Amphiphilic block copolymers by a combination of anionic polymerization and selective post-polymerization functionalization

Eleni Kaditi, Grigoris Mountrichas, Stergios Pispas*

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., 11635 Athens, Greece

Abstract

Anionic polymerization is the oldest known living/controlled polymerization methodology that leads to well defined macromolecules. It has been also used, with considerable success, for the synthesis of amphiphilic block copolymers (AmBC), a class of functional copolymers having interesting self-assembling properties and high potential for applications in various technological fields. The use of mild and effective post-polymerization functionalization/chemical modification reactions on block copolymers has substantially increased the synthetic capabilities of anionic polymerization methodologies, toward the creation of a variety of AmBC. In this feature article we review work done on these directions in the last ten years. Some perspectives and future work on this particular field of polymer science are also discussed.

1. Introduction

Amphiphilic block copolymers (AmBC) remain at the forefront of polymer science research for more than two decades now [1–3]. In the simplest case these intriguing macromolecules are composed of two chemically different homopolymer blocks: the one being hydrophilic (water soluble) the other being hydrophobic (water insoluble). Thanks to advances in synthetic polymer chemistry other non-linear and complex architectures of AmBC have been developed [4–6]. The intense interest in AmBC stems from their ability to self-assemble into ordered nanostructures, when dissolved in aqueous media [1,7–9]. These assemblies have been successfully tested in several applications as nanoreactors, nanotemplates and nanocarriers, especially in drug delivery systems [1,2,10–18]. However, a plethora of basic investigations and potential applications have been also explored for AmBC systems in gel phases, thin films and in the solid state [19,20]. Double hydrophilic block copolymers (DHBC) [21,22] are considered a subclass of AmBC, since in these macromolecular systems amphiphilicity can be provoked/induced by changes in the solubility of one of the blocks in the aqueous medium through pH, temperature and ionic strength changes, as well as through complexation with other building blocks that increases hydrophobicity of the system, leading to nanostructures similar to those observed in conventional AmBC systems. In the aforementioned macromolecular systems the chemical nature of each block and the composition of the copolymers play a decisive role in their self-assembly. Therefore, the behavior of AmBC systems can be decisively and effectively controlled through chemistry and synthetic design.

The most important and effective synthetic strategies leading to the preparation of AmBC involve living/controlled polymerization methodologies, where each block is grown and coupled with the rest in a controlled manner [23–29]. In this way macromolecules with predetermined molecular structures and desired characteristics, including narrow molecular weight distributions, are synthesized.

Anionic polymerization is the oldest living/controlled polymerization methodology [30,31]. Under certain, well chosen and controlled experimental conditions, block
copolymers with predetermined molecular weights (in excess of several hundred thousands g/mol in many cases), chosen lengths of each block and of the copolymer chain, showing narrow molecular weight distributions and low compositional heterogeneity, and having complex macromolecular architectures can be prepared [24,32,33]. The major disadvantage of anionic polymerization is its inherent low tolerance to polar functionalities (usually present in monomers that give polar water-soluble polymers after polymerization). In order to take advantage of the exceptional characteristics of anionic polymerization of producing well-defined block copolymers in the synthesis of novel and interesting AmBC, one must rely on effective and selective chemical functionalization of one or more blocks within the macromolecular chains, after the end of the polymerization step, via utilization of controlled and specific organic chemistry reaction routes [2,34,35]. Such post-polymerization methodologies introduce the desired chemical functionalities in one of the blocks, giving rise to AmBC systems and open large possibilities for chemical tailoring of block copolymer structure and functionality in the molecular and supramolecular level.

In this feature article we present recent advances in the synthesis of AmBC via anionic polymerization routes in order to prepare well-defined block copolymer precursors, which are then transformed to amphiphilic macromolecular systems by selective post-polymerization of at least one of the blocks, utilizing well-behaving organic chemistry reactions. Several examples on the solution and solid state properties of this class of macromolecules are also presented, in order to elucidate the rich array of self-assembled nanostructures that can be formed in macromolecular systems involving AmBC from combined anionic polymerization/post-polymerization functionalization strategies, also pinpointing the potential applications and uses of these well-designed nanosystems. We focus on studies that have appeared in the literature during the last ten years. Some perspectives and future work on the field are also critically discussed.

2. Synthesis of amphiphilic block copolymers (AmBC) by combination of anionic polymerization and selective post-polymerization functionalization

The preparation of amphiphilic block copolymers from precursor copolymers synthesized by anionic polymerization should meet two basic criteria [2,34]: (a) The reaction that would lead to the chemical modification of the initial block copolymer should not in any way alter the molecular characteristics of the precursor e.g. via chain scission and inter- or intra-molecular crosslinking. In the opposite case materials with a broadened molecular weight distribution and considerably altered structure are obtained, which do not correspond to the desired functionality. Ideally, the chemical modification should lead to block copolymers with the same number of monomeric segments, chain architecture and narrow molecular weight distribution as the initial block copolymer. Only changes in the functional groups attached to the monomer segments of the selected block should take place. (b) The chosen functionalization reactions should be mild and effective i.e. should lead to almost 100% percent functionalization of the selected block with the desired functionality. This criterion is not allowed met, and although the properties of the materials may change considerably even with chemical modifications of less than 100%, careful and thorough characterization of the modified product should be realized in order to establish the extend and nature of functionalization (this is also true for 100% modification since the success of the modification should be always verified). Chemical modification of block copolymers prepared by anionic polymerization usually involve deprotection of protected functionalities already existing on the polymerized monomers (e.g. hydrolysis of ester bonds on monomer side chains), nucleophilic addition to C–C double bonds of the main or side chains or on aromatic rings of side chains and multistep reactions (e.g. epoxidation of C–C double bonds with subsequent nucleophilic substitution). In several cases a simple protonation/deprotonation equilibrium in solution can make a block copolymer amphiphilic (e.g. in the case of amine or carboxylic functionalities existing on the copolymer chain). Chemical functionalization can take place selectively on one of the blocks or on more than one of them simultaneously or in steps, providing that the reaction conditions employed allow successive modification steps on separate blocks. It is obvious that judicious choice of monomers and block sequences and overall chemical modification synthetic strategy, allows for great flexibility and variability on the resulting AmBC structures. Some specific examples of synthesis are given in the following sections.

2.1. Amphiphilic diblock copolymers

The synthesis of a variety of amphiphilic diblock copolymers by post-polymerization functionalization of anionically prepared precursor diblocks has been reported so far. The functionalization can be realized with different types of reactions that differ in their complexity and the number of required steps.

In some cases simple changes in solution pH may result in protonation/deprotonation of acidic/basic blocks of copolymers inducing amphiphilicity in the system. A good example of such behavior are the poly(2-vinylpyridine)-b-poly((dimethylamino)ethyl methacrylate) diblock copolymers (P2VP-b-PDMAEMA) synthesized by Jerome and coworkers through living anionic polymerization. The diblock copolymers have been studied as a function of the solution pH and copolymer composition, in relation to the pH-dependent behavior of the constitutive homopolymers. At low pH regime, polydisperse loose aggregates are formed, although the two blocks are protonated. At pH 5, spherical micelles are formed that contain a hydrophobic P2VP core and a protonated PDMAEMA corona. At higher pH regime, micelles consist of a hydrophobic P2VP core surrounded by an essentially uncharged PDMAEMA corona [36].

One of the most widely used functionalization reaction is the quaternization of tertiary nitrogens of several monomers that can be polymerized by anionic polymerization via a controlled pathway. Therefore, the reaction can be performed in nitrogen containing blocks like poly(2-vinylpyridine) (P2VP), poly(4-vinylpyridine) (P4VP) and poly (2-(dimethylamino) ethyl methacrylate) (PDMAEMA). Although usually long reaction times are needed in order
to obtain high yields, the reaction is very versatile since several different alkyl or aryl halides can be used as quaternizing agents. This leads to the formation of cationic sites on the side chains of the polar basic block, which may possess different hydrophobicity depending on the length of the carbon chain of the halide.

Rather recently, Jerome and coworkers reported the synthesis of quaternized poly(2-(dimethylamino) ethyl methacrylate)-b-poly(methyl methacrylate) diblock copolymers (PDMAEMA-b-PMMA) [37]. Many different alkyl bromides (RBr) were utilized for quaternization of the PDMAEMA block (R = ethyl, pentyl, heptyl, n-propyl, n-buty l and tert-buty l). The degree of quaternization was determined by titrating the non-quaternized basic groups with standard HCl solution and the yield of the reaction was found to be nearly quantitative in all cases (Scheme 1).

Manners et al. quaternized the PDMAEMA block of an asymmetric poly(ferrocenyldimethylsilane-b-2-(dimethylamino) ethyl methacrylate) (PFS-b-PDMAEMA) diblock copolymer with excess CH$_3$I in THF [38]. They obtained an amphiphilic block copolymer with a short hydrophobic organometallic block (PFS) and a long hydrophilic, cationic block (QPDMAEMA). The degree of quaternization was quantitative, as indicated by $^1$H NMR in D$_2$O, which selectively solubilizes the QPDMAEMA blocks. Quaternization of PDMAEMA block was found to influence the self-assembly of diblock copolymer and especially the micellar structures in water.

In a recent study on the formation of amphiphilic polymer complex vesicles from mixtures of oppositely charged block polyelectrolytes, a quaternized polystyrene-b-poly(4-vinyl pyridine) (PS-b-QP4VP) was utilized as the cationic component by Schlaad et al. [39]. The precursor polystyrene-b-poly(4-vinyl pyridine) (PS-b-QP4VP) diblock copolymer was prepared by anionic polymerization and then its P4VP block was quaternized by methyl iodide in virtually quantitative yield. The unfunctionalized diblock copolymer presents narrow molecular weight distribution ($M_w/M_n$ is near 1.2), which would also be representative of the molecular weight distribution of the functionalized copolymer.

Sulfonation is a very popular reaction for the chemical modification of diblock copolymers prepared by anionic polymerization routes, since it can be usually realized with success in copolymers containing polystyrene (PS), polyisoprene (PI), and polybutadiene (PB) as one of the blocks. The conditions for the sulfonation of the phenyl side rings of PS are very harsh and can lead to sulfonation of the polydiene blocks. For this reason, sulfonation of PS is used mainly for the synthesis of amphiphilic diblock copolymers on precursor diblocks that contain either a hydrogenated polydiene block or a poly(tert-butyl styrene) block, possessing a sterically protected phenyl ring that resists sulfonation, as the second block [40–42]. The structure of micelles formed by such amphiphilic block copolymers in aqueous media was studied in detail [41,42].

Block copolymers of polystyrene and sulfonated polyisoprene, (PS-b-SPI), were successfully synthesized, utilizing anhydrous sulfuric acid in dioxane. The thus prepared sulfur trioxide-dioxane complex acts as a mild sulfonation agent for the PI block [43]. Under these conditions no sulfonation of the PS block takes place. The amphiphilic PS-b-SPI diblock copolymers synthesized were asymmetric with a short PS block and a much longer SPI block, having different degrees of polymerization (Scheme 2).

A similar sulfonation procedure was adopted for the synthesis of amphiphilic block copolymers of sulfonated polybutadiene (SPB) and poly(ethylene oxide) (PEO) [44]. The degree of sulfonation in the PB block could be varied from 5% to 80%, as it was demonstrated by elemental analysis of the modified copolymers. The sulfonated block copolymers became water-soluble if the degree of sulfonation was about 15% or higher. These novel amphiphilic block copolymers were utilized as macromolecular stabilizers in emulsion polymerization.

A very effective and versatile modification of the polybutadiene block in PB-b-PEO and PB-b-PS diblock copolymers with $\omega$-functional mercaptans has been recently reported by Schlaad and coworkers [45]. A large variety of functional mercaptans could be utilized for incorporation in the C=C double bonds of the PB-1,2 side chains, giving amphiphilic and double hydrophilic block copolymers containing several different polar functional groups. The obtained diblock copolymers present narrow polydispersity (between 1.05 and 1.15 in most cases) as determined by MALDI-TOF MS and size exclusion chromatography (SEC). Conversion of double bonds was usually complete, and the degree of functionalization of the copolymerization.
A diblock copolymer was in the range of 50–85%, typically 70–80%, since some cyclization of two neighboring groups leads to some loss of the desired chemical functionality (Scheme 3).

Novel hybrid peptide amphiphiles comprised of a PB-b-PEO copolymer as the backbone and grafted (L,L)-cysteine-phenylalanine hydrophobic dipeptides on the PB block, were obtained by the aforementioned free-radical addition reaction, involving peptide α-functionalized mercaptans [46]. The reaction was shown to be as effective as the ones involving lower molecular weight mercaptans. The hybridization of the synthetic copolymers with peptides leads to a higher level of sophistication and functionalities of the observed self-assembled structures. The morphologies of this new hybrid peptide show interest because a plethora of self-assembled nanostructures, including spherical micelles, wormlike micelles and vesicles were observed (Scheme 4).

Scheme 2. Reaction scheme for the sulfonation of the polyisoprene block in a PS-b-PI diblock copolymer.

The amphiphilic polystyrene-b-poly((sulfamate-carboxylate)isoprene) diblock copolymer was synthesized from a PS-b-PI precursor by reaction with chlorosulfonyl isocyanate in a first step, followed by alkaline hydrolysis of the lactam groups formed on the PI blocks in the first step [47]. The poly((sulfamate-carboxylate)isoprene) block contains both strong SO$_3^-$ and weak COO$^-$/CO$_2$ acidic groups, which increase the solubility of the SCPI block. The functionalization of the PI block was determined by solid state $^{13}$C NMR spectroscopy and the molar fraction of modified isoprene units was found to be 89%.

Polyethylene-b-poly(tert-butyl methacrylate) (PE-b-PtBMA) diblock copolymers were synthesized by selective hydrogenation of the PB block in polybutadiene-b-poly (tert-butyl methacrylate) copolymers (PB-b-PtBMA), by using the Wilkinson catalyst system [48,49]. The PE block is a semicrystalline material and the PtBMA block is amorphous, resulting in a series of interesting materials in terms of physical properties. When hydrolyzing the PtBMA block of PE-b-PtBMA, polyethylene-b-poly(methacrylic acid) copolymers (PE-b-PMAA) were prepared. The hydrolysis reaction was realized with stoichiometric excess of HCl over the ester groups. Furthermore, the polybutadiene-b-poly(methacrylic acid) and the polybutadiene-b-poly(sodium methacrylate) copolymers were synthesized by hydrolysis of the PB-b-PtBMA diblock copolymers and subsequent neutralization of the COOH groups with NaOH.

A poly(acrylic acid)-b-poly(N,N-diethylacrylamide) diblock copolymer (PAA-b-PDEAAm) was reported by Muller et al. The diblock copolymer was synthesized by hydronogenation of the PtBMA block of a PtBMA-b-PDEAAm copolymer, prepared by anionic polymerization, in dichloromethane with 5-fold molar excess of trifluoroacetic acid, as compared to the ester groups of the PtBA block [50]. The PAA-b-PDEAAm block copolymer formed micelles in aqueous solution with pH-dependent and thermoresponsive structure.

Polystyrene-b-poly(vinylphosphonic acid) diblock copolymers (PS-b-PVPA) were prepared from the corresponding PS-b-PDEV diblock copolymer. Sequential anionic polymerization of styrene and diethyl vinyl phosphonate in THF afforded the PS-PDEV precursors in different comonomer compositions. The phosphonate ester groups of the PDEV block were hydrolyzed with hydrochloric acid in dichloromethane to form the PVPA blocks [51].

A poly(4-tert-butoxystyrene-b-4-vinylpyridine) precursor diblock copolymer (PtBOS-b-P4VP) was modified to poly(vinylphenol-b-4-vinylpyridine) (PVP-b-P4VP) by acidic hydrolysis and subsequent neutralization. The hydrolysis was realized with 10-fold excess of HCl in dioxane/DMF and the neutralization with 10 wt.% NaOH solution to a pH value of 6–7. Strong hydrogen-bonding interactions were found to exist between the hydroxyl group of PVPPh and the pyridine group of P4VP in the bulk phase, as evidenced by DSC and solid-state NMR measurements [52].

Amphiphilic block copolymers containing β-lactam groups on the polyisoprene block were synthesized from polyisoprene-b-poly(ethylene oxide) diblock copolymers [53]. β-lactam functionalization was achieved via reaction of the polyisoprene block with chlorosulfonyl isocyanate in dry diethyl ether. When excess of CSI was used the degree of modification was found to be larger than 70%. Observed changes in the self-assembly behavior after functionalization were also attributed to the higher solubility of the β-lactam functionalized polyisoprene (LPI) blocks, due to the presence of the hydrophilic lactam groups, as well as to the ability for hydrogen bond formation between the lactam groups with water molecules in solution and the PEO blocks in the bulk phase.

Amphiphilic poly(allyl glycidy ether)-b-poly(ethylene oxide) diblock copolymers (PAGE-b-PEO), synthesized by anionic ring opening polymerization, were chemically modified via hydrogenation of the PAGE block. The hydrogenation reaction was realized in THF with cyclohexa-1,4-
diene as a hydrogen donor and palladium as the catalyst [54]. Addition reaction on the double bonds in the PAGE blocks of the same diblocks was realized with methyl sulfonyl acetate in THF, where the double bonds of PAGE were completely functionalized. Finally, radical crosslinking of the micelle core of PAGE-b-PEO micelles in water was accomplished by the radical copolymerization of the copolymer double bonds with 4-methoxystyrene and with 2-hydroxy-2-methyl-1-phenylpropan as a photoinitiator, giving crosslinked nanoparticles.

2.2. Double hydrophilic diblock copolymers

In the case of double hydrophilic diblock copolymers both blocks can be hydrophilic under certain solution conditions. In several systems simple changes in solution pH may result in protonation/deprotonation of acidic/basic blocks of copolymers inducing changes in solubility and amphiphilicity in the system. An illustrative example of such behavior are the poly(2-vinylpyridine)-b-(poly(2-vinylpyridine)-b-(poly(dimethylamino)ethyl methacrylate) diblock copolymers (P2VP-b-PDMAEMA) synthesized by Jerome and coworkers. These copolymers were prepared by living anionic polymerization in THF at \(178^\circ C\), using diphenyl methyl potassium as initiator, in the presence of LiCl. 2VP was polymerized first followed by the addition of DMAEMA. At low pH the two blocks are protonated and water soluble but polydisperse loose aggregates are formed in aqueous solutions. At pH 5, PDMAEMA is protonated but P2VP becomes hydrophobic due to deprotonation. In this regime spherical micelles are formed that contain a P2VP core and a protonated PDMAEMA corona. At higher pH regime, micelles are present in solution consisting of a hydrophobic P2VP core surrounded by an essentially uncharged PDMAEMA corona. This pH-dependent behavior also influenced the adsorption of the particular block copolymers on solid surfaces and the structures formed at different pH regimes [36,55a]. Another rather typical example are poly(2-vinyl pyridine)-b-poly(ethylene oxide) block copolymers (P2VP-b-PEO) [55b], also synthesized by anionic polymerization, where the PEO block is water soluble at all pH values while solubility of the P2VP block changes with pH as discussed above.

Other examples on double hydrophilic block copolymers that follow show the structural variety of block copolymers that can be obtained by a combination of anionic polymerization and post-polymerization functionalization methodologies.

The double hydrophilic diblock copolymer of poly(sodium(2-sulfamate-3-carboxylate)isoprene)-b-poly(ethylene oxide) (SCPI-b-PEO) was prepared by selective post-polymerization reaction of the polyisoprene block with chlorosulfonylisocyanate with 10% molar excess over the double bonds in the PI block, in dry diethyl ether [56]. The resulting block copolymer possesses sulfamate and carboxylate groups at adjacent carbons of the PI double bonds. Functionalized diblock copolymers present narrow molecular weight distributions and the degree of functionalization reported was ca. 75% (Scheme 5).

The synthesis of poly(p-hydroxystyrene-b-methacrylic acid) copolymers (PHOS-b-PAA) was realized by acidic hydrolysis of the precursor poly(p-tert-butoxystyrene-b-tert-butyl methacrylate) (PtBOS-b-PtBMA) diblocks [57]. The reaction was realized with 5-fold molar excess of HCl in dioxane. The presence of hydroxyl and carboxyl functional groups afforded pH responsive character, leading to a complex self-assembling behavior for the hydrophilic block copolymers in aqueous solutions (Scheme 6).

In a similar manner, poly(p-hydroxystyrene-b-ethylene oxide) copolymers (PHOS-b-PEO) were synthesized by acidic hydrolysis of preformed PtBOS-b-PEO diblock copolymers [58]. The PtBOS-b-PEO copolymers were

![Scheme 5. Functionalization reaction of poly(isoprene-b-ethylene oxide) diblock copolymers with chlorosulfonylisocyanate.](image1)

![Scheme 6. Synthesis of PHOS-b-PMAA double hydrophilic block copolymers from PtBOS-b-PMAA precursors.](image2)
subsequently transformed to poly[3,5-bis(dimethylamino)methylene] hydroxyl styrene-b-ethylenoxide] copolymers (NPHOS-b-PEO) using a Mannich type reaction. The reaction was realized by adding dimethylamine and formaldehyde (12-fold molar excess over the hydroxystyrene units). Finally, the dimethylamino groups of the NPHOS blocks were quaternized by treating the copolymers with methyl iodide. The final copolymers contained a QNPHOS block with two quaternized amino groups in nearly every repeat unit and an acidic hydroxyl group (Scheme 7).

DHBC with phosphorylated, sulfonlated and carboxymethylated polyglycidol blocks have been prepared from poly(ethylene oxide)-b-polyglycidol diblock copolymers [59]. Phosphorylation was achieved with POCl3 in dry triethyl phosphate, where the degree of phosphorylation varied and depended upon reaction time and starting molar ratio. Carboxymethylation was done by purified sodium hydride and ethyl bromoacetate in THF. Sulfonylation was performed by reaction with NaH powder and sultone in dry THF. The reported degrees of substitution for phosphorylation were ca. 50% and 100%, for sulfonylation ca. 50% and for carboxymethylation ca. 50%.

2.3. Linear triblock and multiblock copolymers

Large interest has been also focused on the functionalization of linear triblock and multiblock copolymers, prepared by anionic polymerization, in an effort to create linear macromolecules with different arrangements of functional blocks.

A precursor polystyrene-b-poly(tert-butyl acrylate)-b-polystyrene triblock copolymer (PS-b-PtBA-b-PS), synthesized by the use of a difunctional anionic initiator in THF, was converted to the corresponding polystyrene-b-poly(acrylic acid)-b-polystyrene (PS-b-PAA-b-PS) amphiphilic triblock, through acidic hydrolysis of the PtBA middle block. The highly asymmetric triblock (with very short PS end blocks) was found to have a degree of hydrolysis close to 98%. The copolymer was transformed to the sodium salt form by neutralization with NaOH giving the PS-b-NaPAA-b-PS telechelic electrolyte [60,61].

An ABA type triblock copolymer consisting of poly(acrylic acid) outer blocks and a poly(2-vinyl pyridine) middle block was synthesized by Tsitsilianis and coworkers. The double hydrophilic PAA-b-P2VP-b-PAA triblock is another asymmetric copolymer prepared through acidic hydrolysis of protected acrylate ester segments. The triblock copolymer showed narrow molecular weight distribution and the degree of hydrolysis was found to be 95% by 1H NMR and 93.3% by potentiometric titration [62–64].

A double hydrophilic block copolymer poly(ethylene oxide)-b-poly(2-vinyl pyridine)-b-poly(ethylene oxide) (PEO-b-P2VP-b-PEO) has been also synthesized by anionic polymerization. In this system the P2VP block can become hydrophilic by simple protonation at pH lower than 5. The complexation of PEO-P2VP-PEO with PAA, based on the hydrogen bonding association between PEO and PAA blocks has been studied. Complexation weakens with decreasing molar masses of the two associating polymer components [65].

A thermoresponsive double hydrophilic triblock copolymer of the type poly(N,N-diethylacrylamide)-b-poly(acrylic acid)-b-poly(N,N-diethylacrylamide) (PDEAAm-b-PAAs-b-PDEAAm) was synthesized by acidic hydrolysis of the poly(N,N-diethylacrylamide)-b-poly(tert-butyl acrylate)-b-poly(N,N-diethylacrylamide) (PDEAAm-b-PtBA-b-PDEAAm) precursor [66], which was prepared by sequential anionic polymerization of tert-butyl acrylate and N,N-diethylacrylamide in that order. The presence of LiCl was essential for achieving a controlled polymerization and low molecular weight distribution. The degree of hydrolysis of the resulting copolymer was found to be 96.6%. The thermoassociative character of the PDEAAm-b-PAAs-b-PDEAAm triblock is attributed to the temperature sensitive solubility of the PDEAAm block and the pH sensitivity to the PAA block, allowing for a rich self-assembly behavior in aqueous solutions.

The amphiphilic triblock terpolymer poly((sulfamate-carboxylate-isoprene)-b-polystyrene-b-poly(ethylene oxide) (SCPI-b-PS-b-PEO) was synthesized by reaction of the anionically synthesized PI-b-PS-b-PEO triblock with chlorosulfonyl isocyanate [67], which resulted in the modification of the PI block toward a pH sensitive polyelectrolyte. The multifunctional terpolymer contained a SCPI block, with strong and weak acidic groups, a hydrophobic PS block and a neutral hydrophilic PEO block. Characterization by solid state 13C NMR and FTIR spectroscopy established the nature of the functional groups and the degree of functionalization (Scheme 8).

The triblock terpolymer poly(2-vinyl pyridine)-b-poly(acrylic acid)-b-poly(butyl methacrylate) (P2VP-b-PAA-b-PBMA) was synthesized by acidic hydrolysis of the poly(2-vinyl pyridine)-b-poly(tert-butyl acrylate)-b-poly(butyl methacrylate) (P2VP-b-PtBA-b-PBMA) terpolymer [68]. The reaction was performed as usual, with 5-fold molar excess of HCl in dioxane. This double hydrophilic stimuli-responsive terpolymer shows interesting self-assembling properties at various pH. At high pH, a physical gel was formed whereas at low pH three compartment micelles with a positively charged corona and two concentric inner parts were observed.

Scheme 7. Synthesis of QNPHOS-b-PEO diblock copolymer from PtBOS-b-PEO precursor.
An amphiphilic linear triblock terpolymer namely poly(isoprene-b-2-vinylpyridine-b-ethylene oxide) (PI-b-P2VP-b-PEO) has been also prepared by sequential anionic polymerization in THF, using benzyl potassium as the initiator [69]. The terpolymers formed spherical three-layer micelles in aqueous media and the properties of the middle layer, as well as the relative shell and corona widths, could be changed by the solution pH due to the protonation/deprotonation equilibrium of the P2VP block [70].

Finally, a double hydrophilic ABC linear terpolymer with ampholytic/amphiphilic character i.e. having a basic A block, a hydrophobic B block and an acidic C block has been synthesized by hydrolysis of the precursor P2VP-b-PMMA-b-PtBA triblock terpolymer. The obtained P2VP-b-PMMA-b-PAA linear triblock terpolymer formed micelles in aqueous solutions. This double hydrophilic/amphiphilic terpolymer revealed different nanoscale self assemblies depending on the solution pH [71].

In another study, a linear pentablock terpolymer has been modified by hydrolysis. The precursor pentablock terpolymer poly(methyl methacrylate)-b-poly(tert-butyl acrylate)-b-poly(2-vinyl pyridine)-b-poly(tert-butyl acrylate)-b-poly(methyl methacrylate) (PMMA-b-PtBA-b-P2VP-b-PtBA-b-PMMA) was synthesized by living anionic polymerization, in THF by the use of a difunctional anionic polymerization initiator and the sequential monomer addition method. The amphiphilic pentablock terpolymer poly(methyl methacrylate)-b-poly(acrylic acid)-b-poly(2-vinyl pyridine)-b-poly(acrylic acid)-b-poly(methyl methacrylate) (PMMA-b-PAA-b-P2VP-b-PAA-b-PMMA) was synthesized from PMMA-b-PtBA-b-P2VP-b-PtBA-b-PMMA pentablock by acid catalyzed hydrolysis in dioxane [72,73]. The degree of hydrolysis of the resulting copolymer was determined to be more than 97% molar. The specific pentablock copolymer is comprised of two outer hydrophobic blocks (PMAA), two inner pH sensitive acidic blocks (PAA) and a middle pH sensitive, basic block (P2VP). At low pH, a hydrogel is formed, based on a three dimensional network comprising PMMA hydrophobic cores, interconnected by complex bridging chains constituted of...
positively charged P2VP and non-ionic PAA segments. At high pH, the hydrogel is transformed reversibly from a positively to a negatively charged network. In this case the bridging chains are comprised of ionized PAA segments interrupted by hydrophobic P2VP blocks.

2.4. Non-linear architectures

Considerable efforts have been devoted to the synthesis of non-linear well-defined amphiphilic block copolymers. The effects of architecture on the properties of amphiphilic and double hydrophilic block copolymers motivates such synthetic approaches. Since anionic polymerization gives the best control over macromolecular architecture several non-linear block copolymers were synthesized with this polymerization methodology and then were transformed to amphiphilic copolymers by post-polymerization chemical treatments. In the creation of branched architectures via chemical functionalization of preformed block copolymer the reactivity and chemical stability of the branching points during the chemical modification reaction should be also taken into account. This is one reason why some of the aforementioned functionalization reactions have not been applied to branched macromolecules. For example sulfonation of PS containing star copolymers with chlorosilane linked arms is not possible, due to degradation of the central branching point (instability of the Si–C bonds) under the usual conditions employed for sulfonation of PS. Most of the work is focused on the synthesis of star polymers but some graft copolymers have been also reported.

\( (PS)_{n}(P2VP)_{n} \) hetero-arm stars can be synthesized by anionic polymerization, using divinylbenzene for linking preformed PS arms and subsequent polymerization of 2VP monomer using the anionic active sites in the DVB core of the formed star (the “in–out” method). These star copolymers show amphiphilic character due to the protonation/deprotonation of P2VP arms at low and high pH, respectively, and show interesting micellization behavior, as well as complexion properties towards inorganic salts [74,75].

A hetero-arm star copolymer of the type \( A_{n}B_{n} \), composed of polystyrene and poly(acrylic acid) arms was synthesized from \( (PS)_{n}(PtBA)_{n} \) copolymer precursor, via hydrolysis and then neutralized to the \( (polystyrene)_{n}(poly(sodium acrylate))_{n} \), \( (PS)_{n}(NaPAA)_{n} \), form with a stoichiometric amount of NaOH [76]. A high degree of hydrolysis was achieved. The PS/PAA star copolymer was soluble in dioxane when the PS and PAA arms were symmetric and formed micelles with a PAA core. In the case were the hetero-arm star was constituted from short PS and long PAA arms, it was not soluble in dioxane. In an analogous reaction sequence ampholytic \( (P2VP)_{n}(PAA)_{n} \) hetero-arm stars with basic and acidic arms were also synthesized [77]. Using a similar “in–out” methodology, multiarm star-shaped copolymers having the architecture \( A_{n}(B-b-C)_{n} \), where \( A = PS, B = P2VP \) and \( C = PAA \) were synthesized via anionic polymerization and acidic hydrolysis. The amphiphilic/polyampholytic hetero-arm star terpolymers showed interesting behavior in terms of solubility and gelation, under different solution conditions [78].

Sulfonation and neutralization have been also utilized for the synthesis of amphiphilic star block copolymers. The precursor \( (PS-PtBS)_{n} \) star block copolymers, having PS outer arms, were obtained by linking PS-PtBS living chains with DVB. The PS blocks of the stars were selectively sulfonated using \( SO_{3} \) [79]. The degree of sulfonation of the star block copolymers, as determined by elemental analysis, was in the range 85–95%. Neutralization with sodium methoxide in methanol gave the salt form of the amphiphilic star block polyelectrolytes (Scheme 9). Amphiphilic star block copolymers of the inverse molecular architecture were also synthesized.

A novel amphiphilic graft copolymer of the structure poly(ε-caprolactone)-b-quaternized poly(2-vinyl pyridine) (PCL-b-PQ4VP) was synthesized from PCL-b-P4VP precursor graft copolymer, by quaternization with a large excess of iodomethane in DMF [80]. Similarly, the PCL-b-PDMAEMA graft copolymer has been synthesized. The quaternized graft copolymers present improved water solubility and more well defined micellar aggregates than their precursors.

3. Properties of AmBC

The great potential of amphiphilic block copolymers in a wide gamut of polymer and material science research has been recognized since their development. The amphiphilic block copolymers can be considered as macromolecular surfactants. Therefore, one of their fundamental property is the self assembly in selective solvents, i.e. a solvent which is thermodynamically a good solvent for one block but poor solvent for the other. In the particular case of amphiphilic block copolymers synthesized by anionic polymerization, the well defined structure, in terms of molecular weight and polydispersity, gives the advantage of a straight forward correlation between the polymer chain molecular characteristics and the observed physical properties. Moreover, the chemical modification of polymers, using polymer-analogous reactions, offers the ability to add or remove organic groups along the polymer chains in order to design macromolecules with certain functionalities and physical behavior. In this section some characteristic examples of the physical properties and potential applications of chemically modified block copolymers, already synthesized by anionic polymerization, are given. In particular, examples on the solution behavior, complexation ability to other building blocks, solubilization/stabilization of nanostructures, formation of gels or modification of surfaces, are presented, indicating the versatile nature of amphiphilic block copolymers in a variety of applications.

3.1. Properties and self-assembly in solution

The effect of post-polymerization chemical functionalization of macromolecular chains, on their solution properties has been described in a number of publications. An interesting example is the case of PFS-b-PDMAEMA [38]. The particular polymer can form a wide range of morphologies by direct dissolution in water, like spheres, rods, cylinders and hollow structures. However, quaternization of
the PDMAEMA block brought about a significant simplification of the micellization process, since only spherical micelles were observed upon dissolution in water. Nevertheless, cylindrical micelles can be also prepared by dissolution of the quaternized block copolymer in alcohol solvents, like EtOH or PrOH, followed by dialysis against water. The above example indicates that the solubility characteristics of one of the blocks have a great influence on the micellization mechanism and on the resulting supramolecular morphologies.

In a somehow analogous example, Schlaad and coworkers, proposed the post-polymerization functionalization of a diblock copolymer, not with a quaternization reaction, like previously, but with the attachment of an oligopeptide onto one of the blocks [46]. The PB-b-PEO diblock copolymer was found to form spherical micelles upon dissolution in aqueous media. However, after the attachment of a cysteine-containing oligopeptide onto the PB block, the formed copolymer can adopt new supramolecular structures like rods or vesicles (Fig. 1). A key-factor of the final adopted conformation was found to be the hydrophobic/hydrophilic ratio, induced by the extent of oligopeptide attachment.

The post-polymerization addition of \( \beta \)-lactam groups on block copolymers was also reported in the literature. In this case, PEO-PI block copolymers were subjected into a two step reaction, in order to achieve the addition of lactam groups [53]. The solution properties study, both of the precursor and of the lactam-functionalized copolymers, revealed that in both cases spherical aggregates were formed. However, the functionalized copolymers were found to have lower aggregation numbers and higher critical micelle concentration (cmc) values, compared to the precursors, due to the increased polarity of the lactam rings inserted in the PI block.

Post-polymerization functionalization cannot only affect the adopted supramolecular structure and characteristics but also to completely tune the solubility character of the copolymer. An attention-grabbing example in this field is the case of PS-b-SPI where the PI blocks has been sulfonated, leading to a water soluble system [43]. The molecular characteristics of the sulfonated polymer, like the hydrophilic/hydrophobic ratio, were found to play an important role on the aggregation parameters, like the

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critical micelle concentration. Interestingly, the coexistence of micelles and unimers was also reported. Moreover, the influence of environmental conditions, like ionic strength of the aqueous media, was investigated. The conclusion was that the system responds on an increase of the solution ionic strength by decreasing the micellar radius, due to collapse of the polyelectrolyte corona blocks.

Another example of solubility tuning is the case of SCPI-b-PEO. The precursor of the above polymer is the PI-b-PEO block copolymer, which forms micelles in aqueous media. However, after the post-polymerization reaction, which adds sulfamate and carboxylate groups in the PI block, the copolymer became soluble in water. Notably, the whole solution properties of the macromolecular chain were modified, as a result of the chemical treatment, since the polyelectrolyte character of the SCPI block dominates. The result was that, changes in the aqueous media, like changes of the ionic strength, influenced dramatically some properties, like viscosity, of the polymeric solution [56].

The case of diblock copolymers, which can form pH-sensitive supramolecular structures, have attached the interest of many research groups. Uchman et al. has described in detail the case of a functionalized amphiphilic block copolymer, namely PS-b-SCPI [47]. The particular copolymer forms micellar aggregates in aqueous media. However, the aggregation tendency strongly depends on the solution pH, because of the changes in the effective charge density of the water soluble chemically modified PI block. Therefore, at high pH values, where the carboxylic groups of the polyelectrolyte block were dissociated, the aggregates had much smaller molar mass than those formed in acidic media. It is worth mentioning that further investigation of the above system revealed that the formed aggregates were composed of three layers, i.e. the inner PS core, a SCPI block densely packed around the core and an outer SCPI block which is well solvated and extends in the solution [81].

Another interesting example of pH sensitive diblock copolymers is the family of diblocks, formed by chemical modification of PtBOS-b-PEO copolymers. In a first step, deprotection of the PtBOS block, leads to an annealed anionic/nitric/aromatic polyelectrolyte, poly(p-hydroxy styrene)-b-poly(ethylene oxide) (PHOS-b-PEO), which is soluble only at pH values higher than 11. In a second step, addition of dimethylamino groups on the PHOS block, leading to NPHOS-b-PEO block copolymers, had as a result the molecular solubilization of the annealed cationic/neutrall block polyelectrolyte in aqueous media at pH values lower than 8 and precipitation (or formation of micelle, depending on polymer composition) at higher pH values. Finally, quaternionization of the amino groups of the NPHOS block leads to a quenched cationic/neutrall block polyelectrolyte, namely QNPHOS-b-PEO, molecularly dissolved in the whole pH range [58].

The situation is different in the case of a diblock copolymer consisted of two negatively charged annealed polyelectrolyte blocks, namely PHOS-b-PMAA [57]. The aforementioned polymer tends to self-assemble at elevated pH values, forming loose aggregates, due to hydrophobic interactions. At intermediate pH values, only the PMAA block was in the dissociated form, leading to strongly aggregated micellar supramolecular structures, stabilized by PMAA chains. Finally, precipitation of the macromolecular chains was observed in the low pH range, since both blocks were in their protonated form.

Besides diblocks, chemically modified linear triblock copolymers have been found to have an even more complex solution behavior. An indicative example is the case of the SCPI-b-PS-b-PEO triblock terpolymer. The above terpolymer forms kineically frozen multicompartmant micelles in acidic environment, consisted of a core of discrete PS and PSCI domains, while PEO chains were placed in the shell. However, at higher pH values the polymer self-assembled to “regular” micelles with a hydrophobic PS core and a mixed shell of SCPI and PEO (Fig. 2). Noteworthly, the micelles in the alkaline region were not kinetically frozen, having a measurable cmc value [67].

Another example of a triblock terpolymer is the case of PI-b-P2VP-b-PEO, where as chemical modification can be considered the protonation of the P2VP block. The above polymer self-assembled into onion type micelles in aqueous media of neutral and acidic pH. The onion type micelles were consisted of an inner PI core, covered by a P2VP outer shell and protected by a neutral PEO corona. However, this system is pH sensitive, since the P2VP block can be protonated at low pH, leading to micelles with larger diameter, due to the electrostatic repulsion forces between the annealed P2VPH+ polyelectrolyte blocks [69].

Triblock copolymers, of the ABA type, have been found to be also responsible for thermothickening effects. Tzitsilias et al. have described the case of a PAA-P2VP-PAA triblock, which at pH 3,4 behave as a block polyampholyte. The above copolymer presented a pronounced thermothickening behavior upon heating at 35 °C, followed by a weak zero-shear viscosity decrease. The above unusual behavior was attributed to two antagonistic effects, namely the swelling of the polymer, which forces the physical gelation, and the thermal motion of molecules, which speeds-up the molecular dynamics [82].

Copolymer with more than three blocks have been also studied, in terms of their solution properties. One characteristic case is that of PMMA-b-PAA-b-P2VP-b-PMMA pentablock, which was synthesized using anionic polymerization followed by a hydrolysis reaction [72,73]. The above pentablock terpolymer has very interesting solution properties, since changes of pH and/or solvent selectivity can induce the formation of reversible hydrogels. Moreover, depending on the conditions, different kinds of hydrogels can be formed. It is worth mentioning that, besides the formation of hydrogels, the same terpolymer can be also self-assembled into flower like micelles with a core–shell–corona structure.

Examples of self-assembling non-linear copolymer chain architectures have been also presented in the literature. Hetero-arm star copolymers, of the type PS, P2VP, have been studied in aqueous media. A strong effect on the micellar behavior by the molecular characteristics of the hetero-arm star, including number of arms and arm length, has been observed. Moreover, the formation of onion type micelles was detected in aqueous solutions of the above star copolymer in the presence of a water soluble...
PEO-b-P2VP diblock copolymer. The aforementioned micelles are consisted of a PS core, a middle thin and compacted P2VP layer and an outer PEO corona. The onion type micelles are pH sensitive and are formed only at pH values higher than 4.8 [74]. It has to be noted that analysis of the alkalimetric titration data indicates that the inner layer of the P2VP shell, i.e. the layer close to the core, is not fully ionized. The above system is a representative example of how the chemical modification of one of the block, i.e. by protonation, can dramatically affect the properties of the copolymer.

In a continuation of the previous work, Tsitsilianis and coworkers have presented also a similar hetero-arm star copolymer where, instead of P2VP, P2VP-b-PAA blocks were present in the macromolecule. The above hetero-arm star terpolymer was studied under different solution pH values and was found that it was able to form hydrogels, under specific conditions [78]. Other hetero-arm star copolymers have been also presented in the literature, showing similar solution behavior, in a mixed solvent system [76].

An interesting example of micellization of a non-linear block copolymer architecture is the case of an amphiphilic dendrimer like block copolymer, comprised of PMMA inner branches and PHEMA outer blocks, synthesized by deprotection of the silyl-protected PHEMA block [83]. In that case the copolymer was studied by NMR in a system of mixed solvents, namely CDCl₃/CD₃OD, at different ratios. The experimental results indicate the formation of micelles, when the molar ratio of the two solvents was either very high or very low. However, different micelles were obtained in each case. In particular, when CDCl₃ was the solvent in excess, the PHEMA blocks were placed in the micellar core, while in the case of excess CD₃OD PHEMA was placed in the micellar corona.

3.2. Self-assembled nanostructures by complexation of AmBC with low molecular weight amphiphiles, polyelectrolytes and biomacromolecules

The polyelectrolyte nature of the majority of the block copolymers under discussion, allow their electrostatic complexation with oppositely charged moieties and building blocks i.e. low molecular weight surfactants, polyelectrolytes and biomacromolecules.

One example is the complexation of the triblock PI-b-P2VP-b-PEO with both anionic and cationic surfactants, which has been demonstrated by Koutalas et al. [69]. A cationic surfactant namely dodecyltrimethylammonium bromide (DTMAB) was found to interact with the polymeric
micelles mainly through hydrophobic interactions. The micellar mass and size was reduced after addition of a certain amount of the cationic surfactant. In contrast, the anionic surfactant sodium dodecyl sulfate (SDS) seemed to interact electrostatically with the protonated P2VP block, in acidic environment, leading to an initial increase of the micellar mass. However, increased concentration of the anionic surfactant could decrease the micellar mass, due to hydrophobic interactions. Nevertheless, the micellar characteristics of the above system can be easily manipulated by a number of parameters, including the nature and concentration of a low molecular weight surfactant.

The complexation of a hetero-arm star block copolymer, namely PS_n(P2VP-b-PAA)_n with both positively or negatively charged low molecular weight surfactants has been described by Hammond et al. [84]. The study of the system has indicated that the polymer creates insoluble precipitate upon complexation at very high or very low pH values. The above precipitate can adopt either the microstructure of PS spherical beads in a matrix of PAA and P2VP (in the case of complexation with a negatively charged surfactant) or core–shell cylinders (PS core and P2VP shell) in a matrix of PAA complexed with a positively charged surfactant. The adopted microstructure depended on the pH of the system, i.e. at high pH only the PAA block was charged and able to complex forming cylinders, while at low pH values only the P2VP block was charged and able to complex, leading to spherical nanostructures.

Complexes made of a SCPI-b-PEO double hydrophilic block copolymer and a cationic surfactant, DTMAB, as well as a cationic QP2VP polyelectrolyte were also investigated at pH 7, in another report [85]. The driving force was the electrostatic attraction between the SCPI block and DTMAB and SCPI and QP2VP, respectively. In the SCPI-b-PEO/DTMAB system, association of single block copolymer chains with surfactant molecules was observed at low surfactant concentration, while multi-chain micellar like aggregates, with PEO coronas, were formed at high surfactant concentration. In the SCPI-b-PEO/QP2VP system the kinetics of complex formation after mixing of the components were investigated by light scattering techniques. The structural characteristics of the micellar like complexes formed at long times could be tuned by varying the charge mixing ratio and the ionic strength of the solution.

Complexation of oppositely charged block copolymers has been also proposed in the literature [86]. An interesting example of the above case is the complexation of PB-b-PMAA and PS-b-QP4VP diblock amphiphilic polyelectrolytes [39]. In that case the two polyelectrolyte blocks, i.e. PMAA and QP4VP, form complexes, leading to the formation of vesicles with PB blocks inside and PS blocks outside the complex vesicle membrane (Fig. 3). It should be noted that in the above example, the supramolecular vesicles are formed just by mixing two different diblock copolymers with a rather simple macromolecular structure.

Micellar-like nanostructures formed by the complexation of anionically charged SCPI-b-PEO block copolymers and lysozyme, a globular protein carrying positive charges at pH 7, were also studied [87]. The mass and the size of the AmBC/protein complexes were found to depend on the mixing ratio of the components and the molecular charac-

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**Fig. 3.** TEM image and schematic illustration of the vesicles formed after complexation of two oppositely charged block copolymers [39].
teristics of the block copolymers. The complexes showed considerable stability at physiological ionic strength conditions. Furthermore, the structure/conformation of lysozyme was found to remain essentially unaltered in the complexes, as fluorescence and CD measurements indicated. The activity of the enzyme could be manipulated in a wide range via the amount of complexed block copolymer and the ionic strength of the solution. At physiological pH and ionic strength a sustained and extended release of the protein was observed [88], giving promise for the utilization of such hybrid nanostructures in protein drug release systems.

In a more basic study histone/DNA complex mimetic nanoassemblies were formed by complexation of spherical PS-b-QP2VP cationic micelles with DNA [89]. Around stoichiometric charge ratios spherical, rather polydisperse complexes, with large mass and size, engulfing several block copolymers micelles, were formed. At larger excess of DNA small compacted, negatively charged nanoparticles, i.e. isolated PS-b-QP2VP micelles decorated with DNA, could be observed.

Another direction of research related to bionanotechnology is the use of AmBC micelles as nanocarriers of hydrophobic anticancer drugs. Toward this goal the encapsulation and release capabilities of b-lactam functionalized PI-b-PEO copolymers (LPI-b-PEO) against the novel drug curcumin were investigated [90]. Drug encapsulation efficiency and loading capacity was increased as the LPI content increased in the LPI-b-PEO block copolymers. The in vitro release rate of curcumin was higher in FBS solutions compared to solutions in deionized water. Also the micelles with higher LPI content released the drug in a slower rate. Similar in vitro uptake profiles were observed for free curcumin and curcumin-loaded block copolymer micelles.

3.3. AmBC nanoreactors for formation of inorganic nanoparticles – solubilization/functionaization of carbon nanostructures

Chemically modified block copolymers play a critical role in a wide range of potential applications, due to easy-tuning of their physical behavior. Below, some indicative examples pertaining to chemically modified, anionically synthesized block copolymers are discussed.

Functionalized block copolymers have been used for the solubilization of inorganic nanoparticles, like metallic or semiconductor nanoparticles or even carbon nanostructures. In particular, the block copolymer PS-b-SCPI was utilized for the solubilization of carbon nanotubes (CNT). The above copolymer can adsorb on the surface of the nanotubes, through hydrophobic interactions between the PS block and the nonpolar carbon nanostructure. On the other hand, the SCPI block keeps the system in solution due to electrostatic repulsion forces [91,92]. Interestingly, the same block copolymer has been also used for the solubilization of carbon nanohorns (CNH), leading to stable water soluble nanohybrids through an identical solubilization scheme [93] (Fig. 4).

Following, the above described solubilization, the polymer decorated carbon nanostructures were also used for the template synthesis of either metallic or semiconductor nanoparticles. The synthesis [91] and the photophysical properties [94] of CdS nanoparticles on CNT/PS-b-SCPI hybrids have been studied, showing that the nanoparticles are placed in the polyelectrolyte block, because of electrostatic interaction between the cadmium salt precursor and the chemically modified SCPI block. Similarly, in another work, the synthesis of gold metallic nanoparticles has been demonstrated at the periphery of a polymer decorated CNH [93] (Fig. 4). In a similar system carbon nanotubes non-covalently modified with polyisoprene-b-poly(acrylic acid) (PI-b-PAA) amphiphilic block copolymers were used as templates for the biomimetic crystallization of calcium carbonate [95].

The synthesis of inorganic nanoparticles has been also performed in the micellar cores of chemically modified block copolymers from anionic polymerization. In particular, CdS and CdSe nanoparticles have been synthesized in the presence of SPS-b-PtBS or PS-b-SPI block copolymers. The synthesis was performed using a cadmium salt precursor, which induced micellization of the macromolecular

![Fig. 4. Schematic representation of carbon nanohorns solubilization by a block copolymer and of the subsequent gold nanoparticles templated synthesis [93].](image-url)
chains in organic media. The experimental results indicate that semiconductor nanoparticles with well defined size and properties can be prepared under carefully selected experimental conditions [96].

The synthesis of nanoparticles in the micellar core of a P2VP-b-PEO block copolymer has been also described by Anastasiadis and coworkers [97]. In this case, the synthesis of Pt metal nanoparticles was performed, either by introduction of a precursor metal salt in a micellar solution, where it was incorporated within the micellar core, or by addition of the metal salt into a unimers solution, where, under appropriate conditions, micellization was induced. In a second step, the micellar system behaves like a nanoreactor, where metal nanoparticles can be nucleated and grown, upon reduction, into sizes falling in the range of a few nanometers, as was demonstrated by electron microscopy observations.

Au and Ag nanoparticles were also formed in solvent or salt induced micelles of PS-b-P2VP and PI-b-PAA block copolymer, respectively [98]. The morphological changes of the self-assembled hybrid nanostructures formed in solution in the course of nanoparticle formation were studied in detail by dynamic light scattering, FTIR, UV–vis and transmission electron microscopy (TEM). The third order non-linear optical properties of dispersions containing Au nanoparticles embedded in PI-b-PAA micelles were determined by aid of the Z-scan technique [99]. The hybrid colloids were found to exhibit strong optical limiting action.

A SCPI-b-PEO block copolymer was utilized as stabilizer for the production of magnetic Fe3O4 nanoparticles in an attempt to provide biocompatibility to the hybrid nanoassembly [100]. The resulting dispersions showed nanosized dimensions, good colloidal stability and high saturation magnetization.

In another case gold nanoparticles were formed in the corona of PtBS-b-SCPI block copolymer micelles [101]. Formation of Au nanoparticles was achieved in the absence of any reducing agent since the amine groups of the corona SCPI chains were able to promote reduction of the metal precursor (Fig. 5), as evidenced by UV–vis spectroscopy measurements and TEM observations. The hybrid PtBS-b-SCPI/Au nanoparticles micelles were able to complex with lysozyme forming multicomponent/multifunctional hybrid inorganic-(bio)organic nanoparticles.

3.4. Self-assembly and properties of AmBC in the solid state, on surfaces/interfaces and in thin films

Chemically modified block copolymers present particular interest for studying their properties in the solid state or on surfaces. Amphiphilic block copolymers have been utilized in the solid state as nanostructured polymer electrolytes. An interesting example of this case has been recently presented by Jannasch and coworkers [51]. In the aforementioned study, the linear PS-b-PVPA block copolymer was found to form nanophase-separated morphologies with continuous phosphonated domains. The mechanism behind the above morphology is probably the initial formation of spherical micellar nanostructures, with PS cores, followed by the formation of branched arrays of necklace-like nanostructures and finally of a continuous nanophase separated morphology (Fig. 6). Interestingly, the above morphology can reach quite high proton conductivity, namely 30 mS/cm at 130 °C.

![Fig. 5. Schematic illustration of metal nanoparticles preparation protocol in the corona of PtBS-b-SCPI block copolymer micelles, via SCPI block mediated reduction [101].](image-url)
Microphase separated morphology was also observed in the case of polystyrene-b-poly(methacrylic acid) (PS-b-PMAA) block copolymer systems [102]. In the above example, the introduction of Li ions can alter the morphology of the block copolymer into more segregated phase separated domains, due to transformation of the PMAA domains to LiPMAA domains, which contribute to the increase in the ionic conductivity of the resulting amphiphilic block polyelectrolyte. Similar results have been also observed in previous studies, where the addition of Li salt has led to higher organization of block copolymer chains in the solid phase [103,104].

One particular case of bulk amphiphilic block copolymers in the thin film form is the formation of Langmuir–Blodgett (LB) films. An interesting example is the case of a P2VP-b-PS-b-P2VP triblock copolymer, which can form nano-donut like structures, by following the LB technique, as has been described by Park et al. [70]. In this case, the pH value of the solution played a crucial role on the formation (or not) of the nano-donuts structures, due to the chemical modification of the P2VP blocks, via protonation/deprotonation. This is a very nice example of how the environmental changes can chemically modify a polymer chain and consequently change the adopted supramolecular structure when the material is deposited in a form of a very thin film.

The formation of a AmBC monolayer on a surface has been also described by Lupitskyy et al. [105]. In the particular example, a hetero-arm star block copolymer, namely (PS)$_n$(P2VP)$_n$, was attached onto a solid substrate. The attachment was achieved by a quaternization reaction between the P2VP blocks and the Br-alkyl silane chemically modified silica substrate. The result was the formation of a responsive coating, which allowed the switching of the surface properties by changing the selectivity of the supernatant solvent.

The interfacial behavior of PI-b-PEO/PI-b-PAA mixtures, able to form hydrogen bonds due to interactions between the PEO and PAA blocks, at the air–water interface has been also reported [106]. PI-PAA chains were introduced to initially formed PI-b-PEO monolayers. The behavior of the mixed monolayers was found to be pH dependent. At pH 10 and 5.7, where hydrogen bonds cannot be formed due to deprotonation of the carboxylic groups of PAA, no substantial effects are observed to the behavior of the initial PI-b-PEO monolayer. Three regions are observed in π-A isotherms with the aid of neutron reflectivity measurements: (i) region I – a low pressure 2-D pancake structure, (ii) region II – a pseudoplateau, where PEO chains desorb, (iii) region III – the brush regime. At pH 2.5, where carboxylic groups are protonated and hydrogen bonds can be formed, π-A isotherms present only two regions, with the disappearance of the pseudoplateau, and an increased reproducibility of the compression–decompression cycles. The results demonstrate a considerable tuning of the monolayer properties through hydrogen bond formation.

The adsorption mechanism of PtBS-b-NaSPS AmBC onto surfaces has been early described in the literature [107,108]. Recently, Balastre et al. has described brushes of PtBS-b-NaPSS which had been formed at the interface between a hydrophobic mica surface and water. Direct force measurements on this system indicated that it is possible to construct a “universal brush height curve”. The curve takes into account all the parameters that contribute to the final brush height. Interestingly, the experimental results point to the validity of the scaling theory for both osmotic brush and salted brush regime [109].

In another work, diblock copolymer charged layers adsorbed and spread on flexible interfaces were studied. In the above work, the structure and the height fluctuations were detected by means of complimentary techniques, both for the adsorbed and the spread copolymers cases, while the system was in equilibrium. It should be added that, optical and X-ray scattering techniques were used in order to study the buckled deformations of the air water interface [110].

In a more recent example, the adsorption of the above block copolymer was also studied in relation with the hydrophobicity of the surface. In particular, a bare mica (hydrophilic) and an octadecyltriethoxysilane modified mica (hydrophobic) were chosen as the two extreme cases for the above study. The experimental results indicated that in the case of the hydrophobic surface, the polymer is highly adsorbed on the modified mica and the formation of a brush occurs. In contrast, on bare mica, the adsorbed polymer amount was not high enough to form a brush structure [111].

Finally, another study was made on the kinetics of adsorption of PtBS-NaSPS, on germanium surface, which has been followed by attenuated total reflectance IR spectroscopy. The experimental results indicate pronounced differences between the absorption kinetics of the diblock and of the corresponding NaSPS homopolymer. Moreover, it was found that, if the polymer concentration was higher than the cmc, the adsorption mechanism of the diblock copolymer involves chain diffusion, micellar relaxation and a brush-limited process [112].

4. Conclusions and perspectives

The works presented in the previous sections unambiguously show that several well-defined AmBC can be synthesized via anionic polymerization combined with
selective post-polymerization functionalization reactions. Definitely the use of polymer-analogous reactions extends the synthetic capabilities of anionic polymerization, toward molecular structures that would be otherwise unreachable by the particular polymerization mechanism, and in many cases by any other available polymerization methodology. Besides chemistry and synthesis the self-assembly properties, the stimuli responsive character and nanostructure formation, in AmBC based macromolecular systems, are the subject of intense scientific interest, since these studies open ways toward promising nano/bio/technological applications of these polymeric materials.

However, it is the authors’ feeling and belief, that much more work can and should be done in the future on the directions discussed in this article. A natural extension of the work would be the search and adaptation of other efficient and selective functionalization reactions onto block copolymers, taking advantage also of the advances in contemporary organic and organometallic chemistry (for example the “click”-chemistry). The goal would be to increase the nature of available functional groups and chemical diversity of existing systems, as well as to increase efficiency of the modification steps and the homogeneity of the final product.

Another way to go is to increase efforts related to the preparation of novel functional monomers with new protected functionalities. Again the help and support from new knowledge acquired in the field of organic chemistry is valuable and necessary and should be directly applicable to the success of the particular goal. Research along these lines is closely related to the successful and efficient polymerization of the new monomers by existing anionic polymerization protocols, utilizing well-known initiator systems and agents for kinetic control of polymerization reactions via reactive (macro)anions. Of course smart and innovative anionic polymerization methodologies, able to tolerate polar functionalities, should be also devised. The development of novel initiators/catalysts and cofactors and modifiers of polymerization kinetics for mechanism control should produce benefits for polymer science in general. The study of polymerization kinetics of these new systems will also be a valuable attribute to new polymeric materials development. This direction of research on the discussed subject lies at the heart of polymer chemistry.

Full adaptation of existing and new polymerization methodologies for development of AmBC with complex macromolecular architecture, as is done in living/controlled radical polymerization schemes is also necessary. Several reports has been presented so far on the synthesis of linear triblocks, but considerably less attention has been devoted on the synthesis of multiblock and non-linear (star-like and graft) amphiphilic copolymers. Such schemes require the invention of suitable linking/branching chemical pathways, suitably adapted to functional prepolymers and able to sustain/survive subsequent chemical modification reactions that should be controlled as must as possible. Non-linear AmBC architectures hold promise for further elucidating structure–properties relationships in modern polymeric materials, but also may hide unpredictable new properties and physicochemical behavior which may open new and unforeseen possibilities for applications.

It is clear that the efforts described above can lead to the designed synthesis of novel block copolymers. Pairing of polymer synthesis with advanced polymer characterization techniques and the establishment of the inherent properties of new polymeric materials will greatly extend existing understanding and application capabilities of amphiphilic block copolymers and at the same time will widen knowledge on polymer science in general.

References


Eleni Kaditi (born 1982) studied Chemistry at the University of Patras, Greece. She joined the Theoretical and Physical Chemistry Institute at the National Hellenic Research Foundation, Athens, Greece in 2006, in pursuit of a Masters degree, which she obtained from the University of Athens, Greece in 2008. She is currently working on her PhD in the group of Dr. Stergios Pispas. Her research interests focus on the synthesis of functional amphiphilic block copolymers by anionic polymerization and post polymerization functionalization methodologies.

Grigoris Mountrichas (born 1981) studied chemistry at the University of Athens, Greece. He has been working at TPCI-NHRF since 2004 in pursuit of a Masters degree and a PhD degree, which he has received from the Chemistry Department, University of Athens, Greece (in 2006 and 2008 respectively). Currently he is a postdoctoral fellow at the Theoretical and Physical Chemistry Institute of the National Hellenic Research Foundation in Athens, Greece. He had long visits at the ...and the ... in the period ... He has published over 30 papers in refereed scientific journals and made over 30 announcements at international scientific conferences. His research interests include the synthesis and properties of polymers and polymer based hybrid materials, with emphasis on materials containing polymers and carbon nanostructures.

Stergios Pispas (born 1967) studied Chemistry at the University of Athens, Greece and obtained his PhD from the same university in 1994. During 1994 and 1995 he was a Post-doctoral Fellow at the Chemistry Department of the University of Alabama at Birmingham, USA. He then returned to Greece and joined again the Chemistry Department of the University of Athens as a Research Associate. In 2004 he became an Associate Researcher at the Theoretical and Physical Chemistry Institute at the National Hellenic Research Foundation, Athens, Greece. Since 2009 he is Senior Researcher at TPCI-NHRF. He serves as an Editor for the European Physical Journal E: Soft Matter and Biological Physics (since 2003) and is a member of the Editorial Board of the Open Macromolecular Journal (since 2007). He has been awarded the American Institute of Chemists Foundation Award for Outstanding Post-doctoral Fellow (1995) and the A. K. Doolittle Award of the American Chemical Society (2003). He is a coauthor of a book on block copolymers. His current research focuses on the synthesis of functional block copolymers and polyelectrolytes by controlled polymerization methodologies, the study of their self-assembly properties, as well as the development of complex, hybrid, self-organized nanosystems based on designed synthetic polymers and inorganic nanomaterials and biomacromolecules.