
1 Introduction

This book is concerned with the numerous aspects of the self-assembly of block copolymers in solution, and the diverse applications of this. Block copolymers in the melt, or in blends are not considered, and information on this can be found elsewhere.¹

An early review of micellization in block copolymers was presented by Tuzar and Kratochvíl,² and these authors provided a further review of the literature up to 1992.³ Micellar properties of block copolymers were reviewed earlier by Price.⁴ A discussion of micellization was included in the general reviews on block copolymers by Riess *et al.*⁵ and Brown *et al.*⁶ Riess has recently published a very nice review specifically dedicated to micellization in block copolymers.⁷ Excellent reviews focused on the solution properties of a particular class of copolymer, i.e. copolymers of poly(oxyethylene) with poly(oxypropylene), have been presented by several groups.^{8–13} Micellization and micellar association in related poly(oxyethylene)/poly(oxybutylene) copolymers has been summarized by Booth *et al.*^{14–16}

The micellar properties of block copolymers in dilute solution, the properties of adsorbed block copolymers and ordered mesophase (lyotropic liquid crystal phase) formation in more concentrated solutions have been comprehensively discussed.¹ Reviews on structure/rheology relationships in block copolymer gels,¹⁷ and on shear-alignment of ordered mesophases^{18,19} (the latter review incorporates work on block copolymer melts also) have also been provided.

Liu and Armes²⁰, Liu *et al.*²¹ and Förster^{22,23} have reviewed the self-assembly of amphiphilic block copolymers, and the numerous applications of the resulting nanostructures.

Applications of block copolymer surfactants have been the subject of a number of reviews by researchers from Dow in the United States.^{24–26} The texts edited by Nace²⁷ and by Alexandridis and Lindman²⁸ cover many aspects of the behaviour and properties of PEO-based amphiphilic block copolymers, with several chapters devoted to applications.

A standard notation for block copolymers is becoming accepted whereby, for example, PX-*b*-PY denotes a diblock copolymer of polymer X and polymer Y.²⁹ This convention is used here. In the case that a specific polymer with defined chain lengths is considered, the molecule is denoted X_{*m*}-*b*-Y_{*n*}, where *m* and *n* are degrees of polymerization. This notation is somewhat more cumbersome than alternatives. For example, Booth and coworkers use single letters to indicate blocks in

PEO-based copolymers (E for poly(ethylene oxide), etc.), however this system breaks down when considering large numbers of distinct materials, as is the case here. Table 1.1 summarizes the abbreviations used. Note that throughout this book we have used the terms PEG and PEO according to the notation used in the original research—we have not attempted to distinguish carefully between them (PEG differs from PEO by hydroxyl termination as opposed to methyl termination).

Table 1.1 Abbreviations used for polymers

Abbreviation	Polymer/systematic name (where used alternatively)
OEGMA (see also PEGMA)	Oligo(ethylene glycol) methacrylate
PA	Poly(acrylate)
PCsA	Poly(caesium acrylate)
PNaA	Poly(sodium acrylate)
PAA	Poly(acrylic acid)
PAI	Poly[5-(<i>N,N,N</i> -diethylmethylammonium)]isoprene
PAM	Poly(acrylamide)
PAMS	Poly(α -methyl styrene)
PAsp	Poly(α,β -L-aspartic acid)
PB	Poly(butadiene)
PBA	Poly(butyl acrylate)
PBLG	Poly(γ -benzyl L-glutamate)
PBMA	Poly(butyl methacrylate)/poly(<i>n</i> -butyl methacrylate)
PBO	Poly(butylene oxide)/poly(oxybutylene)
PBzMA	Poly(benzyl methacrylate)
PCEMA	Poly(2-cinnamoyloxyethyl methacrylate)
PCL	Poly(ϵ -caprolactone)
PDAMA	Poly[<i>N</i> -(<i>N'</i> , <i>N'</i> -dicarboxymethylaminopropyl)methacrylamide]
PDEA	Poly[(2-diethylamino)ethyl methacrylate]
PDESCB	Poly(diethylsilacyclobutane)
PDLL	Poly(D,L-lactide)
PDMA	Poly[(2-dimethylamino)ethyl methacrylate]
PDMS	Poly(dimethylsiloxane)
PEB	poly(ethylene- <i>co</i> -butylene)
PEE	Poly(ethyleneethylene)
PEGMA	Poly(ethylene glycol) methacrylate
PEHA	Poly(ethylhexyl acrylate)
PEI	Poly(ethyleneimine)
PEMA	Poly(2-phenylethyl methacrylate)
PEO; PEG	Poly(ethylene oxide)/poly(oxyethylene); Poly(ethylene glycol)
PEP	Poly(ethylene- <i>co</i> -propylene)
PE4VP	Poly(<i>N</i> -ethyl-4-vinylpyridinium)
PFMA	Poly(perfluorohexylethyl methacrylate)
PFP	Poly(ferrocenylphenyl phosphine)

Table 1.1 (Continued)

Abbreviation	Polymer/systematic name (where used alternatively)
PFPO	Poly(perfluoropropylene oxide)
PFS	Poly(ferrocenylphenyl silane)
P4FS	Poly(4-fluorostyrene)
PGMA	Poly(glycerol monomethacrylate)
PHEMA	Poly(hydroxyethyl methacrylate)
PhI	Poly(hydrogenated isoprene)
PHIC	Poly(hexyl isocyanate)
PHOVE	Poly(2-hydroxyethyl vinyl ether)
PHPMA	Poly[<i>N</i> -(2-hydroxypropyl)methacrylamide]
PI	Polyisoprene
sPI	Sulfonated polyisoprene
PIBVE	Poly(isobutyl vinyl ether)
PLGA	Poly(D,L-lactic acid- <i>co</i> -glycolic acid)
PLLA	Poly(L-lactic acid)
PLMA	Poly(lauryl methacrylate)
PLys	Poly(L-lysine)
PMA	Poly(methacrylate)
PCsMA	Poly(caesium methacrylate)
PNaMA	Poly(sodium methacrylate)
PMAA	Poly(methacrylic acid)
PMDPS	Poly{3-[<i>N</i> -(2-methacroyloylethyl)- <i>N,N</i> -dimethylammonio]-propane sulfonate}
PME	Poly(methylene)
PMEMA	Poly[2-(<i>N</i> -morpholino)ethyl methacrylate]
PMMA	Poly(methyl methacrylate)
PMOVE	Poly(2-methoxyethyl vinyl ether)
PMOXA	Poly(2-methyloxazoline)
PMPC	Poly(2-methacroyloxy phosphorylcholine)
PMPS	Poly(methylphenyl silane)
P4MS	Poly(4-methyl styrene)
PMTD	Poly(methyltetracyclododecane)
PMTEGVE	Poly[methyl tri(ethylene glycol) vinyl ether]
PMVE	Poly(methyl vinyl ether)
PNBVE	Poly(<i>n</i> -butyl vinyl ether)
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
PPhOVE	Poly(2-phenoxyethyl vinyl ether)
PPO; PPG	Poly(propylene oxide)/poly(oxypropylene); poly(propylene glycol)
PPQ	Poly(phenylquinoline)
PPS	Poly(propylene sulfide)
PS	Polystyrene
PSMA	Poly(solketal methacrylate)
PSO	Poly(styrene oxide)/poly(oxyphenylethylene)
PSS	Poly(styrene sulfonate)

(Continue)

Table 1.1 (Continued)

Abbreviation	Polymer/systematic name (where used alternatively)
PNaSS	Poly(sodium styrene sulfonate)
PSSA	Poly(styrene sulfonic acid)
PTHF	Poly(tetrahydrofuran)
PrBA	Poly(<i>tert</i> -butyl acrylate)
PrBS	Poly(<i>tert</i> -butyl styrene)
PTMEMS	Poly(trimethylammonium ethylacrylate methyl sulfate)
PVA	Poly(vinyl alcohol)
PVBA	Poly[(4-vinyl)benzoic acid]
PVP	Poly(vinyl pyridine) (position of substitution not stated)
PVPh	Poly(vinyl phenol)
P2VP	Poly(2-vinyl pyridine)
P4VP	Poly(4-vinyl pyridine)
qP4VP	Quaternized P4VP
PVPEA	Poly(vinylphenylethyl alcohol)
PVSO	Poly(phenylvinyl sulfoxide)

Abbreviations used for some common solvents and surfactants are listed in Table 1.2. Some technical terms are also abbreviated, but these can be cross-referenced using the index.

Certain topics are omitted from the present text. Associative polymers which may be ‘blocky’ copolymers but are often random copolymers are generally not considered, although some aspects of the self-assembly of telechelic chains is discussed. Texts on this subject are available elsewhere.^{30–32} It should be noted that a telechelic polymer is defined by IUPAC as a ‘prepolymer capable of entering into further polymerization via its reactive endgroups’.³³ We follow common usage here, and use telechelic to refer to an ABA triblock with short endblocks that can undergo physical as well as chemical cross-linking, for example due to association of hydrophobes. The behaviour of block copolymers in blends with homopolymer ‘solvent’ is also not considered (good reviews on this can be found elsewhere¹).

Table 1.2 Abbreviations used for solvents

CPCI	Cetyl pyridinium chloride
CTAB	Cetyl trimethylammonium bromide
DBP	Di- <i>n</i> -butyl phthalate
DEP	Di- <i>n</i> -ethyl phthalate
DMF	Dimethylformamide
DMP	Di- <i>n</i> -methyl phthalate
DOP	Di- <i>n</i> -octyl phthalate
DTAB	Dodecyl trimethylammonium bromide
SDS	Sodium dodecyl sulfate
THF	Tetrahydrofuran

Here we consider self-assembly of block copolymers in low molecular weight solvents. The behaviour of block copolymer melts and nanostructure formation in thin films are also outside the scope of the present volume.

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