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Dispersion polymerization in environmentally benign solvents via reversible deactivation radical polymerization

Xiao Wang, Liangliang Shen, Zesheng An*

Institute of Nanochemistry and Nanobiology, College of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China

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ABSTRACT

There is much recent interest in dispersion polymerization conducted via reversible deactivation radical polymerization (RDRP). This review is focused on RDRP-mediated dispersion polymerization in environmentally benign solvents, including water, supercritical CO_2, ionic liquids, and low-molecular-weight poly(ethylene glycol)s. New trends in employing redox initiator, visible-light control, and enzyme catalysis to conduct dispersion polymerization in these solvents are also highlighted. Finally, we point out the current limitations and future directions that need more attention in this burgeoning field.

Contents

* Corresponding author.
E-mail address: an.zesheng@shu.edu.cn (Z. An).

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Nomenclature

AA acrylic acid
ACAC acetylacetone
AEAM 2-aminoethylacrylamide
AFM atomic force microscope
ALAM allyl acrylamide
ATRP atom transfer radical polymerization
BA butyl acrylate
BIS *N*,*N*′-methylenebis(acrylamide)
BMA *n*-butyl methacrylate
[bmin][PF_6] 1-butyl-3-methylimidazolium hexafluorophosphate
C_2VImBr *N*-vinyl-3-ethyl imidazolium bromide
C_8VImBr *N*-vinyl-3-octylimidazolium bromide
C_{12}VImBr *N*-vinyl-3-dodecylimidazolium bromide
CB [7] cucurbit[7]uril
CCS core cross-linked star
CGT critical gelation temperature
CMRP cobalt-mediated radical polymerization
CRP controlled radical polymerization
CTA chain transfer agent
Đ dispersity
2Dcos two-dimensional correlation spectroscopy
DAAM diacetone acrylamide
DEAM *N*,*N*-diethylacrylamide
DET-RAFT dissociative electron transfer RAFT
DLS dynamic light scattering
DMF *N*,*N*-dimethylformamide
DMSO dimethyl sulfoxide
DP degree of polymerization
EDX energy dispersive X-ray analysis
FTIR Fourier transform infrared spectroscopy
GPC gel permeation chromatography
HEMA 2-hydroxyethyl methacrylate
HPMA 2-hydroxypropyl methacrylate
HRP horseradish peroxidase
IEP isoelectric point
LCST lower critical solution temperature
macro-CTA macromolecular chain transfer agent
MEA 2-methoxyethyl acrylate
[$META^+$][PF_6−] [2-(methacryloyloxy)ethyl]trimethylammonium hexafluorophosphate
MMA monomethyl methacrylate
MW molecular weight
N_{agg} aggregation number
NIPAM *N*-isopropylacrylamide
NMEP *N*-(2-(methacryloyloxy)ethyl)pyrrolidone
NMP nitroxide-mediated radical polymerization
NMR nuclear magnetic resonance
NVP *N*-vinylpyrrolidone
OEGA oligo(ethylene glycol) acrylate
OEGMA oligo(ethylene glycol) methacrylate
p packing parameter
PAMPS poly(sodium 2-acrylamido-2-methylpropanesulfonate)
PDEGA poly(diethylene glycol ethyl acrylate)
PDI polydispersity index
PDMA poly(dimethylacrylamide)
PDMS-MMA poly(dimethylsiloxane monomethyl methacrylate)
PEG poly(ethylene glycol) methyl ether
PFOMA poly(1H,1H,2H,2H-perfluorooctyl methacrylate)
PGMA poly(glycerol monomethacrylate)
PIC polyion complexation
PIESA polymerization-induced electrostatic self-assembly
PIL poly(ionic liquid)
PISA polymerization-induced self-assembly
PITSA polymerization-induced thermal self-assembly
PPEGMA poly(poly(ethylene glycol) methyl ether methacrylate)
PSA poly(sodium acrylate)
RAFT reversible addition-fragmentation chain transfer
RDRP reversible deactivation radical polymerization
RTCP reversible chain transfer catalyzed polymerization
SAXS small-angle X-ray scattering
$scCO_2$ supercritical CO_2
SEM scanning electron microscope
SET-LRP single electron transfer living radical polymerization
SET-RAFT single electron transfer RAFT
SG1 *N*-*t*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide
SPTP sodium phenyl-2,4,6-trimethylbenzoylphosphinate
TEM transmission electron microscope
T_g glass transition temperature
THF tetrahydrofuran
UCST upper critical solution temperature
X Flory-Huggins interaction parameter
ZnTPOR Zn(II) meso-tetra(4-naphthalylmethylpyridyl) porphyrin

1. Introduction

Dispersion polymerization has been the technique of choice for the preparation of microspheres (200 nm to several μm) that find widespread applications in coating, bioassay, print ink, separation, and catalyst support [1]. Key to the formation of stable and uniform microspheres is effective stabilization of the nascent particle seeds during the highly sensitive nucleation stage whereby the growing polymers become insoluble and thus collapse out of the continuous phase [2,3].

The discovery of reversible deactivation radical polymerization (RDRP), also known as controlled radical polymerization (CRP), has revolutionized the field of polymer chemistry, enabling facile access under operationally mild conditions to diverse functional materials with predetermined molecular weights, narrow dispersities and architectures by design [4–11]. Living anionic polymerization requires the use of specialized equipment to meet the stringent polymerization conditions, which has limited their wider adoption both in the laboratory and in industry. In contrast, RDRP techniques can be conducted under routine laboratory conditions; no high vacuum and low temperatures are needed. A wide range of solvents including water can be used in both homogeneous and heterogeneous polymerizations. The high degree of tolerance of functional groups has allowed direct synthesis of an assortment of functional materials without resorting to protection/deprotection, significantly facilitating their application in many fields. RDRP techniques realize polymerization control according to either a reversible deactivation or a degenerative chain transfer mechanism. To date, the most studied RDRP techniques operating via the reversible deactivation mechanism are transition-metal-catalyzed radical polymerization such as atom transfer radical polymerization (ATRP) [7], single electron transfer living radical polymerization (SET-LRP) [11], and nitroxide-mediated polymerization (NMP) [4]. On the other hand, reversible addition-fragmentation chain transfer (RAFT) polymerization [10], including its variants SET-RAFT (single electron transfer RAFT) [12,13] and