

Dispersion Polymerization

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Abstract Dispersion polymerization is an attractive method for producing micron-size monodisperse polymer particles in a single batch process. Great progress in this field has been achieved over the past two decades. This article presents an overview of the recent progress in the preparation of polymeric microspheres via dispersion polymerization in organic media, focusing on the preparation of novel functional particles, the design of microspheres using macromonomers, and on understanding mechanisms for the control of particle size. Examples of functional microspheres obtained by dispersion polymerization in the presence of linear polymers, block polymers, and macromonomers are tabulated, and new developments are highlighted. Particle size control in dispersion polymerization in the presence of macromonomers is discussed, and experimental results for poly(ethylene oxide)-grafted particles are compared with theoretical expectations for ideal core-shell particles.

Keywords Functional microsphere · Macromonomer · Block copolymer · Graft copolymer · Particle size control

Symbols and Abbreviations

AIBN	2,2'-azobisisobutyronitrile
AAm	acrylamide
ATR	attenuated total reflection
BMA	<i>n</i> -butyl methacrylate
<i>Boc</i> -AMST	<i>boc-p</i> -aminostyrene
CMS	chloromethylstyrene
C_s	chain transfer constant
D	mean separation between PEO anchor points
DSM	dynamic swelling method
DVB	divinylbenzene
EDMA	ethylene dimethacrylate
EG	ethylene glycol
ESCA	electron spectroscopy
f	initiator efficiency
FTIR	Fourier transform infrared spectroscopy
GMA	glycidyl methacrylate
GTP	group transfer polymerization
HEMA	2-hydroxyethyl methacrylate
HLB	hydrophobic-lipophilic-balance
HPC	hydroxypropylcellulose
HPMA	2-hydroxypropyl methacrylate
$[I]_0$	initiator concentration
k_d	decomposition rate constant
k_p	propagation rate constant
k_t	termination rate constant
k_2	diffusion-controlled rate constant for coalescence between similar-sized particles
M_D	molecular weight of macromonomer
MMA	methyl methacrylate
MW	molecular weight
M_w	weight average molecular weight
N	number of particles per liter
n	number of chains grafted onto surface
N_A	Avogadro's number
NAD	nonaqueous dispersion
NIPAM	<i>N</i> -isopropyl methacrylate
NMR	nuclear magnetic resonance
NVC	<i>N</i> -vinyl carbazole
PAA	poly(acrylic acid)
PANI	polyaniline
PB	poly(1,3-butadiene)
PBMA	poly(<i>n</i> -butyl methacrylate)
PCL	poly(ϵ -caprolactone)
PDMAEMA	poly(2-(dimethylamino)ethyl methacrylate)
PDMS	poly(dimethylsiloxane)
PDVB	polydivinylbenzene
PE	polyethylene
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)

PGMA	poly(glycidyl methacrylate)
PHEM	Apoly(2-hydroxyethyl methacrylate)
PHSA	poly(12-hydroxystearic acid)
PIB	polyisobutylene
PLMA	poly(lauryl methacrylate)
PMA	poly(methacrylic acid)
PMMA	poly(methyl methacrylate)
PNIPAM	poly(<i>N</i> -isopropylacrylamide)
POXZ	polyoxazolines
PP	polypropylene
PS	polystyrene
P(PP- <i>alt</i> -E)	poly(propylene- <i>alt</i> -ethylene)
PTBA	poly(<i>t</i> -butyl acrylate)
PTBMA	poly(<i>t</i> -butyl methacrylate)
PVA	poly(vinyl alcohol)
PVAcA	poly(<i>N</i> -vinylacetamide)
PVME	poly(vinyl methyl ether)
PVP	poly(vinylpyrrolidone)
P4VP	poly(4-vinylpyridine)
r_i	reactivity ratio of i species
R	radius of particle
ρ	density
S	surface area occupied by a dispersant chain
ST	styrene
$\langle S^2 \rangle$	mean square radius of gyration
S_{crit}	surface area occupied by a macromonomer chain at critical point
TDI	toluene diisocyanate
TEMPO	2,2,6,6-tetramethylpiperidinyloxy
4VBAC	4-vinylbenzyltrimethylammonium chloride
4VP	4-vinylpyridine
Vpy	vinylpyrrolidone
θ	fractional conversion of monomer
θ_{crit}	fractional conversion of monomer at critical point
θ_{D}	fractional conversion of macromonomer
θ_{Dcrit}	fractional conversion of macromonomer at critical point
W_{D}	weight of polymerized macromonomer
W_{Do}	initial weight of macromonomer
W	weight of polymerized monomer
W_{o}	initial weight of monomer

1

Introduction

Micron-size monodisperse polymeric microspheres are used in a wide variety of applications, such as toners, instrument calibration standards, column packing materials for chromatography, spacers for liquid crystal displays, and bio-medical and biochemical analysis [1–3]. Because of the commercial and scientific interest in these particles, research into their preparation has been active

for the past two decades. Micron-size monodisperse particles were usually difficult to obtain because this size is in-between the diameter range of particles produced by conventional emulsion polymerization (0.06–0.7 μm) in a batch process and suspension polymerization (50–1000 μm). Vanderhoff et al. [4, 5] used the successive seeding method to obtain micron-size monodisperse polymer particles. The particles were also prepared by Ugelstad et al. [6, 7] by means of the two-stage swelling method. Omi et al. [8] and Kamiyama [9] used modified suspension polymerizations, and Okubo et al. [10] developed the dynamic monomer swelling method (DSM).

Dispersion polymerization is an attractive and promising alternative to other polymerization methods that affords micron-size monodisperse particles in a single batch process. Dispersion polymerization may be defined as a type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a suitable polymeric stabilizer soluble in the reaction medium. The solvent selected as the reaction medium is a good solvent for both the monomer and the steric stabilizer polymers, but a non-solvent for the polymer being formed. Dispersion polymerization, therefore, involves a homogeneous solution of monomer(s) with initiator and dispersant, in which sterically stabilized polymer particles are formed by the precipitation of the resulting polymers. As a continuous medium, the properties of the solvent also change with increasing monomer conversion. Under favorable circumstances, the polymerization can yield, in a batch step, polymer particles of 0.1–15 μm in diameter, often of excellent monodispersity. This dispersant polymer can be formed as a reactive, polymerizable macromonomer. It can be a block copolymer in which one block has an affinity for the surface of the precipitated polymer, or it can be a soluble polymer (a “stabilizer precursor”) to which grafting is thought to occur during the polymerization reaction. In all instances, this soluble dispersant polymer – a hairy layer – plays a crucial role in the dispersion polymerization process. By adsorbing or becoming incorporated onto the surface of the newly-formed precipitated polymers, it acts as a steric stabilizer, directing the particle size and colloidal stability of the system. This feature of dispersion polymerization is widely appreciated and well understood (Fig. 1).

Dispersion polymerization in organic hydrocarbon media was first developed by Osmond and coworkers at ICI [11]. They polymerized acrylic and vinylic monomers in hydrocarbons with oil soluble polymer stabilizers to produce nonaqueous dispersions (NAD) of polymer particles. Later, Almog et al. [12] extended the concept to dispersion polymerization in polar solvents as a method of forming monodisperse polymeric microspheres. Ober et al. [13–16], Tseng et al. [17], Okubo et al. [18, 19], and Paine et al. [20–24], among other authors, studied this technique in order to control particle size and achieve a narrow particle size distribution. A great deal of research has been devoted to dispersion polymerization during past two decades, as reviewed by Croucher and Winnik [25], Guyot and Tauer [26], Cawse [27], Pichot et al. [28], Asua and Schoonbrood [29], and Ito et al. [30–32]. The present article is intended to discuss state-of-the-art design of microspheres obtained by dis-

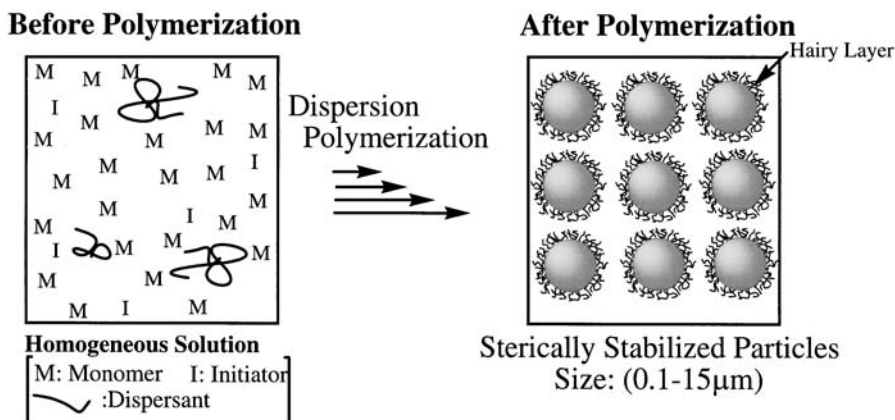


Fig. 1 Schematic description of dispersion polymerization

ersion polymerization, with particular attention paid to the preparation of novel functional particles, the design of microspheres using the macromonomer technique, and to mechanistic aspects for particle size control.

2

Microsphere Syntheses by Linear and Block Polymer Dispersants

2.1

Functional Microspheres

Most research into the study of dispersion polymerization involves common vinyl monomers such as styrene, (meth)acrylates, and their copolymers with stabilizers like polyvinylpyrrolidone (PVP) [33–40], poly(acrylic acid) (PAA) [18, 41], poly(methacrylic acid) [42], or hydroxypropylcellulose (HPC) [43, 44] in polar media (usually alcohols). However, dispersion polymerization is also used widely to prepare functional microspheres in different media [45, 46]. Some recent examples of these preparations include the (co-)polymerization of 2-hydroxyethyl methacrylate (HEMA) [47, 48], 4-vinylpyridine (4VP) [49], glycidyl methacrylate (GMA) [50–53], acrylamide (AAM) [54, 55], chloromethylstyrene (CMS) [56, 57], vinylpyrrolidone (VPy) [58], Boc-*p*-aminostyrene (Boc-AMST) [59], and *N*-vinyl carbazole (NVC) [60] (Table 1). Dispersion polymerization is usually carried out in organic liquids such as alcohols and cyclohexane, or mixed solvent-nonsolvents such as 2-butanol-toluene, alcohol-toluene, DMF-toluene, DMF-methanol, and ethanol-DMSO. In addition to conventional PVP, PAA, and PHC as dispersant, poly(vinyl methyl ether) (PVME) [54], partially hydrolyzed poly(vinyl alcohol) (hydrolysis=35%) [61], and poly(2-(dimethylamino)ethyl methacrylate-*b*-butyl methacrylate)

Table 1 Examples of functional microspheres obtained by dispersion polymerization

Stabilizer	Monomer(s)	Medium	Reference
<i>Functional particles</i>			
PS, PMMA derivatives	HEMA	2-Butanol/toluene	[47]
Cellulose acetate butyrate	HEMA	Alcohol/toluene	[48]
PS- <i>b</i> -PB	4VP	DMF/toluene	[49]
PVP	GMA	MeOH/water or DMF	[50]
PVP	GMA/DVB	Ethanol	[51]
PVP	ST/GMA	Ethanol/water	[52]
Cellulose acetate	GMA	DMF/methanol	[53]
PVME	AAM	<i>t</i> -BuOH/water	[54]
None	AAM	<i>t</i> -BuOH/water	[55]
PVP	CMS	Ethanol/DMSO	[56]
PAA	CMS	Methoxyethanol/MeOH	[57]
PS- <i>b</i> -P(PP- <i>alt</i> -E)	VPy/EDMA	Cyclohexane	[58]
PVP	ST/Boc-AMST	<i>i</i> -Propanol	[59]
PVP	ST/NVC	Ethanol	[60]
PVA- <i>co</i> -PVAc	ST	Methanol	[61]
PDMAEMA- <i>b</i> -PBMA	ST	Alcohols	[62]
<i>Hybrid particles</i>			
Poly(amic acid)	ST/4VBAC	Ethanol/water	[63]
PVP	ST/polyimide prepolymer	<i>i</i> -Propanol	[64]
PVP	GMA/iron oxide	Alcohol/water	[65]
Cellulose acetate butyrate	HEMA/EDMA/iron oxide	Alcohol/toluene	[66]
PVP	HEMA/GMA/iron oxide	Alcohol/toluene	[67]
PVP	ST/SiO ₂	Ethanol/water	[68]
None	4VP/HPMA/SiO ₂	Water	[69]
<i>Crosslinked particles</i>			
PVP	DVB	Acetonitrile or Ethanol	[70]
None	DVB	Acetonitrile	[71]
None	DVB/CMS	Acetonitrile	[72]
Chitosan	NIPAM	Acetic Acid	[73]
PS- <i>b</i> -P(PP- <i>alt</i> -E)	Oxazoline methacrylate	Heptane	[74]
PVP-Aerosol-OT	ST/urethane acrylate	Ethanol	[75]
PVP	ST/2,2'-oxy-bisethanol diacrylate	Ethanol/heptane	[76]
PVP	MMA/EDMA	Ethanol/water	[77]
<i>Dynamic swelling method (DSM)</i>			
None	ST/DVB	Ethanol/water	[10, 78–83]

(PDMAEMA-*b*-PBMA) [62] in alcohols and polystyrene-*b*-polybutadiene (PS-*b*-PB) [49] and polystyrene-*b*-poly(propylene-*alt*-ethylene) (PS-*b*-(PP-*alt*-E)) [58], linear PS [47], and PMMA [47] in hydrocarbon are used.

Dispersion polymerization in supercritical carbon dioxide (scCO₂), pioneered by DeSimone and coworkers, has recently attracted considerable attention as an environmentally friendly alternative to the use of organic solvents. A wide range of monomers have been polymerized to produce the corresponding microspheres in the presence of CO₂-philic polymers and monomers, as reviewed in another chapter.

Core-shell polystyrene-polyimide high performance particles have been successfully prepared by the dispersion copolymerization of styrene with vinylbenzyltrimethyl ammonium chloride (VBAC) in an ethanol-water medium using an aromatic poly(amic acid) as stabilizer, followed by imidization with acetic anhydride [63]. Micron-sized monodisperse polystyrene spheres impregnated with polyimide prepolymer have also been prepared by the conventional dispersion polymerization of styrene in a mixed solvent of isopropanol/2-methoxyethanol in the presence of L-ascorbic acid as an antioxidant [64].

A recent interesting example is the preparation of organic/inorganic hybrid particles by dispersion polymerization. Horák et al. [65–67] have prepared cross-linked poly(2-hydroxyethyl methacrylate) (PHEMA)- and poly(glycidyl methacrylate) (PGMA)-based magnetic microspheres by incorporating iron oxide into cellulose acetate butyrate stabilizer or PVP. Polymer encapsulation of small silica particles has also been achieved using the dispersion polymerization of styrene in ethanol-water medium with PVP [68]. Silica-polymer hybrid particles have also been prepared very recently by the precipitation copolymerization of 4-vinylpyridine with 2-hydroxypropyl methacrylate (HPMA) in water [69]. These organic/inorganic hybrid particles would be expected to lead to a new generation of nanostructured materials with diverse applications such as catalysts, electronic or phonic devices, and sensors.

Highly cross-linked monodisperse polydivinylbenzene (PDVB) microspheres have been prepared in acetonitrile with or without PVP stabilizer [70–72]. Interestingly, PDVB microspheres are very stable without any stabilizer in acetonitrile, possibly due to their highly crosslinking rigid surface. Other examples of the syntheses of crosslinked microspheres [73–77] are listed in Table 1.

The dynamic swelling method (DSM) [10] has also been described for the preparation of crosslinked microspheres with free vinyl groups [78]. Therefore, polystyrene seed particles (1.9 μm) prepared by dispersion polymerization are dispersed in ethanol-water (7/3, w/w) containing divinylbenzene (DVB), benzoyl peroxide, and poly(vinyl alcohol) (PVA). The slow drop-wise addition of water to the mixture causes the DVB phase to separate, and it is continuously imbibed by seed particles to produce relatively large swollen particles (4.3 μm), which are then polymerized to afford the respective PS-PDVB composite particles with free vinyl groups. DSM has recently been developed in order to prepare hollow microspheres and various oddly-shaped polymer particles, including a rugby ball, red blood cells, or snowman structures [79–83].

2.2 Living Dispersion Polymerization

Living dispersion (co-) polymerization is interesting due to its straightforward control of molecular weight with a narrow distribution, and also the functionalization of living end groups that occurs. Living anionic dispersion polymerization of styrene or α -methylstyrene has been achieved in hydrocarbon solvents with block copolymer stabilizers such as PS-*b*-poly(4-trimethylsilylstyrene) [84], PS-*b*-PB [85–87], PS-*b*-poly(4-*tert*-butylstyrene) [88, 89], poly(vinyl ethyl ether) [90], and PS-*b*-polyisobutylene (PS-*b*-PIB) [91], and PS-*b*-P(PP-*alt*-E) [92]. Jenkins and coworkers [93] polymerized methyl methacrylate in *n*-heptane via group transfer polymerization (GTP). Highly crosslinked microspheres have also been prepared by the living anionic copolymerization of *t*-butylstyrene and divinylbenzene in heptane [94].

Living radical dispersion polymerization is a promising way to expand the design and scope of functional polymer colloids to a wider range of other monomers. The 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-mediated living radical dispersion polymerization of styrene has been carried out in presence of PS-*b*-P(PP-*alt*-E) in decane at 135 °C [95] or PVP in alcohol-water at 130 °C [96] in order to produce microspheres with a very broad size distribution, consisting of relatively low molecular weight polystyrene ($M_w=10^4$) with $M_w/M_n=1.1$.

Table 2 Examples of microspheres obtained by living dispersion polymerization

Stabilizer	Monomer	Medium	Reference
<i>Living anionic dispersion polymerization</i>			
PS-poly(4-trimethylsilylstyrene)	ST	Hexane	[84]
PS- <i>b</i> -PB	ST	Hexane	[85, 86]
None	ST/butadiene	Pentane	[87]
PS- <i>b</i> -Poly(4- <i>tert</i> -butylstyrene)	ST	Hexane	[88, 89]
Poly(vinyl ethyl ether)	α -methylstyrene	Heptane	[90]
PS- <i>b</i> -PIB	ST	Hexane	[91]
PS- <i>b</i> -P(PP- <i>alt</i> -E)	ST	Hydrocarbon	[92]
PS- <i>b</i> -P(PP- <i>alt</i> -E)	MMA	Heptane	[93]
None	<i>t</i> -butylstyrene/DVB	Heptane	[94]
<i>Living radical dispersion polymerization</i>			
PS- <i>b</i> -P(PP- <i>alt</i> -E)	ST	Decane	[95]
PVP	ST	Alcohol/water	[96]
<i>Ring opening dispersion polymerization</i>			
Poly(dodecyl methacrylate)- <i>g</i> -poly(ϵ -caprolactone)	ϵ -caprolactone and lactide	Heptane/dioxane	[97,98]

Dispersion polymerization has also been applied to the ring opening polymerization of ϵ -caprolactone and lactide in heptane-dioxane (4/1 v/v) with poly(dodecyl methacrylate)-*g*-poly(ϵ -caprolactone) as stabilizer [97]. Diethylaluminium ethoxide and tin(II) 2-ethylhexanoate were used as initiators in these two systems, respectively, to obtain functional microspheres with a narrow particle size distribution and a narrow molecular weight distribution [98]. Table 2 provides an overview of microspheres obtained by living dispersion polymerization.

2.3

Microspheres from Non-Vinyl Monomers

Microspheres have been prepared by the dispersion polymerization of monomers other than vinyl monomers, such as styrene and (meth-)acrylates. Polyaniline (PANI) is one of the most frequently studied electrically conducting polymers. Since the paper by Armes and Aldissi [99] in 1989, there have been numerous reports on the preparation of PANI dispersions by oxidative

Table 3 Examples of microspheres of monomers other than vinyl monomers obtained by dispersion polymerization

Stabilizer	Monomer	Medium	Reference
<i>Oxidative polymerization</i>			
PVP	Aniline	Alcohol/water	[100, 101]
PVME	Aniline	Alcohol/water	[102, 103]
PVA	Aniline	Water/alcohol	[104–106]
Poly(styrenesulfonic acid)	Aniline	Water	[107]
Methycellulose	Aniline	Water/alcohol	[108]
HPC	Aniline	Water	[109]
PVA	3,5-Xylidine	Water	[110, 111]
Ethylhydroxycellulose	Pyrrole	Ethanol/water	[112, 113]
PVME	Pyrrole	Ethanol/water	[114]
<i>Enzymatic polymerization</i>			
PVME, PVA, PEG	Phenol	Dioxane/phosphate buffer	[115, 116]
PVME	<i>p</i> -Phenylphenol	Dioxane/phosphate buffer	[115, 116]
<i>Polyurethane</i>			
Poly(lauryl methacrylate) diol	TDI/EG	Paraffin oil	[117]
<i>Polyester</i>			
Poly(2-ethylhexyl acrylate- <i>co</i> -styrene- <i>co</i> -acrylic acid)	4-Acetoxybenzoic acid + 2,6-acetoxynaphthoic acid	–	[118]

polymerization. Colloidally-stable submicron-sized PANI particles are produced in the aqueous-alcohol media by the dispersion polymerization of aniline in the presence of a suitable steric stabilizer such as PVP [100, 101], PVME [102, 103], PVA [104–106], poly(styrenesulfonic acid) [107], methycellulose [108], and HPC [109]. The oxidative dispersion polymerization of 3,5-xylidine [110, 111] produced needle-shaped particles in water. Polypyrrole particles were also prepared in aqueous ethanol using FeCl_3 and ammonium persulfate as the oxidant [112–114].

Uyama and Kobayashi et al. [115, 116] were first to prepare nearly mono-disperse sub-micron polyphenol particles by the enzyme-catalyzed dispersion polymerization of phenol and *p*-phenylphenol in a mixture of 1,4-dioxane and phosphate buffer using a water-soluble polymer as stabilizer (such as PVME, PVA, and PEG).

Polyurethane [117] and polyester [118] particles have also been prepared by the dispersion polyaddition of ethylene glycol (EG) and toluene diisocyanate (TDI) in paraffin, and the polycondensation of acid and ester at a high polymerization temperature, respectively. Table 3 provides an overview of microspheres of monomers other than vinyl monomers obtained by dispersion polymerization.

3

Microsphere Syntheses by Reactive Dispersants, Macromonomers, Inimers, and Transurfs

Macromonomers are polymers or oligomers with polymerizable end groups, widely investigated for the preparation of functional polymers and polymer microspheres by dispersion polymerization. For microspheres, the macromonomers should be designed to copolymerize with the main monomers in such a way as to produce graft chains that serve as efficient stabilizers; in other words, their main chain should be firmly bound to the particle surface and the graft chains should extend into the polymerization medium.

Examples of dispersion polymerizations using macromonomers are summarized in Table 4. Non-aqueous dispersion (NAD) polymerization of polar

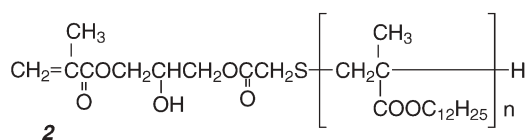
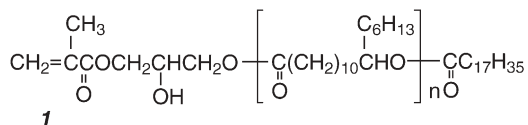
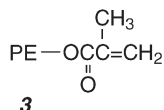


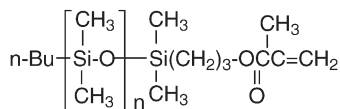
Table 4 Examples of dispersion copolymerization with reactive dispersants

Reactive dispersant	Monomer	Medium	Reference
PHSA 1	MMA	Hydrocarbon	[11]
PLMA 2	MMA	Hydrocarbon	[11]
PE 3	MMA	Dodecane, PE	[119]
PDMS 4	ST	Silicone oil	[120]
POXZ 5	MMA	MeOH/H ₂ O	[121]
POXZ 5	ST	EtOH/H ₂ O	[122]
POXZ 5	CH ₂ =CHNHCHO	MeOH	[123]
POXZ 6	MMA	MeOH/H ₂ O	[124]
PEO 7 (<i>m</i> =1)	MMA, ST	EtOH/H ₂ O	[126, 127]
PEO 8 (<i>m</i> =3, 5, 7)	ST	Ethanol/H ₂ O	[128]
PEO 9a	ST	EtOH/H ₂ O	[129]
PEO 9a, 11	ST	EtOH/H ₂ O	[130]
PEO 7 (<i>m</i> =1, 4, 7)	ST, MMA, BMA	MeOH/H ₂ O	[131–133]
PEO 9b (<i>m</i> =11)	ST	EtOH/H ₂ O	[134]
PEO 10 (<i>m</i> =2.6, 4.1, 6.8)	ST	MeOH/H ₂ O	[135]
PEO 9a, 9b (<i>m</i> =6, 10)	ST, MMA	MeOH/H ₂ O	[125, 137]
PEO 12	ST	EtOH/H ₂ O	[136]
PEO 13	ST	EtOH/H ₂ O	[138]
PVP 14	ST, MMA	EtOH	[139]
PVAcA 15	ST	EtOH	[140]
PVA 16	MMA	EtOH/Water	[141]
P4VP 17	ST	EtOH	[142]
PNIPAM 18	ST	EtOH	[143]
PTBMA 19	ST	EtOH	[144]
PAA 20	MMA	EtOH/H ₂ O	[145]
PDMS 4	MMA, ST	CO ₂	[146]
PCL 21	L,L-Lactide	Heptane/dioxane	[97, 98]
PMA 22	MMA	EtOH/H ₂ O	[147]
PMA 23	ST	MeOH/H ₂ O	[148]
PDMAEMA 24	ST	Alcohols	[150]
PEO 25	ST	MeOH/H ₂ O	[151]
Inimer 26	ST, MMA	Ethanol/H ₂ O	[155]
Transurf 27	ST	Ethanol/H ₂ O	[156]

monomers was first carried out in aliphatic hydrocarbon media with the hydrophobic macromonomers 1 and 2 [11]. These were copolymerized with MMA or other polar monomers to produce comb-graft copolymers, which have limited solubility in pure aliphatic hydrocarbons but adequate solubility in hydrocarbon-monomer mixtures. It is particularly effective in stabilizing PMMA NAD particles. Polyethylene (PE) macromonomers 3 have been used



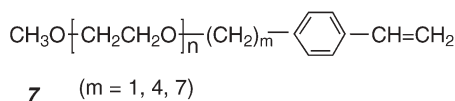
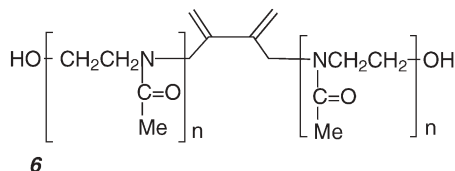
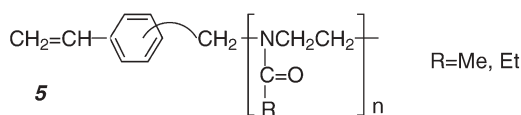
for the dispersion copolymerization of MMA in dodecane and in PE melts to produce stable PMMA dispersions at a high temperature [119]. In the latter case, nanocomposite materials in which submicron-sized fine PMMA particles are uniformly dispersed in the PE bulk can be prepared during the copolymerization. Monodisperse PS particles (0.70 μm), prepared by the dispersion copolymerization of styrene with the poly(dimethylsiloxane) PDMS macromonomer **4** in PDMS-diol (MW=7,500), was allowed (together with trimethylolpropane) to react with hexamethylene diisocyanate using dibutyltin dilaurate as a catalyst. The product of the polyaddition was a tough elastomeric composite with polystyrene particles finely dispersed and strongly anchored in a PDMS-polyurethane matrix [120].

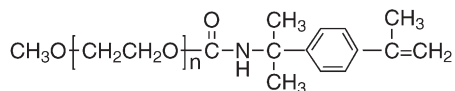
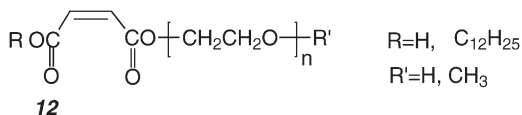
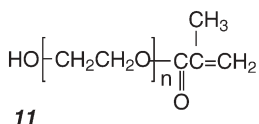
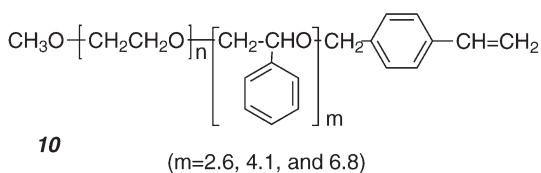
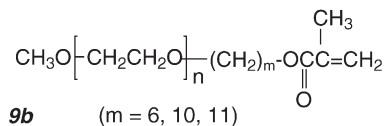
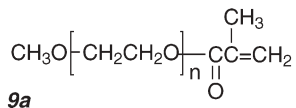
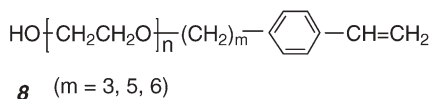


4

This technique has been extended to polar media, especially alcohols and their mixtures with water as a continuous phase. Kobayashi and Uyama et al. [121–124] reported that poly(2-oxazoline) macromonomers such as **5** and **6** are very effective for dispersion copolymerization with styrene, MMA, and *N*-vinylformamide in methanol, ethanol, and mixtures of these alcohols with water. They reported that the particle size decreased with increasing initial macromonomer concentration and that graft-copolymerized poly(2-oxazoline) chains are concentrated on the particle surface to act as steric stabilizers.

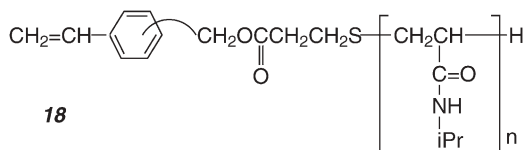
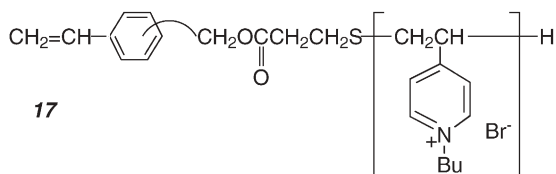
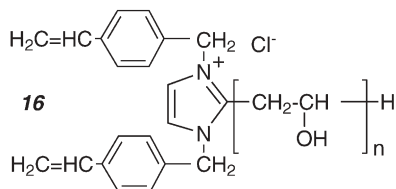
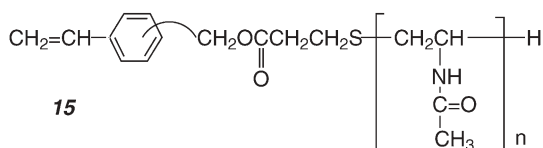
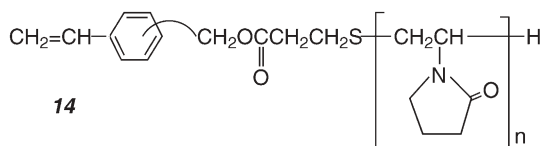
Dispersion copolymerizations that use the poly(ethylene oxide) (PEO) macromonomers **7–13** in alcoholic media have been intensively studied by

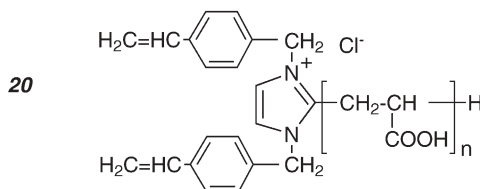
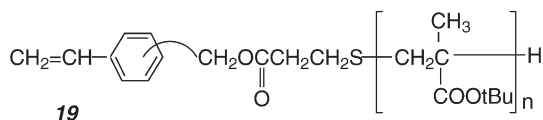




many researchers [125–138]. They produce nearly monodisperse polymeric microspheres of submicron to micron sizes, covered with PEO chains on their surface. Several factors that affect the particles' size and the polymerization kinetics have been studied. Theoretical models for particle nucleation in these systems have also been developed and compared with the experimental observations, as will be discussed later.

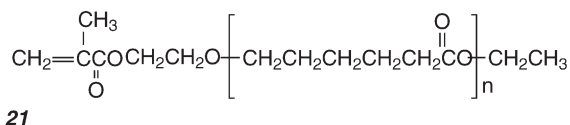
Several other hydrophilic macromonomers including **14–20** have been applied to the dispersion polymerization [139–145]. These macromonomers were synthesized by radical polymerization in the presence of appropriate chain transfer agents, followed by transformation of the end group, as previously summarized [30]. Akashi et al. [143] used poly(*N*-isopropylacrylamide) (PNIPAM) macromonomer **18** in ethanol and prepared thermosensitive microspheres 0.4–1.2 μm in diameter consisting of a PS core and PNIPAM branches on their surface. The particles are particularly useful for many biomedical applications. Indeed, the particles have been reported to flocculate and change in light transmittance with increasing temperature.



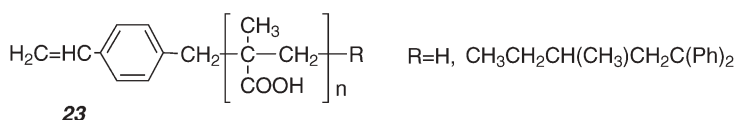
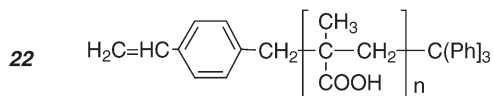


DeSimone and his co-workers have intensively studied polymerization reactions in an environmentally friendly solvent, CO_2 . In the presence of the CO_2 -philic silicone-based macromonomer **4**, relatively monodisperse micron-sized polymer particles were obtained by the polymerization of MMA and styrene in supercritical CO_2 , as shown in another chapter [146].

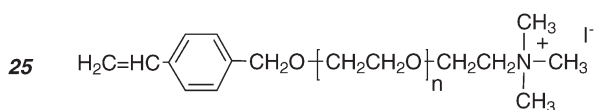
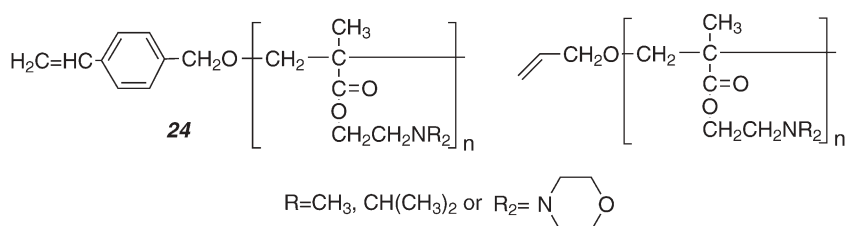
Sosnowski et al. [97, 98] have reported that uniform biodegradable polymeric particles with diameters of less than $5 \mu\text{m}$ can be prepared by ring-opening dispersion polymerization of L,L-lactide in heptane-dioxane mixed solvent in the presence of poly(dodecyl acrylate)-*g*-poly(ϵ -caprolactone), which were synthesized by the copolymerization of dodecyl acrylate with the poly(ϵ -caprolactone) macromonomers **21**. Note that the polymer particles consist of well-defined poly(L,L-lactide) polymers with $M_n \approx 1 \times 10^4$ and $M_w/M_n \approx 1.06$.



The polyelectrolyte macromonomers **17**, **20**, **22**, and **23** [142, 143, 147, 148] were prepared and applied to dispersion copolymerizations to produce polymeric particles covered with polyelectrolyte chains. Evidently, the dependence of the conformational properties of polyelectrolyte brush chains attached to the latex surface on the pH, the degree of neutralization, and the salt concentration have been the subject of growing experimental and theoretical effort.



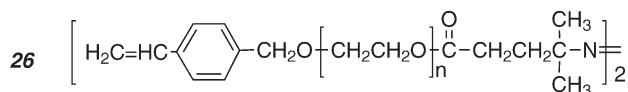
Some novel water soluble macromonomers, **24**, have been synthesized by the oxyanionic polymerization [149] of 2-(dimethylamino)ethyl, 2-(diisopropylamino)ethyl, and 2-(*N*-morpholino)ethyl methacrylate, and conducted to dispersion copolymerization of styrene in alcohol media [150]. Sufobetaine-based macromonomer was prepared by the polymer reaction of **24** ($R=CH_3$) with propane sultone, and was found to be useful in the dispersion polymerization of styrene even at high electrolyte levels (up to 1 M NaCl). Ito et al. [151] synthesized new PEO macromonomers with a cationic charge at the ω -end, **25**, and examined the influence of the charge on the particles' size in dispersion copolymerization with styrene in alcohol media.



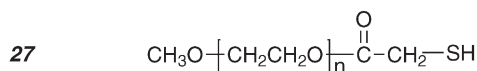
Poly(HEMA-*co*-MMA-*g*-PMMA) graft copolymer was also prepared with a commercially available poly(methyl methacrylate) (PMMA) macromonomer, HEMA, and MMA, and used as an efficient dispersant for the dispersion polymerization of styrene in ethanol [152].

Recently, Akashi and coworkers [153, 154] synthesized novel spherical particles on which nano-projections are uniformly distributed over the whole surface like “confetti” by the one-step dispersion terpolymerization of acrylonitrile, styrene, and the PEO macromonomer **9a** in ethanol/water media. The control of nanoparticle morphology by a one-step synthetic procedure is important to self-organization at the polymer chain level, which is a basis for the formation of biological nanoconstructs such as viruses and organelles.

Dispersion polymerization in the presence of reactive surfactants including surfmers, inisurfs and transurfs is also a versatile method for producing functional microspheres [26]. For example, the macromonomeric azoinitiator **26** is an effective inisurf in the preparation of PS and PMMA particles [155].



Similarly, the thiol-ended transurf 27 shows higher stabilizing efficiency than PVP in the dispersion polymerization of styrene and MMA in water-ethanol [156].



In all instances of the dispersion polymerization, amphiphilic graft copolymers produced in a selective solvent for the branches play a crucial role. Schematically, a microsphere obtained by copolymerization in this way with a small amount of macromonomer has a core-shell structure as given in Fig. 2, with the core occupied by the insoluble substrate polymer chains and the shell by the soluble, graft-copolymerized macromonomer chains. The backbone chains of the graft copolymers, which must be insoluble in the medium, serve as the anchors into the core. The following section presents general criteria for the size control of polymeric microspheres by dispersion copolymerization using macromonomers.

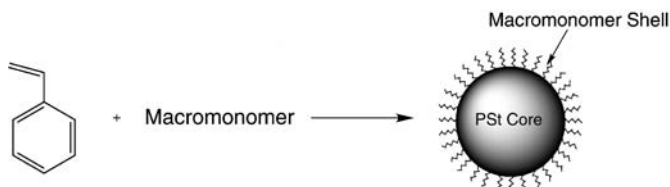


Fig. 2 Schematic description of dispersion copolymerization of styrene with macromonomer

4

Particle Size Control in Dispersion (Co-)Polymerization

4.1

Theoretical Model

According to the aggregative and coagulative nucleation theories [157] which all originally derive from the homogeneous nucleation theory [158], the most important point when determining particle number is the instant at which sterically-stabilized particles form [159]. After this point, coagulation between similar-sized particles no longer occurs, and the number of particles present in the reaction medium remains constant. Sufficient particle stabilization may be achieved with physically adsorbed stabilizers in the case of linear soluble polymers, copolymers, and block copolymers. For covalent bonding, polymerization is performed in the presence of macromonomer stabilizers, which copolymerize with monomer(s) to graft stabilizer on the particles' surface [26, 31]. The graft copolymer may be also produced by the chain transfer reaction of a propagating radical with a soluble polymer chain.

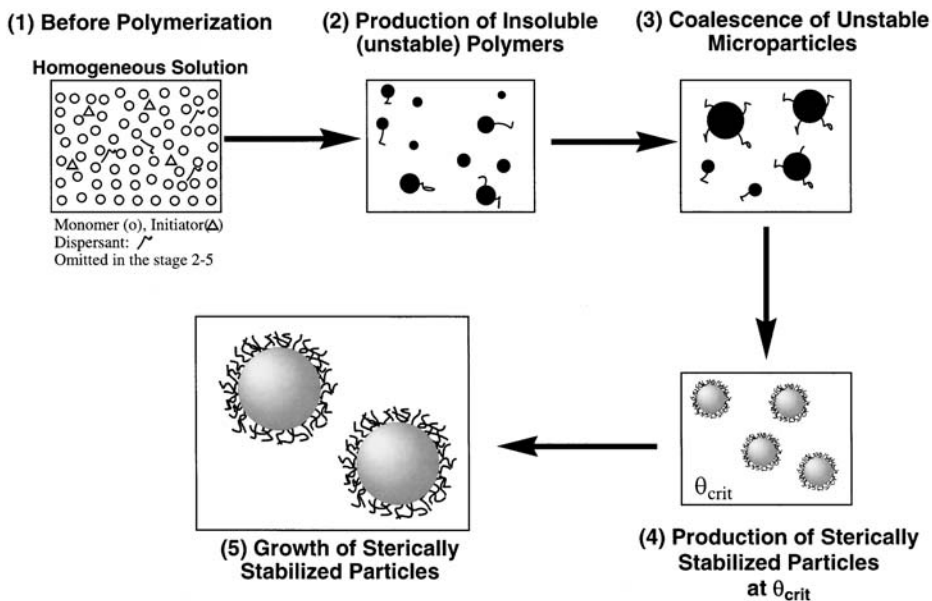


Fig. 3 Schematic model for the particle nucleation and growth of sterically-stabilized particles in dispersion polymerization

As shown in Fig. 3, the dispersion polymerization is considered to proceed as follows:

1. Before polymerization, the reaction mixture dissolves completely into the continuous phase.
2. When the reaction mixture is heated, free radicals are formed by initiator decomposition and grow in the continuous phase to produce linear oligomer, polymers, and/or graft copolymers. The solubility of these polymers is a function of their molecular weight (MW) and the composition of the graft copolymers. Polymers with a MW larger than a certain critical value precipitate and begin to coagulate to form unstable particles.
3. These particles coagulate on contact, and the coagulation among them continues until sterically-stabilized particles form.
4. This point is referred to as the critical point, and it occurs when all of the particles contain sufficient stabilizer polymer chains on the surface to provide colloidal stability.
5. After this point, no new nuclei or particles are formed and the particles may grow both by the diffusive capture of oligomers and the coagulation of very small unstable particles (nuclei, precursors) produced in the continuous phase and by the polymerization of the monomer included within the particles until all of the monomer is consumed. The total number of such sterically-stabilized particles remains constant so that their size is only a function of the amount of polymer produced.

In 1990, Paine [24] first developed a multibin kinetic model for the aggregation of precipitated radicals or unstabilized particles in dispersion polymerization, based on diffusion-controlled particle aggregation, which was described by Smoluchowski [160] and Frenklach [161]. The stabilized particles whose surfaces are completely covered with grafted polyvinylpyrrolidone (PVP) chains do not aggregate. This was the first model that quantitatively simulated the role of the stabilizer molecules at the particle formation stage. Assuming ideal core-shell structures in which the main monomer forms the core, and dispersant the shell, one can readily establish a basic relationship between microsphere size and weights of main core polymer and stabilizer polymer attached on the particle surface, as given by the following equations:

$$W = W_o \theta = \frac{4}{3} \pi R^3 \rho N \quad (1)$$

and

$$nS = \frac{W_{D_o} \theta_D N_A S}{NM_D} = 4\pi R^2 \quad (2)$$

Here, W (g/l) is the weight of monomer polymerized, W_o is the weight of monomer feed, θ is the fractional conversion of monomer, R is the particle core radius (cm), ρ is the core polymer density, N is the particle number per liter, n is the number of dispersant molecules on one particle, S is the area of particle surface covered by one dispersant molecule, W_{D_o} is the weight (in g/l) of dispersants in feed, M_D is the molecular weight of dispersant, θ_D is the fraction of adsorbed or grafted dispersant on particle surface, and N_A is Avogadro's number. Combining Eqs. 1 and 2 produces a universal relationship between the particle radius and the extent of polymerization for the microspheres obtained by an ideally grafted steric stabilizer:

$$R = \frac{3W_o \theta}{\rho N_A W_{D_o} \theta_D \left(\frac{S}{M_D} \right)} \quad (3)$$

In spite of different mechanisms of particle formation and growth, Eq. 3 predicts larger particles with increasing amounts of main polymer, and with lower surface coverage by individual dispersant molecules (S/M_D), but smaller particles with increasing amounts of dispersant. Also, S/M_D increases with the solvency of the dispersion medium, and hence the particle radius should be smaller in media that are good solvents for the dispersant.

One problem is the estimation of θ_D and S with respect to the monomer conversion (θ) and the attachment of the dispersant to particles. For adsorbed dispersants, θ_D is determined by the partition of dispersant between the particle surface ($4\pi R^2 N$) and the continuous medium. For chemical grafting via chain transfer, Paine [24] derived the equation

$$R = \theta^{\frac{1}{3}} \left(\frac{3W_o}{\rho N_A} \right)^{\frac{2}{3}} \left(\frac{M_D}{C_S W_{Do} S_{crit}} \right)^{\frac{1}{2}} \left(\frac{0.386k_2}{4\pi k_t} \right)^{\frac{1}{6}} \left(\frac{k_t}{2k_d f[I]_o} \right)^{\frac{1}{12}} \quad (4)$$

where C_s is the chain transfer constant to dispersant polymer chains, S_{crit} is S at critical point, k_2 is the diffusion-controlled rate constant for coalescence between similar-sized particles ($M^{-1}s^{-1}$), k_p is the propagation rate constant ($M^{-1}s^{-1}$), k_t is the termination rate constant ($M^{-1}s^{-1}$), $[I]_o$ is the initiator concentration (M), and f is the initiator efficiency and k_d is the initiator decomposition rate constant (s^{-1}).

Equation 4 was found to explain particle size data fairly well, with reasonable kinetic and coverage parameter values (k 's and S_{crit}), in the dispersion polymerization of styrene in ethanol with PVP dispersant [24]. Many other dispersion polymerization systems with homopolymer dispersants appear to be explained by Eq. 4, except for the frequently observed direct particle size dependence on initiator concentration [27].

For dispersion polymerization with macromonomer stabilizers, we use Eq. 5 and Eq. 6 [31, 32, 131–133].

$$R = \theta^{\frac{1}{3}} \left(\frac{3W_o}{\rho N_A} \right)^{\frac{2}{3}} \left(\frac{M_D r_1}{W_{Do} S_{crit}} \right)^{\frac{1}{2}} \left(\frac{0.386k_2}{4\pi k_p} \right)^{\frac{1}{6}} \left(\frac{k_t}{2k_d f[I]_o} \right)^{\frac{1}{12}} \quad (5)$$

$$S = \theta^{-\frac{1}{3}} \left(\frac{3W_o}{\rho N_A} \right)^{\frac{1}{3}} \left(\frac{M_D S_{crit}}{r_1 W_{Do}} \right)^{\frac{1}{2}} \left(\frac{4\pi k_p}{0.386k_2} \right)^{\frac{1}{6}} \left(\frac{2k_d f[I]_o}{k_t} \right)^{\frac{1}{12}} \left(\frac{\theta}{\theta_D} \right) \quad (6)$$

Here r_1 is the reactivity ratio ($=\theta_{crit}/\theta_{Dcrit}$) of the monomer (M_1) in a copolymerization with the macromonomer (M_2) at critical stabilization.

In Eqs. 4 and 5, one sees that the radius of the latex particle follows simple scaling relationships with the key parameters in the system: $\theta^{1/3}$, $[\text{monomer}]_o^{2/3}$, $[\text{dispersant}]_o^{-1/2}$, $[\text{initiator}]_o^{-1/12}$, where $[]_o$ means initial concentration. These equations predict that the particle size and stabilization are determined by the magnitude of r_1 . In addition, looking at Eq. 6, it is apparent that the surface area occupied by a stabilizer chain follows $\theta^{-1/3}$, and in the case of azeotropic copolymerization, $\theta = \theta_D$. This means that the chain conformation for the grafts on the latex particle will change with grafting density. The S value is closely related to the conformation of a single polymer chain as a stabilizer grafted onto the surface of a latex particle. According to de Gennes' "mushroom" model [162] for a polymer grafted to a noninteracting surface, the polymer chain occupies a volume determined by its mean-squared radius of gyration $\langle S^2 \rangle$. When the surface becomes crowded with chains, additional energy is needed to deform the polymer mushrooms into brushes. When the particle surfaces are completely covered with random coils of the polymer, they are also sterically-stabilized against coagulation with other particles. One, therefore, defines S_{crit} as the maximum surface area occupied by a single polymer chain in the continuous phase.

4.2

Comparison of Experiment with Theory

For dispersion copolymerization with PEO macromonomers, the power law exponents in Eq. 5 have been experimentally determined and compared, as summarized in Table 5. Initial monomer concentration has a major influence on the final particle radius. The experimental power law exponents (0.82–1.02) are usually significantly larger than those in Eqs. 4 and 5, except for 0.63 for styrene as a monomer with 7 ($m=4, n=45$). This is likely to be due to a solvency effect of the monomer. The values of the exponents for the macromonomer and initiator concentration dependences in the polymerization of hydrophobic monomer, styrene and *n*-butyl methacrylate are in good agreement with those from Eq. 5. Figure 4a shows a comparison of Eq. 5 with the particle radius obtained for the dispersion copolymerization of styrene with the PEO macromonomer 7 ($m=4, n=45$), in methanol-water medium (9/1 v/v). One sees that the experimental particle radius is quantitatively described by the model with reasonable constants, $\theta=1$, $\rho=1.05 \text{ g cm}^{-3}$, $N_A=6.02 \times 10^{23}$, $k_2=10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_p=352 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_t=6.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_d=3.2 \times 10^{-7} \text{ s}^{-1}$, $f=1$, and $S_{\text{crit}}/r_1=10 \text{ nm}^2$, $r_1=1$.

In remarkable contrast, unusually high exponent values (~ 1.2) have been obtained in the dispersion copolymerization of a polar monomer, MMA in methanol-water (8:2 and 7:3 v/v) media. The value of the exponent drops to 0.51 when the water content is increased to higher than 40%, as shown in

Table 5 Values of the exponents in $R=K [\text{Monomer}]^a [\text{Macromonomer}]^b [\text{Initiator}]^c$ (see also Eq. 5) for dispersion copolymerizations with macromonomers

Macromonomer	Monomer	Medium	<i>a</i>	<i>b</i>	<i>c</i>	Reference
Theory (Eq. 5)	–	–	0.67	–0.50	–0.083	–
7, $m=4, n=45$	ST	MeOH/H ₂ O (9:1)	0.63	–0.52	–0.068	[131]
7, $m=1, 4, 7,$ $n=53, 110$	BMA	MeOH/H ₂ O (8:2)	0.82	–0.54	–0.10	[132]
9b, $m=11, n=40$	ST	EtOH/H ₂ O (9:1)	1.02	–0.60	–0.090	[134]
10, $m=2.6, n=41$	ST	MeOH/H ₂ O (9:1)	–	–0.47	–	[135]
10, $m=4.1, n=41$	ST	MeOH/H ₂ O (9:1)	–	–0.40	–	[135]
10, $m=2.6, n=41$	ST	MeOH/H ₂ O (9:1)	–	–0.59	–	[135]
8, $m=3, 5, 6, n=50$	ST	MeOH/H ₂ O (9:1)	–	–0.50	–	[128]
4, $n=130$	ST	Silicone oil ($M=2700$)	–	–0.40	–	[120]
7, $m=1, n=45$	MMA	MeOH/H ₂ O (8:2)	–	–1.17	–	[133]
7, $m=1, n=45$	MMA	MeOH/H ₂ O (7:3)	0.85	–1.15	–0.030	[133]
7, $m=1, n=45$	MMA	MeOH/H ₂ O (6:4)	–	–0.51	–	[133]
7, $m=1, n=45$	MMA	MeOH/H ₂ O (5:5)	–	–0.52	–	[133]
7, $m=1, n=36$	ST/AN	Ethanol/H ₂ O (8:2)	–	–0.68	–	[153]

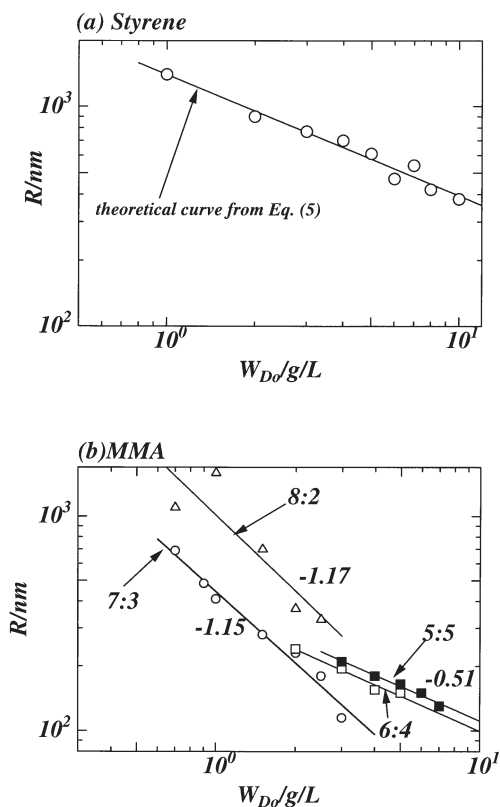


Fig. 4 Double logarithmic plots of average particle radius (R) as a function of weight (W_{D0}) of PEO macromonomer. **a** Styrene 7 ($m=4$ and $n=45$), $W_0=100$ g/L, $[I]_0=0.0122$ mol/L, $\theta=1$ at 60°C . The straight line is a theoretical curve calculated from Eq. 5 with the parameters in the text. **b** MMA 7 ($m=1$ and $n=45$), $W_0=100$ g/L, $[I]_0=0.012$ mol/L, $\theta=1$ at 60°C in methanol: water=8:2 (empty triangles), =7:3 (empty circles), =6:4 (empty squares), and =5:5 (filled squares)

Fig. 4b. The significant change in the value of the exponent with the polarity of the continuous phase cannot be simply explained by the current model, so further refinements [163–165] are needed.

The criteria for designing PEO macromonomers to be used as efficient dispersants in dispersion polymerization have been thoroughly studied by Ito et al. [128, 131, 135, 151], who examined the effects of the length of spacer (m), the degree of polymerization of PEO chain (n) of 7, and charge group at the ω -end of 25 on particle size.

5 Chain Conformation of Grafted Polymer Chains at the Particle Surface

Polymer adsorption has been a subject of both theoretical and experimental interest, because the adsorption behavior of the polymer at the solid-liquid interface is strongly connected with many technologically important processes such as flocculation, adhesion, coating, and lubrication in addition to the colloidal stabilization already discussed above. This subject has been recently reviewed by Cosgrove, Griffiths [166], Flerer et al. [167], and Kawaguchi and Takahashi [168]. Among a variety of adsorbed polymers, two are of particular interest with respect to macromonomers. One is the adsorption of comb and graft copolymers with highly grafted chain density onto the solid surface, which is referred to as “brush adsorption”, as illustrated in (a) of Fig. 5. Another is the attachment of the double bond of the macromonomer with the solid surface by chemical reaction, which is referred to as “terminally-attached

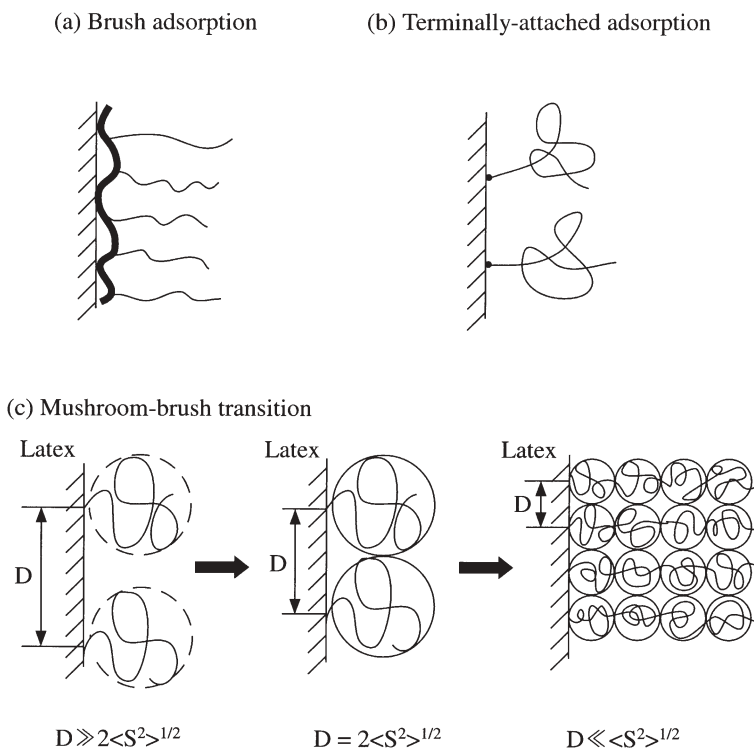


Fig. 5 Schematic representation of the possible conformations of adsorbed (co)polymers prepared using the macromonomer technique. **a** Brush adsorption of graft copolymer; **b** terminally-attached adsorption, and; **c** the mushroom-brush transition for strongly overlapping chains as proposed by de Gennes [162] and Alexander [170]

adsorption”, as illustrated in (b) of Fig. 5. The conformational properties of these grafted polymer chains have been the subject of growing attention, from the point of view of the “mushroom-brush” transition proposed by de Gennes [162, 169] and Alexander [170], as shown in (c) of Fig. 5.

While there have been many studies on the conformational properties of terminally-attached polymer chains, prepared either by the adsorption of block copolymers in a selective solvent onto a solid surface [171] or by the reaction of a solid surface with reactive groups of polymer [172], little has been reported for graft copolymer chains prepared from macromonomers. Cairns et al. [173] carried out a SANS study of a non-aqueous dispersion system comprised of deuterated PMMA latex grafted with poly(12-hydroxystearic acid), **1**. The thickness of the layer was found to correspond to about 2/3 of the extended chain length. Comb-like PEO gradient surfaces were grafted onto low density PE sheets by corona discharge treatment followed by the homopolymerization of the PEO macromonomers **9b** ($n=1, 5$ and 10) and the gradient PEO concentration at the surface was characterized by measuring the water contact angle, by FTIR-ATR, and by ESCA [174]. The gradient surfaces can be used to investigate the interactions between biological species and the surface PEO chains. Hadziioannou and coworkers [175] prepared a terminally-attached cationic polyelectrolyte brush on a gold-coated Si-wafer by end-grafting styryl-terminated poly(vinylpyridine) macromonomer, followed by quarternarization with methyl iodide. The surface was characterized by means of scanning force microscopy, ellipsometry, and FTIR-ATR.

Wu et al. [176] studied the surface properties of PS and PMMA microspheres stabilized by the PEO macromonomer **7** ($m=1$) using dynamic light scattering, and claimed that for PMMA microspheres the surface area occupied by a PEO molecule is nearly twice as large as that for PS microspheres, assuming that 100% macromonomer is copolymerized to attach to the latex surface. However, this is not the case for styrene copolymerization with PEO macromonomers in which only 10% PEO macromonomer was copolymerized [131]. In contrast, it was confirmed that 100% of PEO macromonomers were copolymerized for the MMA and BMA dispersion copolymerization [132, 133].

¹H NMR studies have been carried out for the dispersion copolymerization of BMA with the PEO macromonomer **7** ($m=7$), in a deuterated methanol-water medium [177]. The fractional composition and surface-grafted PEO concentration were monitored as functions of conversion and particle size. In Fig. 6, the mobile fraction of PEO chains incorporated into the particles is plotted against the interchain spacing D , as shown in (c) of Fig. 5, which can be calculated using particle size values and conversions. One sees that the values of the mobile fraction increase sharply with decreasing D in the region of $D < 1.6$ nm and become constant below $D = 1.4$ nm. The radius of gyration of the PEO chain coil in methanol is calculated to be 1.6 nm, which corresponds to the D value at which a sharp increase in mobile fraction occurs. This result may suggest that the onset of a pancake-to-brush transition of grafted chains at the interface

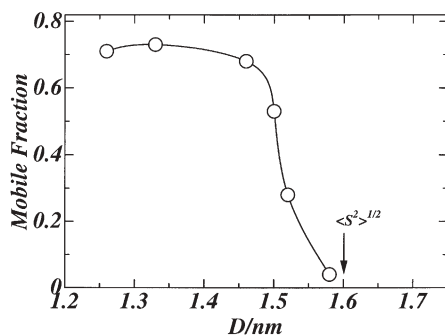


Fig. 6 Plots of mobile fraction of surface anchored PEO chains against the estimated mean separation D between PEO anchor points on the surface of the particles. The D values were calculated from the particle size and number, assuming that all PEO chains were located at the surface

occurs when, say, $D \approx \langle S^2 \rangle^{1/2}$, as expected by theory [162, 169, 170]. This subject should lead to a better understanding of the true nature of the steric stabilization that exists in many dispersion systems.

6

Conclusions and Future

A wide variety of polymer microspheres can be made by dispersion polymerization. A key component in all of these systems is the stabilizer (dispersant) both during particle formation and for the stability of the resulting colloidal particles. Functionality can be introduced into colloidal particles in various ways: by copolymerization of functional monomers (like HEMA), or incorporation of functional dispersants, initiators, chain transfer agents, or macromonomers. Many different types of macromonomer are prepared and used to prepare functional microspheres. Amphiphilic macromonomers provide a particularly versatile component in these systems, being the source of both stabilizer and functional residue. They act as stabilizer because they are covalently grafted onto the particles' surface by copolymerization with main monomers, and form tightly bound hairy shells on the particles' surface.

The experimental details of dispersion polymerization with various polymeric dispersants and macromonomers are fairly well established. A basic expression for particle size control has also been derived for the formation of clear-cut core-shell particles based on highly incompatible core-shells such as polystyrene-PVP and polystyrene-PEO. However, results deviate considerably from theory in compatible polymers such as PMMA with PEO macromonomer. The detailed structures of the "hairy" shells need to be discovered in order to better understand the exact mechanism of their formation and stabilizing function.

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