

## Index

### **a**

ALB<sub>2</sub> binary systems  
     crystal structure 260, 261  
     optimal linker strength and average  
         hybridization percentage 265,  
         267  
 α-chymotrypsin 141  
 amines and trimethyl ammonium  
     surfactants 112  
 amino acid sequence, of  
     ELP–cysteine–ELP block  
     copolymer 225, 226  
 amphiphile/amphiphilic molecules *see*  
     *also* giant surfactants  
     amphiphile headgroups *vs.*  
         solute/solvent molecules  
         interactions 106  
     chemical structures of 101, 102  
 amphiphile production catalyst  
     configurations 121–123  
 amphiphilic nanoparticles 34–36  
 Anderson–C<sub>16</sub> giant surfactant 313,  
     314  
 angiogenesis, PA scaffolds in 195  
 antisense cyanine 5 labeled LPA 168,  
     169  
 antisense fluorescein labeled LPA  
     (AS-FL-LPA) 168, 169  
 ascorbic acid 87

asymmetric Janus particles 288–290  
 azobenzene trimethylammonium  
     bromide (azoTAB) 91, 93

### **b**

basic leucine zipper (bZip) peptide  
     amphiphiles 184, 187, 192  
 β-sheet forming peptides, drawback of  
     215  
 β-sheet protein copolymers 215–219  
 bioconjugation chemistry 229, 230  
 biomedical applications, PAMs in  
     diagnostic and therapeutic PAMs  
         195–199  
     tissue engineering and regenerative  
         medicine 192–195  
 biomimetic silaffin R5 peptide  
     225–226  
 biomineralization, nanofibrous PAMs  
     in 194, 195  
 biomolecules 137  
 biomolecule-surfactant assemblies,  
     control of 84–87  
 biopolymer synthesis 118  
 4,4'-bis(trimethylammoniumhexyloxy)  
     azobenzene bromide (BTHA)  
     90, 92  
 bis(11-ferrocenylundecyl)  
     dimethylammonium bromide  
     (BFDMA) 78, 84–87

- block copolymer micelles
  - de Gennes model for 11–13
  - formation of 11, 12
  - geometrical relations for 19
  - mean field model of 17–20
  - star polymer model for 15–17
- block copolymers 1, 2
  - industrial applications 207
- bottom-up approach 257
- bovine serum albumin
  - (BSA)-b-poly(methyl methacrylate) micelles 232
- bovine serum albumin (BSA)-PS giant surfactant 316
- branched micellar networks 53–55
  - entropic networks
    - mean-field theory 57, 58
    - phase separation 56, 58, 60
    - statistical associating fluid theory 58, 59
    - statistical mechanical theory 60
    - topological defects 57
    - Zilman-Safran theory 60
  - examples of 41–43
  - shape and free energy
    - curvature dependence 61
    - electrostatic contribution 63
    - endcap (junction) 61, 62, 64
    - equilibrium aggregate free energy 65
    - numerical minimization technique 61, 63
    - total aggregation free energy 63
  - swollen polyelectrolyte corona 64, 65
  - theoretical studies of 44
- C**
- carbon contents of carbonaceous
  - chondrite meteorites 103
- carboxyfluorescein 125
- carboxylic acid-functionalized
  - polyhedral oligomeric silsesquioxane–polystyrene (APOSS-PSs) giant surfactant 316, 317
- catalysis compartmentalization, with SCAs 116–118
  - enclosed protocell models 118–120
  - interfacial protocell models 120–123
  - membranes as energy transduction systems 124–126
- charged SCAs, mixtures of 112–113
- chemical gradients, formation of 125
- cholesterol 113–114
- classical Odijk-Skolnick-Fixman (OSF) theory 52, 53
- click chemistry 311
- coarse-grained model 257, 258
- coiled-coils 191, 209, 214, 215
- coil-like protein copolymers 223–229
- corona crosslinked micelles 225
- critical aggregate concentration (CAC) 106, 107
- critical micelle concentration (CMC) 181
- critical packing parameter 182
- Cr<sub>3</sub>Si binary systems
  - crystal structure 260, 261
  - optimal linker strength and average hybridization percentage 265, 267
- cryo-transmission electron microscopy (cryo-TEM) 26, 43
- CsCl binary systems
  - crystal structure 260, 261
  - optimal linker strength and average hybridization percentage 265, 267
- cyclic peptides (CPs)
  - CP–polymer conjugates 221–223
  - from D-alt-L linear peptides 220
  - nanotubes 221
  - N-methylation 223
  - solid-phase synthesis 221

- cyclic protein copolymers 220–223  
 cylindrical micelles, formation of 9  
 cysteine–arginine–glutamic  
   acid–lysine–alanine (CREKA)  
   195, 196
- d**
- decanoic acid bilayers 115, 123  
 decyl trimethylammonium bromide  
   (DTAB) 112–113  
 de Gennes model, for block copolymer  
   micelles 11–13  
 dehydration–rehydration method  
   119  
 dendritic amphiphiles  
   aggregation behavior of 26, 27  
   headgroups and tailgroups of 25  
   steric repulsions 26  
 Derjaguin approximation 272  
 dexamethasone 196  
 diblock copolymers 1–3 *see also*  
   block copolymers  
   ELP–ELP  
     schematic representation and  
     amino acid sequence 226, 227  
     spherical and cylindrical micelles  
     of 224, 225  
   ELP–PEG 228–229  
   PAA–VG2 229  
   poly(benzyl-L-glutamate)-coil 209,  
   210  
 dipalmitoylphosphatidylcholine  
   (DPPC) membranes 283  
 dissipative particle dynamics (DPD)  
   advantageous features of 278  
   conservative force 279  
   drag force 280  
   hydrodynamic behavior 280  
   random force 280  
 DNA amphiphiles 27–29  
 DNA-functionalized anisotropic  
   nanoparticles 258  
 DNA-mediated nanoparticle  
   crystallization, in Wulff  
   polyhedra 268–272  
 DNA nanotechnology 153  
 DNA–polymer amphiphiles  
   categories 159  
   DNA-brush copolymers 163, 164  
   DNA micelle formation 160  
   endonuclease resistance 165, 167  
   fluorescence studies 163, 165  
   positional ordering along DNA  
     nanotubes 171  
   preparation 165, 166  
   ss-DNA-b-PPO micelles  
     hybridization 161, 162  
 DNA-programmable nanoparticle  
   assembly  
   schematic illustration 263  
   thermally active hybridization  
   263–268  
 DNA-programmed micelle systems  
   151, 153–154  
   DNA–polymer amphiphiles  
   159–171  
   lipid-like DNA amphiphiles  
   154–159  
 dynamical micellar branching 68
- e**
- elastin-like polypeptides (ELP) 223  
   sharp solubility transition 224  
   transition temperature 224  
 elastin-mimetic hybrid copolymers  
   229  
 electrostatic interactions 188  
 electrostatic persistence length, of  
   wormlike micelles 53, 54  
 ELP–ELP diblock copolymers  
   schematic representation and amino  
   acid sequence 226, 227  
   spherical and cylindrical micelles of  
   224, 225

ELP-PEG diblock copolymers  
228–229

emulsion compartments 108–109

enclosed protocell models 118–120

enhanced green fluorescent protein  
(EGFP) 84, 316

entangled wormlike micelles,  
viscoelasticity of 44–50

breaking time 45

characteristic lengths 46, 48

Cole–Cole plot 46, 48, 49

concentration dependence 50

contour length 45, 49

for dilute and semidilute solutions  
44

Maxwell model 46

reptation model 45

storage and loss moduli, frequency  
dependence of 46, 47

terminal relaxation time 50

entropic networks, branched micelles

mean-field theory 57, 58

phase separation 56, 58, 60

statistical associating fluid theory  
58, 59

statistical mechanical theory 60

topological defects 57

Zilman-Safran theory 60

enzyme catalyzed dephosphorylation  
reaction, of Fmoc-FpY 139,  
140

enzyme-triggered degradation, of  
PEG-peptide micelle 141

enzyme-triggered PA hydrogel  
formation 191

ethyl(hydroxyethyl) cellulose (EHEC)  
83

ethylene oxide (EO) linkers 184, 187

**f**

ferrocenyl surfactants 77–78

11-ferrocenylundecylammonium  
bromide (11-FAB)

bulk solution properties 82

molecular structure 78

11-ferrocenylundecyltrimethyl-  
ammonium bromide (FTMA)

excess surface concentration 79

globular micelles with hydrodynamic  
diameter 82

Marangoni flow generation 87

molecular structure 78

surface tensions 79, 80

fibronectin-mimetic peptide

amphiphiles 193

fluorinated polyhedral oligomeric  
silsesquioxane  
(FPOSS)-polystyrene-block-  
polyethylene oxide (PS-*b*-PEO)

giant surfactants 323

Fourier transform pulsed field gradient  
spin-echo NMR 43

fusion proteins 227, 235

fusogenic GALA peptide 197

**g**

gemi surfactants 187, 320, 321

genetic engineering 217

geometrical relations

for block copolymer aggregates 19

for spherical and cylindrical micelles  
and bilayers 4, 5

giant surfactants 35

with block copolymer tails  
321–324

gemi surfactants 320, 321

molecular architecture of 311–312

with multiheads and multitailes  
319–321

phase behaviors and self-assembled  
morphologies of 318

with short nonpolymeric tails  
312–315

with single head and polymer tail  
315–319

- globular protein-based giant surfactants 316  
 globular protein copolymers 229–236
- h**
- helical protein copolymers  
   coiled-coils 209, 214, 215  
   helix-to-sheet transitions 213  
   *N*-carboxy anhydride (NCA)  
     polymerization 209  
   PBLG-oligostyrene conjugates 211, 212  
   poly(carbobenzoxy-L-lysine) (PZLLys) 211  
   poly(benzyl-L-glutamate)-coil diblock copolymer 209, 210  
   rod-coil block copolymers, phase diagrams of 210  
   rod-rod polymers 211–212  
   short helix-alkyl chain diblock system 213  
 helix-to-sheet transitions 213  
 horseradish peroxidase (HRP)-polyethylene oxide-block-polystyrene (PEO-*b*-PS) giant surfactants 322  
 hydrophobic effect 105
- i**
- interfacial protocell models 120–123  
 ionic micelles  
   growth of 51–52  
   persistence length of 52–53  
 ionic surfactants, spherical micelles from 8–9  
 ion-specific effect, on micellar growth and branching 55–56
- j**
- Janus particles  
   asymmetric 288–290  
   deposition on patterned surface  
     step trench 295–298  
     sticky stripe 301–303  
     wedge trench 298–301  
   and lipid vesicles (*see* lipid vesicles-Janus nanoparticle interaction)  
   symmetric 285–288
- k**
- Keggin POM-based giant surfactants 313  
 KLAK PA 189, 198
- l**
- light energy harvesting  
   and chemical conversion 124  
   phosphate-chemicals high-energy bond conversion 125–126  
 light-responsive surfactants  
   azobenzene 90  
   biomolecule-surfactant interactions 91–93  
   bulk solution properties 90–91  
   interfacial properties 90  
   spatial control of 93  
 light-reversible transition, of NaOA and C<sub>0</sub>AZOC<sub>2</sub>IMB binary mixtures 91, 94  
 Lindqvist POM-based giant surfactants 313  
 lipase-PS giant surfactant 315, 316  
 lipid-like DNA amphiphiles 154–159  
 lipid membranes 101  
 lipid vesicles-Janus nanoparticle interaction  
   adhesive interactions 282–283  
   asymmetric Janus particles 288–290  
   dissipative particle dynamics 278, 279  
   advantageous features of 278  
   conservative force 279  
   drag force 280

lipid vesicles-Janus nanoparticle interaction (*contd.*)  
 hydrodynamic behavior 280  
 random force 280  
 multiple Janus particles 291–294  
 on patterned surfaces  
 step trench 295–298  
 sticky stripe 301–303  
 wedge trench 298–301  
 Peclet number 284  
 shear flow 283  
 spherical amphiphilic Janus nanoparticles 278  
 composition 280–281  
 deposition on patterned surfaces 295–303  
 face-centered cubic lattice structure 280  
 symmetric Janus particles 285–288  
 locked nucleic acid (LNA)-polymer amphiphile-based micelles (LPA) 166, 168

## **m**

Marangoni flows 87, 93, 95, 96  
 matrix metalloproteinases-7-mediated hydrogelation 139, 140  
 matrix metalloproteinases-responsive fluorescent micellar nanoparticles 148  
 Matrixyl 195  
 mCherry-b-PNIPAM block copolymers 232, 233  
 mCherry-ELP fusion block copolymers 234, 235  
 mean field model, of block copolymer micelles 17–20  
 medium-hydrocarbon-chain fatty acid(MCFA) 111, 119, 120  
 membrane proteins 234–236  
 membrane scaffold proteins (MSPs) 236

micelles, 2 *see also* protein analogous micelles (PAMs)  
 corona crosslinked 225  
 cylindrical micelles, formation of 9  
 ionic 51–53  
 nonionic micelles, growth of 50–51  
 PEO–PPO block copolymer 19, 20  
 shell-crosslinked 225  
 wormlike (*see* wormlike micelles)  
 mixed phospholipids/oleic acid bilayers 113  
 molecular beacon micelle flares (MBMFs) 158–159  
 molecular dynamics (MD) simulations advantages 259  
 DNA-mediated nanoparticle crystallization using 260, 261, 263  
 of scale-accurate coarse-grained model with DNA chains 259–263  
 molecular nanoparticles 35  
 molecular packing parameter 3, 7  
 molecular thermodynamic models 63, 68  
 Monte Carlo (MC) method 259  
 multiheaded/multitailed giant surfactants 319–321 *see also* giant surfactants  
 myoglobin-b-polystyrene-block-poly(ethylene glycol) (Mb-PS-b-PEG) triblocks 230, 231

## **n**

nanofiber-based PA system 197  
 nanocarriers 277  
 nanoscopic lipid vesicles 277 *see also* lipid vesicles-Janus nanoparticle interaction  
 N-carboxy anhydride (NCA) polymerization 209

- neurite-promoting laminin epitope  
194
- N-methylation, of cyclic peptides 223
- nonclassical amphiphiles  
amphiphilic nanoparticles 34–36  
dendritic amphiphiles 25–27  
DNA amphiphiles 27–29  
peptide amphiphiles 29–31  
protein–polymer conjugates 31–34
- nonionic micelles, growth of 50–51
- nonionic surfactants, spherical micelles  
from 8
- nonsense fluorescein labeled LPA  
(NS-FL-LPA) 168, 169
- nucleic acids 151, 153
- P**
- PAA-VG2 diblock copolymers 229
- packing parameter 106, 108–109
- Peclet number 284
- PEG-peptide micelle, enzyme-triggered  
degradation of 141
- PEO–PPO block copolymer micelles  
19, 20
- PEO–PPO–PPO triblock copolymers  
23
- peptide amphiphiles (PAs) 139–141,  
179  
in anti-aging skin creams 195  
in aqueous solutions 30  
basic leucine zipper (bZip) 184,  
187, 192  
 $\beta$ -sheet secondary structure  
183–185  
biomimetic assemblies 180  
fibronectin-mimetic 193  
hydrophobic tails, role of 185, 186  
IKVAV neurite-promoting laminin  
epitope 194  
for materials design applications  
29–30  
molecular structure and chain  
conformation 31
- nanofiber-based system 197
- photocleavable nitrobenzyl group  
191, 192
- physicochemical properties of  
181–192
- Prodan drug addition 196
- randomly and flow aligned 193
- thermodynamic behavior 181
- peptide-containing micelles 138
- peptide amphiphiles 139–141
- peptide–polymer amphiphiles  
141–151
- peptide–polymer amphiphiles (PPAs)  
 $\alpha$ -chymotrypsin 141  
cancer-associated enzymes 142  
fluorogenic micellar nanoparticles  
145, 146  
FRET-active species 146, 147  
FRET signal 148–151  
MMP-responsive fluorescent  
micellar nanoparticles 148
- phosphorylation/dephosphorylation  
reactions 142, 143
- polymer properties, structure, and  
characterization 142, 143
- SEC-MALS 142
- synthesis of 151, 152
- TEM 146, 147
- percolating active network 68
- persistence length, of ionic micelles  
52–53
- phosphatases 139
- photoresponsive surfactants 91, 93,  
96
- physicochemical properties, of peptide  
amphiphiles 181–192
- poly(carbobenzoxy-L-lysine) (PZLLys)  
211
- poly(benzyl-L-glutamate)-coil diblock  
copolymer 209, 210
- polycyclic aromatic hydrocarbons  
(PAHs) 114

- poly(ethyleneglycol)-DNA polymer
    - structure 170
  - poly(benzyl-L-glutamate)
    - (PBLG)-oligostyrene conjugates 211, 212
  - polyoxometalate (POM) amphiphiles 34, 35
  - polyoxometalate (POM)-based giant surfactants 313, 318–319
  - protein analogous micelles (PAMs) *see also* peptide amphiphiles (PAs)
    - advantages 198
    - $\beta$ -sheet formation 182, 183
    - in biomedical applications 192–199
    - cell penetration and internalization 197
    - for controlled drug release 196
    - description 179
    - electrostatic interactions 188
    - in immunotherapeutic applications 198
    - inhibition of cancer cell proliferation 196
    - mixed micelles 188–189
    - multiple headgroups, role of 186–187
    - pH 190
    - properties of 181
    - protein resembling dendrimer templated nanospheres 187–188
    - scaffolds 192
    - secondary structures, role of 182–185
    - spherical and cylindrical 179, 180
    - stabilizing spherical structure 187–188
    - stimuli-responsive 190–192
    - for tissue engineering applications 198–199
  - protein–polymer conjugates
    - aggregation patterns 34
    - headgroup repulsions 33
    - schematic representations 31, 32
    - shapes of 208, 209
  - protein resembling dendrimer templated nanospheres (PRTNs) 187–188
  - proteins 208
  - protocells 103
    - designs 116, 117
    - development 118
    - energy uptake and transduction 118
- r**
- redox-active surfactants
    - biomolecule-surfactant assemblies, control of 84–87
    - bulk solution properties, reversible changes in 82–84
    - ferrocenyl surfactants 77–78
    - interfacial properties, reversible changes in 78–82
    - Marangoni flows 87
    - micelle concentration, spatial gradients in 87
    - microfluidic channels 89
  - RGD-based nanofibers 192–193
  - rhombic dodecahedra (RD)
    - microcrystals formation 268
  - rod-coil block copolymers, phase diagrams 210
  - rod–rod polymers 211–212
- s**
- SCAs *see* single-hydrocarbon-chain amphiphiles (SCAs)
  - self-assembled recombinant triblock polypeptide 219
  - semi-synthetic, biohybrid
    - supramolecular systems 137
  - shell-crosslinked micelles 225
  - short helix-alkyl chain diblock system 213



- silk-elastin-like protein polymers (SELPs) 217–219
  - silk-mimetic block copolymers 217
  - silk-mimetic hybrid nanostructures 217
  - silk-to-elastin block ratio 219
  - single-head/single-tail giant surfactants 315–319 *see also* giant surfactants
  - single-hydrocarbon-chain amphiphiles (SCAs)
    - amphiphile headgroups *vs.* solute/solvent molecules interactions 106
    - catalysis compartmentalization with 116–126
    - critical aggregate concentration 106, 107
    - dynamism 126–127
    - headgroup-to-headgroup interactions 105–106
    - interaction with solid surfaces 116
    - membrane formation in prebiotic context 104
    - mixtures of 110
      - charged species 112–113
      - and lipids 113–114
      - and neutral co-surfactants 111–112
      - and nucleobases 114, 115
      - and polycyclic aromatic hydrocarbons 114
      - with same functional headgroups 111
    - packing parameter 106, 108–109
    - self-assembly on surfaces 115–116
    - single species of 109–110
    - van der Waals forces and hydrophobic effect 104–105
  - slow-cooling method 268, 269
  - small-molecule surfactants 309
  - sodium dodecylsulfate (SDS) 90
  - sodium (11-ferrocenylundecyl) sulfonate (SFS)
    - critical aggregation concentration (CAC) 81
    - globular micelles with hydrodynamic diameter 82
    - molecular structure 78
    - surface tension 81, 82
  - solution self-assembly, of giant surfactants *see* giant surfactants
  - spherical amphiphilic Janus nanoparticles 278 *see also* lipid vesicles-Janus nanoparticle interaction
    - composition 280–281
    - deposition on patterned surfaces 295–303
    - face-centered cubic lattice structure 280
  - spherical bilayer vesicles, formation of 9–10
  - spherical micelles
    - from ionic surfactants 8–9
    - from nonionic surfactants 8
    - from zwitterionic surfactants 8
  - spherical nucleic acids (SNAs) 272
  - star polymer model, for block copolymer micelles 15–17
  - statistical associating fluid theory (SAFT) 58
  - step trench, vesicle-particle assembly behavior 295–298
  - sticky stripe, vesicle-particle assembly behavior 301–303
  - stimuli-responsive PAMs 190–192
  - strain promoted azide-alkyne cycloaddition (SPAAC) 225
  - surface energy ratios 268
  - surface tension-driven (Marangoni) flows 87
  - surfactant micelles/aggregates
    - dodecyl alkane tail effects on shape transitions 20–22

surfactant micelles/aggregates (*contd.*)

schematic representation of 4

Tanford model for 4–11

surfactant molecules 1

surfactant self-assembly model 13–15

switchable aptamer micelle flares

(SAMFs) 155–157

symmetric Janus particle-lipid vesicles

interaction 285–288

## t

Tanford model, for surfactant micelles

critical micelle concentration 6

cylindrical micelles formation 9

equilibrium aggregation behavior 6

Gibbs equilibrium condition 4

hydrophobic domain 4

molecular packing parameter and  
aggregate shape 7

spherical bilayer vesicles formation  
9–10

spherical micelles formation

from ionic surfactants 8–9

from nonionic/zwitterionic  
surfactants 8

standard free energy change 5–6

vesicle interior volume per molecule,  
tail length dependence of 10,  
11

template-directed RNA polymerase

ribozyme 121

thermally active hybridization,

DNA-programmable

nanoparticle assembly

263–268

thermo-responsive micelle conjugates

322

tropoelastin 224

twin-tailed amphiphilic lipid molecules

280, 281

## u

UV light effect, BTHA/SDS mixture

91–93

## v

van der Waals attractive forces

104–105

velocity-Verlet algorithm 280

vesicles 4, 108, 119–120 *see also* lipid

vesicles-Janus nanoparticle

interaction

azoTAB 91

decanoic acid 110

fatty acid vesicle formation and

stability 110

formation and disruption 82, 83

nanoscopic 277, 278

spherical bilayer vesicles formation

9–10

VG2-PAA-VG2 triblock copolymers

229

viscoelasticity, of entangled wormlike

micelles *see also* wormlike

micelles

breaking time 45

characteristic lengths 46, 48

Cole–Cole plot 46, 48, 49

concentration dependence 50

contour length 45, 49

for dilute and semidilute solutions

44

Maxwell model 46

reptation model 45

storage and loss moduli, frequency

dependence of 46, 47

terminal relaxation time 50

## w

wedge-shaped trench, vesicle-particle

assembly behavior 298–301

- wormlike micelles
    - branching 43
    - entropic networks 56–60
    - shape and free energy 61–66
  - entangled, viscoelasticity of 44–50
  - rheology and structure of 44–56
  - transformation in multiconnected perforated structure 65–66
  - Wulff polyhedra, DNA-mediated nanoparticle crystallization in 268–272
- Z**
- Zilman-Safran theory 60, 61, 64
  - zwitterionic surfactants, spherical micelles from 8

