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Temperature responsive bio-compatible polymers based on poly(ethylene oxide) and poly(2-oxazoline)s

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ABSTRACT

This review covers the LCST behavior of two important polymer classes in aqueous solution, namely poly(2-oxazoline)s and systems whose thermo-responsiveness is based on their structural similarity to poly(ethylene oxide) (PEO). In order to elucidate the progress that has been made in the design of new thermo-responsive copolymers, experimental data that were obtained by different research groups are compared in detail. Copolymerization with hydrophilic or hydrophobic comonomers represents a suitable method to tune the coil to globule transition temperature of several homopolymers, and incorporation of other monomers provided further interesting features, such as pH responsiveness or sensing properties. In addition, living and controlled polymerization techniques enabled access to defined end groups and more advanced polymer architectures, such as graft copolymers or double responsive block copolymers. The effect of such structural variations on the temperature responsive behavior of the (co)polymers is discussed in detail.

Contents

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Nomenclature

AGET ATRP Activator generated by electron transfer ATRP
ATRP Atom transfer radical polymerization
BMDO 5,6-Benzo-2-methylene-1,3-dioxepane
BOx 2-Butenyl-2-oxazoline
BuMA Butyl methacrylate
BuOx 2-Butyl-2-oxazoline
CROP Cationic ring opening polymerization
DLS Dynamic light scattering
DMAEMA *N*,*N*-dimethyl aminoethyl methacrylate
DP Degree of polymerization
DR Disperse red
DSC Differential scanning calorimetry
EGFP Enhanced green fluorescent protein
EO Ethylene oxide
FRP Free radical polymerization
HEA Hydroxy ethyl acrylate
HS-DSC High sensitivity differential scanning calorimetry
LCSC Lower critical solution concentration
LCST Lower critical solution temperature
MAA Methacrylic acid
MMA Methyl methacrylate
NBA *o*-Nitrobenzyl acrylate
NiPAm *N*-*iso*-propylacrylamide
NMP Nitroxide mediated polymerization
PBS Phosphate buffered saline
PCL Poly(ε-caprolactone)
P*c*PrOx Poly(2-*cyclo*-2-propyl-2-oxazoline)
PTCO Poly(1,3,6-trioxacyclooctane)
PDI Polydispersity index
PDMAEMA Poly(*N*,*N*-dimethyl aminoethyl methacrylate)
PDXL Poly(1,3-dioxolane)
PEG Poly(ethylene glycol)
PEO Poly(ethylene oxide)
PEtOx Poly(2-ethyl-2-oxazoline)
PhOx 2-Phenyl-2-oxazoline
PIC Polyion complex
PLGA Poly(lactide-*co*-glycolide)
PMeOx Poly(2-methyl-2-oxazoline)
PMO Poly(methylene oxide)
PNiPAm Poly(*N*-*iso*-propylacrylamide)
PNonOx Poly(2-*n*-nonyl-2-oxazoline)
PO Propylene oxide
POx Poly(2-oxazoline)
PPC Pressure perturbation calorimetry
PPO Poly(propylene oxide)
PPrOx Poly(2-propyl-2-oxazoline)
PTCU Poly(1,3,6,9-tetraoxacycloundecane)
RAFT Reversible addition-fragmentation chain transfer
SLS Static light scattering
T_{cp} Cloud point temperature
TEM Transmission electron microscopy
TMAEMA$^+$ Methacryl oxyethyl trimethylammonium chloride
UCST Upper critical solution temperature
XRD X-ray diffraction

1. Introduction

Polymers that respond with a property alteration towards environmental changes are often referred to as “stimuli-responsive”, “smart”, or “intelligent” materials. In cases where the external trigger is temperature, the polymer is said to exhibit thermo-responsive properties. An interesting feature that can be influenced by changes in temperature is the solubility of the polymer in aqueous systems. Besides individually dissolved polymer chains, thermo-responsive polymers can be designed to exist in various physical forms, such as hydrogels, functionalized surfaces, membranes, micelles and various types of