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Review

Micellization of synthetic and polysaccharides-based graft copolymers in aqueous media

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ABSTRACT

This review highlights recent advances in the micellization of synthetic graft copolymers and those based on natural precursors, particularly polysaccharides. Synthesis and characterization of a broad range of architectures are discussed, along with different micellization procedures and fundamental micellar characteristics, such as morphology and size. Micelle formation by synthetic graft copolymers in aqueous media is examined in detail for different architectures of nonionic, ionic, and temperature and pH stimuli-responsive "*double hydrophilic*" copolymers. In this context, the problems associated with unimolecular micelles and the correlations between molecular characteristics are further addressed. In addition to backbone and side chain molecular weights, grafting density and topology are the major parameters that directly influence graft copolymer micellization. A similar overview is provided for graft copolymers based on polysaccharides, such as cellulose, chitosan, dextran, and starch. Finally, an outlook is given on the prospects for further development in this area.

Contents

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Nomenclature

AFM	Atomic force microscopy
ATRP	Atom-transfer radical polymerization
CAC	Critical association concentration
CMC	Critical micelle concentration
C.M.C	Carboxymethylcellulose
CMT	Critical micelle temperature
CHMA	Cyclohexylmethacrylate
COs	Chitosan oligosaccharides
CRP	Controlled radical polymerization
CS	Chitosan
DEX	Dextran
DDA	Dodecylamine
D_h	Hydrodynamic diameter
DLLA	d,l-lactide
DLS	Dynamic light scattering
DNA	Deoxyribonucleic acid
DS	Degree of substitution
DSC	Differential scanning calorimetry
DSeDPA	3,3′-diselenodipropionic acid
EC	Ethylcellulose
FTIR	Fourier transform infrared spectroscopy
HDI	1,6-hexamethylenediisocyanate
HEC	Hydroxyethylcellulose
HEMA	Hydroxyethylmethacrylate
HES	Hydroxyethylstarch
HMssEt	Methacrylate monomer bearing pendant disulfide linkage
HPC	Hydroxypropylcelllulose
HPLC	High performance liquid chromatography
GA	Glutaraldehyde
GPC	Gel permeation chromatography
LCST	Lower critical solution temperature
LMA	Lauryl-methacrylate
MAA	Methacrylic acid
MEO_2MA	2-(2-methoxyethoxy) ethylmethacrylate
MH	Maltoheptaose
MMA	Methylmethacrylate
MPEG	Methoxy polyethylene glycol
N_{agg}	Micellar aggregation number
NMP	Nitroxide mediated radical polymerization
NMR	Nuclear magnetic resonance spectroscopy
OEOMA	Oligo(ethylene oxide methacrylate)
OEGMA	Oligo (ethylene glycol) methacrylate
PAA	Poly(acrylic acid)
PAHMA	Poly(N-amidino)hexyl methacrylamide
PAN	Poly(acrylonitrile)
PnBA	Poly(n-butyl acrylate)
PtBA	Poly(tert-butyl acrylate)
PtBMA	Poly(tert-butyl methacrylate)
PBIEM	Poly[(2-(2-bromoisobutyryloxy)ethyl methacrylate)]
PBMA	Poly(butyl methacrylate)
PC	Polycarbonate
PCL	Poly(ε-caprolactone)
PCEMA	[Poly(2-cinnamoyl-oxyethyl methacrylate)]
PCMS	Poly(chloromethylstyrene)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PEI	Poly(ethylene imine)
PDAEMA	Poly(2-(N,N-dimethylamino) ethyl methacrylate
PDEA	Poly[2-(diethylamino)ethyl methacrylate]
PDMA	Poly(N,N-dimethylacrylamide)
PDMAEMA	Poly(N,N-dimethylamino-2-ethyl methacrylate)
PDMAPS	Poly[3-dimethyl (methacryloyloxyethyl) ammonium propanesulfonate]
PDMS	Poly(dimethyl siloxane)
PEGMEMA	Poly(ethylene glycol methyl ether methacrylate)
PGA	Poly(glutamic acid)
PGMA	Poly(glycidyl methacrylate)
PHEA	Poly(N-hydroxyethylacrylamide)
PHFBMA	Poly(4,4,4,3,3,2-hexafluorobutyl methacrylate)
P(HFMA-co-NaSS)	Poly(hexafluorobutyl methacrylate-co-sodium 4-vinylbenzenesulfonate)
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic acid)
PLL	Poly(L-lysine)
PMA	Poly(methyl acrylate)
P(MOx)	Poly(2-methyl-2-oxazoline)
PMO_2MA	Poly(2-2 methoxy-ethoxy ethyl methyl methacrylate)
PNAM	Poly(N-acryloylmorpholine)
PNDH	Poly[(*N*-isopropylacrylamide-co-*N*,*N*-dimethylacrylamide-co-*N*(hydroxymethyl)acrylamide)]
PNIPAM	Poly(N-isopropyl acrylamide)