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Micellization of block copolymers

Gérard Riess*

Lab de Chimie Macromoleculaire, Ecole Nationale Supérieure de Chimie de Mulhouse, Institut de Chimie des Surfaces et Interfaces, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

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Abstract

This article deals with recent progress including the author's work in the field of block copolymer self-assembly in solution and on solid surfaces. The synthesis methods for producing block copolymers with well-defined structures, molecular weights and composition are outlined with emphasis on ionic and controlled free radical polymerization techniques. A general overview of the preparation, characterization and theories of block copolymer micellar systems is presented. Selected examples of micelle formation in aqueous and organic medium are given for di- and triblock copolymers, as well as for block copolymers with more complex architectures. Current and potential application possibilities of block copolymer colloidal assemblies as stabilizers, flocculants, nanoreservoir in, among others, controlled delivery of bioactive agents, catalysis, latex agglomeration and stabilization of non-aqueous emulsion are also discussed.

Keywords: Block copolymers; Synthesis; Micellization; Micelles; Micellar architectures; Comicellization; Colloidal nanostructures; Self-aggregation; Self-assembly; Controlled drug delivery; Polyion micellar complexes; Metal nanoparticles; Surface modification

Contents

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* Tel.: +33-389-33-68-47; fax: +33-389-33-68-54.
E-mail address: g.riess@uha.fr (G. Riess).

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1. Introduction

Block copolymers are generally defined as macromolecules with linear and/or radial arrangement of two or more different blocks of varying monomer composition. Details of definition, nomenclature, synthesis and properties of block copolymers have been reviewed previously [1].

In the last decade, the synthesis techniques have been widely extended, and especially ionic and controlled free radical methods can now be employed to prepare block copolymers with well defined

Nomenclature

For some polymers the abbreviations are those of the corresponding monomers, e.g. MMA methylmethacrylate with PMMA being the corresponding polymer.

AFM	atomic force microscopy
ATRP	atom-transfer radical polymerization
BAEMA	butylaminoethylmethacrylate
CAC	critical association concentration
CMC	critical micelle concentration
CMT	critical micelle temperature
CHMA	cyclohexylmethacrylate
CRP	controlled radical polymerization
DEAEMA	diethylaminoethylmethacrylate
DMAEMA	*N*,*N*-dimethylaminoethylmethacrylate
DPAEMA	*N*,*N*-diisopropylaminoethylmethacrylate
DLS	dynamic light scattering
EHMA	ethylhexyl methacrylate
EOVE	2-ethoxyethyl vinyl ether
GTP	group transfer polymerization
MeCH	methylcyclohexane
MAA	methacrylic acid
MEMA	2-(*N*-morpholinoethyl) methacrylate
MMA	methylmethacrylate
MM 212	'methylidene malonate' (1-ethoxycarbonyl-1-ethoxycarbonylmethylenoxy carbonyl ethene)
MOVE	2-methoxyethyl vinyl ether
NIPAAM	*N*-isopropyl acrylamide
OEGMA	oligo(ethylene glycol) methacrylate
PAA	poly(acrylic acid)
PANa	neutralized PAA (Na counter ion)
PB	polybutadiene
PFMA	poly(perfluoromethacrylate)
PhB	poly(hydrogenated butadiene)
P*t*BA	poly(*tertio*-butylacrylate)
PBO	poly(butylene oxide)
PnBMA	poly(*n*-butyl methacrylate)
P*t*BMA	poly(*tertio*-butyl methacrylate)
P*t*BS	poly(*tertio*-butylstyrene)
PCEMA	poly(cinnamoylethyl methacrylate)
PCL	poly(caprolactone)
PDMS	poly(dimethylsiloxane)
PE	polyethylene
PEB	poly(ethylene–butylene)
PEG	poly(ethylene glycol)
PEI	poly(ethylene imine)
PEO	poly(ethylene oxide)
PI	poly(isoprene)
PIB	poly(isobutylene)
PIC	polyion complex
PLA	poly(lactic acid)
PLGA	poly(lactic-glycolic acid)
PMANa	neutralized PMAA (Na counter ion)
PP	polypropylene
PPO	poly(propylene oxide)
PQVP	poly(vinylpyridine) quaternized
PS	polystyrene
PVC	poly(vinylchloride)
RAFT	reversible addition–fragmentation transfer
ROP	ring opening polymerization
SEC	size exclusion chromatography
s.c. CO_2	supercritical CO_2
SCK	'shell cross-linked knedel-like micelles'
SFRP	stable free radical polymerization
SLS	static light scattering
TEMPO	2,2,6,6-tetramethylpiperidine-*N*-oxy
THF	tetrahydrofuran
VA	vinyl acetate
VBA	vinyl benzyl alcohol
VME	vinyl methyl ether
2VP	2-vinylpyridine
4VP	4-vinylpyridine

compositions, molecular weights and structures of very elaborate architectures.

The increasing interest in block copolymers arises mainly from their unique solution and associative properties as a consequence of their molecular structure. In particular their surfactive and self-associative characteristics leading to micellar systems are directly related to their segmental incompatibility.

Thus micellization of block copolymers in a selective solvent of one of the blocks is a typical aspect of their colloidal properties. In fact when a block copolymer is dissolved in a liquid that is a thermodynamical good solvent for one block and a precipitant for the other, the copolymer chains may associate reversibly to form micellar aggregates which resemble in most of their aspects to those obtained with classical low molecular weight surfactants. The micelles consist of a more or less swollen core of the insoluble blocks surrounded by a flexible fringe of soluble blocks. These micelles are generally spherical with narrow size distribution but may change in shape and size distribution under certain conditions.

The research on the colloidal behavior of block and graft copolymers has developed gradually from a few isolated observations to a sizeable body of knowledge. The first discovery of micelle formation was apparently Merret's [2] observation for grafted natural rubber, followed by the pioneering work of Molau in the mid-60s [3].

Later on, the colloidal aspects of block copolymers in solution have been surveyed from experimental and theoretical points of view by Price [4], Piirma [5], Tuzar and Kratochvil [6], Riess and co-workers [1], Webber et al. [7], Alexandridis and Hatton [8], Nace [9], Hamley [10], and quite recently by Alexandridis and Lindman [11], by Riess and co-workers [12] as well as by Xie and Xie [13] who focused their review mainly on the synthesis of block- and graft copolymers containing poly(oxyethylene) segments.

In the following we intend to present an overview on some more recent results, including the author's contributions, concerning the synthesis of well defined block copolymers, the preparation and characterization techniques with typical examples of micellar systems in aqueous and organic medium. The existing theories, including those of micellization kinetics and the solubilization phenomenon in micelles, will be discussed to a minor extent as these topics have been treated recently in detail [6,7, 9–11]. An outlook will then be given on less classical micelles, such as functionalized, cross-linked, ABC or mixed micelles, on the self-aggregation of block copolymers with liquid crystalline structures or more complex architecture, as well as on interpolymer complexes of block copolymers.

Section 8 provides a concise overview on current and potential application possibilities of block copolymer colloidal assemblies as stabilizers, flocculants, nanoreservoirs in, among others, controlled drug delivery, gene therapy, phase transfer catalysis, surface modification, metal nanoparticles, latex agglomeration, stabilization of non-aqueous emulsions, etc.

With the increasing number of publications on these different topics, a detailed description with reference to all of them would exceed the scope of this review which has rather the purpose to highlight some specific aspects of block copolymer micellization in aqueous and organic solvent media that have appeared in the recent years.

Block copolymers are mostly referred to in the following by abbreviation of their segments, such as PS–PMMA instead of PS-*b*-PMMA for poly (styrene)-*b*-poly(methylmethacrylate). Full names of block copolymers discussed in the text are provided in the nomenclature.

2. Synthesis and structures of block copolymers

Block copolymers, consisting of connected blocks (sequences) formed by two or more different monomer species, can be in a linear and/or radial arrangement. In the simplest case, a diblock copolymer AB consists of two different homopolymers linked end to end. Extension of this concept leads to ABA or BAB triblocks and to $(AB)_n$ linear multiblocks, whereas ABC copolymers are obtained by the incorporation of a polymer sequence having a third composition. Radial arrangements of block copolymers are in the simplest case star-shaped structures, where n block copolymer chains are linked by one of their ends to a multifunctional moiety. Another structural possibility designated by heteroarm block copolymers is to link n homopolymer sequences to a given junction point.

The synthesis of block copolymers, mainly di- and triblock copolymers has been studied extensively and a general overview can be found in the literature [1, 12,14].

More specific topics, such as block copolymer synthesis by changing the polymerization mechanism [15], by step-growth polymerization [16], via macroinitiators [17] or 'living' free radical polymerization [18] were reviewed later on, as well as the synthesis of selected block copolymer types, e.g. hydrophilic–hydrophilic copolymers [19], copolymers based on PEO [9,13].

With the increasing number of papers published in this area over the last few years, it will be impossible, in the frame of this review article, to make reference to all of them. Our attempt will rather be to outline typical synthesis strategies, mainly by ‘living’ polymerization techniques, and to indicate some recent trends concerning the preparation of block copolymers with well-defined structure, molecular weight and composition. A first part will be devoted to typical examples of block copolymers with linear architecture, e.g. di- and triblock copolymers which up to now have mostly been used in micellization studies whereas in a second part we will focus more specifically on block copolymers with more complex architectures, e.g. star blocks, heteroarm blocks, ‘palm tree’ copolymers, etc. Additional references concerning this type of copolymers will also be given in the other sections of this review.

2.1. Block copolymers with linear A–B and A–B–A architecture

The polymerization methods leading to linear diblock, triblock or segmented block copolymers are based on two general reaction schemes. In a first one, α or α,ω active sites are generated on a polymer chain poly A which then initiate the polymerization of a second monomer B. Such a polymerization can be of free radical, anionic or cationic type. The second method, which is usually called condensation or coupling, is a reaction between chemical functional groups present at the end of different polymers.

The selection of a given synthesis technique will depend on the following criteria:

- the polymerization mechanism, e.g. free radical, anionic or cationic polymerization for the monomer A and/or B; the most suitable case will be that where both monomers A and B are polymerizable by the same mechanism, although mechanism switching is at present an interesting alternative
- the structure of the copolymer, e.g. diblock, triblock, multiblock, star-shaped, etc.
- the desired molecular weight range, knowing that condensation reactions are usually preferred for the preparation of block copolymers of lower molecular weight, e.g. from 1000 to 50 000
- the required monodispersity of each block and the purity of the end product (absence of homopolymers in a diblock or absence of diblock contaminant in a triblock copolymer).

2.1.1. Free radical polymerization

The first identified block copolymer was obtained by Melville by quenching the macroradicals of growing PMMA chains followed by the polymerization of styrene [20]. Since that time a large variety of A–B and A–B–A block copolymers were prepared by free radical polymerization by using as well macroinitiators with active chain ends, either peroxide or azo groups, as polyinitiators, e.g. polyazoesters [17]. These techniques are still used at present for the preparation of different types of polyelectrolyte block copolymers, because charge carrying monomers are in general not directly polymerizable by ionic techniques.

A typical example is that reported by Jaeger and Lieske [21], where poly(ethylene glycol) (PEG) macroinitiators of variable chain length were used to initiate the polymerization of alkylsubstituted quaternary diallylammonium compounds.

The structure of these block copolymers is dependent upon the mode of termination of the growing polymer. If the polymerization is terminated by disproportionation, AB block copolymers are formed. Combination as well as termination by primary radicals lead to ABA block copolymers. This example demonstrates that free radical polymerization could be the preferred mechanism for many vinyl monomers since, unlike ionic polymerization, it is tolerant of trace impurities and monomer functionality. However, one of its major drawbacks is the lack of control over the molecular weight distribution due to intrinsic termination reactions. Furthermore, the efficiency factor of the initiator decreases by the so-called cage effect, e.g. by recombination of the primary free radical, with increasing molecular weight of the macroinitiator [22]. This normally prevents the synthesis of block copolymers with controlled architectures, narrow molecular weight distributions and well-defined molecular weights.

Remarkable progress was made in recent years by so-called ‘living radical’ or controlled radical polymerization (CRP), which is based on the concept of reversible chain termination pioneered by Otsu and Yoshita [23]. The first breakthrough was achieved when free radical polymerizations, initiated with classical initiators such as benzoyl peroxide, were carried out in the presence of selected stable nitroxy radicals, e.g. 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (abbreviated TEMPO) [18,24–26]. A large variety of AB and ABA block copolymers could be obtained by this technique for instance by using mono- or difunctional nitroxides.

The advantage of this nitroxy mediated technique is that the first block could be isolated and characterized before starting the polymerization of the second block. This SFRP (*Stable Free Radical polymerization*) process is mainly limited to styrenic monomers forming adducts with a sufficient low bond-enthalpy of the C–O bond between the dormant chain and the *N*-oxyl moiety.

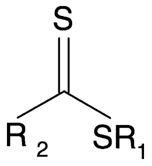
Another generation of CRP is atom transfer radical polymerization (ATRP) first described by Matyjaszewski and Wang [27] and by Sawamoto et al. [28]. This technique, since reviewed in a number of monographies and feature articles [29–32] involves the reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between the organic halide and a copper^{I} halide (in the presence of a ligand, e.g. bipyridine) which yields the initiating radical and the oxidized copper complex:

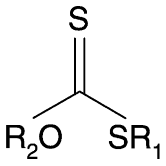
$$RX + Cu^{I}(Bipy)_2 \rightleftarrows R^0 + X - Cu^{II}(Bipy)_2$$

As the polymer chain-end still contains a halogen group, this can be used to initiate the polymerization of a second monomer for the preparation of block copolymers.

Numerous examples were reported for the preparation of AB and ABA block copolymers by using either sequential monomer addition or macroinitiators, e.g. ω- or α,ω-bromine functionalized polymeric precursors [33].

An extension to CRP is the 'reversible addition–fragmentation transfer' (RAFT) technique pioneered by Rizzardo and co-workers [34,35]. The RAFT technique, as well as the recently MADIX process claimed by Rhodia [36] for the 'Molecular Design via Interchange to Xanthates', are based on the rapid and reversible chain transfer of the growing free radical chains on dithioesters, respectively, xanthates of the following structures:





These ATRP and RAFT techniques, which are very tolerant to almost any functional groups and impurities, have further the advantage that a wide range of block copolymers can be obtained in a variety of solvents including water [37–41].

2.1.2. Anionic polymerization

Anionic polymerization has been the first and the most used technique for the preparation of well-defined block copolymer. Since its discovery by Szwarc [42] in 1956 a large variety of block copolymers were prepared from styrene, dienes, methacrylates, oxiranes, thiiranes, lactones, cyclic siloxanes [1,12,14]. Typical examples of such block copolymers are PS–poly(diene) di- and triblock, PPO–PEO as hydrophilic–hydrophobic copolymers, acrylic copolymers and many others.

A–B structures are generally obtained by sequential addition of the monomers, either by adding directly the second monomer on the living first block, or by end-capping this first block with 1,1-diphenylethylene in order to avoid different side reactions as reported in the synthesis of PS–PMMA. A–B–A structures could be obtained either with anionic difunctional organometallic initiators or by coupling the living AB copolymer with suitable difunctional reagents, like phosgene, dihalides, esters, etc. [1]. All acrylic di- and triblock copolymers have been prepared such as PMMA–P*t*BA, with the interesting fact that the P*t*BA sequence can be easily transformed in a water-soluble PAA sequence, by elimination of isobutene from the *t*-butyl group or by its selective hydrolysis.

A wide range of functionalized block copolymers also became available by anionic polymerization, with the specific functionality either at the junction of the A and B block, or as endstanding functionality. Of special interest for micellization studies is the functionalization of block copolymers, e.g. PS–PEO with fluorescent labels like anthracenyl or phenanthrenyl groups built in at the junction of the two block [43].

The main limitation in the synthesis of block copolymers by anionic polymerization, is that it is applicable to a limited number of monomers and that the relative reactivity of the monomers has to be taken into account for their sequential addition. In fact, it is generally difficult to polymerize functional monomers, e.g. monomers having hydroxy, mercapto, amino, carbonyl, etc. groups, because they undergo side reactions with either the initiator or the living chain end. This problem could be solved, as shown by Nakahama and Hirao [44] by using suitable protecting groups, like *tert*-butyldimethyl silyl groups.

An important extension of anionic polymerization of acrylic monomers was the discovery of group transfer polymerization (GTP), by Webster et al. [45], which allowed the synthesis of acrylic and methacrylic polymers in a 'living' reaction at ambient temperature or above. A wide range of 'all-(meth)acrylic block' copolymers as well hydrophilic–hydrophobic, as 'double hydrophilic' copolymers which are of special interest for micellization studies, could be prepared by Armes et al. [46].

2.1.3. Cationic polymerization

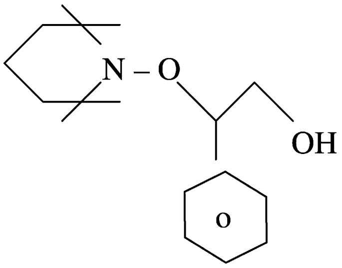
Living cationic polymerization is also finding an extensive application in the preparation of block copolymers. After the first examples of Dreyfuss and Dreyfuss [47] concerning block copolymers derived from tetrahydrofuran and 3,3-bis-chloromethyl oxetane, and those of Higashimura et al. [48], a large variety of block copolymers based on styrene derivatives, isobutene, vinyl ethers, could be obtained as reported by Faust et al. [49,50].

Special mention should also be made for poly(2-ethyl-2-oxazoline)-*b*-poly(L-lactide) block copolymers prepared by Kim et al. [51], which is a typical example where both blocks are biocompatible.

2.1.4. Mechanism switching—difunctional initiators

The range of possible monomer combinations in block copolymers is greatly extended by devising processes by which the polymerization mechanism can be changed at will to suit the reactivity of the monomer being polymerized sequentially. Since the pioneering work of Richards et al. [52], the possibilities of monomer combinations in block copolymers have expanded by changing the polymerization mechanism, and many examples have been reported [53,54]. This topic has been reviewed by Riess et al. [1,12] and by Yağci and Mishra [15].

An alternative to mechanism switching is the use of difunctional initiators, each functionality being selective for a given polymerization mechanism. This concept has, for instance, been demonstrated by Hawker et al. [55] for the preparation of PS–PCL copolymers with the following difunctional initiator:



After anionic ring opening polymerization of the lactone initiated by the OH group, the living free radical polymerization of styrene could be started with the nitroxide moiety. The versatility of this approach has further been demonstrated by showing that the block copolymer could be grown in any order, either the polystyrene block followed by the poly(-caprolactone) block or vice versa.

2.1.5. Coupling reactions

Numerous examples have been reported in the literature for the preparation of block copolymers by coupling end-functionalized polymers, either by direct coupling of 'living' polymers, by reacting two different polymers functionalized with suitable reactive end-groups or by using so-called difunctional coupling agents [1].

The first report concerning the direct coupling of 'living' polymers was given by Berger et al. [56] who investigated the reaction between an anionic difunctional polystyrene and a cationic poly(tetrahydrofuran) leading to a triblock copolymer. Mc Grath et al. [57] succeeded in obtaining an almost quantitative efficiency by coupling a living cationic poly(vinylether) with PMMA initiated by group transfer polymerization.

A typical example of coupling two polymers with suitable end-groups is that reported by Fock et al. [58]. These authors have taken advantage of the fact that the end-standing ester group of a PMMA chain, obtained by free radical polymerization in the presence of mercaptanes as chain transfer agents, is about 50 times more reactive than the other ester groups. Thus in a transesterification reaction of PMMA having a molecular weight below 5000 in the presence of hydroxy-terminated PEO, PMMA-*b*-PEO block copolymers are obtained in this highly selective end-group reaction.

2.1.6. Chemical modification of precursor block copolymers

As for homopolymers, the chemical modification of a given block, for instance, by hydrogenation, halogenation, hydrolysis, etc. gives access to new types of copolymers such as those containing poly(vinyl alcohol) or linear poly(ethylene imine) blocks [59,60].

2.2. Block copolymers with complex molecular architecture

The synthesis concepts developed in Section 2.1 have been extended in the recent years to the preparation of block copolymers with complex architectures where polymer segments of different type and different architecture are combined in the same molecule.

With the significant progress in the 'living polymerization techniques', in the design of multifunctional initiators and the control in coupling reactions a large variety of block copolymers with sophisticated architecture became available such as cyclic, H and star shaped, multiarm and 'palm-tree' or dumbell structures, dendritic blocks linked to linear blocks, etc.

In the following typical examples of these new amphiphilic structures will be outlined, by considering at first block copolymers with poly A/poly B sequences and then those comprising poly A/poly B/poly C blocks. As an illustration some of the synthesis routes will be given. Further details and informations especially on star block copolymers can be found in the excellent review articles recently published by Hadjichristidis [61], Hirao et al. [62] and Quirk et al. [63].

2.2.1. Block copolymers with poly A/poly B sequences

In Table 1 are schematically indicated the typical block copolymer structures which can be obtained by combining poly A and poly B sequences.

In a given block copolymer one can therefore combine rigid and/or 'soft' blocks, hydrophobic and/or hydrophilic blocks, the later ones being either of ionic or non-ionic type, as well as coil and/or helix structures. With regard to the solid-state properties this combination is possible between amorphous and/or crystallizable, or between isotropic and nematic blocks. Of special interest in this range of block copolymers are also those comprising biocompatible or biodegradable blocks, as well as functionalized block copolymers, e.g. copolymers with given functional or targeting groups.

2.2.2. Block copolymers with poly A/poly B/poly C sequences

Linear A–B–C block copolymers prepared by sequential anionic polymerization were already reported in the early 1980s [84] and were then developed systematically by Lerch [85], by Stadler et al. [86] and by several other groups [87–89].

More complex architectures such as multiarm star block copolymers were reported by Isono et al. [90], who used as a starting point a 1,1-diphenyl end-capped macromonomer A_n as shown in Fig. 1(a). This non-homopolymerizable macromonomer reacts with a 'living' chain B_m^- leading to a carbanionic species that allows to initiate the polymerization of the third monomer C (see Fig. 1(a)).

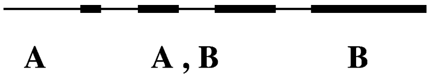
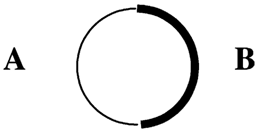
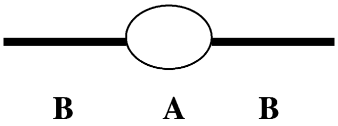
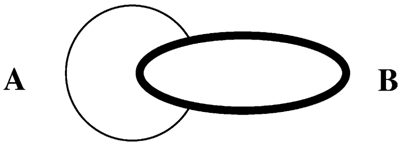
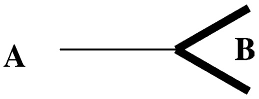
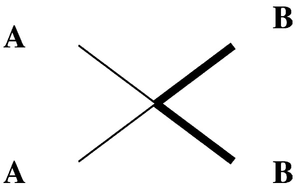
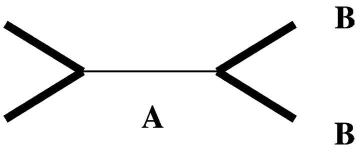
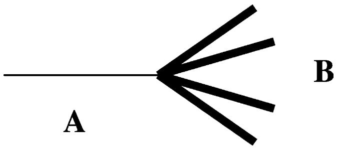
Triarm also called 'miktoarm' star block copolymers were for instance prepared by Dumas et al. [92, 93] using this strategy. A macro bifunctional initiator is obtained by end-capping of living polystyrene with a functional 1,1-diphenyl ethylene derivative given in Fig. 1(b). A second block is started by 'classical anionic way and a third by ring opening polymerization initiated by an alcoholate [91] or an alkoxide [92] generated by cleavage of the silyl protecting group. PS-arm-PEO-arm-PCL and PS-arm-PMMA-arm-poly(L-lactide) star block copolymers could be synthesized by this technique.

The application of 1,1-diphenyl ethylene chemistry in anionic synthesis of block copolymers with controlled structures was extensively developed by Quirk and co-workers [63] as well as by Dumas et al. [93].

As an alternative the recently developed multifunctional initiators by Sogah et al. [94,95] appeared to be as one of the most efficient routes for the synthesis of multiarm star block copolymers.

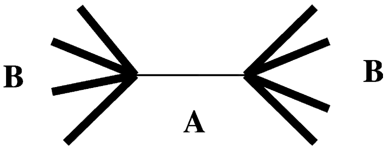
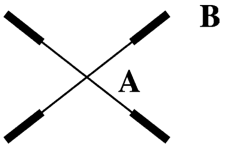
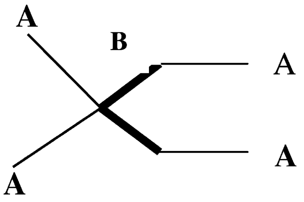
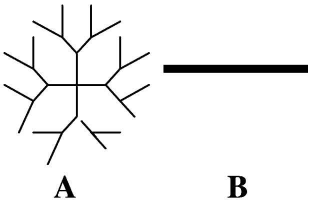
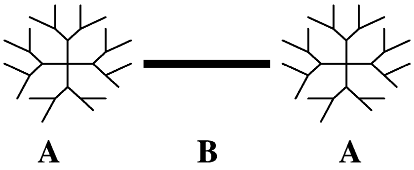
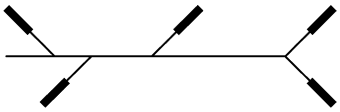
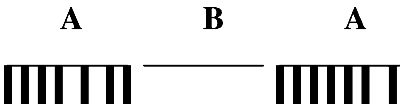
In Table 2 are given the various structures of block copolymers combining in the same molecule poly A, poly B and poly C structure.

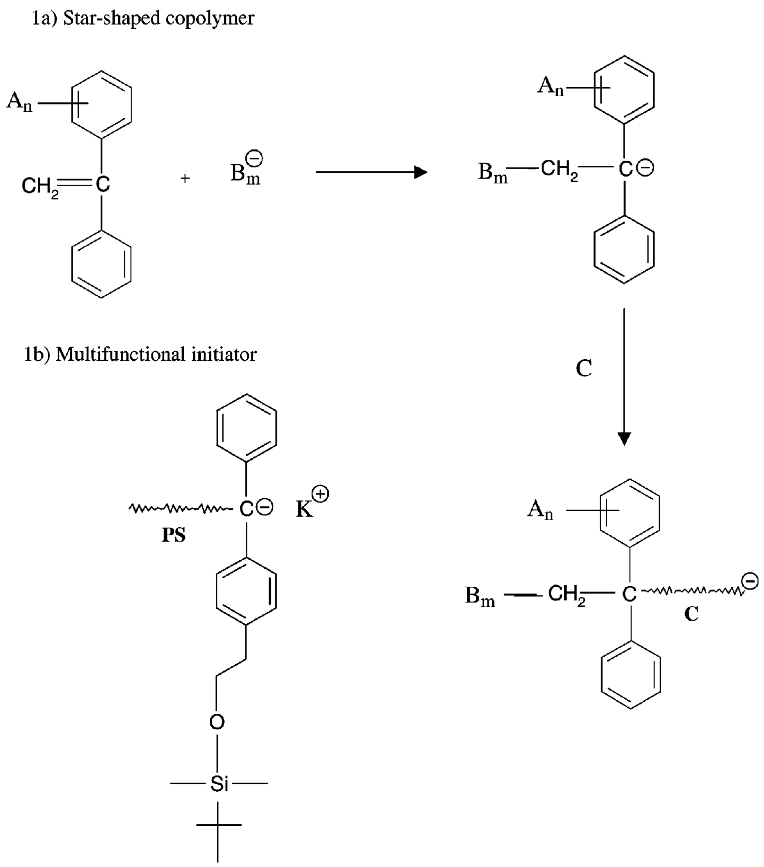
Table 1
Poly A/poly B block copolymers with complex architectures: schematic structures

Structure	Type	A	B	Polymerization technique	Reference
	Tapered, overlap	PS	PB	Anionic	[1]
	Ring diblock	PEO	PBO	Anionic	[64]
	Coil–cycle–coil	phenyl-ethinyl	PS	Coupling	[65]
	Catenated diblock	PS	P2VP	Anionic	[66]
	AB_2 star	PS $(PS)_2$	PI_2	Anionic	[67]
	(miktoarm star)		PMMA, POE, PCL	Anionic	[100]
	Heteroarm	PIB (A_2)	PMeVE (B_2)	Cationic	[68]
	star A_nB_n	PS (A_2)	PB, PI (B_2)	Anionic	[69]
	H shaped B_2AB_2	PS	PI	Anionic	[70]
	‘Palm-tree’ AB_n	PB	PEO	Anionic	[71]

(*continued on next page*)

Table 1 (*continued*)

Structure	Type	A	B	Polymerization technique	Reference
	Dumb-bell 'pom-pom'	PDMS	PS	Anionic	[72]
	Star–block	PnBMA	PDMAEMA	ATRP ($n = 3$)	[73]
	$(A–B)_n$	PMMA	PAA	ATRP ($n = 6$)	[74]
	Star–block $A_2(BA)_2$	PS	PB	Anionic	[75]
	Dendrimer-	styrene and	styrene and	Nitroxide ATRP	[76]
	linear	(meth)acrylic polyamido-amine dendrimer	(meth)acrylic poly(2-methyl-2-oxazoline)		[77]
	Linear-	PEG	Poly(chloro-methylstyrene)	ATRP	[78]
	dendrimer	PEO	Poly(benzyl ether)	Coupling	[79]
	Arborescent	PIB	PS	Cationic inimers, initiator-monomer	[80]
		PS	PLA methacrylic macromonomer	CRP (TEMPO)	[81]
		PMAA	POE methacrylic macromonomer	GTP	[82]
		PEO	PPO methacrylic macromonomer	ATRP	[83]


1a) Star-shaped copolymer

1b) Multifunctional initiator

Fig. 1. Synthesis of block copolymers with ABC sequences (see text).

3. Block copolymer micelles: preparation techniques and characteristics

It is now well established that micellization occurs in dilute solutions of block copolymers in a selective solvent at a fixed temperature above a concentration called the critical micelle concentration (CMC), which is also called critical association concentration for polymeric micelles.

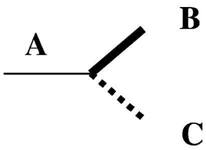
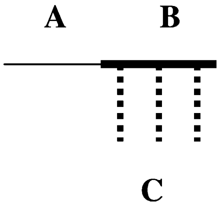
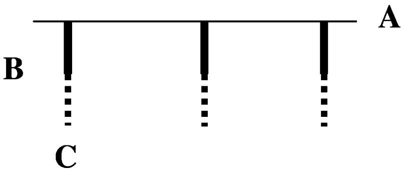
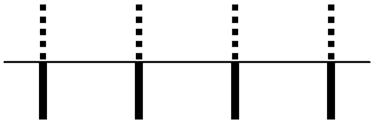
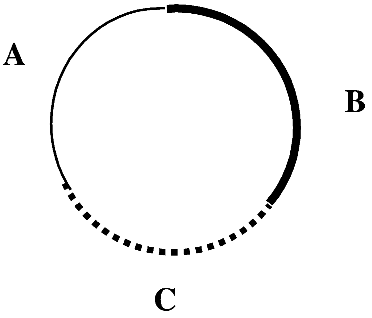
The classical methods for the preparation and the study of block copolymer micellar systems, mostly worked out in the 80' and beginning 90', have been reviewed by quite a number of authors [1,4–11] so that in the present section it will not be necessary to cover this topic in detail. Our aim is rather to outline the basic concepts and to focus on some practical informations also worked out in our group.

This section is therefore organized in the following manner: after a recall of the typical micellar characteristics, the various preparation techniques are presented, followed by the experimental characterization techniques. The dynamics and solubilization in micellar systems is outlined briefly at the end of this section.

3.1. Micellization of block copolymer—generalities

It can in general be assumed that block copolymers in a selective solvent form micelles via a so-called closed association process, characterized by a certain CMC, below which only molecularly dissolved copolymer is present in solution, usually as unimers. Above CMC, multimolecular micelles are in equilibrium with the unimers. This situation, analogous to classical low

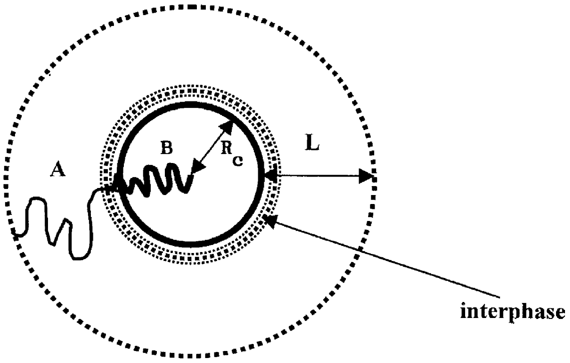
Table 2
Poly A/poly B/poly C block copolymers with complex architectures—schematic structures

Structure	Type	A	B	C	Polymerization technique	Reference
		ABC triblock methacrylates			GTP	[87]
	Triblock	PMMA	P*t*BMA	PS	ATRP/ nitroxide	[88]
		P*t*BA	PMA	PS	ATRP	[89]
	Star block miktoarm	PS PS PS	PI POE PMMA	PB PCL POE	Anionic Anionic Anionic	[96] [93] [93]
	Graft block	PS	PI	PEG	Anionic	[97]
	Graft block	PMMA	P2VP	PS	Anionic free radical	[98]
		P(oxazoline)	P2VP	PS	Nitroxide Free radical cationic or ROP	[94] [95]
	Cyclic triblock	PS	PI	PMMA	Amide ring closure	[99]

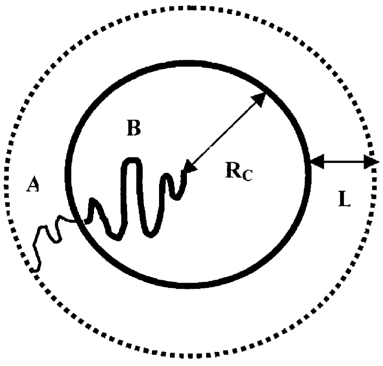
molecular weight surfactants is schematically represented in Fig. 2 for a A–B diblock copolymer in a selective solvent for the A block.

Such a micellar system is characterized by:

- the equilibrium constant unimers ↔ micelles
- the CMC and CMT, respectively, the critical micelle concentration and the critical micelle temperature
- the morphology which in the simplest case can be considered as spherical
- M^{m}, the molecular weight of the micelle
- Z, the aggregation or association number, e.g. the average number of polymer chains in a micelle, deduced from M^{m} and the molecular weight M^{u} of the unimer with $Z = M^{\mathrm{m}}/M^{\mathrm{u}}$ (note that different symbols, such as P, f, N, etc.) are used for this characteristic value by different authors
- R_{g}, the radius of gyration of the micelle
- R_{h}, the total hydrodynamic radius of the micelle
- the ratio $R_{\mathrm{g}}/R_{\mathrm{h}}$ which is informative of the shape
- R_{c}, the micellar core radius
- L, the thickness of the shell (corona) formed by the soluble blocks.



"hairy micelle" **L>>R$_c$**



"crew-cut" micelle" L < R$_c$

Fig. 2. Schematic representation of AB diblock copolymer micelles in a selective solvent of the A block. R_{c} : core radius; L : shell (corona) thickness.

3.2. Preparation techniques

Block copolymer micellar systems are generally produced by one of the following two procedures.

In the first technique, the copolymer is dissolved molecularly in a common solvent e.g. that is 'good' for both blocks, and then the conditions such as temperature or composition of the solvent, are changed in the way that requires formation of micelles. This is commonly achieved by adding gradually a selective precipitant of one of the blocks, eventually followed by stripping the common solvent. An alternative, that is often recommended is the dialysis technique by which the common solvent is gradually replaced by the selective solvent.

In a second technique, a solid sample of the copolymer is directly dissolved in a selective solvent; the micellar solution is let to anneal by standing and/or the annealing process is made by thermal treatment, eventually under ultrasonic agitation.

From our own experience, and also from literature, it appeared with both of these techniques, that depending on the block copolymer system, an equilibrium situation is not necessarily reached, especially if the core-forming polymer has a high glass transition temperature (T_{g}). In this case, e.g. with PS–PEO and PEO–PS–PEO di- and triblock copolymers so-called 'frozen micelles' are formed. Moreover, ultrasonic treatment is not recommended as demonstrated by Hurtrez for this type of micelles [101]. By size exclusion chromatography (SEC) this author has shown that chain degradation of the PEO fringe occurs, especially for high molecular weight blocks.

As mentioned by Munk [102] micelle formation by direct dissolution in a selective solvent is in general not very suitable. In fact the resulting micelles will depend on the two-phase morphology of the bulk sample as well as on the interactive properties of the selective solvent with respect to the polymer microphases in presence. In order to reach an equilibrium within a reasonable time, it would be necessary that the selective solvent also swells quite extensively the insoluble block. Advantage has however been taken from this 'memory effect' of the organized structure of block copolymers in the solid state, to acceed to fibrillar or Janus type micelles as indicated later on in Section 7.4.

The step-wise dialysis technique, pioneered by Tuzar and Kratochvil [6], is therefore the preferred preparation technique for micellar systems, mainly in aqueous medium, as demonstrated by Munk [102] for PS–PMAA block copolymers and as experienced by our group for various micellar systems [101]. Even if the formation of large aggregates can be suppressed by this technique, it does however not avoid the 'freezing-in' of a given unimer-micelle equilibrium, e.g. by the formation of a 'glassy' micellar core at a given temperature and/or at a specific solvent/non-solvent composition. Moreover under such conditions, the step-wise dialysis of a copolymer sample, with a polydispersity in composition and/or molecular weight, can generate a polydispersity of the resulting micellar characteristics, such as in size, in composition, in aggregation number, etc.

3.3. Characterization of block copolymer micelles—experimental techniques

The physical methods for the characterization of block copolymer micellar systems have been reviewed extensively by Tuzar [103], Munk [104]), Chu and Zhou [105], Webber [106] and by Hamley [10] who has also listed systematically the different techniques which have been applied for given block copolymers. These reviews were completed recently by that of Mortensen [107] related to small-angle scattering techniques and that of Zana [108] dealing with fluorescence studies.

In a first approach, these characterization techniques, some of them having already been applied for several decades in micellar systems studies, can be classified in scattering, spectroscopic and in a wide range of other physical techniques which are summarized in Table 3 according to the listing provided by Chu and Zhou [105].

Table 3
Experimental techniques for micelle characterization

Techniques	Micelle characteristics
TEM	Shape, size
SANS and SAXS	Molecular weight (weight-average), R_g, R_{core}, macrolattice structures
SLS	Molecular weight (weight-average), R_g
DLS	R_h
SEC	R_h, dynamics of micellar equilibrium
Ultracentrifugation	Micelle density, molecular weight (Z average), micelle/unimer weight ratio
Fluorescence techniques	Chain dynamics, CMC, hybridization of micelles
NMR	Chain dynamics
Viscometry	R_h, intrinsic viscosity
Stop flow techniques	Kinetics of micelle formation and dissociation

It will not be possible to cover in this section the background of all these techniques and in the following our aim is to only outline some typical aspects, some encountered in our own studies, and which could be of interest for the general practice.

3.3.1. Critical micelle concentration

For low molecular weight surfactants, the CMC, as well as the critical micelle temperature (CMT), can be determined by various scattering techniques (SLS, SAXS, etc.), fluorescence or dye solubilization technique, surface tension measurements, etc. These techniques are also applicable to block copolymer micellar systems, however by keeping in mind that copolymers can have very low CMC values and furthermore that, due to their low diffusion coefficient, equilibrium situations are only reached after a very long time period, without forgetting that the unimer–micelle equilibrium is not attainable for 'frozen-in' micellar systems. This specific behavior is illustrated for PMMA–PEO and PS–PEO diblock copolymers in the following examples.

In our attempt to determine by surface tension measurement the CMC of PMMA–PEO copolymers, even of relatively low molecular weight, e.g. 2000–7000, it could be observed that unexpectedly

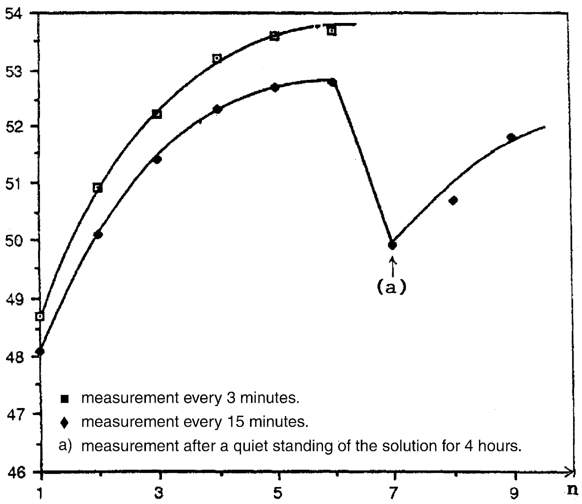


Fig. 3. Surface tension in mN/m versus the number *n* of consecutive measurements on the same copolymer solution. Aqueous solution of a $PMMA_{10} - PEO_{68}$ diblock copolymer ($M_n = 4000$) at an initial concentration of 112 mg/l; first measurement (Wilhelmy plate technique) after an equilibration time of 6 days.

the surface tension increases for two successive measurements if the time interval between these measurement is short, e.g. from several minutes to hours depending on the molecular weight.

Moreover it turned out that surface aggregates of copolymer are withdrawn from the surface and that the resulting surface depletion is only compensated by slow diffusion of copolymer molecules from the bulk solution to the water/air interface. This phenomena, systematically studied by Peter [109], is illustrated in Fig. 3 with the experimental details given in its caption.

Fluorescence techniques, as outlined for instance by Zana [108] and by Jada et al. [110], either with 'free' probes like pyrene solubilization or covalently fixed fluoroprobes, might therefore be a preferred technique for CMC and CMT determinations. A typical example is given in Fig. 4 for PS–PEO copolymer labeled at the junction of the two blocks with an anthracenyl as 'acceptor' group, respectively, a phenanthrenyl as 'donor' group. These two groups

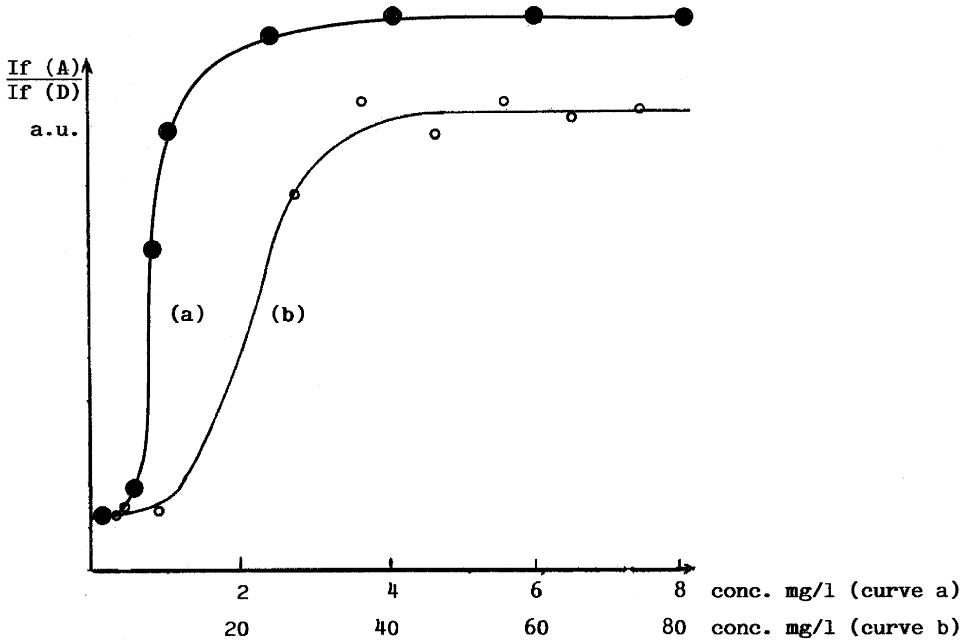


Fig. 4. CMC determination in aqueous medium of PS–PEO diblock copolymers labelled at the junction of the two blocks with an anthracenyl as 'acceptor' group, respectively a phenanthrenyl as 'donor' group. Fluorescence intensity ratio If (A)/If (D) (in arbitrary units) versus the copolymer concentration in mg/l. Excitation at 299 nm. If (A) determined at 370 nm and if (D) determined at 425 nm then Curve (a): PS–Anth–PEO, $M_n = 28\,000$ (43 wt% PS); PS–Phen–PEO, $M_n = 25\,000$ (40 wt% PS); equimolar ratio, CMC = 0.4 mg/l. Curve (b): PS–Anth–PEO, $M_n = 114\,000$ (7 wt% PS); PS–Phen–PEO, $M_n = 114\,000$ (7 wt% PS); equimolar ratio, CMC = 20 mg/l.

are capable to produce a non-radiative energy transfer if they are close together in the interfacial area between core and fringe of a micelle.

This technique of covalently fixed fluoroprobes, we developed in collaboration with Winnik's group [111], is similar to that described by Webber [106]. It is not only of interest for CMC determination but also for kinetic studies of micellar block copolymer systems [101]. However, as mentioned by Zana [108] it should be recalled that a covalently attached probe might not yield the same information as the same probe in the free state.

3.3.2. Morphology

For linear AB and ABA block copolymer Price [4] has already shown in the early 80's by transmission electron microscopy (TEM) the spherical shape of PS-*b*-PI micelles, as well as their monodispersity in size distribution. This observation was confirmed more recently by Esselink [112] and by Lam et al. [113] with cryo-TEM, a very valuable technique for the study of colloidal systems as demonstrated in the review article of Goldraich and Talmon [114]. A similar result, but directly in the presence of the selective solvent, was found by Tuzar and Kratochvil [6] by sedimentation velocity analysis of a PS–PB–PS block copolymer.

Other micellar morphologies, such as slightly elliptic, rod-like, vesicles, 'crew-cut micelles', flower-like micelles, etc. were reported more recently by different authors [115,116]. Concerning the chain conformation of the soluble A block in the micelle fringe, there is a definite difference in structure between A–B and A–B–A copolymers on the one side and B–A–B on the other. In fact B–A–B copolymers, with B being the insoluble block, have a tendency to form 'flower-like micelles' or to lead to micellar bridging.

3.3.3. Size, molecular weight

The dimensions and the molecular weight of block copolymer micelles can be determined by quite a number of techniques, especially scattering and hydrodynamic characterization techniques as summarized in Table 3. In general practice the hydrodynamic radius R_h is determined by dynamic light scattering (DLS) techniques. By treating the micelles as hydrodynamically equivalent spheres and using the Stokes–Einstein relation, R_h can be evaluated from the translational diffusion coefficient extrapolated to infinite dilution D_0 :

$$R_h = kT/6\pi\eta D_0$$

where k is the Boltzmann constant; T, the absolute temperature; η is the viscosity of the solvent.

R_h can also be obtained from SEC experiments with the so-called universal calibration technique. In the general case, as demonstrated by Tuzar and Kratochvil [6], static light scattering (SLS) would lead, if unimers and micelles are simultaneously present, to an apparent molecular weight M_w^{app} (weight average), defined as

$$M_w^{app} = M_w^{(u)}x + M_w^{(m)}(1-x)$$

where (u) and (m) stand for unimer and micelles, respectively, and x is the weight fraction of unimers. Since the unimer molar weight is known, its weight fraction in the micellar system can be determined by techniques like ultracentrifugation or SEC. In the simplest case, for block copolymer systems with low CMC, the unimer concentration can even be considered as negligible.

For copolymers that are heterogeneous in composition and whose blocks have significantly different refractive indexes, SLS provides only an apparent molar weight. These problems related to SLS experiments of micellar systems have been discussed in detail by Tuzar and Kratochvil [6]. As mentioned by these authors, typical values of unimer molar weight are in the order of 10^3–10^5 and those of micellar molar weight in the range of 10^6–10^8 g/mol.

3.4. Dynamics of micellar systems

Concerning the dynamics of block copolymers in solution, we have to consider on the one side the kinetics of micellization, which corresponds to the dynamic of the micellar equilibrium unimers ↔ micelles as well as to the problem of hybridization in micellar systems and on the other to the chain dynamics in the micellar core and in its corona.

3.4.1. Kinetics of micellization

Kinetic studies of micelle formation and dissociation by direct methods are scarce as already mentioned by Tuzar and Kratochvil [6,103] and later on by Hamley [10]. Informations can be obtained by fast reaction techniques, such as stop-flow, temperature or pressure jump techniques, as well as by steady state methods, e.g. ultrasonic absorption, NMR, ESR.

Stop-flow experiments have been performed by Tuzar and Kratochvil [6] and more recently by Kositza et al. [117]. In analogy to low molar weight surfactants, it could be shown that two relaxation processes have to be considered for block copolymer micellar systems: a faster process attributed to unimer ↔ micelle equilibration at constant micelle concentration, and a slower process assigned to an association ↔ dissociation equilibration, accompanied by changes in micellar concentration. Major differences were observed between AB di- and ABA triblock copolymers, which could be explained by the fact that the escape of a unimer, which has to disentangle from the micellar core, might be much easier in a diblock than in a triblock structure.

Indirect methods for obtaining information on the kinetics of the association/dissociation phenomena includes SEC and ultracentrifugational techniques. By SEC, for instance, two well-separated peaks are observed due to the slow dynamic unimer ↔ micelle equilibrium. However, no quantitative conclusions can be obtained from SEC or sedimentation experiments.

3.4.2. Micelle hybridization

The hybridization of micellar systems corresponding to the exchange of unimers between two micelle populations with formation of so-called ‘mixed micelles’ is a rather complex phenomena as it is governed by thermodynamic and kinetic parameters, which in turn are very sensitive to the copolymer structures, to their molecular weights and compositions. The more, equilibrium situations might not always be reached during the whole process as a result of frozen micelle formation.

This kind of problem was approached in a very systematic way by Munk and Tuzar [102,103] for PS–PMAA diblock micelles of different sizes in water–dioxane mixtures and by using sedimentation velocity as experimental technique. According to these authors the mechanism of hybridization consists primarily in the transfer of unimers among the micelles of both type and the driving force for this phenomena is the increase of entropy when the two types of unimers are mixed within the micelles.

Hybridization of micellar systems was more extensively studied by fluorescence techniques. As mentioned by Webber [106], the chain exchange between micelles can be characterized by mixing micelles composed of block copolymers that are similar or identical except that they are tagged with different fluorophores. Thus, when two micelle populations, the one tagged with donor- the other with acceptor groups, are mixed and the donor is excited, primarily donor fluorescence is observed. As the chromophore tagged chains are exchanged between micelles the donor will sensitize the fluorescence of the acceptor.

A typical example of this kind of study concerned PS–(F)–PEO diblock copolymers where (F), the chromophore, is either a donor- (naphthalene) or an acceptor (pyrene) group, placed at the junction of the hydrophobic and the hydrophilic sequence. Even for relatively low molar weight copolymers no hybridization was observed at room temperature in aqueous solution. Riess and Hurtrez [118] came to a similar conclusion for PS–(F)–PEO diblock copolymer tagged with anthracenyl acceptor and phenanthrenyl donor groups, respectively.

Rager et al. [119] have recently studied by non-radiative energy transfer techniques the micelle formation of PAA–PMMA–(F) block copolymers, tagged with pyrene or naphthalene, in mixtures of water with organic solvents. By addition of dimethyladipate to the micellar system, acting as a plasticizer of the PMMA core, these authors concluded that under their experimental conditions, the micelle–unimer exchange equilibrium is not kinetically hindered, e.g. determined by the T_g of the core material of the micelle, but controlled by a strong thermodynamic preference for the aggregated state.

The problem of kinetic hindrance for chain exchange is however still under debate, as Winnik et al. [120] reported the presence of non-equilibrating structures in acetonitrile, for PI–PMMA block copolymer micelles, having a PI core of low T_g.

A more complex situation of micelle hybridization was examined by Jérôme and co-workers [121]. These authors studied by steady-state fluorescence spectroscopy the dynamics of unimer exchange between aqueous micelles formed by two amphiphilic block copolymers PS–PMA$^-$Na$^+$ and P*t*BS–PMA$^-$Na$^+$. No exchange rate could be detected at room temperature, while at 60 °C the exchange rate was measurable.

3.4.3. Chain dynamics

Scattering and fluorimetric techniques, recently reviewed by Alexandridis and Hatton [8], Procházka et al. [122] and by Zana [108], are excellent tools for studying the dynamics and the chain conformation in the micellar core as well as in its shell.

From these overviews it appeared that the compactness and the rigidity of the micellar core could be confirmed for different systems, however very little seems to be known about the detailed conformation of the insoluble blocks in the core. Some stretching of the core forming blocks could be observed for PS–PMMA block copolymers in xylene, as well as the stretching of the corona chains beyond the calculated end-to-end distance for free PDMS chains compared to those of PS–PDMS block copolymers in decane. Depending on the χ_{AB} interaction parameter of the two blocks and on the corresponding interaction parameter with the solvent, the interface between core and shell can be more or less extended. For highly incompatible blocks, most of the small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) studies confirm the presence of a sharp core–shell interface. However, for more compatible blocks a partial mixing and the presence of an interphase could be demonstrated.

Informations on the chain mobility and thus on the micellar structure can further be obtained by NMR. In fact, a decreased mobility of protons in polymer chains with hindered motion causes broadening of the respective NMR lines and even disappearance of the corresponding signal when the polymer is in the glassy state. This phenomena has been observed already in the early 80s by Spevacek [123] for PS–PB in a selective solvent for the aliphatic block. The aromatic signal of PS could not be detected at all in high resolution spectra at 26 °C, demonstrating that the PS in the micellar core is in the glassy state; at 87 °C the signal becomes comparable to that of PS in a good solvent.

A similar study was performed by Riess et al. [118] on PMMA–PAA diblock copolymers of the same composition (43 wt% AA) in CD_3OD, a selective solvent of PAA, as a function of temperature and the total molar weight.

An interesting approach to chain dynamics at the segment level in the micelle corona formed by ionic block copolymers was reported by Eisenberg et al. [124] using ^{2}H NMR experiments. The structure of the PS-neutralized PAA block copolymer used in that study was as follows:

$(PS)_j-(PS-d_8)_k-(PS)_m-(PANa)_n$

where $(PS-d_8)_k$ is a perdeuterated PS block of about three monomer units ($k \sim 3$) j and m can be varied from 0 to about 70–90 styrene units.

The original fact in this series of copolymers is that the deuterated PS block can be placed in a controlled distance from the hydrophilic PANa block forming the micellar core in CCl_4. The distance between the ^{2}H-labelled PS segment and the ionic core is thus controlled by the number of styrene units $(PS)_m$ separating the labelled segment from the ionic $(PANa)_n$ segment. NMR linewidths, signal intensity and relaxation times indicated that the mobility of the soluble PS segments near the ionic cores was dramatically reduced. At a distance of 25 repeat units ($m = 25$) from PS–PANa block junction, the mobility was still significantly lower than in single chains, while at a distance of 50 repeat units ($m = 50$) from the junction, the mobility was essentially the same as that in the single chains.

3.5. Solubilization in micelles

One of the most useful properties of micellar aggregates is their ability to enhance the aqueous solubility of hydrophobic substances which otherwise are only sparingly soluble in water. The enhancement in the solubility arises from the fact that the micellar cores, for classical low molar mass surfactants as well as for block copolymer micelles, can serve as compatible microenvironment for water-insoluble solute molecules. This phenomenon of enhanced solubility is referred as ‘solubilization’.

As pointed out by Nagarajan [125], who has recently reviewed this characteristic feature of block copolymer micelles, the solubilization in such micellar systems holds great potential for the development of aqueous block copolymer solutions as environment friendly substitutes for organic solvents and as tissue-specific drug delivery systems. For this reason, mainly all the studies in this area are devoted to hydrophobic–hydrophilic block copolymers forming micelles in aqueous phase.

PPO–PEO block copolymers have been studied quite extensively, as they are commercially available in a large range of compositions and molecular weights. In addition, their biocompatibility makes them very attractive for biomedical applications. For these systems it was therefore of interest to determine:

- the change in size and shape of the micelles as a consequence of solubilization
- the change in the CMC due to the presence of the solubilizates
- the solubilization capacity of the micelles for different hydrophobic substances
- the partition coefficients of the solubilizate in a mixture of components.

The solubilization characteristics of the block copolymer micelles are usually given in terms of micelle–water *partition coefficients* defined as the ratio between the concentration of the solubilizate inside the micelle and the concentration of the solubilizate that is molecularly dispersed in the aqueous phase. The *solubilization capacity* can be expressed either in the form of the volume or mass fraction of the solubilizate in the micellar core, or as the number of moles solubilized per gram of hydrophobic block.

For PPO–PEO block copolymer it could be found that the solubilization capacity of the micellar core is correlated to the Flory–Huggins interaction parameter $\chi_{\mathrm{s,core}}$, which can be expressed in terms of the solubility parameters δ_{s} and δ_{core} for the solubilizate s and the core-forming block, respectively

$$\chi_{\mathrm{s,core}} = (\delta_{\mathrm{s}} - \delta_{\mathrm{core}})v_{\mathrm{s}}/kT$$

where v_{s} is the molar volume of the solubilizate s; k, the Boltzmann constant; T is the absolute temperature.

Nagarajan has also developed the theory of solubilization based on the thermodynamic considerations of block copolymers, with the assumption that the micelles containing the solubilizate can be considered as a pseudo-phase in equilibrium with the solubilizate and the block copolymer molecules in solution. This thermodynamic treatment of solubilization established for a series of PEO–PPO diblock and PPO–PEO–PPO triblock copolymers in aqueous medium, allowed the explicit calculation of the solubilization capacity of the micelles, the dimensions of the hydrophobic core swollen by the solubilizate, the hydrophilic PEO shell, as well as the change in aggregation number Z and in the CMC. Reasonable agreement could be found between the experimental values of the solubilization capacity and the predicted values. For PEO–PPO diblock copolymers in water and benzene as solubilizate, it could be shown that η, the volume fraction of solubilizate in the micellar core, scales as

$$\eta \sim N_{\mathrm{B}}^{0.17} N_{\mathrm{A}}^{-0.017}$$

This observation confirms the conclusions given by Tuzar and Kratochvil [6] that the amount of solubilized compound is mainly controlled by the Flory–Huggins parameter characterizing the interaction between the solubilizate and the core-forming copolymer block. This feature also explains the high selectivity in the solubilization of a given component, which is observed when a micellar systems is in presence of a mixture of solubilizates. Thus, aromatic hydrocarbons are solubilized in micelles with PS cores to a much greater extent than aliphatic ones. Advantage has been taken from the solubilization of aromatic fluorescent labels, such as pyrene or phenanthrene, for the determination of the CMC and to probe the interior of polymeric micelles. This problem of solubilization and release of fluorescent labels has been studied in detail by Webber [106,126] and by Arca [127].

Numerous theoretical and experimental studies have demonstrated already in the early 70' that homopolymers can be solubilized to some extent by block copolymer micellar system. Tuzar and Kratochvil [6], for instance, have shown that solubilization of PB homopolymer in PS–PB–PS micelles becomes possible if the molecular weight of the PB homopolymer is lower than that of the core-forming PB chain of the copolymer, and when its amount does not exceed a certain saturation limit. Similar studies on the solubilization of PIB by micelles of PS–poly(ethylene-*co*-butylene)–PS triblock copolymers in methyl isobutylketone were published by Quintana et al. [128].

4. Theories and computer simulations

Quite a number of theories were developed over the years in order to predict the structural parameters of a micelle (CMC, association number Z, core radius R_c, shell thickness L, hydrodynamic radius R_h) as a function of the copolymer characteristics, e.g. its molecular weight and composition. For A–B diblock copolymers which were mainly examined and where the B sequence is forming the micellar core, these characteristics are defined by the corresponding polymerization degrees N_A and N_B. In all these theories and by using various models and mathematical approaches, the total Gibbs free energy $G^{(m)}$ of the micelle is expressed as the sum of several contributions, mainly those related to the core $G^{(\text{core})}$, the shell $G^{(\text{shell})}$ and the core/shell interface $G^{(\text{interface})}$:

$$G(\text{micelle}) = G(\text{core}) + G(\text{shell}) + G(\text{interface})$$

Minimization of this equation with respect to parameters characterizing the micelle leads to correlations between the copolymer and micellar characteristics.

According to the reviews published by Tuzar [6], Hamley [10], Gast [129] and recently by Linse [130], these theories are based on one side on the scaling concepts derived from the Alexander–De Gennes theories and on other on the mean field theories first developed by Noolandi and Hong [131], Leibler et al. [132], Nagarajan and Ganesh [133] and by Hurter et al. [134]. These theoretical efforts, completed by computer simulations as demonstrated, for instance, by Binder and Muller [135,136] and by Mattice and Haliloğlu [137], have contributed to the understanding of the self-assembly of block copolymers into micellar structures. A concise overview on the thermodynamic background and of these different approaches will be given in the following, completed by some recent developments.

4.1. Thermodynamic background

From the early results of Price [4] and Quintana [138], it is now well established that the micellization of block copolymers in organic medium is an enthalpic driven process. It could be shown that the negative standard Gibbs energy (ΔG^0)

$$\Delta G^0 = \Delta^0 H - T\Delta S^0$$

results from the dominant ΔH^0 values with respect to ΔS^0 which is also negative. These negative values of ΔS^0, unfavorable to micellization, arise from the loss in the combinatorial entropy because the copolymer chains are less swollen in the micelles than in the unassociated state and furthermore the number of possible conformations is also decreased due to the placement of block junctions at the core/shell interface of the micelles. The negative values of ΔH^0 arise from the exothermic energy interchange which results from the replacement of polymer/solvent interactions by polymer/polymer and solvent/solvent interactions. The formation of the micellar core is therefore the main contribution to the exothermic process.

This situation is quite opposite to that reported for the micellization in aqueous medium, for low molecular weight surfactants as well as for hydrophilic–hydrophobic block copolymers in water. Typical examples are those reported by different authors for PEO–PPO–PEO block copolymers for which the micellization is an entropy driven process [103,138,139]. According to Liu et al. [140] this phenomenon is mainly the consequence of hydrophobic interactions and changes of the water structure in vicinity of the polymer chains. Guo et al. [141] have recently studied by FT-Raman spectroscopy this problem of hydration in the case of PEO–PPO–PEO copolymers.

For a closed-association process of block copolymers in a selective organic solvent, the standard enthalpy and the Gibbs free energy of micellization can be calculated in a first approximation by the following equations

$$\Delta G^0 = RT\ln(\text{CMC}) \qquad \Delta H^0 = R[\text{d}\ln(\text{CMC})/\text{d}(1/T)]$$

where the CMC, the critical micelle concentration, is expressed in mole fraction units. Under the assumption that Z, the aggregation number, and ΔH^0 are independent of temperature, integration leads to

$$\ln \mathrm{CMC} = \Delta H^0/RT + \text{constant}$$

4.2. Scaling theories

The concept of the scaling theories is to establish on the basis of simple model the correlations between the molecular characteristics of a given block copolymer, mainly diblock copolymers AB, and the characteristics, such as the core radius R_c, the corona thickness L and the aggregation number Z of the resulting micelle in a selective solvent for one of the blocks. In this approach, monodispersed AB diblock copolymers are generally considered, where N_A and N_B are the number of A and B monomer units in the corresponding blocks.

According to Linse [130] two limiting cases were mainly examined for AB diblock copolymers, with B being the insoluble block, the one where $N_B \gg N_A$ leading to so-called *crew-cut micelles* with $R_c \gg L$, the other where *hairy micelles* are formed when $N_B \ll N_A$. A schematic representation of these two possibilities is given in Fig. 2. In the first case, that of *crew-cut micelles* the scaling relations for micellar systems were developed from the De Gennes/Alexander theories for polymer brush. Thus, by assuming uniformly stretched chains for the core radius R_c, with an aggregation number Z, the following relationships are predicted

$$R_c \sim \gamma^{1/3} N_B^{2/3} a \qquad Z \sim \gamma N_B$$

where γ is the A/B interfacial tension and a the segment length.

In the second case, that of *hairy micelles*, the star polymer theory of Daoud and Cotton [142] can be applied. These authors defined for star-like polymers in good solvents the segment density profile as a function of the distance of the core center. Their model predicts that the star polymer radius scales as

$$R \sim N_A^{3/5} f^{1/5}$$

with f being the number of arms. As in a block copolymer micelle the number of arms corresponds to the aggregation number Z, it follows that $L \sim Z^{1/5} N_A^{3/5}$ with $Z \sim N_B^{4/5}$.

Similar scaling relations were also derived by Halperin [143] and by Zhulina and Birshtein [144], who considered for the scaling modelization four possibilities for the relative values of N_A and N_B.

In the typical case of *hairy micelles* in a good solvent of A blocks, where $N_A > N_B^{4/5}$, the aggregation number Z scales as $N_B^{4/5}$, R_c as $N_B^{3/5}$ and L as $N_A^{3/5} N_B^{6/25}$, in close agreement with the relations derived by Daoud–Cotton [142]. A similar result for a star model was obtained by Halperin [145], with a scaling relationship for the total micellar radius R such as

$$\mathrm{R} \sim N_A^{3/5}\, N_B^{4/25}$$

which demonstrates the predominant contribution of the corona thicknesss L to the micelle size. The same author also examined within a scaling approach the self-assembly of A–B-C triblock copolymers by taking into account the incompatibility effects between the A and C blocks forming the shell of the micelle [146]. This theory was then extended to ABA and ABC coil-rod-coil triblock copolymers, by analyzing the equilibrium structures of micelles and lamellae [147].

The application of the scaling concepts to the description of the polymer concentration profiles and free energy in micellar systems is largely restricted to long polymer chains in good solvents. In fact scaling models presented above are unable to include finite chain effects and polymer/solvent interactions. Furthermore, numerical values of the micellar characteristics are not directly accessible, as the scaling laws only predict the trends, e.g. how a given micellar parameter scales with a given copolymer parameter. The scaling models have thus to be complemented by more detailed mean-field calculations and molecular simulations, which are concisely outlined in the following.

4.3. Mean-field theories

The development of the self-consistent mean-field formalism provided the means to calculate the polymer concentration profiles in a relatively tractable form. Excellent reviews of the mean field theories applied to the micellization of block copolymers were recently presented by Hamley [10] and by Linse [130], who considered on the one side the semi-analytical mean-field models and on the other the numerical self-consistent mean-field descriptions.

With respect to the first type of approaches, theories of block copolymer micellization were formulated in 1983 by Noolandi et al. [131] and by Leibler et al. [132]. The first authors derived the micellar characteristics by minimizing the Gibbs energy of an isolated micelle. They calculated the characteristics of the micelle formed by a PS-*b*-PB diblock copolymer in heptane, a selective solvent for the PB block, using numerical values of the Flory–Huggins interaction parameters χ, molecular weight and composition of the copolymer. Their theoretical values were in a fair agreement with those obtained experimentally. An improvement of this theory was that of Leibler et al. who minimized the total Gibbs energy not only for one micelle but for the whole micellar system.

In a similar approach, Nagarajan and Ganesh [133] developed their theory by taking into account the molar volumes of the selective solvent v_s and of the blocks v_A and v_B respectively. The effective number of repeating units is therefore no longer N_A and N_B, the polymerization degrees of the blocks, but $N'_A = v_A/v_s$ and $N'_B = v_B/v_s$. The micellar characteristics could thus be correlated to N'_A and N'_B, by knowing γ_{BS} the interfacial tension and the interaction parameter χ_{AS}. As typical examples, Nagarajan and Ganesh calculated the scaling relations for PPO–PEO block copolymer in water, which is a good solvent for POE

$$R_c \sim N_A^{-0.17} N_B^{0.73} \qquad L \sim N_A^{0.74} N_B^{0.06}$$

$$Z \sim N_A^{-0.51} N_B^{1.19}$$

From these results it appeared that, in contrast to the earlier theories, the coronal A block can have a strong influence on the micellar characteristics especially when the solvent is very good for the A block. By this type of approach, Nagarajan and Ganesh could obtain ‘universal’ correlations for R_c, Z and L as a function of N_A, N_B, χ_{AS}, γ_{BS} and v_s.

Linse [130] has used the lattice self-consistent mean-field theory to calculate the effects of the copolymer architecture on the association behavior of PEO/PPO block copolymers and this study was recently extended to charged polymeric micelles [148]. In a similar way Monzen et al. [149] investigated the structures and the phase behavior of micelles prepared from symmetric and asymmetric triblock copolymers with different architecture. They demonstrated that asymmetry between the two end-blocks as well as the block architecture strongly affects the micellization behavior.

4.4. Computer simulations

Analytical theories and computational simulations, mainly Monte Carlo type simulations, are complementary methods for the study of the self-assembly of block copolymers as demonstrated by Mattice and Haliloğlu [137] and by Binder et al. [150].

The background of the simulation techniques and detailed reviews of simulation studies have been published by Binder and Muller [136] and by Shelley and Shelley [151]. Scaling and other field theories offer the important advantage of the insight that can be gained directly from a given equation and the speed with which numerical results can be generated. Sometimes however, the theories are limited by certain approximations which are necessary to make the problem tractable. In contrast, computer simulation proceeds in general straightforward with relatively very few approximations and without preassumption of micelle geometry or chain conformation that are very often needed in the other theoretical treatments. In computer simulations it is possible also to vary intermolecular forces at will in a well-controlled manner. The main limitation of the simulation is the requirement for extensive computation and therefore simulations are mostly reported for ‘short’ block copolymers, e.g. with N_A or N_B from 2 to about 30.

Several aspects of the self-association of AB, ABA and BAB block copolymers in a selective solvent of A have been studied by Monte Carlo simulations based on bead models for the copolymer chains in a cubic lattice. $A_{10}B_{10}$ and $A_5B_{10}A_5$ were, for instance, compared as reported by Linse [130].

Kim et al. [152,153] performed a Monte Carlo simulation in order to compare the micellization behavior of ABA and BAB type triblock copolymers as well as of star block copolymers A_2B_2 in a selective solvent of A. The basic micellar characteristics, such as the micellar shape, size, size distribution and core structure could be established and compared for these systems. Furthermore, the thermodynamic analysis confirmed that the additional entropy loss due to the looping conformation of the middle block of BAB copolymers induces a higher CMC value and therefore reduces their capability of self-assembling. In contrast, A_2B_2 star block copolymers form micelles easier than the corresponding triblock copolymer.

These computer simulations have been extended in order to consider other aspects of block copolymer self-association such as:

- the chain length dependence [150]
- the dynamics of chain exchange between micelles of AB block copolymers [137]
- the formation of surface micelles [154]
- the solubilization of low molecular weight compounds, e.g. hydrophobic drug molecules in a micellar core [155,156]; from the study of Chen and Shew [156] it appeared that depending on the interaction parameters, the drug molecules distribute in the micellar core in a non-uniform fashion, either near the core/shell interface or quite inside the core
- the chain density profile and the thickness of the interfacial region [130]

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5. Micellization in aqueous medium

Micellization of block copolymers in aqueous medium was recognized quite early and the first systematic studies with well-defined products started with the development of anionic polymerization. The increasing interest in aqueous micellar systems of block copolymers is due, as mentioned by Tuzar in a recent review [139], to the improvement of the synthesis techniques and to their widespread application possibilities in technical and especially biomedical areas. In analogy to classical low molecular weight surfactants, hydrophilic–hydrophobic block copolymers can be classified in three categories by considering their hydrophilic blocs:

- the non-ionic copolymers mainly based on PEO, such as PEO–PPO, PEO–PBO, PEO–PS di- and triblock structures
- the anionic copolymers with PAA or PMAA blocks
- those containing blocks of cationic or cationizible monomer units, such as P2VP, P4VP, poly(amino(meth)acrylates), etc.

An interesting feature of block copolymers is that even hydrophilic–hydrophilic structures are able to form micellar systems, under suitable thermal or pH conditions.

Since this aspect of block copolymers was recently the subject of detailed review articles [5,6,8–11] we shall limit ourself in summarizing some of the major conclusions of these previous studies and by illustrating them with selected examples of the recent literature, as well as with various contributions to this topic by our group. Mainly AB, ABA and BAB structures are considered at this point, whereas more elaborate block architecture will be examined in Section 7.

5.1. Micellization of non-ionic hydrophilic–hydrophobic block copolymers

Most of the amphiphilic block copolymers of this type comprise PEO as hydrophilic block(s), whereas the hydrophobic block(s) are PPO, PBO, PS, PMMA, polyesters, etc. PEO, in addition to its adjustable water solubility with temperature, has the advantage to be non-toxic and non-immunogenic, which are the requirements for biomedical applications.

In this section, we intend to examine successively the micellization behavior of PEO–poly(oxyalkylene), and PEO–PS block copolymers which have been studied the most extensively up to now, then that of PEO based block copolymers with other hydrophobic blocks and finally that of block copolymers with hydrophilic sequences other than PEO.

5.1.1. PEO–poly(oxyalkylene) copolymers

PEO–PPO, and later on PEO–PBO copolymers, represent a bridge between classical low molecular weight non-ionic surfactants and polymeric surfactants. These commercially available products (formerly known as PLURICARE, PLURONICS, SYNPERONICS), mainly with di- and triblock structures can form, depending on temperature and concentration, true solutions, micelles of different shapes and physical gels. Their micellization behavior has been studied quite extensively and the experimental as well as the theoretical results were summarized in the review articles of Chu and Zhou [105], Almgren et al. [157], Hamley [10], Booth et al. [64,158], Wanka et al. [159].

In the most recent ones, Booth and co-workers [64, 158] outlined not only the various characterization techniques, but also the correlations between the molecular characteristics (composition, structure, molecular weight) and the corresponding micellar characteristics, such as the CMC and CMT, the micellization enthalpy, the micelle size and association number, etc. These characteristic features were studied by SLS, DLS, SAXS, NS, NMR, etc.

By SAXS it could, for instance, be demonstrated that not only spherical but, depending on molecular weight, composition, temperature, concentration, salt content, also rod-like micelles are formed [105,157]. Mortensen and Pedersen [160] have shown that in case of spherical micelles the PPO core is surrounded by a dense layer of PEO and an outer corona of flexible PEO chains.

By studying the influence of the block architecture on the micellar properties for PEO–PBO, PBO–PEO–PBO and PEO–PBO–PEO copolymers, Booth and co-workers [64,158] came to the conclusion that at constant composition, the CMC varies as follows

$$\begin{aligned}&(\mathrm{PEO})_m-(\mathrm{PBO})_n \ll (\mathrm{PBO})_{n/2}-(\mathrm{PEO})m-(\mathrm{PBO})_{n/2}\\ &\quad\leq (\mathrm{PEO})_{m/2}-(\mathrm{PBO})_n-(\mathrm{PEO})_{m/2}\end{aligned}$$

and that the aggregation number Z increases with n and is the highest for a diblock series. These trends were confirmed by Yu and Krumnov [161].

The studies on PEO–PPO, PEO–PBO di- and triblock copolymers were completed recently by Bahadur et al. [162] who examined the role of various additives on the micellization behavior, by Guo et al. [141] who used FT-Raman spectroscopy to study the hydration and conformation as a function of temperature, by Chaibundit et al. [163] who were mainly interested in PEO/PBO block copolymers with long PEO sequences.

5.1.2. PS–PEO copolymers

One of the first systematic study on PS–PEO di- and triblock copolymers with controlled molecular characteristics, and in a large range of molecular weights and compositions, was reported by Riess and Rogez [164,165]. It could be shown that the micellar aggregation number increases with the copolymer molecular weight at constant composition and decreases with the PEO content for a given molecular weight. It was further observed that PEO–PS–PEO triblocks are less aggregated than the corresponding PS–PEO diblocks. In extension of this work, homologous series of PS–POE and POE–PS–POE with exactly the same PS precursor sequence and increasing molecular weights of the PEO block could thus be prepared [101,111,166,167]. Such series of diblock copolymers, are now also commercially available from Goldschmidt however in a more limited range of molecular weights, e.g. 2000–7000. With respect to PPO and PBO, PS being highly hydrophobic would have the advantage to decrease the CMC for a given molecular weight of the hydrophobic blocks. However, due to the higher T_g of PS, typical non-equilibrium situations could occur, with formation of so-called ‘frozen micelles’ having a ‘glassy’ micellar core.

Some specific features will be given in the following concerning the micellization behaviors of PS–PEO and PEO–PS–PEO, studied in our group in collaboration with Winnik and co-workers [168] and with Ballauff et al. [169]. This type of copolymers were also examined by Eisenberg [170] especially for copolymer with high PS content, and by Khokhlov et al. [171,172]. Eisenberg and co-workers could for instance demonstrate that with increasing PS contents the dominant morphologies are spherical micelles, then rod and lamellae and finally vesicles.

In our approach, we were mainly interested in the micellization behavior of PS–PEO copolymers in a wide compositional and molecular weight range, e.g. $5\ \text{wt}\% \leq \text{PS} \leq 75\ \text{wt}\%$ and $2000 < M_n < 100\,000$, in homologous series having the same PS precursor and in fluorescent labelled copolymers. From the DLS determinations of the micellar hydrodynamic radius R_h for 23 diblock and 14 triblock copolymers in the indicated compositional and molecular weight range, it appeared that neither the Noolandi–Hong theory

[131] nor Halperin's theory [145] could be applied directly to these systems as the requirement of thermodynamic equilibrium is not fulfilled in that case. Empirical correlations, with fair linear regression coefficients could however be established between R_h and N_{PS}, N_{PEO}, the polymerization degrees of the PS, respectively, of the PEO block. According to Halperin's theory

$$R_h \sim N_{PEO}^{0.6} N_{PS}^{0.16}$$

whereas the experimental results lead to the following relationships, with R_h given in nm

$$R_h = 1.77 N_{PEO}^{0.31} N_{PS}^{0.09} \text{ for diblocks} \qquad \text{with } r = 0.989$$

$$R_h = -1.14 + 0.78 N_{PEO}^{0.42} N_{PS}^{0.14} \text{ for triblocks}$$

with $r = 0.962$

r being the linear regression coefficients and N_{PEO} the total number of PEO units in the case of triblock copolymers [101,167].

For two homologous PS–PEO series, having a constant PS block: $N_{PS} = 10$ and $N_{PS} = 38$, respectively, additional and more detailed informations could be obtained by DLS, SAXS and viscometry. These characteristics are given in Table 4.

Table 4
Experimental characteristics of micellar systems prepared from two homologous series of PS–PEO block copolymers

Sample	N_{PS}	N_{PEO}	R_g (nm)	R_h (nm)	R_c (nm)	Z	$L = R_h - R_c$ (nm)
SE 10-10	10	23	6.3	8.6	5.2	370	3.4
SE 10-20	10	46	7.2	10.8	4.5	227	6.3
SE 10-30	10	69	7.9	14.3	3.6	122	10.7
SE 10-50	10	115	9.2	17.3	3.1	77	14.2
HH 1	38	90	6.7	9.2	5.5	110	3.7
HH 2	38	148	7.9	11.4	5.4	104	6.0
HH 3	38	249	9.9	14.5	5.3	103	9.2
HH 4	38	445	12.0	16.6	5.2	100	11.4
HH 5	38	704	13.1	17.9	5.1	91	12.8

Micelles from series SE are prepared by direct solubilization in water. Micelles from series HH are prepared by stepwise dialysis starting from a THF solution (for experimental details see Ref. [166], table adapted from Ref. [166]). R_g : radius of gyration, R_h : hydrodynamic radius, L : corona thickness, R_c : core radius, Z : aggregation number.

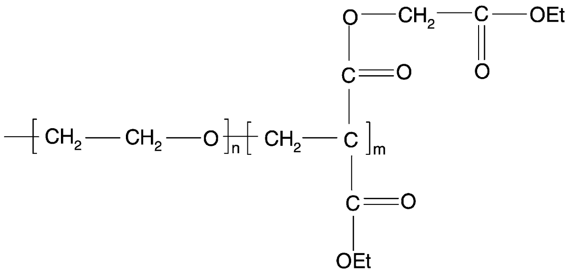
From this table it appears as predicted by theory, that R_g, R_h, and L increase with increasing N_{PEO} for both series. R_c, the micellar core radius, L, the thickness of the PEO fringe and Z, the aggregation number however decrease, as expected from the theoretical predictions, only for the lower molecular weight series. For the higher molecular weight series (series HH), where R_c and Z are almost constant, it can therefore be assumed that frozen micelles are formed even if the micelles are prepared by a stepwise dialysis technique. This freezing-in phenomena is also in agreement with the observation that there is almost no hybridization, e.g. an exchange of unimers between micelles, when two populations of fluorescent labelled PS–PEO copolymers micellar systems are mixed [118]. On the other hand by direct solubilization of the copolymer it cannot be excluded that a given fraction of the PEO gets solubilized more or less in the core, as it could be demonstrated for the SE 10-10 sample by SAXS technique with contrast variation, e.g. by adding given amounts of glycerol to the aqueous phase [169].

5.1.3. Miscellaneous non-ionic copolymers

In addition to the extensively studied block copolymers based on PEO with PPO, PBO and PS hydrophobic blocks, there are quite a number of other possibilities for non-ionic copolymers with A–B, A–B–A and B–A–B structures, where A is either PEO or a non-ionic water-soluble block and where B are hydrophobic blocks such as polydienes, polymethacrylates, polyesters, poly(amino acids), etc.

Typical examples of micelle formation in aqueous medium will be outlined in the following for these di- and triblock structures. Other examples with A–B–C structures, one of the blocks being PEO, or with more complex structures will be given in Section 7.

Micellization of polydiene copolymers was examined by Petrak et al. [173] in the case of PEO–PI–PEO for the development of controlled drug release systems. This interest in biomedical applications was also the starting point for extensive studies on micellar systems obtained with PEO–poly(amino acid) [174, 175], PEO–polyesters block copolymers [176] and PEO–poly (methylidene malonate), also designated by PEO–PMM 212, of the following structure:



which by hydrolysis or enzymatic degradation of the ester side-groups leads to a block copolymer with two water-soluble sequences [177]. In agreement with the theory of Zhulina–Birshtein it could be shown that the hydrodynamic radius R_h of PEO–PMM 212 scales as

$$R_h/N_B^{0.6} = K + K'N_A^{0.6}N_B^{-0.4}$$

where N_A and N_B are the polymerization degrees of PEO, respectively, of PMM 212.

Additional information on block copolymer micelles in biomedical applications will be given in Section 8.

Preliminary micellization studies were reported by Tondeur [178] for PMMA–PEO diblock copolymers which are commercially available from Goldschmidt as homologous series with M_n from 1000 to 3000 for PMMA and PEO. CMC and particle size were found in the same range as for the corresponding PS–PEO copolymers. PIB–PEO block copolymers micelles studied by Kennedy [179] should finally be mentioned as the PIB hydrophobic block of very low T_g could favorize the unimer–micelle equilibrium.

Concerning block copolymers with non-ionic hydrophilic block other than PEO, typical examples are those reported by Binder and Gruber [180] for poly(2-methyl-2-oxazoline)-*b*-poly(2-alkyl-2-oxazoline) and by Cho et al. [181] for poly(*N*-isopropylacrylamide)-*b*-poly(γ-benzyl L-glutamate). These PNIPAM based copolymers, are typical for the preparation of thermosensitive micelles, with a coil–globule transition of the PNIPAAM fringe at around 31–32 °C [182].

5.2. Micellization of anionic amphiphilic block copolymers

Block copolymer micelles with a polyelectrolyte corona are representative of colloidal particles which are strongly influenced by many parameters, e.g. by the degree of dissociation, the pH and the salt concentration, the presence of water-miscible solvent, the polar interactions, etc. These micelles provide unique colloids in which the polyelectrolyte properties can be studied at a very high segment concentration.

Typical examples of well-defined amphiphilic anionic block copolymers are PS–PAA and PS–PMAA in the neutralized form (PS–PANa and PS–PMANa) which have been studied extensively over the last years by Tuzar [103,139] and by Eisenberg and co-workers [116,183] who have also recently reviewed this topic of self-assembly of polyelectrolytes. These copolymers with a PAA or PMAA sequence have been examined in a very wide compositional and molar mass range as well in aqueous medium, as in water/dioxane or water/DMF mixtures. At high pH, the (meth)acrylic blocks are ionized resulting in stable micelles with extended shell regions, due to the electrostatic repulsion of the shell-forming chains.

Typical polyelectrolyte behavior could be found for this type of micelles. Tuzar et al. [184] have shown for PS–PMAA the steep increase of the hydrodynamic radius R_h and of the electrophoretic mobility at a pH around 7, corresponding to the increases in dissociation of the carboxy groups when the pH was changed from 5 to 10 in various buffer solutions. According to these authors, the shift of the inflexion point, from about pH 5 for PMAA homopolymer to a pH 7 for the PS–PMAA copolymer, may indicate that PMAA chains of the micellar system, and more likely those close to the micelle core, experience a lower ‘effective pH’ than that of a given buffer. They concluded that the degree of dissociation decreases from the shell outer layer to the core–shell interface.

It was further demonstrated by Eisenberg et al. [183] that by decreasing PAA/PS ratio of the blocks or by increasing amounts of salt, the morphology of the colloidal dispersion changed from spheres, to rods, to vesicles and even to more complex structures, such as multiple micellar morphologies. Similar effects were observed by changing the water/solvent ratio. The thermodynamics, the kinetics and the mechanism of formation of these block copolymer morphologies could be established by these authors [185]. They have also shown the formation of 'crew-cut' micelles with very asymmetric block copolymers, e.g. those having a short coronal PANa block attached to a long core block. Further studies on PS–PAA and PS–PMAA in their acid or neutralized form were reported by Maarel et al. [186] who examined by SANS with contrast matching in water the structural arrangements in the micelles and by Prochazka and Stepanek [187] who determined by potentiometric titration, light scattering and fluorometry the time-dependant behavior of these polyelectrolyte micelles.

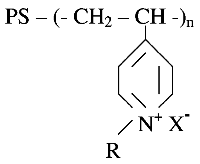
Similar studies were carried out by Wegner et al. [119] on fluorescent labelled PMMA–PAA copolymers in mixtures of water with organic solvents such as methanol or dioxane. From their fluorescence and NMR measurements these authors came to the conclusion that the block copolymer multimerization is preceded by the collapse of the hydrophobic block and that the micelle–unimer exchange equilibrium might not be kinetically hindered under given conditions, such as by the glassy state of the micellar core, but could be controlled by a strong thermodynamic preference for the aggregated state.

In addition to PAA and PMAA based block copolymers, which are the most extensively studied systems, there are a few reports concerning the micellization of copolymers with a carboxylated PS [188] or a sulfonated PI sequence [189].

5.3. *Micellization of cationic amphiphilic copolymers*

The number of publications concerning the micellization of block copolymers containing cationic or cationizable sequences are considerably less than those of copolymers with anionic or nonionic sequences. The earlier studies in this area, mostly those of Gallot and Selb [190], were devoted to vinylpyridine (2VP and 4VP) containing block copolymers, readily accessible by anionic sequential polymerization and which could be transformed into water-soluble cationic species by quaternization or by simple protonation at low pH. The more recent development, pioneered by Armes and co-workers [38,46,82,191], concerns the micellization of amino-methacrylate based block copolymers.

In fact, the first systematic micellization studies of copolymers containing cationic hydrophilic blocks were those of Selb and Gallot, who have also given a review of this topic in 1985 [190]. The typical polyelectrolyte copolymers studied by these authors were polystyrene-*b*-poly(quaternized 4 vinylpyridine) PS–PQV4P with the following structure



with R = CH_3 or C_2H_5 $X^- = Br^-, I^-$

Systematic studies by light scattering, viscometry, ultracentrifugation, etc. were performed on these copolymers in water, methanol or mixtures of both solvents. The typical behavior of polyelectrolyte micelles could thus be demonstrated.

Similar to their work on anionic block copolymers, Eisenberg and co-workers [183,192] have shown that 'crew-cut' micelles can be obtained with PS–PQ4VP of high PS content, when the micelles are formed from DMF solutions of the copolymer dialysed against water. P*t*BS–P2VP copolymers were also studied by these authors, who could furthermore demonstrate with this type of copolymers the concept of two-dimensional micellization on a water–air interface.

A typical example of the polyelectrolyte effect of quaternized PS–P4VP copolymers was reported by Riess et al. [115,118]. The P4VP block is soluble in methanol, whereas the corresponding quaternized block PQ4VP, obtained with methyl iodide, is soluble in water. The micellar characteristics of a diblock copolymer with $N_{PS} = 154$ and $N_{P4VP} = N_{PQ4VP} = 381$ are given in Table 5.

One can notice from this table that:

- the aggregation number Z is highest for PS–P4VP in methanol, whereas Z is similar for the micelles in water before and after addition of KI as electrolyte

Table 5
Characteristics of PS–P4VP and quaternized PS–P4VP$^+$I$^-$ in methanol

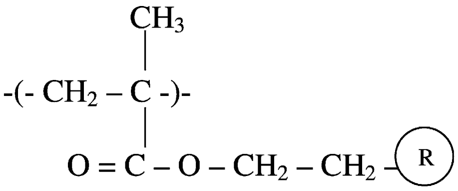
	Solvent	R_h (nm)	Z	φ (g/cm^3)
PS–P4VP	Methanol	22.7	75	0.14
PS–P4VP$^+$I$^-$	Water	26.0	37	0.05
PS–P4VP$^+$I$^-$	Water + KI (7.2 × 10^{-3} mol/l)	20.6	42	0.20

R_h : hydrodynamic radius; Z : aggregation number; φ : density of the corona.

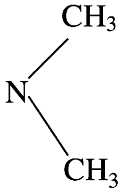
- the density of the micellar fringe is lowest for PQ4VP in water, which corresponds to an important stretching of the PQ4VP chains; the addition of an electrolyte such as KI leads as expected to a denser packing of the chains in the micellar fringe and to a decrease of the hydrodynamic radius R_h of the micelles.

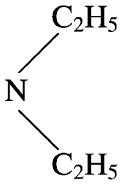
Another approach to cationic block copolymers is that reported by Dautzenberg et al. [193]. These authors synthesized via controlled free radical polymerization diblock copolymers of styrene and vinylbenzyl chloride, which were then quantitatively converted into cationic polyelectrolytes by reaction with different types of tertiary amines. The micellar characteristics of these copolymers were examined by SLS, SEC and ultracentrifugation.

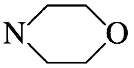
Block copolymers containing tertiary amine methacrylic sequences developed in the recent years by Armes, Billingham and co-workers [38,46,82,191,194,195] offer interesting combinations of solubility properties versus pH, temperature and electrolytes that makes them very attractive for micellization studies. These authors investigated essentially three types of tertiary amine ethylmethacrylates with the following structures:



with R :


dimethylamino DMAEMA


diethylamino DEAEMA


N-morpholino MEMA

- cloud point 34-45°C at pH = 7

These different polymers, that are water-soluble at low pH or by quaternization, are interesting candidates for stimuli-responsive micelles as their solubility can easily be tuned by changing the pH, the temperature and/or the electrolyte concentration.

Hydrophilic aminoethyl methacrylate blocks can therefore be combined with various hydrophobic blocks as shown also by Jérôme et al. [196]. PDMAEMA–PMMA diblock and star–block copolymers, quaternized on the PDMAEMA block with different alkyl halides were synthesized by these authors who could demonstrate that with short alkyl halides the diblock copolymers behave like classical amphiphiles on micellization, whereas their behavior becomes similar to polysoaps in the case of long alkyl halides.

The particular interest of the strategy developed by Armes and Liu [191] is that a new category of hydrophilic–hydrophilic block copolymers becomes available for micellar studies as outlined in Section 5.4.

5.4. Micellization of double hydrophilic block copolymers

Hydrophilic–hydrophilic also called double hydrophilic block copolymers, consist of water soluble blocks of different chemical nature. In aqueous solution they behave as unimers like classical polymers or polyelectrolytes, whereas their amphiphilic characteristics, such as surface activity and micelle formation, only appear under the influence of a given external stimuli, mainly temperature, pH or ionic strength changes. Micellization of these copolymers can further be induced by complex formation of one of their blocks, either by electrostatic interaction with oppositely charged polymers, by hydrophobic interactions such as with surfactants, or by insolubilization in the presence of metal derivatives. These polymer intercomplexes, mainly polyion complexes (PIC), with their application possibilities will be outlined in more detail in Section 7.

Among the first examples of double hydrophilic block copolymers leading to micelle formation by pH change and metal complexation, one could mention that of protonated P2VP–PEO developed in our group by Ossenbach-Sauter [197]. Although numerous examples concerning the synthesis of this category of block copolymer were reported, only relatively few before the beginning of the 90s, were characterized by their micellization behavior.

Their interest as colloidal systems has however dramatically increased in the last 10–15 years as shown by Cölfen in a recent review article [19]. A very systematic overview, including the synthesis techniques, the properties and the application possibilities of these copolymers has been published by this author. The following will therefore be limited to an outline of the micelle formation of these double hydrophilic block copolymers by considering, mainly for A–B diblock copolymers, the various combinations of non-ionic, anionic and cationic blocks (Fig. 5).

Block copolymers with anionic and a cationic (cationizable) sequence are designated by polyampholites and those with a zwitterionic sequence can be classified, depending on the pH, in the one or the other above mentioned categories.

Typical examples of water soluble block copolymers containing at least one non-ionic sequence are listed in Table 6.

It can be noticed that the majority of copolymers in this category contain a PEO or a PVME sequence and that for completely non-ionic systems micellization is mainly induced by a temperature change. For those copolymers with an ionic and a non-ionic sequence micellization becomes also possible by pH changes or by addition of electrolytes.

A second category of water soluble block copolymers are those comprising two ionic sequences, either of the same type, e.g. anionic/anionic or cationic/cationic, or those of polyampholite types where one

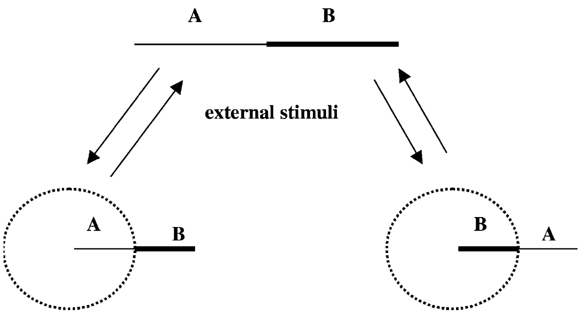


Fig. 5. Reversible micellization of hydrophilic–hydrophilic diblock copolymers under the influence of external stimuli, e.g. temperature, pH, electrolyte, etc. (schematic representation).

Table 6
Micellization of hydrophilic–hydrophilic A–B diblock copolymers containing at least one non-ionic sequence

A block	B block	Type (B block)	Stimulus	Reference
EOVE	MOVE	Non-ionic	T	[198]
MVE	VA	Non-ionic	T	[199]
EO	NIPAAM	Non-ionic	T	[200]
VBA	OEGMA	Non-ionic	pH	[201]
OEGMA	MAA	Anionic	Electrolyte, pH	[82]
EO	Vinylbenzoate	Anionic	pH, T	[202]
EO	MAA	Anionic	Cationic surfactant	[203]
			pH	[204]
EO	2VP	Cationic	pH	[197,205]
EO	DMAEMA, DPAEMA	Cationic	T, pH	[206]
PO	DEAEMA	Cationic	T, pH	[207]

sequence is of anionic the other of cationic type. The corresponding examples are listed in Table 7.

Of special interest are those block copolymers based on tertiary amine methacrylates studied in a very systematic way by Billingham, Armes and co-workers [191]. In addition to the examples already given in Section 5.3, these authors have developed a wide range of water-soluble block copolymers containing two different tertiary amine methacrylate sequences, e.g. methacrylates with dimethylamino (DMA), diethylamino (DEA) and morpholino (M) substituents, which lead under proper stimuli conditions (pH, electrolytes, temperature or combinations of these parameters) to reversible micellar systems.

6. Micellization of block copolymers in organic medium

The micellization behavior of amphiphilic block copolymers in selective organic solvents was recognized quite early and a great deal of experimental and theoretical work has been devoted to this problem, as outlined in different reviews published in the 1980s [1,4,6,7]. An extensive list of block copolymer/selective solvent micellar systems has been given more recently by Hamley [10] from which it appears that a wide range of styrene, (meth)acrylates, dienes based block copolymer were investigated in organic medium.

In one of the most recent overviews on this topic, Chu and co-workers [214] have summarized the main conclusions related to the formation of amphiphilic block copolymer micelles in organic solvents, which in this case is mainly an enthalpy driven process, whereas the micelle formation in aqueous systems can be considered as an entropy driven process.

With a slightly different approach to that of Chu et al. we intend to examine in this section some of the more recent work, at first of hydrophobic–hydrophilic AB and ABA block copolymer where A or B is a water-soluble sequence, mainly PEO, PAA, PMAA, etc. blocks, which are also soluble in polar organic

Table 7
Micellization of hydrophilic–hydrophilic A–B diblock copolymers containing two ionic sequences

A block	B block	Type	Stimulus	Reference
DMAEMA	DEAEMA	Cationic/cationic	pH	[208]
DMAEMA	DEAEMA or DPAEMA	Cationic/cationic	pH, T, electrolyte	[209]
Vinylbenzyltrimethyl-ammonium chloride	*N*,*N*-dimethyl vinylbenzyl amine	Cationic/cationic	pH	[210]
MAA	4VP	Zwitterionic	pH	[211]
MAA	DMAEMA	Zwitterionic	pH	[212]
PS sulfonate	PSCOONa	Anionic/anionic	pH	[210,213]

liquids such as alcohols or mixtures of water and water miscible solvents. As an extension it will be shown that these types of copolymers are able to form *reverse micelles* or other colloidal structures by crystallization of one of the blocks, mainly PEO, in non-polar organic solvents.

A second part will be devoted to the micellization of typical hydrophobic–hydrophobic block copolymers in a variety of selective solvents including alcohols and supercritical CO_2.

Micellization of AB and ABA block copolymers with a liquid crystalline or 'rigid' block and novel micellar architectures, e.g. those obtained by selective cross-linking, will be examined in Section 7.

6.1. Micellization of hydrophobic–hydrophilic block copolymers

From Section 5 it turns out that the micellization behavior of hydrophobic–hydrophilic block copolymer has been studied extensively in aqueous medium and only little attention has been paid to their self-aggregation in non-aqueous solvents, although this kind of study could be quite informative for the understanding of the aggregation mechanism. This prompted us to review in a first part, those studies concerning the micellization of hydrophobic–hydrophilic block copolymer, typically copolymer containing a PEO, PAA or a PMAA sequence, in non-aqueous polar solvents. In the second part, the formation of reverse micelles with these copolymers will be outlined.

6.1.1. Micellization in polar non-aqueous solvents

Micellization of low molecular weight surfactants has been studied to some extent in non-aqueous polar solvents, such as alcohols, glycols, *N*-methylformamide, formamide, etc. Although PEO, PAA or PMAA are known to be soluble in these solvents, only very few studies were reported concerning the micellization of block copolymers in this type of media. The first studies were those of Lindmann and co-workers [215,216]. These authors, who examined the phase behavior of PEO–PPO block copolymers in various formamides, have shown that the cloud point is higher in formamide than in aqueous solution.

A systematic study of the micellization of poly (alkylene oxide) block copolymers in formamide and formamide–water mixtures was performed more recently by Alexandridis and Yang [217,218]. For a PEO–PPO–PEO block copolymer (Pluronic 105 $EO_{37}PO_{58}EO_{37}$), the concentration–temperature phase diagram was established by SANS measurements and it could be shown that micelles are formed in formamide upon increasing the temperature, indicating an endothermic micellization process, similar to that in aqueous phase. However, the enthalpy and entropy of micellization in formamide are about three times smaller than the respective values in water. From the evaluations of the CMC, CMT, micellar size and association number, these authors concluded that formamide is a better solvent than water for PEO–PPO–PEO block copolymers.

Table 8
Micellar characteristics of PB–PEO diblock copolymers in methanol at 20 °C

Sample	M_n copolymer	PEO (wt%)	R_h (nm)	Z^a
B209-E193[b]	19 800	43.0	17.5	187
B202-E157[b]	18 200	38.7	18.3	283

[a] Association number.
[b] polymerization degrees DP_n of each sequence.

For different applications of PEO containing block copolymers, especially for their use as stabilizers of non-aqueous emulsions, we became interested in our group by the micellar characteristics of PB–PEO and PS–PEO copolymers in alcohols and glycols [219, 220]. A typical example of PB–PEO micelles in methanol as selective solvent is given in Table 8, their characteristics having been determined by SLS, DLS and viscometry.

It can be noticed that for these copolymers with a constant PB sequence, the association number Z decreases as expected from theory with increasing PEO content. A similar study for PMMA–PAA diblock copolymers in methanol and mixtures of water with organic solvents was performed by Wegner and co-workers [119].

6.1.2. Micellization in non-polar solvents

With block copolymers having a PAA, PMAA or PEO hydrophilic sequence, micellar systems, so-called 'reverse micelles', can be formed in non-polar solvents that are selective solvents of their hydrophobic blocks.

Over the past decade, the aggregation behavior of block ionomers, such as PS–PAA or PS–PMAA in their neutralized form, has been studied quite extensively by Eisenberg and co-workers [116,183] in order to determine fundamental micellar parameters as a function of the block copolymer characteristics. These studies were mainly focused on PS based diblock ionomers, with relatively long PS blocks linked to short PAA or PMAA ionic segments in form of Na or Cs salts. With different experimental techniques (SEC, DLS, SLS, SAXS, EM, etc.), these authors could demonstrate that in various selective solvents of PS, such as toluene or CCl_4, spherical and very stable micelles are formed, with an ionic core radii that scales roughly as $N_B^{3/5}$, N_B being the number of repeat units of the ionic block. Moreover, they established that the segmental mobility of the PS corona is considerably restricted close to the ionic core and that within the corona the PS segment mobility becomes even more restricted as the size of the ionic core increases.

The micellization of PMMA–PAA diblock copolymers with the PAA in its acid form, has also been studied in *n*-butylacetate which is a non-solvent for PAA and a Θ solvent for PMMA [221]. According to the model designed by Halperin [222] for this particular situation, we could establish that the hydrodynamic radius R_h of the micelles scales such as

$$R_h \sim N_{PMMA}^{0.5} N_{PAA}^{0.09}$$

with N being the number of the corresponding monomer units in a block. Similar studies were performed by Fillod [223] for PCHMA–PAA and PEHMA–PAA in methylcyclohexane and in dodecane, respectively.

The formation of reverse micelles in organic medium with PEO based block copolymers is in general a more complex process as PEO has a tendency to crystallize under given conditions. This problem of crystallization of PS–PEO and PB–PEO in the presence of selective solvents for the PS and PB blocks was first studied over a wide concentration range by Gallot and Gervais [224], by Kovacs and Manson [225] and later on also by Gast et al. [226–228] and by Wu and Chu [229] in the case of PEO–PPO–PEO. These authors have clearly shown that one of the key parameter in this process is the amount of water present in the system with respect to the PEO content. Gast et al. [228] for instance demonstrated by that PS–PEO copolymers in cyclopentane form star-like polymeric micelles having aggregation numbers between 17 and in the order of 100 depending on the copolymer concentration and on the water content. Wu and Chu [229], and more recently Guo et al. [230] came to similar conclusions in their study on water induced micelles formation of PEO–PPO–PEO copolymers in *o*- or *p*-xylene, by showing that the micellar characteristics, as well as the shape transitions from spheres to ellipsoids, are controlled by the water/PEO ratio.

In the absence of water however it could be shown, first by Kovacs et al. and then by Gast et al. that lamellar microcrystals or shish-kebab structures are formed by chain-folding crystallization of the PEO sequences. These lamellar microcrystals, called ‘platelets’ by Gast et al., are typically formed by a central part of PEO, with a lamellar thickness depending on the crystallization conditions, having on their surface a fringe of PS blocks solubilized in the organic solvent.

The schematic structure and a micrograph of these ‘platelets’ is indicated in Fig. 6.

The same type of morphologies was also observed more recently in our group by Reiter et al. [231], Hoerner [219] and Krikorian [232] for a wide range of diblock copolymers such as PB–PEO, PhB–PEO, P*t*BS–PEO, PEB–PEO in cycloaliphatic solvents. Moreover, these authors could demonstrate that under well-defined crystallization conditions it is possible to generate the above mentioned platelets and/or ‘vermicelle’ like colloidal particles with a core of crystallized PEO.

6.2. Micellization of hydrophobic–hydrophobic block copolymers

In the recent publication of Liu et al. [214] and Hamley [10] the basic concepts of block copolymer micellization in organic solvents has been reviewed, the similarities and differences between aqueous and organic based systems were given, illustrated by numerous examples of block copolymer/selective solvent systems.

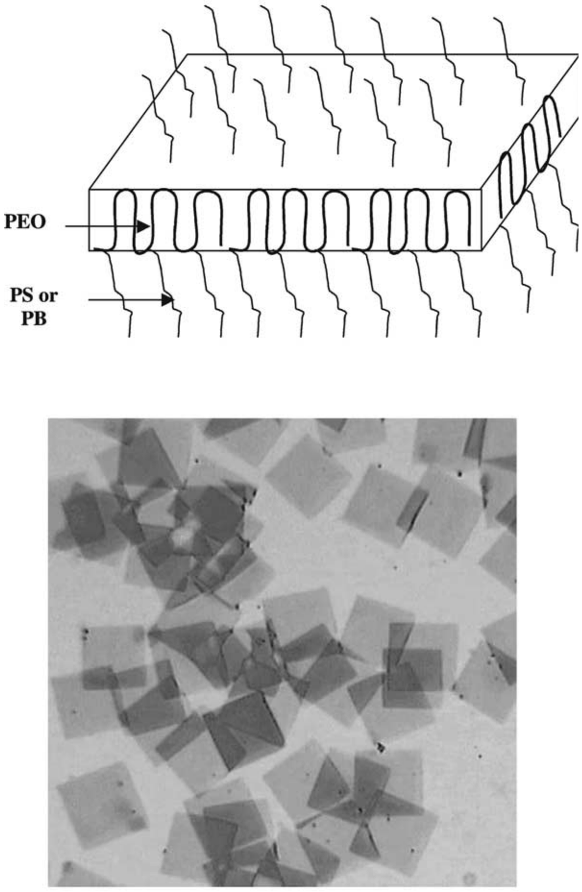


Fig. 6. Schematic structure of lamellar microcrystals (platelets) formed by controlled crystallization of PS–PEO or PB–PEO diblock copolymers. Crystallized PEO in the center of the platelets with a fringe of PS or PB solubilized in organic solvents, e.g. methylcyclohexane. (a) Self-assembly of crystallizable PS_{100}-PEO_{2500} diblock copolymer. Micrograph of platelets. Total size of the picture $200 \times 200\ \mu m^2$.

In the following we intend to complete these overviews with some of the recent publications and in part with typical results of our group which have not yet been published. The description will be limited to the micelle formation in organic medium, including alcohols and s.c. CO_2, of AB and ABA copolymers where neither the A block nor the B block is water-soluble.

According to the main conclusions of Liu et al. [214], the solvent and its interaction with the copolymer blocks plays a dominant role on their micellization behavior. This solvent effect on micellization, very often studied in solvent mixtures of a common- and a selective solvent, was also confirmed recently by Pitsikalis et al. [233]. These authors observed large differences in the micelle characteristics, e.g. hydrodynamic radius, aggregation number, etc., for styrene–stearylmethacrylate diblock copolymers either in ethyl- and methylacetate.

Moreover, it is quite obvious that the temperature dependent solvent–polymer interaction parameter directly determines the CMT (critical micellization temperature) of a given system and thus its CMC as well as its aggregation number at a fixed temperature. This behavior has been well illustrated in the literature and especially by Quintana et al. [128,234] who have clearly shown the decrease of CMC with increasing temperature for PS–PE/PP copolymers in alkanes. Another typical example of the temperature influence is that reported by Fillod [223] for PCHMA–P2VP, which are of practical interest as 'viscosity improvers in motor-oil formulations'. Their micellar characteristics in methylcyclohexane as a function of temperature are given in Table 9.

The second point mentioned by Liu et al. [214] in the summary of their review article is that of 'flower-like micelles' formed with ABA triblock copolymers in a selective solvent of the B middle block. Although numerous examples were reported concerning this type of micellar structure, Hosotte [235] in our group has demonstrated that flower-like structures and/or end-group association could be induced even in organic medium by an initiator end group of an AB diblock copolymer. This demonstration could be supported by the fact that PMMA–P*t*BA have the unique property that their synthesis can be started either with the PMMA sequence or with the P*t*BA sequence. It follows that the initiator group will be in the first case at the PMMA end and in the second case at the P*t*BA end.

By micellization in methanol, which is a selective solvent for P*t*BA, the more hydrophobic initiator end group Ⓘ will therefore be either in the micellar core for copolymer of type 1 or at the end of the P*t*BA fringe in the case of type 2 as indicated schematically in Fig. 7. By following the diffusion coefficient *D* as determined by DLS versus the copolymer concentration, an important difference appears between both cases as shown in Fig. 7, especially at a concentration

Table 9
Micellar characteristics of P2VP–PCHMA copolymers in methylcyclohexane versus temperature

Sample type	DP of the blocks	M_n total	Temperature (°C)	R_h (nm)	$[\eta]$ (ml/g)	Z
P2VP–PCHMA	V_{47}–C_{260}	48 500	20	24.7	21.9	89
			40	24.5	22.7	84
			50	24.1	23.0	79
P2VP–P*t*BMA–PCHMA	V_{25}–T_{12}–C_{173}	33 300	20	17.9	16.9	65
			40	15.4	17.3	40
			50	14.0	17.0	31

R_h : hydrodynamic radius; $[\eta]$: intrinsic viscosity; Z aggregation number.

$C > C^*$, where C^* is the concentration at which the corona chains of different micelles start to overlap.

This is also a direct evidence that labeling and especially end-group labeling of block copolymers for fluorescence experiments can modify to some extent the micellar characteristics of the copolymer under study.

In order to complete the literature survey of Hamley [10] and of Liu et al. [214] we have collected in Table 10 typical examples of recent studies related to AB and ABA block copolymer micellization, the more elaborated structures being discussed in Section 7.

From this table it appears that micellization is still a relative active field of investigation with ongoing studies on special acrylic, silicone or fluorinated copolymers and on their micellization in special organic solvents such as alcohols and supercritical CO_2 [236–238].

7. Novel micellar architectures

As outlined in the previous sections, the theoretical and experimental aspects of block copolymer micellization was mainly examined in the case of AB diblock and ABA triblock copolymers leading in general to spherical micelles. Already in the early 70s it was found however that micelles could change shape under the influence of external parameters, such as temperature or solvent composition. Prolate ellipsoids were thus reported by different authors [245,246].

A number of other morphologies since developed with AB and ABA copolymers will be reviewed in the first part of this section. The stabilization of micellar systems derived from linear AB and ABA copolymers by selective cross-linking, either of the micellar core or of the corona will then be examined.

With the development of the controlled synthesis techniques block copolymers with well-defined architectures became available, such as:

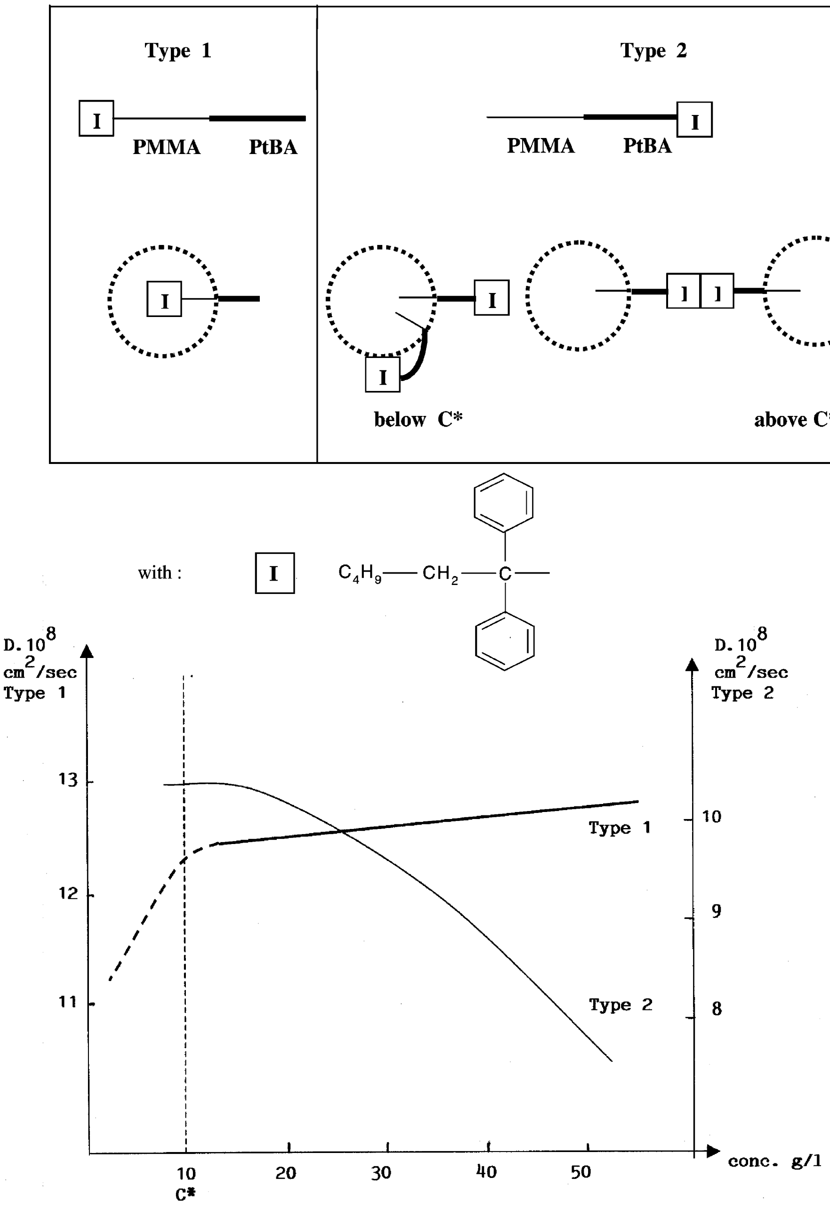
- AB and ABA copolymers with *non-linear structures*
- *functionalized block copolymers* with typical structures like ABF or AFB where F is a functional group
- *ABC triblock copolymers*, mainly with linear arrangements of the three blocks of different chemical nature.

Typical examples of these possibilities will be given and finally it will be of interest to consider the formation of micellar systems by:

- comicellization of AB and BC block copolymers having one type of sequences in common
- polar interaction between oppositely charged block copolymers, leading to PIC micelles
- low molecular weight surfactant–block copolymer interactions.

7.1. Micellar architectures derived from linear AB and ABA block copolymers

AB and ABA copolymers, with a coil–coil conformation in a common solvent of both blocks, have a tendency to self-associate in form of star-like micelles in the presence of a selective solvent for the A blocks. ‘Flower-like’ micelles would be formed



Diffusion coefficient versus concentration :
Type 1 PMMA384 - PtBA194
Type 2 PMMA438 - PtBA502

Fig. 7. Micellization of PMMA-P*t*BA in methanol, a selective solvent of P*t*BA. Initiator end-group [I] effect on the diffusion coefficient D of the micelles. Schematic representation.

with ABA triblock copolymers in a selective solvent of the B block, as already mentioned previously.

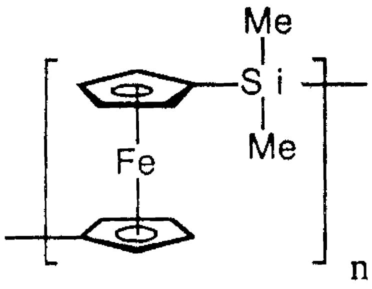
The problem of morphological transitions in block copolymers and especially in block polyelectrolytes was studied extensively by Eisenberg and co-workers [116,183]. These authors examined the morphologies formed by PS–PAA diblock copolymers in aqueous medium as the PAA block length was decreased from PAA_{21} to PAA_4 at constant PS block length (PS_{200}). Spherical crew-cut micelles

Table 10
Studies on AB and ABA block copolymer micellization in organic medium

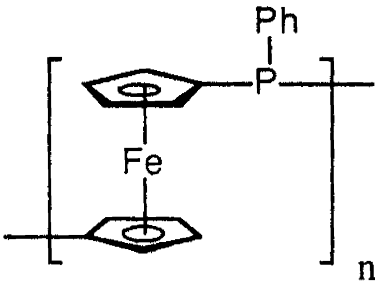
Copolymer type	Solvent	Type of study	Technique	Reference
PMMA–P*t*BA	Ethanol	R_h, $[\eta]$, Z	DLS, viscometry	[239]
PCHMA–PAA	MeCH	R_h, $[\eta]$, Z	DLS, NMR	[223]
PCHMA–P2VP	MeCH	R_h, $[\eta]$, Z	NMR	[223]
PEHMA–PAA	Dodecane	R_h, $[\eta]$, Z	NMR	[223]
PS–PMMA	*p*-Cymene + toluene	Comicellization		[240]
PS–PDMS	1,2-Chlorobenzene + benzylalcohol	'Anomalous' micellization	DLS, SLS	[241]
PDMAEMA–PDMS		R_h		[242]
PMMA–PFMA	Acetonitrile, $CHCl_3$	R_c, R_h, Z	SANS, SLS, cryo-TEM, AFM	[243]
P*t*BMA–PFMA	s.c. CO_2	R_h	SLS, SANS	[244]

were observed for PS_{200}–PAA_{21}, whereas rod-like micelles were formed for PS_{200}–PAA_{15}. Vesicular aggregates and complex micellar structures appeared for lower PAA contents.

An interesting development of novel organometallic nanostructures derived from amphiphilic poly(ferrocene) block copolymers was recently reported by Winnik and co-workers [247–249]. These authors prepared a series of copolymers with an organometallic block either of poly(ferrocenylsilane) (PFS) or of poly(ferrocenylphosphine) (PFP) with the following structures



PFS



PFP

The solubilizing block of these copolymers could be either PDMS, PS, PI or even PEO. Depending on the copolymer type and its composition various morphologies were obtained ranging from spherical star-like micelles to cylindrical micelles also called 'worm-like' micelles, as well as to original flower-like structures.

The self-assembly of rod–coil block copolymers was extensively studied especially in the case with a helix type 'rigid' block as already reported in the 80s by Douy and Gallot [250]. The introduction of a rigid segment in the block copolymer results in a stiffness asymmetry which leads to an increase of the Flory–Huggins χ parameter. An interesting consequence of the increase of χ is that phase separation already occurs at much lower molecular weights in comparison to coil–coil diblock copolymer [251]. pH sensitive vesicular aggregates in a size range of 100–150 nm were for instance obtained by Lecommandoux et al. [252] with polybutadiene–poly(glutamic acid, sodium salt) (PB_{40}–$PGANa_{100}$). Similar results for PEG–polypeptide diblock copolymers were reported by Klok et al. [253].

The self-assembly of rod–coil block copolymers was further studied by Jenekhe and Chen [254] using poly(phenylquinoline) as rigid block linked to a PS coil forming block. The interesting feature of this type of block copolymers is that, unlike to conventional micelles, spherical or tubular aggregates in the 1–50 μm range, having a large hollow cavity akin to vesicles, can be formed under proper conditions and especially in the presence of a selective solvent of the rigid block. Large amounts of fullerenes C_{60} and C_{70} could be solubilized and encapsulated in these structures.

The structure formation of liquid-crystalline isotropic AB block copolymers in nematic solvents was first reported by Finkelman et al. [255,256]. These authors have shown that block copolymers consisting of a 'nematophilic' liquid-crystalline block and a 'nematophobic' segment are able to form thermoreversible thread-like aggregates of micellar type with ordered superstructure in dilute nematic solvents. It could be assumed that these thread-like aggregates with a uniform diameter of 2–3 μm consist of bilayered vesicles with a rod-like shape.

7.2. Cross-linked micellar structures

Although micelles are stable in time at fixed conditions, their characteristics depend for a given system on the thermodynamic quality of the solvent and on temperature. For this reason it is impossible to study that system under different conditions, e.g. in a different solvent, at a different temperature or at various concentrations. The idea of Prochaska and Baloch [257] and of Tuzar [258] to circumvent this problem was to stabilize a particular micellar structure such as block copolymers with a PB block by cross-linking of the micellar core, either by UV or fast electron irradiation.

A similar approach was made by Wilson and Riess [259], who studied the UV photocross-linking of a range of SB diblock copolymers differing in structure, molecular weight and composition. It could be shown that cross-linking induces a reduction of the hydrodynamic radius of the micelle and that the cross-linking efficiency, typically between 65 and 85% depends on the molecular weight of the PB block. The unimers remaining in the system after cross-linking can easily be removed by fractional precipitation or dialysis.

Systematic studies on photocross-linking block copolymer micelles, with a core of poly(cinnamoylethyl methacrylate) (PCEMA) were published more recently by Liu and co-workers [260]. By changing the shell-forming block (e.g. PS, PAA), these authors could demonstrate by SLS, DLS, TEM and SEC that photocross-linking of PCEMA locked in the initial structure of the micelles without any significant change in their aggregation number and size distribution.

The other possibility, at first examined by Wooley and co-workers [261,262] is to cross-link the corona of the micelles, as indicated schematically in Fig. 8.

These kind of nanoparticles are designated by shell cross-linked knedel-like micelles by these authors. Wooley et al. have applied this concept to a large variety of block copolymers, mainly hydrophobic–hydrophilic copolymers with PAA or quaternized PVP as the water soluble block, which can be chemically cross-linked in their micellar form. A similar approach has been described by Armes and co-workers [263] for the synthesis of shell cross-linked micelles where core and shell are both hydrophilic.

An alternative to form core cross-linked nanoparticles was reported by Ishizu [264], who started from a PS–P4VP diblock copolymer having a spherical microphase separated mesomorphic structure in the solid state. A film of this material, having P4VP spherical microdomains dispersed in the PS matrix, is treated with 1,4-dibromobutane in order to cross-link the P4VP domains. The core–shell microspheres obtained by dissolution in benzene were characterized by SAXS.

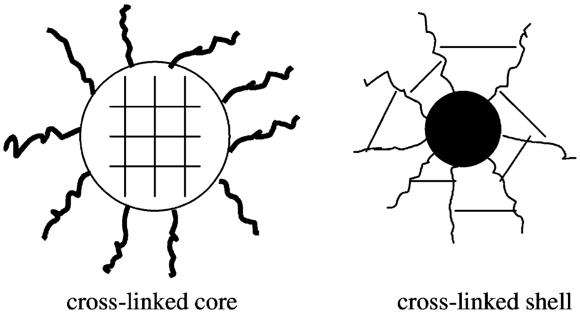


Fig. 8. Cross-linked micellar structures (schematic representation).

7.3. Micellization of AB block copolymers with non-linear architecture

The influence of the block architecture on micelle formation was usually limited to comparisons of AB, ABA and/or BAB linear structures in a selective solvent of A. Among the large variety of AB block copolymers with non-linear structures as outlined in Section 2, only very few of them have been studied with respect to their micellization behavior. Typical examples of these recent studies are discussed in the following.

In a very systematic study of PEO–PBO copolymers, Booth and co-workers [64] have also compared linear to the corresponding cyclic structures. Their general conclusion was that the micellization of a cyclic diblock copolymer is favored over that of its corresponding linear precursor triblock.

The micellization of quite a number of star–block copolymers with well defined structures of type AB_2, AB_3 and A_2B_2, as well water soluble as organosoluble copolymers were studied, usually in comparison to the corresponding AB diblock structure. The general observed trend is that star architectures have higher CMC values and thus less tendency to micellization than the corresponding linear block copolymers.

Pispas et al. [67] who examined the micellization of PS–PI star–block in decane, a selective solvent for PI, found that the hydrodynamic radius R_h and the aggregation number Z increased in the following order $I_2S < S_2I <$ SI. Similar conclusions could be drawn by Sotiriou et al. [265] and by Allgaier et al. [266] who have studied by SANS and LALLS in addition to the I_2S structure S_2I_2, I_3SI_3 and $(SI)_4$ architectures. Theoretical models could be developed for these micellar structures which are schematically given in Fig. 9.

By increasing the number of arms for $(AB)_n$ star block copolymers, Miller and co-workers [74,267] could demonstrate with fluorescence techniques the formation of unimolecular micelles for $n = 6$ or 12.

The micellization behavior in aqueous and organic medium of heteroarm star copolymers A_nB_n was studied by Tsitsilianis and Kouli [268], by Voulgaris et al. [269] and by Kanaoka et al. [270]. The architecture of these copolymers is not as well defined as that of the previously mentioned star blocks, due to the presence of the central dense core of divinylbenzene. Nevertheless, it could be shown that the aggregation number decreases, with the possible formation of unimolecular micelles, by increasing the number and the molecular weight of the soluble chains.

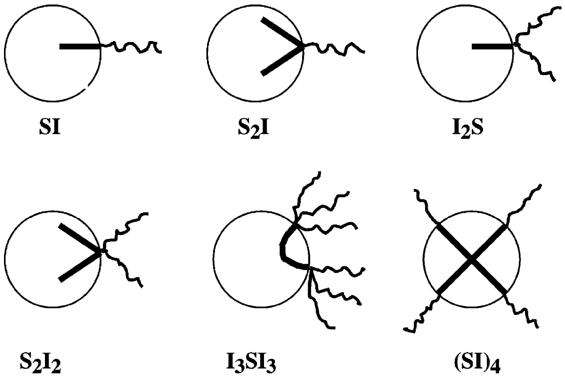


Fig. 9. Star–block copolymers: schematic representation of micellar structures for polystyrene (S)-polyisoprene (I) copolymers.

Unimolecular micelles in form of cylindrical brushes were reported by Schmidt et al. [98] for PS–P2VP poly(blockcomacromonomers) in toluene as selective solvent of the PS block. Micellization of ‘palm-tree’ structures derived from oligo PEO macromonomers were studied by Armes and co-workers [82] and by Graf and Müller [71]. PEO based linear-dendridic structures were further examined by Gitsov [79] and finally it is worthwhile to mention the recent example of supramolecular brushes formed by self aggregation of coil–ring–coil block copolymers [65].

7.4. Micellization of functionalized block copolymers and of ABC triblock copolymers

For specific applications of block copolymer micellar systems, especially in the biomedical area and for analytical purposes, it is of interest to fix covalently, either on the micellar surface or at the core–fringe interface, specific functional groups such as amino, aldehyde, carboxy, sugar moieties, fluorescent labels, etc. The synthesis of these structures has been outlined in Section 2 and in several review articles, knowing that an end-functionality can be introduced in the block copolymer chain either in the initiation or the termination step [1,118].

A wide range of functionalized block copolymers were developed, mainly for application purposes, and a typical example is that described by Hurtrez [101] for PEO–PS–PEO end-functionalized with carboxy or sulfonate groups. By increasing the hydrophilic character of the copolymer it appeared that the micelles formed in aqueous solution decrease generally in size and aggregation number with respect to the micelles obtained with an unlabelled copolymer. On the contrary hydrophobic end-groups could have a tendency to self-aggregate leading to micellar bridging or to 'flower-like' structures as previously mentioned. This typical behavior of ω-functionalized copolymers was recently confirmed by Hadjichristidis and co-workers in the case of ω-PS–PI sulfonates [271]. Another example of functionalized micelles is that reported by Kataoka et al. [272] for PEG–polylactide copolymers having a sugar group at the PEG chain end.

Photocleavable PS–PMMA diblock copolymers having at their junction point an anthracene $[4+4]$ photodimer were recently reported by Goldbach et al. [273].

ABC triblock copolymers, with a linear arrangement of three different blocks, have attracted increasing attention because they display in the solid state a very large variety of mesomorphic structures [84,86]. Their synthesis is well documented, however their colloidal properties, and especially their micellization behavior in selective solvent, have not yet been studied in detail.

One of the first examples might be that of Patrickios et al. [274] who demonstrated the micelle formation as a function of pH for a polyampholyte triblock copolymer consisting of PDMAEMA–PMMA–PMAA prepared by GTP polymerization. A similar approach with the same type of triblock copolymer was that of Triftaridou et al. [275] who determined by aqueous GPC the micellar size as a function of the sequence arrangement which has a profound effect on the self-assembly behavior. This type of study was recently completed by Patrickios et al. [87] by preparing the three equimolar structures ABC, ACB and BAC, with one hydrophobic PMMA sequence, and two hydrophilic sequences PDMAEMA and hexa(ethylene glycol) methacrylate respectively.

Micelle formation of ABC copolymers in organic medium was reported by Tsitsilianis and Sfika [276]. For PS–P2VP–PMMA in toluene, a selective solvent for both end blocks, these authors observed the formation of spherical micelles with a dense P2VP core, surrounded by PS and PMMA chains in the corona. For this micellar architecture, similar to that of heteroarm star copolymers, it could be shown that the aggregation number and the micellar size are strongly influenced by the length of the P2VP middle block.

In our group we became interested a few years ago in ABC block copolymers able to form micelles in organic as well as in aqueous medium, with the practical goal to develop 'universal' pigment dispersants, e.g. copolymers that are efficient as dispersants and stabilizers for pigments in aqueous and organic medium [85]. The study was focused on PB–P2VP–PEO triblock copolymers and their micellization behavior was examined in water and in heptane, which are selective solvents of PEO and PB respectively, whereas P2VP is insoluble in both of these solvents.

The composition domain could be determined where micellization was possible in aqueous medium, by step-wise dialysis from a 50:50 v/v mixture of THF/CH_3OH, and in heptane, by azeotropic distillation from a THF/heptane mixture. For a given copolymer, micelles can be formed in water and in heptane, with less than 1% larger aggregates, if its PEO and PB contents are at least 20 wt%.

The micellar characteristics as determined by DLS and viscometry are summarized in Table 11.

The theories developed in recent years to predict the micellar characteristics as a function of the block copolymer parameters concern almost exclusively AB and ABA copolymers. Our intention was therefore to verify if the classical theories for AB diblock copolymer are applicable to our PB–P2VP–PEO copolymers by considering that in aqueous medium such a copolymer has:

- a hydrophilic sequence of PEO with N_{PEO} monomer units
- a hydrophobic moiety comprising the PB and the P2VP blocks with N_{PB} and N_{PVP} monomer units, respectively, in such a way that the total number of hydrophobic units N_{B} is given by $N_{\mathrm{B}} = N_{\mathrm{PVP}} + N_{\mathrm{PB}}$. Furthermore, in order to take into account the difference in molar volumes of the vinylpyridine and butadiene units as suggested in the theory of

Table 11
Micellar characteristics of PB–P2VP–PEO triblock copolymers in water and in *n*-heptane

Sample	N_{PB}	N_{PVP}	N_{PEO}	Water			*n*-Heptane		
				R_h	$[\eta]$	Z	R_h	$[\eta]$	Z
JPL 3	100	100	104	22.5	13.69	256	22.6	12.87	276
JPL 4	185	108	154	25.1	7.38	479	28.5	15.93	325
JPL 301	89	145	125	24.0	12.12	281	24.2	10.12	345
JPL 302	113	67	218	23.5	11.52	313	26.3	17.19	294
JPL 305	131	219	322	38.6	11.50	712	37.6	10.77	703

$[\eta]$: intrinsic viscosity in cm^3/g at 20 °C; R_h in nm, determined by DLS at 20 °C.

Nagarajan and Ganesh [277], the number of hydrophobic monomer units has been 'normalized' with respect to the vinylpyridine monomer units. The total number of hydrophobic units is therefore given by

$$N'_B = N_{PVP} + 0.65N_{PB}$$

where the correcting factor is calculated from the respective densities $\varphi(PB) = 0.89\ g/cm^3$ and $\varphi(PVP) = 1.13\ g/cm^3$. In a similar way, for micelles in heptane, where PB is the soluble block of N_{PB} units, the total number of monomer units of the insoluble blocks becomes:

$$N'_B = N_{PVP} + 0.39\ PEO$$

The exponents of the scaling laws from the experimental results are given in Table 12 for the micellization in water and in heptane.

The same type of approach as the one proposed by Lerch [85] is that developed by Webber et al. [278] for PMAA–PMMA–PDMS copolymers. This type of copolymer acts with its PDMS block as stabilizer for PMMA latexes prepared in s.c. CO_2. This latex is then easily transferred in aqueous medium, where the stabilization is achieved by the PMAA block.

Cross-linking of ABC micellar structure was performed in analogy to AB structures as mentioned in Section 7.2. Wooley and Ma [89] reported the cross-linking of PAA_{90}–PMA_{80}–PS_{98} micelles in aqueous medium by amidation of the PAA shell. Liu and co-workers [279,280] focused their study on PI–poly(2-cinnamoyl ethylmethacrylate)–P*t*BA triblock copolymers where the central block can easily be cross-linked by UV irradiation. In addition hollow nanospheres and nanotubes were obtained by ozonolysis of the PI micellar core. Armes et al. [281] have also extended their pioneering work on aminoacrylate based block copolymers to micellar studies of ABC copolymers such as PEO–PDMAEMA–PDEAEMA and PEO–PDMAEMA–PBAEMA in which the central PDMAEMA block was cross-linked by a difunctional alkyl iodide.

So-called spherical 'Janus micelles' with a central core of cross-linked PB, a fringe of PS chains on the one side and a PMMA fringe on the other were recently obtained by Müller et al. [282] starting with

Table 12
Scaling laws exponents: comparison of the experimental and theoretical values (micellization of PB–P2VP–PEO in water and *n*-heptane)

Micellar characteristics	Solvent	Theory[a]	Experimental values	Experimental values 'corrected'[b]
R_h	Water	0.68	0.67, r = 0.905	0.68, $r = 0.970$
hydrodynamic radius	Heptane	0.68	0.66, $r = 0.994$	0.70, $r = 0.964$
Z	Water	0.90	1.08, $r = 0.935$	1.08, $r = 0.969$
aggregation number	Heptane	0.90	1.15, $r = 0.832$	1.26, $r = 0.913$

r : correlation coefficient.

[a] According to the theory of Noolandi–Hong [131] $R_h \sim N^{0.68}$, $Z \sim N^{0.90}$ with $N = N_{PB} + N_{PVP} + N_{PEO}$.

[b] Values of N 'corrected': 'normalization' with respect to the VP monomer units by taking into account the molar volumes of the butadiene and ethylene oxide units.

a PS–PB–PMMA triblock copolymer having a typical PB sphere–PS/PMMA lamellar mesomorphic structure in the solide state. Similar results on 'Janus' micelles were also reported by Saito et al. [283].

In the case of ABC copolymers micellization studies were mainly reported in recent years for linear architecture. ABC star structures have not yet been examined in detail and the only report we are aware of is a preliminary study of Dumas et al. [93]. These authors have examined the micellization behavior of a three star [$PS_{40}PMMA_{26}PEO_{289}$] in aqueous medium by comparing the hydrodynamic radius R_h of the micelles to those of an 'equivalent' $PS_{66}PEO_{289}$ diblock copolymer. As no major influence of the PMMA block on the micellar size could be detected, the authors assumed the miscibility of the short PS and PMMA block in the micellar core.

7.5. Comicellization and complex formation

The complex formation by polymer-surfactant interaction has been extensively studied, as well for ionic and non-ionic polymers as for the different surfactant types, e.g. anionic, cationic and non-ionic low molecular weight surfactants. The driving forces for these complex formation are in general electrostatic or hydrophobic–hydrophobic interactions between polymer and surfactant. These concepts have been extended to block copolymer systems mainly to those containing a water-soluble PEO block, such as PPO–PEO, PS–PEO, PEO–PMAA, PMMA–PEO in the presence of anionic or cationic surfactants [284,109].

Also 'mixed' micelles could be obtained by comicellization of PPO–PEO based copolymers in the presence of a non-ionic $C_{12}(EO)_5$ low molecular weight surfactant [285]. This topic will not be reviewed further and the following will mainly be focused on supramolecular assemblies formed through specific interactions between a given block copolymer and either a homopolymer or another block copolymers.

The different concepts of comicellization and complex formation are schematically indicated in Fig. 10.

Let's consider at first a block copolymer AB where the sequence B can interact specifically, say by electrostatic interaction or hydrogen bonding, with a homopolymer C. In this case a PIC micelle can be formed having a BC core and a stabilizing corona of A (see Fig. 10(a)). This possibility was examined in our group by Fillod [223] by addition of P2VP to a PCHMA–PAA diblock copolymer dissolved in dioxane, a common solvent of all the polymeric components. At a stoichiometric amount of P2VP with respect to PAA, stable micelles are formed with a PAA/P2VP complex core and a PCHMA corona. Their hydrodynamic radius R_h could be varied between 13 and 30 nm with aggregation numbers ranging from 150 to 800 depending on the molecular characteristics of the precursor block and homopolymer.

A second possibility is that where the starting copolymer AB is already under its micellar form. By complexing the B chains in the corona with the polymer C the micellar structure could remain at low ratios of C versus B, however at a stoichiometric amount flocculation could occur (see Fig. 10(b)). Examples of this behavior have been examined in our group by Lee [286] for PDMS–P2VP micelles in methanol complexed afterwards with PAA and by Mechergui [287] for PS–PEO micelles where the complex formation occurs by hydrogen bonding between PEO and PMAA in aqueous medium at low pH. A similar system was reported recently by Müller and co-workers [288] where an interpolyelectrolyte complex was formed between $PIB–PMAA^{-}Na^{+}$ micelles in aqueous medium and a cationic polyelectrolyte such as poly(*N*-ethyl-4-vinylpyridinium bromide).

The most interesting situation is that where the complex formation occurs between two block copolymers AB and AC, respectively CD, with specific interactions between the blocks B and C (see Fig. 10(c)). Such PIC, also called block ionomer complexes (BIC) have been studied quite extensively in aqueous medium by Kataoka and Harada [289,290] and by Kabanov and Alakhov [291] due to their practical interest in controlled delivery systems. Kataoka and co-workers have for instance shown that water-soluble PICs for biomedical applications are formed by combination of PEO–poly(L-lysine) and PEO–poly(α,β-aspartic acid). These authors have further demonstrated that the PIC micelles prepared under charge-neutralized conditions have an extremely narrow size distribution if matched pairs

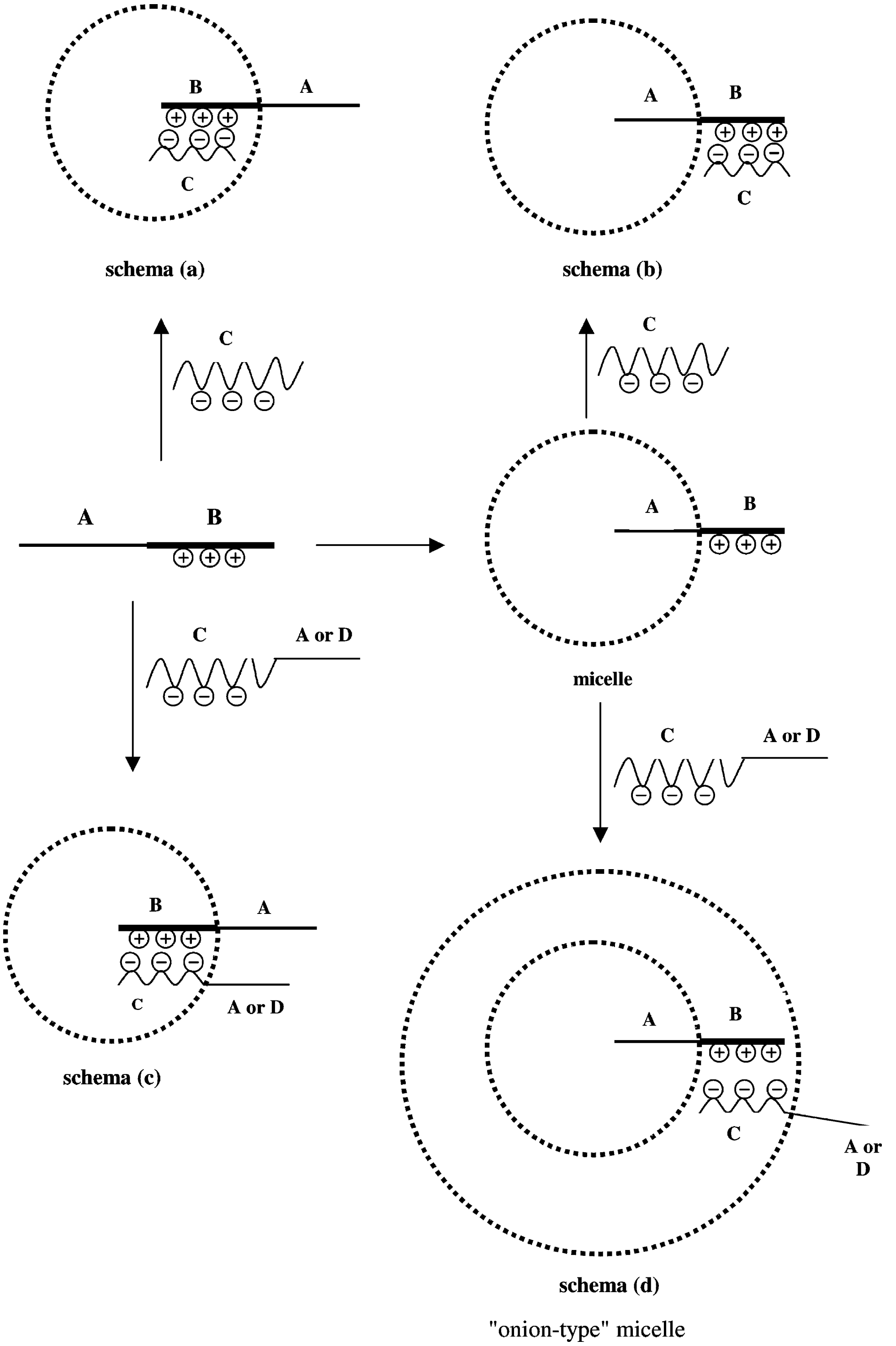


Fig. 10. Schematic micellar structures of PIC.

of copolymers with the same block lengths of polyanions and polycations are combined. PIC systems in organic medium have furthermore been investigated by Fillod [223] in the case of complex formation between PCHMA–PAA and PCHMA–P2VP.

The PIC systems that have mostly been examined were those of type AB + CA, e.g. with a common soluble sequence A. However, Liu et al. [292] mentioned the micellization of block copolymers and a random copolymer in a non selective solvent caused by interpolymer hydrogen bonding complexation and quite recently Antonietti et al. [293] reported the interpolymer complex formation in organic medium of a system AB + CD, where A and D are long PS and PB segments respectively, with B and C being PMAA and P4VP. 'Janus' type micelles are claimed to be formed under these conditions due to the incompatibility of the A and D blocks.

A different approach for AB + BC systems described by Prochazka et al. [294] leads to the formation of onion-type micelles as schematically outlined in Fig. 10(d). Such structured micelles could be obtained by starting with P*t*BA–P2VP precursor micelles in acidic aqueous solution having a P*t*BA core and a protonated P2VP corona. When this micellar solution is brought to a pH higher than 4.8, the P2VP shell of the micelles collapses and the copolymer precipitates. However, by addition of a water-soluble P2VP–PEO diblock copolymer, its P2VP block coprecipitates with the P2VP corona of the micelles. The complex onion structure is thus stabilized by the PEO blocks. Similar onion type micelles obtained by combination of PS_nP2VP_n heteroarm star copolymers with a P2VP–PEO diblock copolymer were reported recently by Tsitsilianis et al. [295].

8. Application possibilities of block copolymer micellar systems

The surface activity of block copolymers, a well established fact as outlined in several review articles, make them of great practical interest as dispersants, emulsifiers, wetting agents, foam stabilizers, flocculants, demulsifies, viscosity modifiers, etc., in many industrial and pharmaceutical preparations [1,9,11]. In fact, with respect to classical low molecular weight surfactants, block copolymers have in general a very low CMC and a low diffusion coefficient which is of benefit for micellar systems where the concentration of unimers in equilibrium with the micelles has to be kept to a minimum. Block copolymers have furthermore the unique property to act under proper conditions not only as a surfactant for oil–water but also for oil–oil two-phase systems [1].

A detailed description of all these application possibilities of block copolymers would exceed the scope of this review. Our aim is rather to highlight some specific aspects where the applications of block copolymers are directly related to their self-organization into micellar systems. This is for instance the case where block copolymers, in form of colloidal dispersions, are of interest for controlled delivery of drugs, diagnostic agents and more recently in gene transfection (gene therapy). These biomedical application possibilities, based on the solubilization of active components in block copolymer micelles, will be briefly outlined in a first section mainly under the viewpoint of polymer colloids, rather than on biological and medical aspects, such as drug efficiency or toxicity, specific interactions with cells, etc.

Some aspects concerning nanoparticles obtained by metal complexation of block copolymers will then be reviewed. Typical features related to the surface modification, will be indicated as well as some miscellaneous application possibilities of block copolymer micellar systems.

8.1. Solubilization of active components in block copolymer micelles: biomedical applications

In addition to their applications as biomaterials, such as implants, block copolymers have found since the mid-70s a strong interest in their colloidal form especially as controlled drug delivery systems, as carriers of diagnostic agents and more recently in gene therapy. These aspects, essentially based on the solubilization capacity of block copolymers micellar systems have been recently reviewed by Riess et al. [12], Malmsten [296], Arshady [297], Torchilin [298]. The major contributions in this area have come from the groups of Kataoka and Kabanov and their recent overviews illustrate perfectly the current status of the field [291,299–301].

According to Kabanov and Alakov [291] three major systems have to be considered for the use of block copolymer micelles in drug delivery:

- micelle forming conjugates of drugs and block copolymer, where the drug is covalently linked to one of the sequences of the copolymer
- drugs non-covalently incorporated into the block copolymer micelles with formation of so-called ‘micellar microcontainers’
- polyelectrolyte complexes formed between polynucleotides and cationic block copolymers designated by BIC.

For these different systems, the main requirements which have to be met, such as biocompatibility, biodegradability, particle size, etc. have been summarized by Kabanov et al. [291,300].

8.1.1. Drug loaded micelles

Various colloidal systems, such as liposomes, microspheres, emulsions have been described as drug targeting devices. Block copolymers in their micellar form or as steric stabilizers for colloidal particles are well suited for drug delivery and diagnostic systems if they meet the requirement of biocompatibility and preferably of biodegradability [302,303].

The first work on micelle-forming block copolymers, with the drug covalently linked to one of the blocks of the copolymer, was reported in early 80s by Ringsdorf et al. [304]. Starting with a poly(ethylene oxide)-*b*-poly(L-lysine) diblock copolymer, these authors fixed covalently the drug ‘cyclophosphamide’ on the L-lysine block leading to micelles with a hydrophobic core of modified L-lysine and a hydrophilic PEO fringe. A similar approach was later described by Yokoyama and co-workers [305] using PEO–poly(aspartic acid) block copolymer modified with doxorubicin. Even more elaborate structures were developed for this type of copolymers in order to increase the activity of drug and to reach the level of the free drug, by introducing spacer groups and cleavable bonds, such as disulfide bonds, between the polymer backbone and the drug moiety. If this approach is still of interest for water soluble drugs, the main limitation for the controlled drug release of hydrophobic drug molecules by this strategy is that specific block copolymers, with suitable functional groups, spacers and cleavable bonds, have to be designed for a given kind of drug.

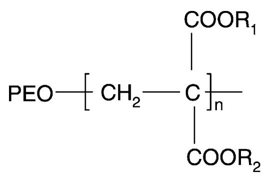
‘Micellar microcontainers’, where the drug is solubilized, e.g. non-covalently fixed, in the hydrophobic core of block copolymers micelles, became therefore the preferred strategy during the last decade, especially with the possibility to provide these micellar systems with targeting function and stimuli sensitive properties.

The large variety of amphiphilic block copolymers developed for temporary biomedical applications are those containing a poly(aminoacid), a poly(ester) or a poly(anhydride) hydrolytic and/or enzymatic degradable block, with their hydrophilic moiety mostly based on ethylene oxide oligomers or polymers: PEG or PEO. This type of water soluble polymers, approved by FDA for biotechnological applications, have numerous other advantages, such as rapid clearance from the body, lack of immunogeneicity, etc. [306]. PLA–PEO, PLGA–PEO and PCL–PEO are typical examples of polyester based block copolymers that have extensively been studied over the last years in view of their biomedical applications.

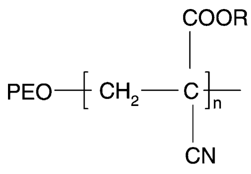
PEO–PPO di-, tri- or multiblock structures (trade names: PLURONICS, TETRONICS, POLOXAMER), were certainly one of the first types of amphiphilic block copolymers described in the literature. Their properties and biomedical application possibilities having extensively been described by Kabanov et al. [291,300], we will not further consider this type of copolymer.

Various other combinations of hydrophobic–hydrophilic blocks are of interest as ‘micellar microcontainers’ in drug delivery applications, such as poly(DL-lactide)-poly(*N*-vinyl-2 pyrrolidone [307], poly(lactide)–depsipeptide [308], poly(malic acid)–poly(malic ester) [309], PEO–PPO–PCL triblock copolymers [310], dendrimer unimolecular micelles [311], etc.

A final example of amphiphilic block copolymers recently developed in our group for biomedical applications in micellar form is that of PEO–poly(methylidene malonates) [177,312]. These diblock copolymers with the following schematic structure are somehow analogous to poly(cyanoacrylate) copolymers developed by Couvreur [313].



$\text{PEO}-[\text{CH}_2-\text{C}(\text{COOR}_1)(\text{COOR}_2)]_n-$



$\text{PEO}-[\text{CH}_2-\text{C}(\text{COOR})(\text{CN})]_n-$

Of special interest are the malonate sequences with $R_1{=}C_2H_5$ and $R_2{=}CH_2{-}COO{-}C_2H_5$ abbreviated PMM 212 for which it was shown by Lescure et al. [314] that the degradation occurs in vivo by elimination of ethanol and glycolic acid. After bioerosion of the poly(malonate) sequence the block copolymer will be formed by two water-soluble sequences which in contrast to the starting PEO–PMM 212 copolymer has no longer a tendency to form micelles. Solubilization of drugs in this type of bioerodible micelles appeared to be very promising as drug carrier and controlled delivery systems because their toxicity is quite reduced with respect to poly(cyanoacrylates).

In continuation of their pioneering work on polymeric micelles as drug release systems Kataoka and co-worker [299,301,315] have introduced the concept of active targeting for micellar systems. A typical example described by these authors is that of heterotelechelic PEG–poly(lactide) block copolymers of the following structure:

PLA–PEG–X

where X can be an aldehyde, amino or a saccharide moiety. Other examples were reported by Lim et al. [316].

Promising developments are finally expected from stimuli sensitive, mainly pH and thermoresponsive systems that change their volume and shape according to external physicochemical factors. Typical examples of such block copolymer micelles mainly based on PNIPAAM were described by different authors [181,182,317].

As clearly pointed out by Kabanov and Alakhov [291,300], the major interest of block copolymers in form of 'micellar microcontainers' is that one can adjust the chemical nature of blocks as well as the molecular characteristics (molecular weight, composition, presence of functional groups for active targeting) within an homologous block copolymer series to optimize the performance of the drug for a given drug delivery situation.

The advantages of block copolymers are furthermore that

- the micelle dimension are easily adjustable in the range of 10–100 nm
- the CMC, the diffusion coefficient of the micelles and that of the corresponding unimers are generally very low, as compared to low molecular weight surfactants; these parameters are important for a drug delivery applications since they determine the thermodynamic and kinetic stability of the micelles during dilution occuring in biological fluids
- end-group functionalization increases the targeting efficiency
- frozen micelles are unique in that they may remain intact or dissociate only slowly into unimers even at concentration levels below their CMC which allows the longer retention of the loaded drug and a higher drug concentration at the target site [302]
- the partition coefficient of the drug, e.g. its distribution between the micelles and the aqueous phase, as well as the total amount of solubilized drug can be adjusted as a function of the micellar characteristics as clearly demonstrated by Nagarajan and Ganesh [133] and by Kozlov et al. [318].

8.1.2. Polyion micellar complexes

A new development in block copolymer micelles for controlled delivery is the formation of PIC in aqueous media as proposed by Kataoka [289,290] and by Kabanov and Alakhov [291] as outlined in Section 7.5. Various cationic block copolymers, such as polylysine [319,320–322], PEI [323] or PDMAEMA [324] in combination with PEO, have been examined for the complexation of oligonucleotides in order to provide new pharmaceutical forms for gene therapy [325].

Loading of block copolymer micelles by complexation with contrast agents, e.g. with colloidal metals or heavy elements such as bromine or iodine, opens interesting application possibilities in medical diagnostic imaging. This concept will be discussed below in more detail.

8.2. Metal nanoparticles

Colloidal particles (nanoparticles) are of current interest because their large surface area (100–3000 m^2/g) makes them very useful in a wide range of chemical and physical applications [326]. Various nanoparticles are produced in presence of block copolymers in selective solvents, where they form micelles and encapsulate particles such as metal salts. These, in turn, are reduced or chemically converted to finely divided colloidal metal particles with interesting catalytic, non-linear optic, semiconductor and magnetic properties [327].

The classical method to prepare such nanoparticles is to trap metal salts in amphiphilic block copolymer micelles formed in selective solvents. The core is able to entrap particles by complexation or association, and the shell provides stabilization. These micellar structures can be considered as very small reactors in which minute metal particles are formed by chemical transformation. However, the block copolymer must be selected in such a way that one block has affinity with the metal or metal salt, and the other block with the liquid medium. For example, P4VP block is mostly used for its strong metal chelating ability. The second block, usually PS, must be incompatible with P4VP block in order to form micellar structure. This means that in this case, the medium in which the particles form must be an organic liquid.

One of the first examples of metal ions complexed in micellar structures might be that of Ossenbach-Sauter [197], who complexed Cu^{++} with P2VP–PEO diblock copolymers in benzene, which is a selective solvent in this case of PEO.

A large variety of metal nanoparticles, mainly Au, Pd, Pt, Rc, Rh, Co, etc. have been prepared in organic medium with block copolymer micelles, such as those based on P2VP or P4VP [327–331], PEO [332–335], epoxidized polybutadiene [336], amide modified PS–P*t*BMA [337], PS–PMMA [332], PS–PB di- or triblocks [338], amphiphilic poly(oxazoline) [339], PS–poly(vinyl-triphenylphosphine) [340].

Metal nanoparticles were also prepared in aqueous medium. A typical example is that reported by Kataoka et al. [341] who used PEO–poly(α,β-aspartic acid) block copolymers for complexation of *cis*-dichlorodiamineplatinum. Interaction of P2VP–PEO diblock copolymers with noble metal compounds in aqueous medium and metal nanoparticles formation in such systems were studied by Bronstein et al. [342]. Double hydrophilic block copolymers like PEO–PEI are also suitable for metal complexation as reported by Sidorov et al. [343].

8.3. Adsorption and surface modification by block copolymer micelles

Block copolymers, like homopolymers, are known to adsorb on solid surfaces. A great number of experimental and theoretical studies have been published concerning the surface modification by block copolymers in order to promote specific characteristics, e.g. wetting, dispersibility and stabilization of solid pigment particles in a liquid or in a solid phase, improved biocompatibility, etc. As many technical processes depend on such adsorption it is important to determine not only the conformation and the surfaces density of the adsorbed chains in form of a brush, but also the kinetics of this phenomena which in fact will depend on the unimer–micelle equilibrium.

The theories and the experimental aspects concerning self-assembly of block copolymers at surfaces have recently been reviewed by Tirrell [344] and by Hamley [10]. Hamley has given in addition an overview on the various morphologies of thin block copolymer films confined on a surface and on the surface induced ordering, e.g. formation of lamellar structures, hexagonal packing, ‘surface islands’, when the film, cast from solution, is further annealed by thermal treatment. This classical situation when a AB block copolymer is adsorbed from a common solvent of both blocks will not be further outlined in this section in which we intend to focus on the interaction, either by physical or chemical bonding, of micellar block copolymer systems on a substrate and on the surface modification by block copolymer micelles.

These different interaction possibilities between a substrate and a copolymer, as such or in its micellar form, are represented schematically in Fig. 11.

A distinction can be made between physical interaction (scheme a and b) and chemical linking, either by surface grafting of block copolymer chains (scheme c) or by attachment of functionalized micelles on the surface (scheme d).

In the first case which is that of physical interaction, we have to consider two possibilities for a block copolymer in a selective solvent:

- Only the insoluble block B has affinity to the surface; in this case it is generally assumed that the anchoring block B, present either as unimer at a concentration below CMC or slowly dissociated from the micelle, covers the surface. However as demonstrated by Munch and Gast [345] for the adsorption of PS–P2VP on a silver surface, or by Xu et al. [346] for the interaction between PS latex particles and PS–POE block copolymer micelles, the first stage of the process corresponds to a rapid adsorption of micelles, with a possible rearrangement on the surface,

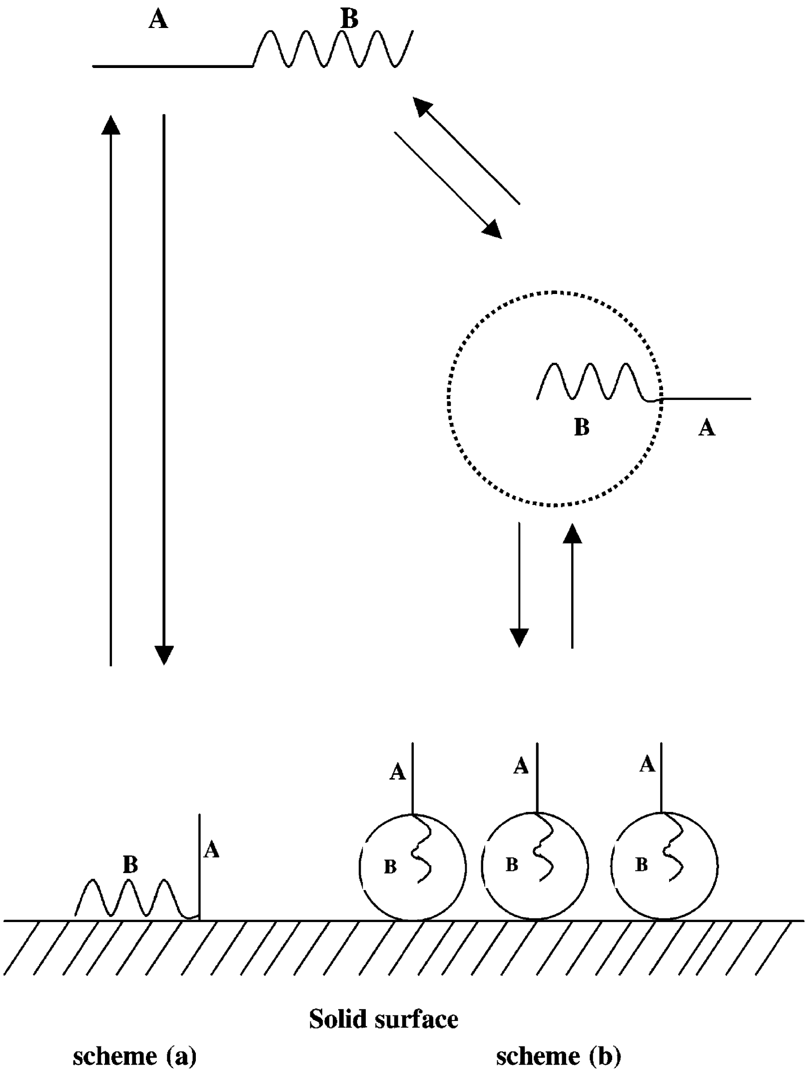


Fig. 11. (a) Surface modification of solid surfaces by block copolymers and block copolymer micelles. (b) Surface modification of solid surfaces by functionalized block copolymers and functionalized block copolymer micelles.

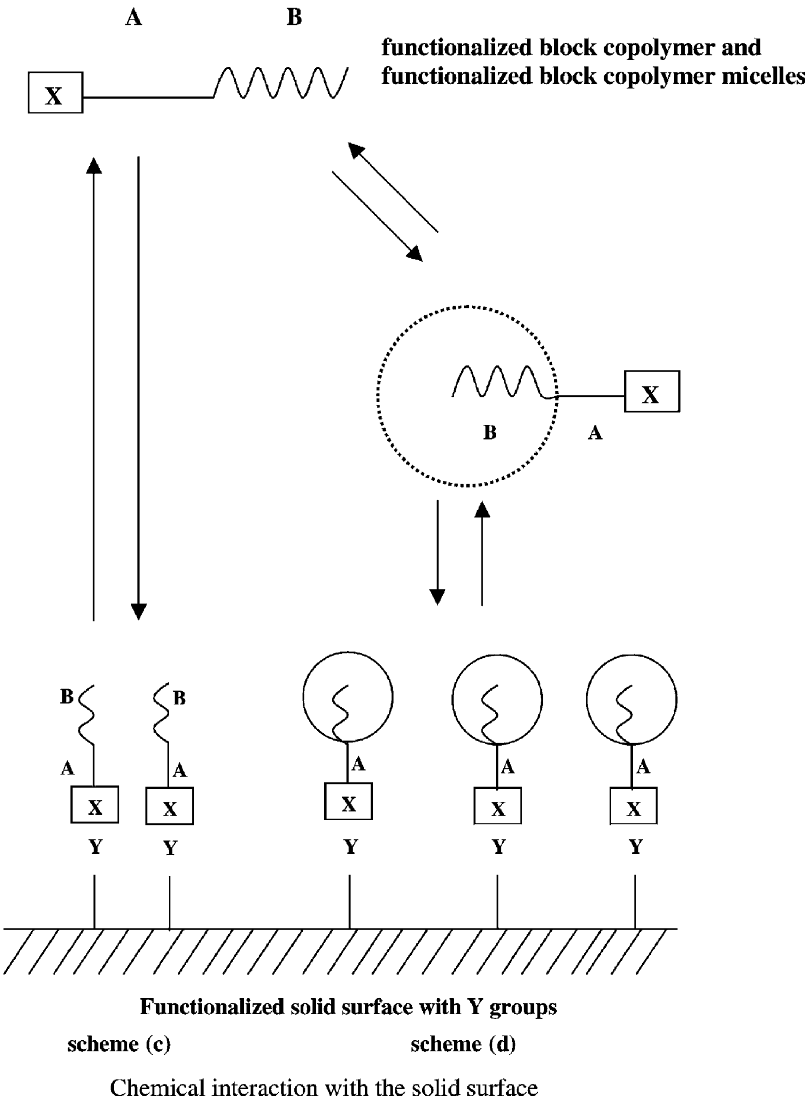


Fig. 11 (*continued*)

whereas the adsorption of unimers is a much slower process leading to a more homogeneous and thus enhanced brush-type coverage.

- Only the soluble A block has affinity to the surface, so that above CMC the entire micelles, especially those having a 'frozen' core, might be adsorbed in form of a micellar monolayer (Fig. 11, scheme b). Also in this case reorganization of the surface structures, especially by solvent evaporation and eventual subsequent thermal treatment, could occur as shown by Antonietti et al. [347] with formation of organized films having periodic structures. Micelles with a glassy core can even be piled up on the surface as multilayered structures.

Another typical example and application of physical interactions between a surface and a micellar block copolymer systems, is that of controlled agglomeration for polymer latexes, e.g. PS, PB, PVC, etc., developed by Thyebault [348] and later on by Peter [109]. This process consists in the addition of PEO based block copolymer micelles, mainly from PS–PEO di- and triblock copolymers, to a PB or PVC 'seed-latex' of 0.1–0.5 μm stabilized by anionic surfactants, in order to obtain agglomerates of controlled size and distribution in the range of 1–40 μm. The driving force of this agglomeration process is on the one side the complex formation between the PEO blocks and the anionic surfactant as demonstrated by Cabane [349], which decreases the surface coverage of latex and thus its stability, and on the other to PS–POE micelle adsorption on the latex [346]. The resulting 'hairy latexes' promote the bridging and thus the agglomeration of the latex particles.

Surface micelles have also been observed for a number of ionic diblock copolymers on air-water interfaces by Eisenberg and co-workers [350].Various two-dimensional structures, called 'starfish' and 'jellyfish' micelles by these authors, were obtained by spreading a monolayer of quaternized PS–P4VP block copolymers at the air–water interface. These hemimicelles, transferred from the Langmuir–Blodgett film on a carbon-coated copper grid, could be examined by TEM and atomic force microscopy.

Similar surface structures are those reported by Huang et al. [351] who demonstrated the self-assembly or surface micellization of immobilized block copolymers by their chain ends to a gold surface, followed by their treatment with selective solvents (Fig. 11, scheme c). Block copolymers brushes, chemically linked to a substrate, are therefore attractive for surface patterning at a nanometer scale.

An original and major contribution to the surface modification by micellar diblock copolymer systems has been proposed by Webber and co-workers [352]. These authors studied the adsorption of PS–PMAA block copolymer micelles onto a polystyrene surface in a solvent mixture composed of 80:20 dioxane:water which swells the PS core but does not destroy the micelle. Similar approaches of surface modification by micelles were described by Farinha et al. [353] and by Spatz et al. [354]. Webber et al. [355] extended this procedure by chemical linking of PS–PMAA micelles having carboxy surface groups to an aminated surface using carbodiimide chemistry (Fig. 11, scheme d).

Starting from this concept Kataoka and co-workers [356] prepared non-fouling surfaces by coating them with core-polymerized PEG–PLA block copolymer micelles having an aldehyde-ended PEG shell. These core-polymerized reactive micelles were coated to a primary amine-containing polypropylene plate that was prepared by a plasma treatment. A reductive amination reaction was employed for the covalent linkage of the micelles to the surface. These type of materials with high surface density of PEG chains and excellent stability of the micellar coating is of special interest for biomedical and bioanalytical applications. By extension of this concept multilayered thin films on a substrate were obtained by Kataoka et al. [357, 358]. Their approach consisted in the treatment of an aminated surface with PEG–PLA micelles having acetal groups at the PEG chain ends in the corona, followed by alternative coatings with polyallylamine and reactive micelles in the presence of a reducing agent. In order to promote the surface modification by block copolymer micelles, Ma and Webber [359] have developed a new technique in which the surface is first modified by covalently attaching monocarboxy-terminated PS on a activated quartz surface followed by micellization of PS–PMAA in the presence of that PS modified quartz. It could be demonstrated that these anchored PS chains serve as nucleation sites for the aggregation of PS–PMAA.

The various application possibilities of these highly ordered arrays and ultrathin structured films derived from block copolymer micellar systems has recently been reviewed by Webber et al. [360] and by Kataoka and co-workers [358].

8.4. Miscellaneous applications

In addition to the above mentioned application possibilities, the variety of block copolymers which are now available, and the unique combination of properties they offer, make them further attractive for many chemical and industrial applications based on their surface activity, micellar or interfacial function in two-phase systems.

Among the general overviews previously indicated, one has to mention those concerning block copolymer applications as emulsifiers [1,361], as stabilizer in latex technology [1,5,12,362], as compatibilizers in polymer blends [1,10] and as active component in separation processes [363]. In addition, several recent reviews as those of Holmberg [364] and of Edens [365]. concerned more specifically the applications of PPO–PEO and PBO–PEO block copolymers. The following will therefore be limited to some typical application examples where the effect of block copolymer micelles was clearly identified.

Thus the ability of micelles to solubilize or encapsulate various compounds, as previously outlined for biomedical applications, can also be employed for purification and separation processes as well as for specific chemical reactions. For example, if removal of oil and organic pollutants in waste water was already achieved with conventional surfactants, the use of block copolymers such as PEO–PPO could significantly improve these processes [363,366,367].

Jenekhe and Chen [254] reported the solubilization and encapsulation of fullerenes in poly(phenylquinoline)–PS block copolymer micelles. As much as 20% of fullerene with respect to the copolymer could thus be solubilized in binary solvents like trifluoracetic acid/CH_2Cl_2.

Typical applications in chemical processes include use of PB–PEO [368] block copolymers as phase transfer catalysts in a Williamson reaction, thus confirming the catalytic effect previously reported for PS–PEO [369].

Ion complexation by block copolymers is not only attracting interest in biomedical applications, as previously mentioned, but also in catalysis [339], in solar energy-conversion and photoinduced electron transfer processes as indicated by Hou and Chan [331] for polymer aggregates formed by PS–P4VP functionalized with rhenium 2,2′-bipyridyl complexes.

As already demonstrated by Price [4] in the early 80s, block copolymers are of practical use as viscosity improvers of motor oil which may be related to association–dissociation of their micelles as a function of temperature. Asymmetric triblock copolymers were reported more recently in the patent literature [370]. For poly(alkylacrylates)–P2VP block copolymers developed in our group it could be shown that these products are not only viscosity improvers but also efficient dispersants and stabilizers for carbon black, a good model for sludge [223]. Fetters [371] pointed out that the platelet structures generated from PEO–PEP diblock copolymers by crystallization of their PEO sequence are efficient pour-point depressing additives for fuel oils. Such platelets and crystallized colloidal particles derived from PEO based block copolymers were further claimed as efficient stabilizers for polymeric oil-in-oil emulsions of large particle size [219,372].

The application of block copolymers as steric stabilizers of solid dispersions in a liquid, of the various types of emulsions, e.g. water/oil, water/oil/-water, oil/oil, and in emulsion polymerization for the preparation of ‘hairy latexes’ having recently been reviewed [12], this topic will not be covered further in the present overview as the stabilizing effect of the copolymer can mainly be attributed not to the micelles but to the unimers located at the solid/liquid or liquid/liquid interface.

9. Concluding remarks

From the number of research and review papers published over the last decade, it turns out that block copolymer micellization, which is a unique example to achieve self-assembled nanoparticles with well-defined morphologies, is an area of increasing interest for the fundamental understanding and in view of practical application possibilities.

As concluding remarks of the present review, some of the remaining problems and various perspectives for further investigations on copolymer self-assembly are outlined in the following.

Concerning the synthesis of tailor-made block copolymers remarkable progress has been made, especially by ‘living’ ionic polymerization, controlled free radical polymerization and the design of multifunctional initiators. Numerous examples of linear A–B and A–B–A were described in addition with the possibility to functionalize these copolymers with specific groups, either at the chain ends and/or at the junction of the blocks.

Quite a number of more sophisticated structures such as linear or star-shaped AB or ABC, H-shaped, block-graft copolymers, etc. have been prepared and examined to some extent with respect to their micellization behavior.

There is almost no limits in the design and optimization for novel types of block copolymers and of new structures. Interesting developments can for instance be expected from

- organo-metallic or metal containing copolymers as shown recently by Winnik et al. [247–249]
- non-covalent block copolymers of poly(pseudorotaxane) type as mentioned by Gibson et al. [373]
- various combinations of linear with ring- or dendrimeric sequences.

Even for more classical AB and ABA copolymers there is definitely a need for homologous series of a given block copolymer type, e.g. series of copolymers having exactly the same A sequence but B sequences of increasing molecular weights, copolymers of constant composition and increasing molecular weights, copolymers of different structures at given composition and molecular weight. Up till now only a limited number of examples have been reported in this respect.

Another challenge for the synthesis chemist is to provide 'ultrapure' block copolymers, especially freed from hydrophobic impurities (trace amounts of impurities remaining from the initiator, homopolymers) which could have a strong influence on the micellization process as pointed out by Zana [108].

A large number of techniques, mainly scattering and fluorescence techniques, are nowadays available for the characterization of micellar systems in general, and those based on block copolymers in particular.

A considerable set of data is available concerning micellar size, morphology, interphase characteristics, chain dynamics in the core and corona, etc. However, even for a given type of block copolymer, it is not always straightforward to correlate the different data as the starting samples are often incompletely characterized, mainly with respect to their molecular weight and their polydispersity in composition. Moreover, great attention has to be paid to the preparation step of the micellar system. In fact, one has to be aware that the simple dissolution of the block copolymer in a selective solvent, or even the preparation of the micellar system by step-wise dialysis could lead to *non-equilibrium situations* to so-called 'frozen micelles', and to fractionation during the micellization process, which is inherent to the polydispersity of the starting sample. This phenomena of forming frozen micelles could be thus of practical interest however it raises more fundamental questions related to micellization kinetics and CMC determinations, to the problem of unimer exchange and hybridization of micelles. These features are of considerable research interest and still under debate.

There is substantial body of theoretical work on micellization of block copolymers. The simplest approaches are the scaling theories which account quite successfully for scaling the micellar characteristics, e.g. R_h, R_c, Z,etc. to the molecular characteristics of the copolymer. Rather detailed mean-field theories have been developed and interesting studies are in progress by computer simulations. According to Linse [130] the expected developments in this area is the treatment of more complex models of self-assembly of polyelectrolytes and ionomers. Further, in order to mimic real systems it will be necessary to make suitable assignments concerning short range interactions characterized by the χ parameter of polymer systems.

Micellization of AB, ABA or BAB hydrophobic/hydrophilic block copolymers in aqueous medium, with comparison of these different structures, is well documented, especially in the case of the commercial available alkylene oxide copolymers, which offer a large variety of application possibilities.

From a more theoretical point of view, block copolymer micelles with an ionic shell provide unique colloids in which the polyelectrolyte properties can be studied at a very high segment density. There have been significant advances in the understanding of such systems, however, this is still an area of considerable research interest.

The last decade was also marked by a large number of publications dealing with the micellization of block copolymers in organic solvents, including polar solvents like alcohols or glycols as well as supercritical CO_2. Studies on ABC block copolymers and on those with more 'exotic' structures have been started but much remain to be done to provide systematic informations in this area. Hydrophilic–hydrophilic block copolymers have recently attracted special interest. A great development potential is expected from this category of copolymers.

Micelles of complex architectures, such as ABC core–shell–corona structures, core- or shell cross-linked micelles, Janus- and onion- skin micelles, which have appeared in these last years, are of interest and they need to be further developed. This is also the case for liposome type micelles or 'mixed micelles' formed by comicellization of two block copolymers AB and BC having a sequence of the same type.

Although spherical morphologies are the most typical for block copolymer micelles, there is almost no limits in developing colloidal systems with platelets, 'vermicelle', thread-like or other structures.

Micelle formation on liquid/air or solid/liquid interfaces would need further investigations as this topic has been examined only very scarcely up till now.

Concentrated solutions where micelles could have the tendency to form gels, has only recently begun to be examined. Systematic studies would be necessary to enhance the understanding of such concentrated colloidal systems.

Concerning the application possibilities, block copolymer micelles and assemblies are of great technological importance. They offer in fact attractive properties for biomedical applications and other uses as emulsion stabilizers, viscosity regulators, catalyst supporters, surface modifiers, etc. Of special interest are amphiphilic block copolymers with biocompatible and/or biodegradable sequences, which are studied quite extensively for drug delivery systems and as potential carriers in gene therapy. A further interesting potential is the preparation of stable metallic nanoparticles in aqueous or organic medium useful as catalysts and as precursors of nanostructured materials.

For all these applications, the further challenge is to tune and to control the molecular characteristics of the precursor block copolymer and to develop appropriate preparation conditions to achieve the required size and microstructure of the micellar system.

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