



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).

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Nomenclature

AOMEc	2-Allyloxymethyl-2-ethyl-trimethylene carbonate
ATRP	Atom-transfer radical polymerization
nBA	<i>n</i> -Butyl acrylate
BEMP	2-Tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
B(C ₆ F 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
<i>t</i> -BuP ₂	1-Tert-butyl-2,2,4,4,4-pentakis(dimethylamino)-2 λ ⁵ ,4 λ ⁵ -catenadi(phosphazene)
<i>t</i> -BuP ₄	1-Tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylideneamino]-2 λ ⁵ ,4 λ ⁵ -catenadi(phosphazene)
C ₆ F ₅ CHTf ₂	Pentafluorophenylbis(triflyl)methane
ε CL	ε -Caprolactone
CTA	Chain-transfer agent
D_M	Molar mass distribution
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DHC	3,4-Dihydrocoumarin
DLA	(3 <i>R</i> ,6 <i>R</i>)-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)

<i>rac</i> LA	3,6-Dimethyl-1,4-dioxane-2,5-dione (<i>rac</i> -lactide)
LCRP	Living/controlled radical polymerization
LLA	(3 <i>S</i> ,6 <i>S</i>)-(–)-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 ₂ IMe	1,3,4,5-Tetramethylimidazol-2-ylidene
Me ₂ IPr	1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene
Me ₃ SiNTf ₂	<i>N</i> -(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 ₆ F ₅	MTC pentafluorophenyl ester
M _n	Number-average molar mass
M _w	Weight-average molar mass
NCA	α -Amino acid <i>N</i> -carboxyanhydride
NHC	<i>N</i> -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
PnBA	Poly(<i>n</i> -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(<i>n</i> -hexyl isocyanate)

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