerization
OC-GTP Organocatalytic group transfer polymerization
OC-ROP Organocatalytic ring-opening polymerization
OC-ZROP Organocatalytic zwitterionic ring-opening polymerization
OEGMA Oligo(ethylene glycol) methyl ether methacrylate
P*n*BA Poly(*n*-butyl acrylate)
PBd Polybutadiene
PBL Poly(*β*-butyrolactone)
PCL Poly(*ε*-caprolactone)
PDL *ω*-Pentadecalactone
PEO Poly(ethylene oxide)
PEO-diol *α*-*ω*-Dihydroxy-poly(ethylene oxide)
PEO-OH *α*-Methoxy-*ω*-hydroxy-poly(ethylene oxide)
PEO-NH_2 *α*-Methoxy-*ω*-amino-poly(ethylene oxide)
PHIC Poly(*n*-hexyl isocyanate)