



Linear and non-linear triblock terpolymers. Synthesis, self-assembly in selective solvents and in bulk

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Abbreviations ATRP, atom transfer radical polymerization; BAE, (*t*-butylamino)ethyl methacrylate; BIEE, 1,2-bis(2-iodo ethoxy)ethane; BSI, poly(butadiene-*b*-styrene-*b*-isoprene); BzMA, benzyl methacrylate; BuA, *n*-butyl acrylate; CROP, cationic ring opening polymerization; D₃, hexamethylcyclotrisiloxane; DABCO, 1,4-diazabicyclo[2.2.2]octane; DBM, diagonal bond method; DDFT, dynamic density functional theory; DMAC, dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSA, 3-(dimethoxymethylsilyl)propyl acrylate; DMSO, dimethyl sulfoxide; *dn*Nbpy, 4,4'-di-*n*-nonyl-2,2'-bipyridine; DPE, 1,1-diphenylethylene; EB, poly(ethylene-*co*-butylene); EF-TEM, energy-filtering transmission electron microscopy; EVE, ethyl vinyl ether; GTP, group transfer polymerization; HEEDTA, hydroxyethyl-ethylenediaminetriacetic acid sodium salt; $I = M_w/M_n$, polydispersity index; IMDS, intermaterial dividing surface; IR, infrared; Is, isoprene; ISD, poly(isoprene-*b*-styrene-*b*-dimethyl siloxane); ISP, poly(isoprene-*b*-styrene-*b*-vinyl pyridine); LALLS, low angle laser light scattering; MALLS, multi angle laser light scattering; MeNQ, 2-methyl-1,4-naphthoquinone; M_n , number-average molecular weight; MO, membrane osmometry; MPEO, poly(ethylene oxide)methyl ether; MTEGVE, methyl tri(ethylene glycol) vinyl methyl ether; MVE, methyl vinyl ether; M_w , weight-average molecular weight; M_w/M_n , molecular weight distribution; NIPA, *N*-isopropyl acrylamide; NMR, nuclear magnetic resonance; NMRP, nitroxide mediated radical polymerization; ODT, order disorder transition; OTDD, ordered tricontinuous double diamond; P2VP, poly(2-vinylpyridine); P4VP, poly(4-vinylpyridine); P4MeS, poly(4-methyl styrene); PA, poly(acrylic acid); PBd, polybutadiene; PBMA, poly(*n*-butyl methacrylate); PCEMA, poly(cinnamoyl ethyl methacrylate); PCHD, poly(1,3-cyclohexadiene); PCL, poly(ϵ -caprolactone); PCP, polycyclopentene; PDEA, poly[2-(diethylamino)ethyl methacrylate]; PDIPAEMA, poly[2-(diisopropylamino)ethyl methacrylate]; PDMA, poly[2-(dimethylamino)ethyl methacrylate]; PDMAA, poly(*N,N*-dimethylacrylamide); PDMS, poly(dimethyl siloxane); PDMSA, poly[3-(dimethoxymethylsilyl)propyl acrylate]; PEG, poly(ethylene glycol); PEHA, poly(2-ethyl hexyl acrylate); PEMA, phenyl methacrylate; PEO, poly(ethylene oxide); PFP, poly(ferrocenylphenyl phosphine); PFS, poly(ferrocenyldimethylsilane); PGMA, poly(glycerol monomethacrylate); PHEGMA, poly[hexa(ethylene glycol)methacrylate]; PHEMA, poly(2-hydroxy ethyl methacrylate); PI, polyisoprene; PIBVE, poly(isobutyl vinyl ether); PLLA, poly(L-lactide); PMA, poly(methacrylic acid); PMEMA, poly[2-(*N*-morpholino)ethyl methacrylate]; PMMA, poly(methyl methacrylate); PMOXA, poly(2-methyl oxazoline); PNaAc, poly(sodium acrylate); PNIPAM, poly(*N*-isopropylacrylamide); POEGMA, poly[oligo(ethylene glycol) methacrylate]; PPO, poly(propylene oxide); PS, polystyrene; PSEMA, poly(succinyl oxy ethyl methacrylate); PTA, phosphotungstic acid; PrBuA, poly(*tert*-butyl acrylate); PrBuMA, poly(*tert*-butyl methacrylate); PrBuS, poly(*t*-butylstyrene); P α MeS, poly(α -methyl styrene); RAFT, reversible addition-fragmentation chain transfer; ROP, ring opening polymerization; SANS, small angle neutron scattering; SAXS, small angle X-ray scattering; SBI, poly(styrene-*b*-butadiene-*b*-isoprene); SBM, poly(styrene-*b*-butadiene-*b*-methyl methacrylate); *s*-BuLi, *sec*-butyllithium; SBV, poly(styrene-*b*-butadiene-*b*-2-vinyl pyridine); SCL, shell crosslinked (micelles); SEC, size exclusion chromatography; SIO, poly(styrene-*b*-isoprene-*b*-ethylene oxide); SLS, static light scattering; SSL, strong segregation limit; St, styrene; TEM, transmission electron microscopy; THF, tetrahydrofuran; THPMA, tetrahydropyranyl methacrylate; TMEDA, *N,N,N',N'*-tetramethylethylenediamine; TMSMA, trimethylsilyl methacrylate; ϕ , volume fraction.

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Abstract

The synthesis of linear and non-linear (star, cyclic) triblock terpolymers through living, controlled/living polymerization methods and their combinations are reviewed. The theoretical predictions and the experimental results concerning the self-assembly of these materials in selective solvents and in bulk are also discussed. A plethora of self-assembled structures have been detected either in solution or in bulk, potentially leading to a rich variety of high-tech applications. First results regarding the synthesis and morphology of multicomponent multiblock (tetrablock quarter and pentablock quinto) polymers are also given.

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Keywords: Triblock terpolymers; Linear; Miktoarm star; Cyclic; Synthesis; Living polymerization; Living/controlled polymerizations; Self-assembly; Selective solvents; Bulk

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1. Introduction

Emerging technologies in medicine, microelectronics and optics require the availability of novel

polymeric materials with ever more sophisticated properties and performances. Living and controlled/living polymerization methods have allowed for the synthesis of tailor-made macromolecules of varying

chemical structure, composition, molecular characteristics and architecture. Among the different architectures, block copolymers definitely play a central role in polymer science. The covalent bonding of two or more thermodynamically incompatible polymeric chains leads to a rich variety of microstructures both in bulk and in solution. Block copolymers are pre-eminent self-assembly materials since they offer control over length scale, morphology and domain functionality. The domain dimensions of the block copolymer microstructures can be manipulated through the monomer structure, composition and molecular weight and vary between 5 and 50 nm. In solutions the nature of the selective solvent is crucial in determining the size and shape of the micellar structures formed.

An enormous amount of work has been published using diblock copolymers of the AB type. In bulk, four different ordered structures can be obtained (alternating lamellae, cylinders, body-centered cubic arrays of spheres and gyroid) depending on the copolymer composition and architecture. Considerably less extended is the work dedicated to the synthesis, solution and bulk properties of triblock terpolymers of the ABC type. It is well known that the addition of a third block leads to a much richer variety of phases (over 30 phases have been identified to date in bulk). These materials have the potential to generate a variety of well-controlled multiphase microdomain structures with nanosized structural units in bulk and thin films and to provide supramolecular structures in solution with a mesoscopic length scale. Therefore, numerous applications such as multifunctional sensors, multiselective catalysts for sequential or simultaneous chemical reactions, separation membranes, filters, etc., are possible.

In the present work, the more recent advances in the synthesis, micellization properties in selective solvents and microphase separation of ABC triblock terpolymers are reviewed. Of all the possible arrangements of the blocks (see Fig. 49), only pure linear, star and cyclic terpolymers have been prepared and studied. It is not the aim of the present work to offer an exhaustive coverage of the field. Special interest is given by providing the advantages and limitations of the different polymerization techniques for the synthesis of well-defined structures.

2. Synthesis of ABC triblock terpolymers

2.1. Linear ABC triblock terpolymers

2.1.1. Anionic polymerization

The usual synthetic approach for the synthesis of linear triblock terpolymers is the sequential three step addition of monomers to an appropriate anionic initiator. The key parameter for the successful synthesis of the terpolymers by this method is the order of the addition of the monomers. The initiation rate at each step should be faster than the corresponding propagation rate, for each monomer. If this requirement cannot be fulfilled, either modification of the active site or coupling methodology is necessary in order to produce ABCs with high molecular weight and compositional homogeneity.

By using the sequential approach, Matsushita and collaborators [1,2] synthesized a series of poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (I-S-2VP) as well as poly(styrene-*b*-isoprene-*b*-2-vinylpyridine) (S-I-2VP) terpolymers in THF using cumyl potassium. Due to the presence of THF, PI exhibited high 3,4 as the initiator content. As an example, the synthetic route for S-I-2VP is given in Fig. 1. The precursors along with the terpolymers were extensively characterized by membrane osmometry (MO), size exclusion chromatography (SEC) and NMR spectroscopy. The final terpolymers exhibited low polydispersity indices, and their molecular weights were the expected ones from stoichiometry, indicating high degree of molecular and compositional homogeneity. These terpolymers were used to examine their morphological features.

Watanabe and collaborators [3] synthesized poly(styrene-*b*-2-vinylpyridine-*b*-butadiene) (S-2VP-Bd) triblock terpolymers first by reacting poly(styrene-*b*-2-vinylpyridine)Li living diblock copolymers with excess *p*-xylene dichloride. The excess dichloride was removed by successive precipitation/dissolution procedures, under high vacuum, in a specially designed apparatus. Heptane/THF was used as the non-solvent/solvent pair. The resulting functionalized S-2VP-Cl diblock copolymer was subsequently reacted with a large excess of living polybutadiene end-capped with diphenylethylene (DPE), in order to attenuate the basicity of the living center (Fig. 2). Finally, excess PBd was removed by fractionation. The final products

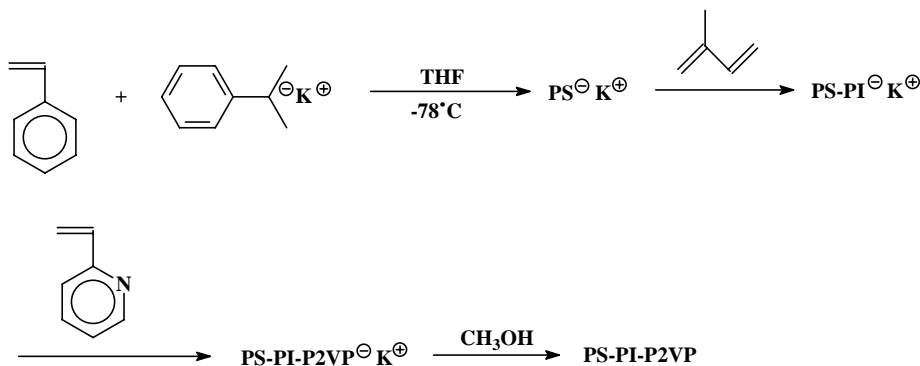


Fig. 1. Synthesis of PS-*b*-PI-*b*-P2VP triblock terpolymers by anionic polymerization.

were characterized by SEC with both refractive index and low angle laser light scattering detectors. The polydispersity indices were close to 1.1, and the molecular weights agreed with the corresponding one calculated by the stoichiometry.

Poly(styrene-*b*-butadiene-*b*-methyl methacrylate) (S-Bd-MMA) triblocks were prepared by Stadler and collaborators [4] by sequential anionic polymerization of styrene, butadiene and methyl

methacrylate in THF with *s*-BuLi as the initiator, under inert atmosphere (Fig. 3). Since the polymerization was performed in THF, the microstructure of the resulting PBd was 90% 1,2. The polydispersity indices were close to 1.1, as determined by SEC. The same authors in a subsequent work selectively hydrogenated the PBd 1,2 middle block to produce the triblock terpolymer polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-poly(methyl methacrylate) [5].

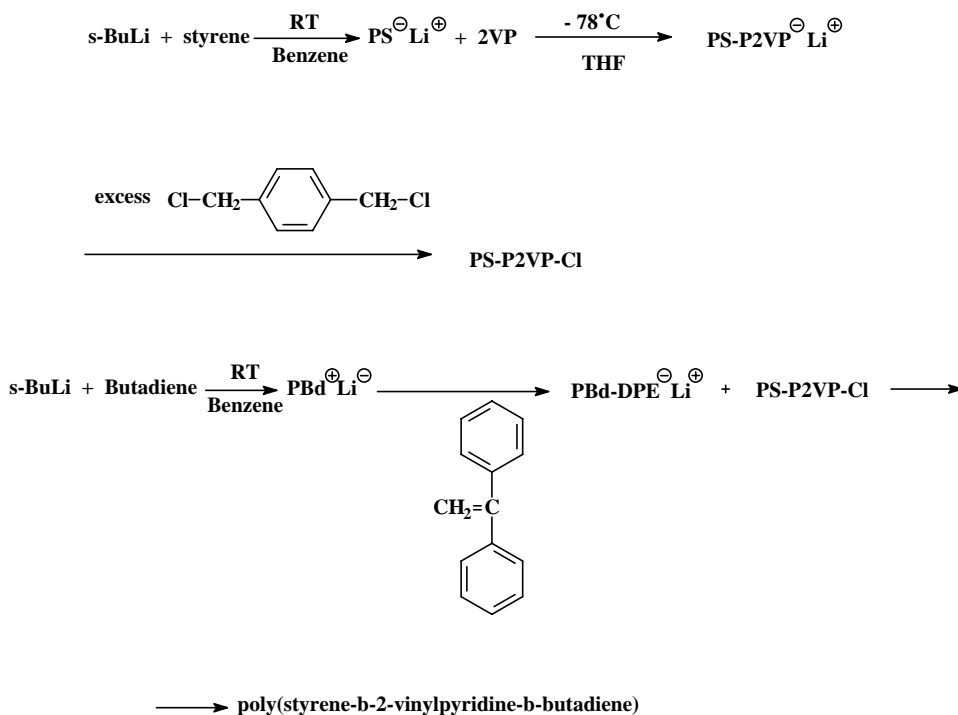


Fig. 2. Synthesis of PS-*b*-P2VP-*b*-PBd triblock terpolymers by anionic polymerization.

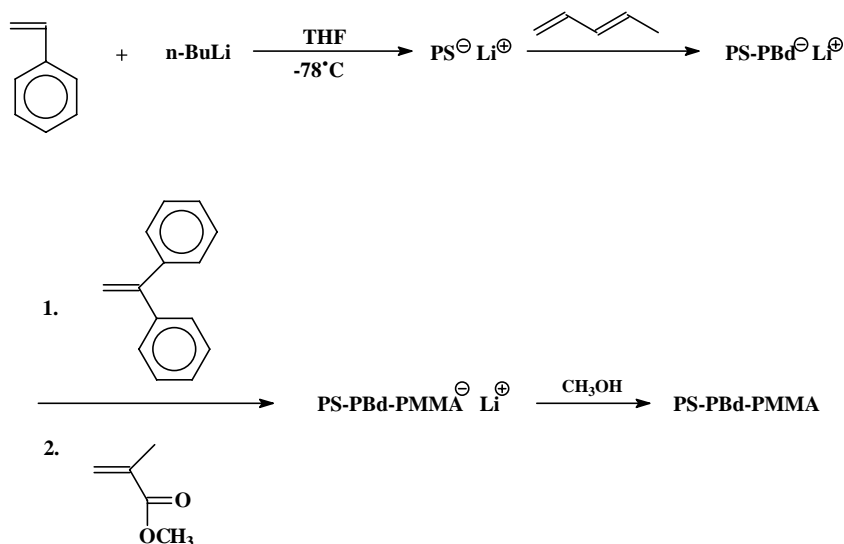


Fig. 3. Synthesis of PS-*b*-PBd-*b*-PMMA triblock terpolymers by anionic polymerization.

By using sequential anionic polymerization, Stadler and co-workers [6] synthesized well-defined triblock terpolymers containing styrene, either 2- or 4-vinylpyridine and *tert*-butyl methacrylate (*t*BuMA) in THF with *s*-BuLi as the initiator, at $-78\text{ }^{\circ}\text{C}$ (Fig. 4). The terpolymers were characterized only with SEC, while the molecular weights were calculated from the stoichiometric amounts of the initiator and monomers. During the addition of the second monomer (2- or 4-vinylpyridine), a small amount of the living PS chains was terminated due to

the impurities introduced with the monomer, resulting in high polydispersity indices (I) (~ 1.31).

Sequential addition of the monomers was also used by Abetz et al. [7] to synthesize poly(1,4-isoprene-*b*-1,2-butadiene-*b*-polystyrene) triblock terpolymers with *s*-BuLi in benzene. In order to obtain PBd *1,2* as the second block a small amount of THF was added before the addition of butadiene. Characterization by SEC revealed $I=1.02\text{--}1.06$.

Triblock terpolymers containing PS, PMMA and poly(*tert*-butyl acrylate) (*Pt*BuA) were synthesized by

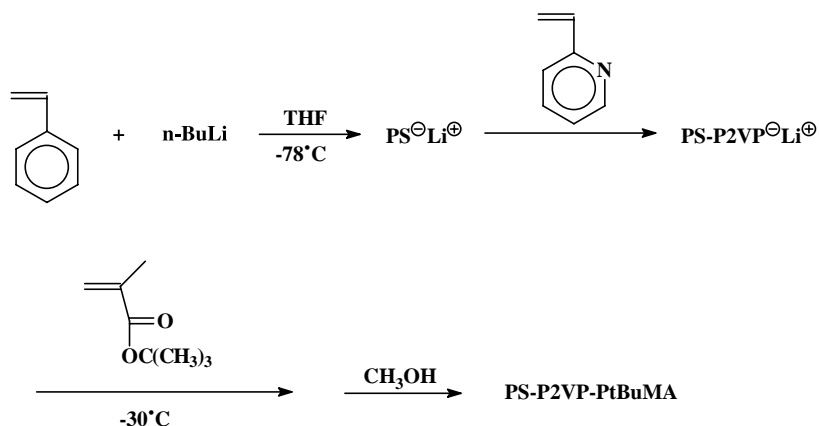


Fig. 4. Synthesis of PS-*b*-P2VP-*b*-*Pt*BuMA triblock terpolymers by anionic polymerization.

Eisenberg and co-workers [8] for aggregation phenomena studies in solution. The synthetic approach involved the sequential addition of the three monomers to *s*-BuLi in THF at $-78\text{ }^{\circ}\text{C}$. The poly(*tert*-butyl acrylate) block was further hydrolyzed to polyacrylic acid (PA) to afford the S-MMA-A amphiphilic terpolymer. The molecular weight of the first block was obtained by SEC, calibrated with PS standards; whereas the molecular weights of the other two blocks were calculated from the NMR spectra and the molecular weight of the first block. The polydispersity indices were around 1.1.

The sequential addition approach along with post polymerization reactions were also followed by Liu et al. [9] for the synthesis of one poly(isoprene-*b*-2-cinnamoyl ethyl methacrylate-*b*-*tert*-butyl acrylate) triblock terpolymer. Isoprene was polymerized in cyclohexane with *s*-BuLi, the living PI chain ends were then end-capped with diphenyl ethylene, followed by addition of a significant amount of THF. The temperature was lowered to $-78\text{ }^{\circ}\text{C}$, and 2-trimethylsiloxyethyl methacrylate (the second monomer) was added, followed by *tert*-butyl acrylate. The trimethylsilyl group of the poly(2-trimethylsiloxyethyl methacrylate) block was then removed by precipitation of the terpolymer in methanol, to yield poly(2-hydroxyethyl methacrylate), which was converted to poly(2-cinnamoyl ethyl methacrylate) by reacting the pendant hydroxyl groups with excess cinnamoyl chloride (Fig. 5). The excess cinnamoyl chloride was removed by repeated precipitation from methanol. The absolute molecular weight of the first

block was measured by LALLS and the molecular weights of the other two blocks were calculated by NMR spectroscopy. The polydispersity index was 1.16. The terpolymer was used to study the micellar behavior in selective solvents.

Bates and collaborators [10] provided another example with the synthesis of poly(isoprene-*b*-styrene-*b*-dimethylsiloxane) (PI-*b*-PS-*b*-PDMS) triblock terpolymers. The synthetic approach involves the polymerization of isoprene in a hydrocarbon solvent, with *s*-BuLi to give a high *1,4* content. A significant amount of THF was then added, followed by addition of styrene and D_3 monomer (Fig. 6). The polymerization was terminated with trimethylchlorosilane. The polydispersity index of the terpolymer was 1.18, and its bulk morphology was investigated by TEM, SAXS, and SANS.

A polystyrene-*b*-poly(sodium acrylate)-*b*-poly(*n*-butyl methacrylate) triblock terpolymer was synthesized by Tsitsilianis et al. [11]. Sequential anionic polymerization of styrene, *tert*-butyl acrylate and *n*-butyl methacrylate, in THF at $-40\text{ }^{\circ}\text{C}$ with *s*-BuLi initially gave poly(styrene-*b*-*tert* butyl acrylate-*b*-*n*-butyl methacrylate) triblock terpolymer. A six-fold excess of LiCl with respect to the active sites, was added in order to create ‘living’ conditions for the polymerization of the second monomer. The middle polymeric block of *tert*-butyl acrylate was then modified by selective acidic hydrolysis followed by neutralization of the produced carboxylic group to give the final product. The polymers were characterized by SEC and LALLS.

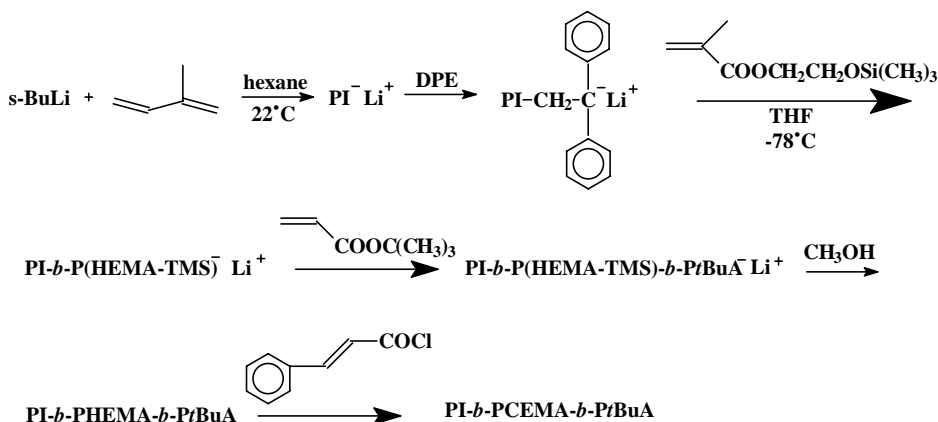


Fig. 5. Synthesis of PS-*b*-PCEMA-*b*-PtBuA triblock terpolymers by anionic polymerization.

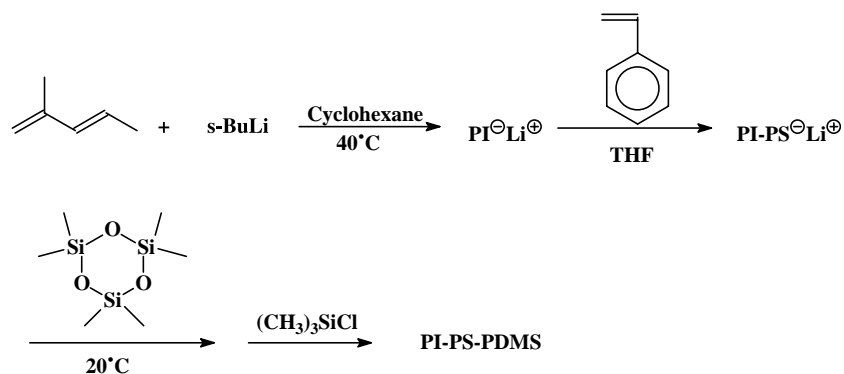


Fig. 6. Synthesis of PS-*b*-PI-*b*-PDMS triblock terpolymers by anionic polymerization.

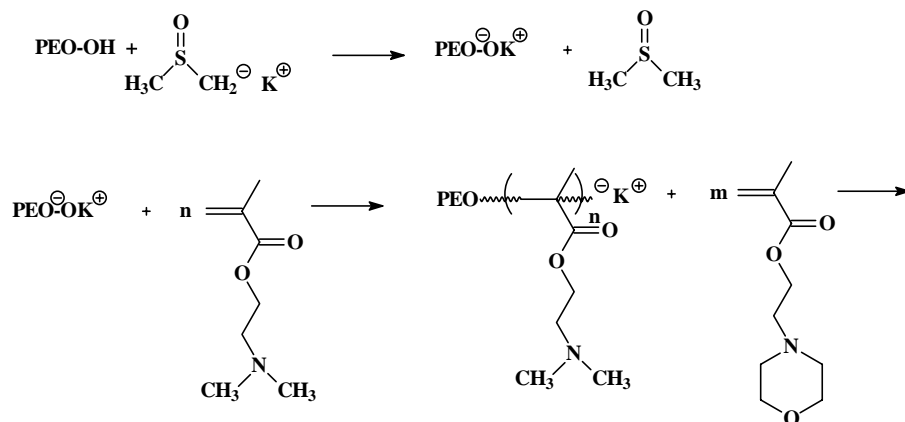
Abetz et al. [12] synthesized two series of linear triblock terpolymers with styrene as the first block and butadiene and 2-vinyl pyridine as the other two blocks, in different orders. The synthesis of S-Bd-2VP involved the sequential polymerization in THF of the corresponding monomers with *s*-BuLi. The Bd-S-2VP terpolymers were prepared by sequential polymerization of butadiene and styrene in benzene at 40 °C. In order for the polybutadiene block to have a similar *1,2* content to that of the S-Bd-2VP terpolymers, 1 ml of THF was added to the solvent prior to addition of butadiene. The living chains were then end-capped with 1,1-diphenyl ethylene to reduce the reactivity of the active centers, followed by the addition of a large amount of THF (THF/benzene = 3/1) and lowering the temperature to –80 °C, before the addition of 2-vinylpyridine. Both series were examined for their microphase separation behavior. The polydispersity indices and the number average molecular weights were obtained by SEC and membrane osmometry, respectively. Triblocks composition was verified by NMR spectroscopy.

By utilizing anionic polymerization high vacuum techniques and the sequential addition methodology, Hadjichristidis and collaborators [13] synthesized triblock terpolymers of isoprene, 2-vinyl pyridine and ethylene oxide. Benzyl potassium was employed as the initiator, and the polymerization of the three monomers was performed in THF at –78 °C. The polyisoprene block exhibited high *3,4* content, since it was polymerized in a polar solvent. Molecular characteristics were obtained by NMR spectroscopy and SEC. The polydispersity index was found to be around 1.05.

Jérôme and co-workers [14] synthesized a triblock terpolymer of styrene, 2-vinyl pyridine and ethylene oxide. Initially, they prepared ω -OH poly(styrene-*b*-2-vinyl pyridine) with *s*-BuLi in the presence of LiCl and termination of the living diblock with ethylene oxide. The end-hydroxy groups were then converted to potassium alcoholate with potassium naphthalene, followed by addition of the EO monomer at 0 °C to afford the final product.

A series of triblock terpolymers of 5-(*N,N*-dimethylamino) isoprene, styrene and methacrylic acid was synthesized by Muller et al. [15], by sequential addition of 5-(*N,N*-dimethylamino) isoprene, styrene and *t*-butyl methacrylate onto *s*-BuLi. The polymerization of 5-(*N,N*-dimethylamino) isoprene was performed in toluene at –40 °C. After completion of the polymerization, THF was added, the temperature was lowered to –65 °C, followed by addition of styrene. Upon completion of the polymerization, *t*-butyl methacrylate was introduced to the reaction solution. The poly(*t*-butyl methacrylate) block was hydrolyzed with hydrochloric acid. The terpolymers were characterized by SEC, NMR spectroscopy and membrane osmometry (MO).

Armes and collaborators [16] synthesized triblock terpolymers of ethylene oxide (EO), 2-(dimethylamino)ethyl methacrylate (DMA), 2-(*N*-morpholino)ethyl methacrylate (MEMA) or *t*-(butylamino)ethyl methacrylate (BAE), and of MEMA, DMA and 2-(diethylamino)ethyl methacrylate (DEA), by using the sequential monomer addition methodology. One example is shown in Fig. 7. The synthetic approach for the terpolymers incorporating



PEO-*b*-PDMA-*b*-PMEMA

Fig. 7. Synthesis of PEO-*b*-PDMA-*b*-PMEMA triblock terpolymers by anionic polymerization.

PEO blocks involved the use of an ω -potassium poly(ethylene oxide), produced from the reaction of hydroxyl end-functionalized PEO with the potassium salt of DMSO. The same initiator was also employed for the synthesis of the PMEMA-*b*-PDMA-*b*-PDEA triblock terpolymers. SEC, NMR and UV spectroscopy revealed the stoichiometrically expected molecular weights and composition, and relatively broad molecular weight distributions ($I=1.32$). The increased polydispersities implies that termination reactions occurred during the addition of the second and third monomers.

The synthesis of two triblock terpolymers of styrene, 2-vinyl pyridine and methyl methacrylate was reported by Tsitsilianis et al. [17]. The polymerization was performed under argon atmosphere, with THF as the solvent and by sequentially addition of the monomers. The polymerization of styrene was initiated with *s*-BuLi at $-40\text{ }^{\circ}\text{C}$ in THF. A five-fold excess of LiCl with respect to the active sites was present in the reaction medium, in order to provide the living conditions of the polymerization of the second and third monomer. After total consumption of styrene, the solution was cooled to $-70\text{ }^{\circ}\text{C}$, and 2VP was added dropwise. Upon completion of the polymerization, MMA was introduced at $-60\text{ }^{\circ}\text{C}$. Characterization by SEC and NMR spectroscopy indicated a slight termination of the precursors, and the traces of the side products were thus removed by extraction. The final terpolymers exhibited

polydispersity indices of 1.17, and molecular weights of $70\text{--}84 \times 10^3\text{ g/mol}$.

Schubert et al. [18] employed an alternative method, for the synthesis of a triblock terpolymer of styrene, 2VP and EO. Their approach involves the synthesis of terpyridine-terminated PEO and S-2VP, followed by linking through the formation of a Ru complex. More details are given in Fig. 8. The formation of the triblock terpolymer was evidenced by UV-VIS spectroscopy.

A series of well-defined coil-crystalline-coil triblock terpolymers of poly(ferrocenylphenylphosphine)-*b*-poly(ferrocenyldimethylsilane)-*b*-poly(dimethylsiloxane) of narrow polydispersity were prepared by Manners et al. [19] through sequential anionic ring-opening polymerization of phosphoferrocenophane, silaferrocenophane and hexamethyl cyclotrisiloxane (Fig. 9). The polymerization of the first two monomers took place in THF, at $23\text{ }^{\circ}\text{C}$, whereas the polymerization of the third monomer at $0\text{ }^{\circ}\text{C}$. The terpolymers were characterized by SEC and NMR spectroscopy. The polydispersity indices of the terpolymers were lower than 1.1, indicating that no termination reactions occurred during the sequential addition of the monomers.

Lodge and collaborators [20] synthesized linear triblock terpolymers of PBd 1,2, PS and PEO by sequential anionic polymerization of butadiene and styrene in THF at $-60\text{ }^{\circ}\text{C}$, followed by termination of the living ends with ethylene oxide. The resulting

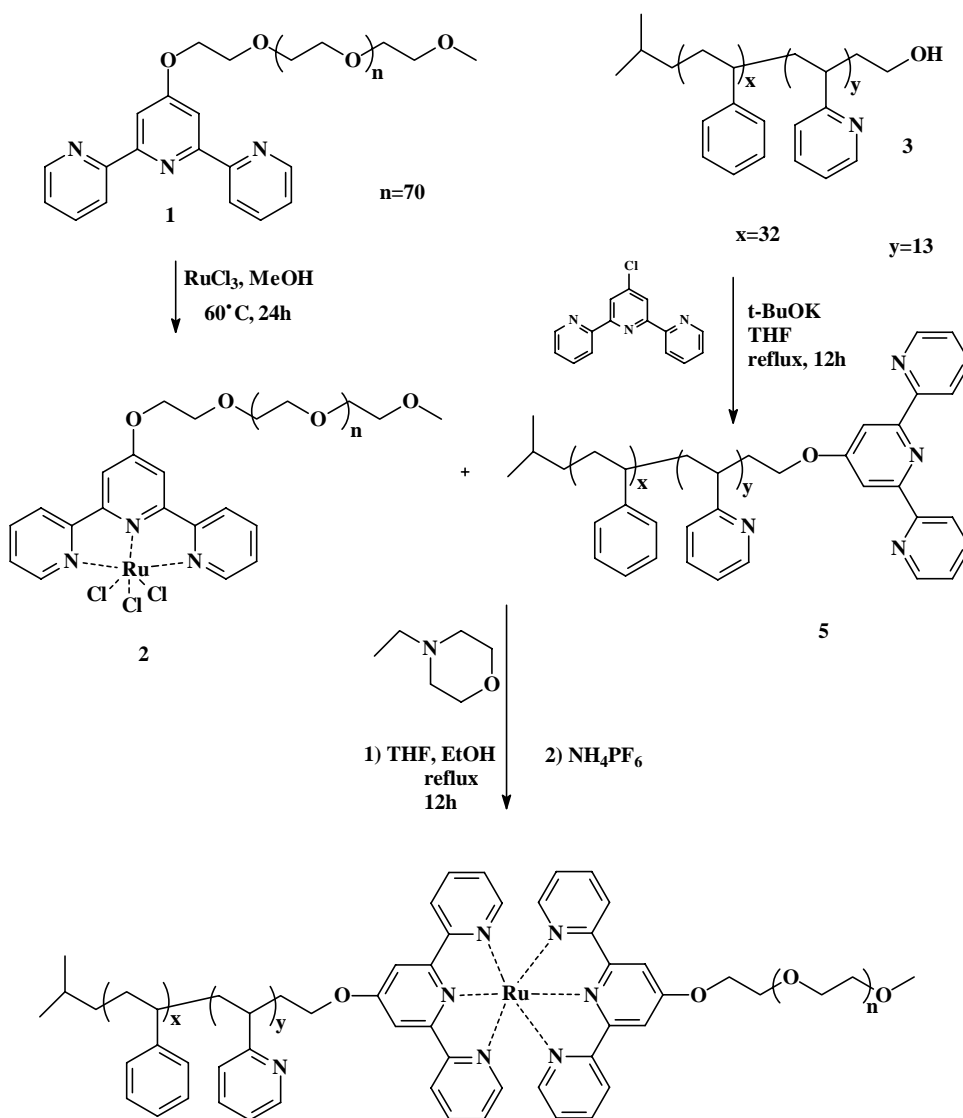


Fig. 8. Synthesis of PS-*b*-P2VP-*b*-PEO triblock terpolymers by linking through the formation of a Ru complex.

$-\text{OH}$ groups were then transformed to $-\text{O}^- \text{K}^+$, by reaction with potassium naphthalenide, which acted as the initiating sites for the polymerization of ethylene oxide. The terpolymers were characterized by SEC and NMR spectroscopy. The B blocks were further fluorinated with *n*-perfluorohexyl iodide, and the micellar behavior of the resulting terpolymers in selective solvents was examined.

New biodegradable/biocompatible terpolymers of ethylene oxide glycidol and L-lactide were

synthesized by Sosnowski et al. [21] by sequential monomer addition onto potassium 2-methoxyethanolate in THF. EO and 1-ethoxyethylglycidyl ether monomers, were polymerized at 37°C , while the polymerization of L-lactide took place at room temperature. Before addition of the second and third monomer, a small aliquot was removed in order to characterize the intermediate products. Deprotection of the hydroxyl groups in poly(L-ethoxyethylglycidol) segments was carried out in acidic conditions to result

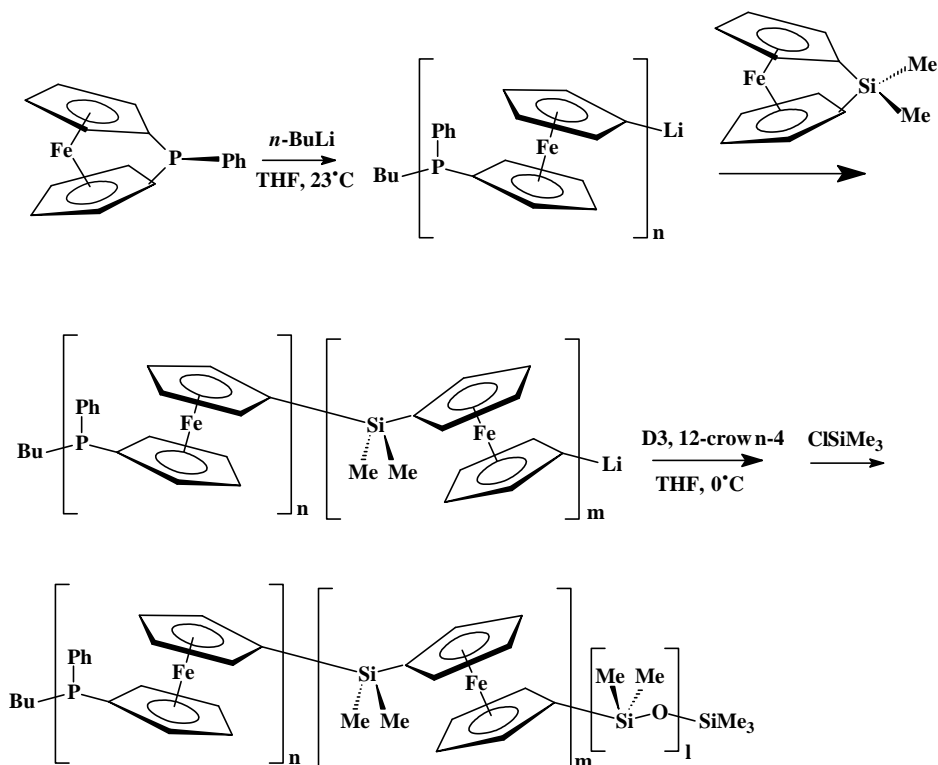


Fig. 9. Synthesis of poly(ferrocenylphenylphosphine)-*b*-poly(ferrocenyldimethyl silane)-*b*-poly(dimethylsiloxane) triblock terpolymers by anionic polymerization.

the polyglycidol middle block, as shown in Fig. 10. The terpolymers were extensively characterized by SEC, with a MALLS detector, along with NMR and IR spectroscopy, and the polydispersity indices were between 1.03 and 1.21.

Liu and Eisenberg reported the synthesis of the *t*BuA-S-4VP triblock terpolymer using anionic polymerization and the macro-monomer method [22]. *Pt*BuA macro-monomer with styryl end group was prepared by polymerizing *t*BuA with the lithium amide shown in Fig. 11. This macromonomer was polymerized with the initiator α -methylstyryllithium, produced from *s*-BuLi and α -methyl styrene. The bulky structure and the reduced nucleophilicity of the initiator were effective in suppressing the side reactions with the acrylate ester groups. However, termination reactions and broader molecular weight distributions were observed during this procedure. The living *Pt*BuA chains were subsequently used for the

sequential polymerization of styrene and 4-vinyl pyridine, leading to the desired well-defined triblock terpolymer.

2.1.2. Cationic polymerization

Water soluble ABC triblock copolymers of methyl vinyl ether (MVE), ethyl vinyl ether (EVE) and methyl tri(ethylene glycol) vinyl methyl ether (MTEGVE) were synthesized by Patrickios et al. [23] through cationic polymerization. The degree of polymerization of each block was around 20. The synthesis involved polymerization of the three monomers via sequential addition in dichloromethane with the $\text{SnCl}_4/n\text{Bu}_4\text{NCl}$ catalyst/cocatalyst system. The polymerization of MVE and EVE took place at -78°C , while the reaction temperature of MTEGVE was -20°C (Fig. 12). By changing the reaction sequence, MVE-MTEGVE-EVE, MTEGVE-MEV-EVE and EVE-MEV-MTEGVE triblock terpolymers were also synthesized. Characterization by SEC and

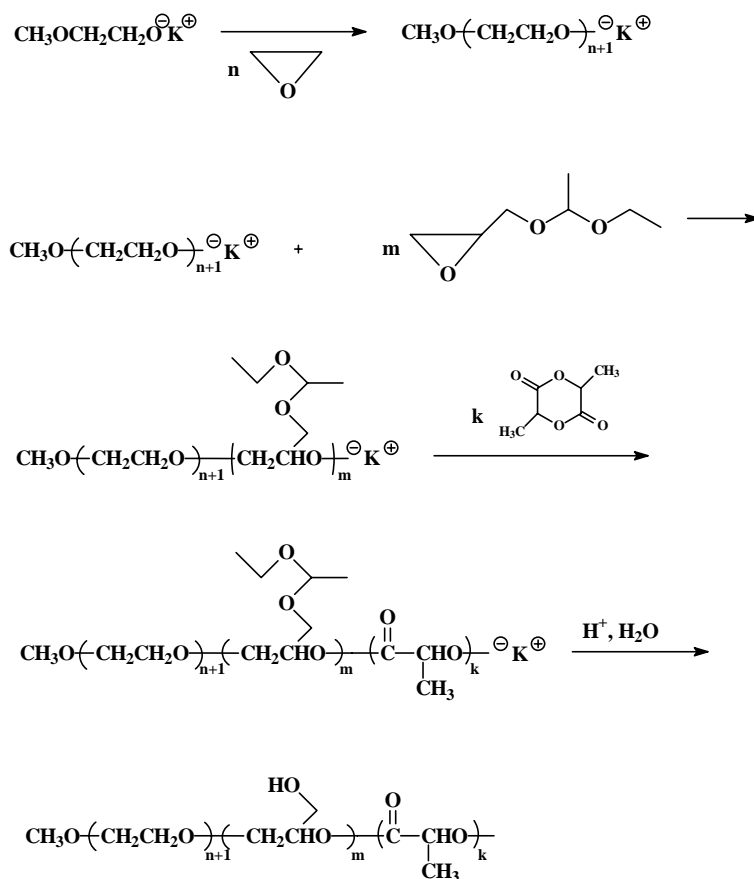


Fig. 10. Synthesis of PEO-*b*-polyglycidol-*b*-PLLA triblock terpolymers by anionic polymerization.

NMR spectroscopy revealed that the molecular weights obtained were rather low, ranging between 5030 and 6800. The polydispersity indices were close to 1.3.

2.1.3. Atom transfer radical polymerization (ATRP)

Matyjaszewski and co-workers [24] reported the synthesis of a *PtBuA-b-PS-b-PMA* triblock terpolymer by means of the three-step sequential monomer addition methodology (Fig. 13). *tert*-Butyl acrylate was polymerized first, using 2-bromopropionate/CuBr/bpy initiating system, followed by the addition of styrene and methyl acrylate. After the polymerization of each monomer, the intermediate product was isolated and purified, mainly to eliminate the unreacted monomer. Elimination of the previous monomer was a key parameter for the successful

synthesis of the terpolymers, since they were allowed to react up to 90%, in order to ensure the formation of pure blocks. The final terpolymer had a molecular weight of 24,800 and a polydispersity of 1.1, thus indicating high molecular and compositional homogeneity.

Armes and collaborators [25] used an ω -functionalized poly(propylene oxide) bromide (PPO-Br) as a macro-initiator for the ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and subsequent polymerization of methoxy-capped oligo(ethylene glycol) methacrylate (OEGM) for the preparation of PPO-PDMAEMA-POEGM terpolymer. The PPO-Br macroinitiator was prepared by reacting monohydroxy-terminated PPO with 2-bromoisobutyl bromide in the presence of triethylamine. 1,1,4,7,10,10-hexamethyltriethylenetetramine/Cu(I)Cl, in a molar

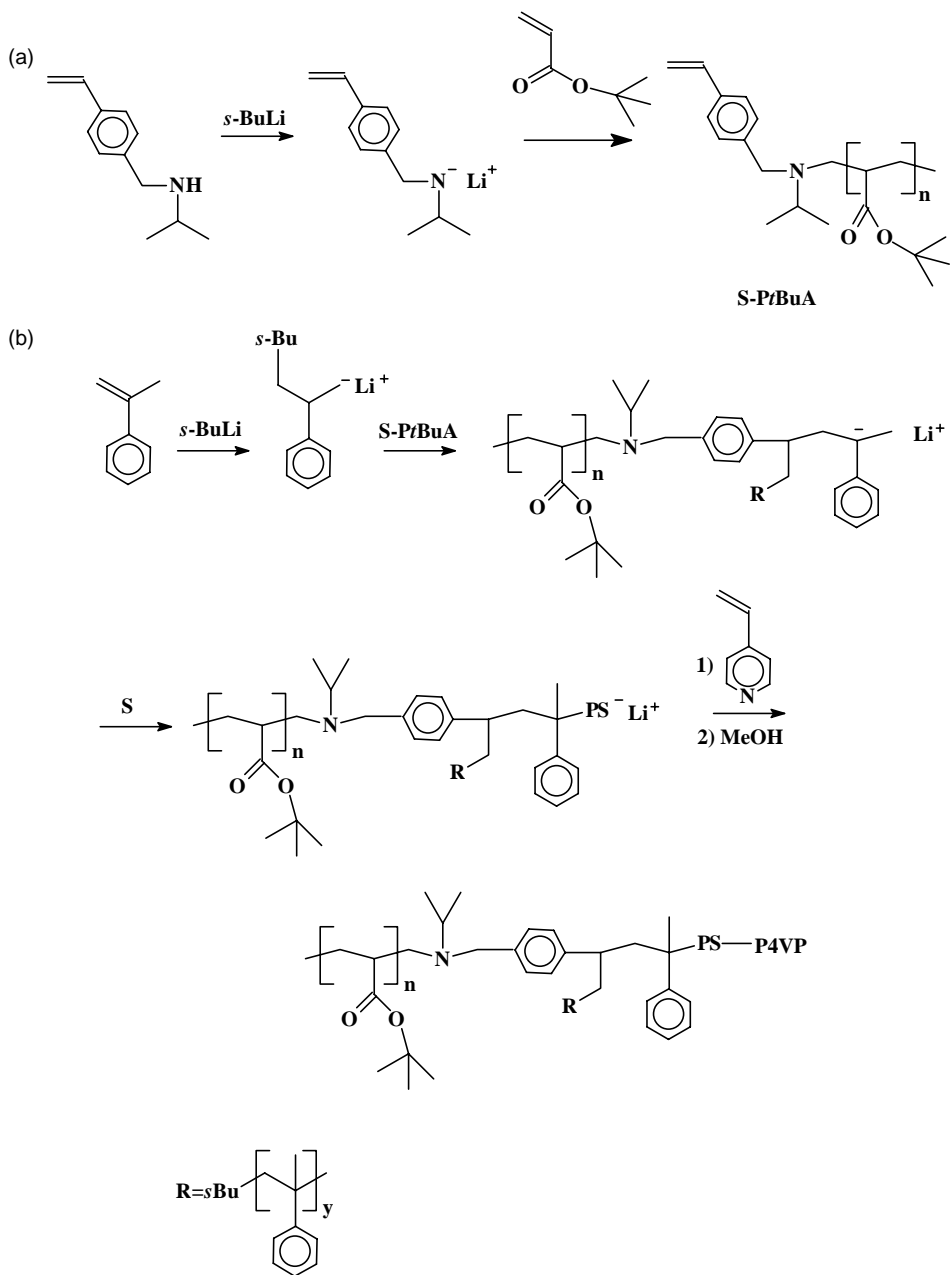


Fig. 11. Synthesis of PrBuMA-*b*-PS-*b*-P2VP triblock terpolymers by anionic polymerization.

ratio of 1:1:1 in respect to the PPO-Br species was the complementary initiating system. Characterization by SEC and NMR spectroscopy revealed a terpolymer molecular weight of 25,000 and a polydispersity index of 1.20 (Fig. 14).

Armes and co-workers [26,27] used the same methodology to synthesize poly(ethylene oxide)-*b*-glycerol monomethacrylate-*b*-2-(diethylamino)ethyl methacrylate and poly(ethylene oxide)-*b*-hydroxyethyl methacrylate-*b*-2-(diethylamino)ethyl

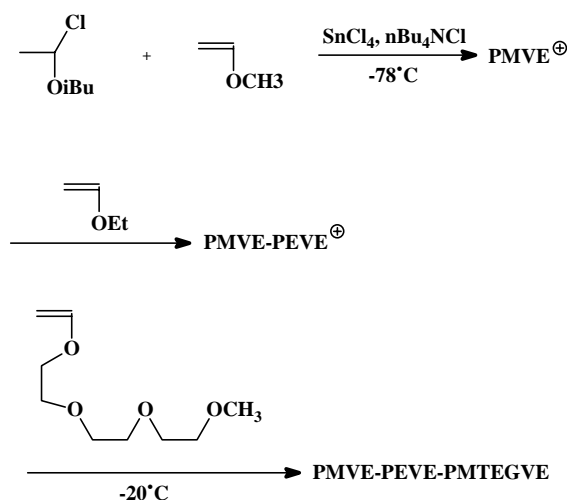


Fig. 12. Synthesis of PMVE-*b*-PEVE-*b*-PMTEGVE triblock terpolymers by cationic polymerization.

methacrylate triblock terpolymers, as well as poly(ethylene oxide)-*b*-2-(dimethylamino)ethyl methacrylate-*b*-2-(diethylamino)ethyl methacrylate via ATRP, without resorting to protecting group chemistry. The polymerization was performed under nitrogen atmosphere, at room temperature. The polydispersity indices obtained by SEC was ranged between 1.17 and 1.23, and the composition of the terpolymers was obtained by NMR spectroscopy.

Poly(ethylene oxide) bromide (PEO-Br) was employed as a macroinitiator for the successive polymerization of 2-(diethylamino)ethyl methacrylate, DEA, and 2-hydroxyethyl methacrylate, HEMA, to afford PEO-*b*-PDEA-*b*-PHEMA triblock terpolymers [28]. PEO macroinitiator and PEO-*b*-PDEA diblock copolymer impurities were removed by

precipitation in excess *n*-hexane. SEC analysis revealed the presence of ashoulder at the higher molecular weight range and a molecular weight distribution equal to 1.20. The products were transformed to PEO-*b*-PDEA-*b*-PSEMA, where PSEMA is poly(succinyloxyethyl methacrylate), by the transesterification reaction of the hydroxyl groups of the HEMA blocks with succinic anhydride in anhydrous pyridine at 20 °C.

2.1.4. Group transfer polymerization

Patrickios et al. [29] reported the synthesis of ABC triblock terpolymers of DMAEMA, MMA (or phenyl methacrylate, PEMA) and methacrylic acid (Fig. 15), with the last block being derived from postpolymerization deprotection of trimethylsilylmethacrylate (TMSMA) or tetrahydropyranyl methacrylate (THPMA), by means of a sequential three-step addition of monomers. The initiator used was 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-pentene, and tetrabutylammonium biacetate served as the catalyst. The methacrylic acid precursor block was always formed last, and the non-ionic block (PMMA) was always used as the middle block. The polymers obtained exhibited relatively narrow molecular weight distributions but rather low molecular weights.

In a subsequent work, Patrickios et al. [30] described the synthesis of ABC, ACB and BAC triblock terpolymers of MMA, DMAEMA and THPMA. The length of each block was around 12 monomeric units in all cases, and the block sequence was varied in order to synthesize different topological isomers, as shown in Fig. 16. The polydispersities of the low molecular weight terpolymers were rather low and the compositions determined by NMR were in good agreement with those theoretically expected.

More recently, Patrickios et al. [31] synthesized ABC triblock methacrylate terpolymers, where A, B, C are hexa(ethylene glycol) methacrylate, MMA, and DMA, respectively, by the sequential addition methodology in THF at temperatures ranging between 26 and 37.8 °C, depending on the monomer. SEC characterization revealed that the terpolymers had relatively low polydispersity indices, and the composition expected from stoichiometry agreed with that obtained by NMR spectroscopy. A series of ABC, ACB and BAC triblock terpolymers, where A, B, C are benzyl methacrylate, BzMA, DMA and

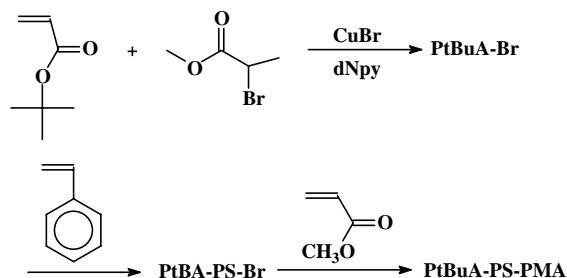


Fig. 13. Synthesis of PtBuA-*b*-PS-*b*-PMA triblock terpolymers by ATRP.

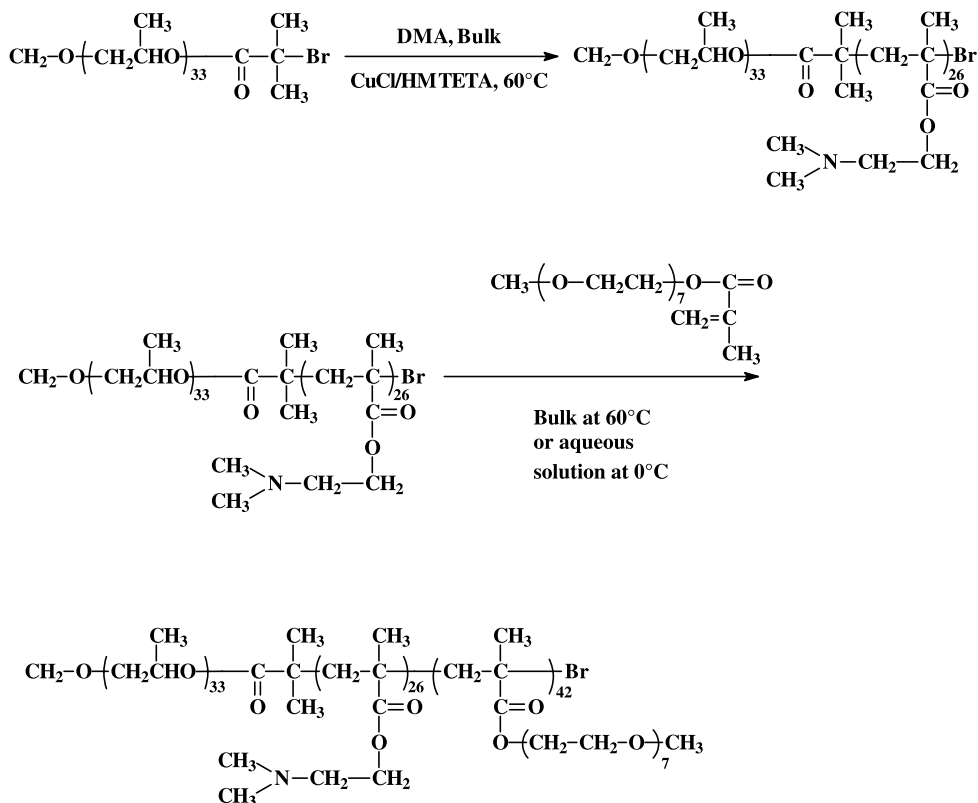


Fig. 14. Synthesis of PPO-*b*-PDMAEMA-*b*-POEGM triblock terpolymers by ATRP.

methoxyhexa(ethylene glycol) methacrylate, respectively, was also synthesized by the same author [32]. Low molecular weight polymers of narrow molecular weight distributions were obtained.

Triblock terpolymers of poly(2-ethylhexyl acrylate)-*b*-poly(methyl methacrylate)-*b*-poly(acrylic acid) were also synthesized by Kriz et al. [33]. The synthetic approach involved the sequential polymerization of 2-ethylhexyl acrylate, MMA and *tert*-butyl acrylate. Hydrolysis of the poly(*tert*-butyl acrylate) block resulted in the final triblock terpolymer.

2.1.5. Combination of different polymerization methods

Different polymerization methods can be combined for the synthesis of terpolymers containing blocks that cannot be produced by the same polymerization technique. An interesting example is the preparation of poly(ethylene oxide)-

b-poly(dimethylsiloxane)-*b*-poly(2-methyloxazoline), PEO-*b*-PDMS-*b*-PMOXA triblock terpolymers [34]. Poly(ethylene oxide) monomethyl ether was transformed to the corresponding alcoholate using potassium hydride in THF in the presence of 18-crown-6. The resulting living anion promoted the anionic ring opening polymerization of octamethyltetracyclosiloxane, *D*₄. The living diblock was then terminated with methacryloyloxydimethylchlorosilane. The macromonomer, thus produced, was purified by column chromatography and ultrafiltration. The ester end group was reduced to the corresponding alcohol and the ring opening cationic polymerization of MOXA was initiated in the presence of Et₃N and CF₃SO₃H at 0°C. Unfortunately, no molecular characterization data were provided.

Combination of anionic and ATRP polymerization methods were employed by Matyjaszewski and collaborators for the synthesis of ABC triblock terpolymers containing PS, PDMS and poly(meth)

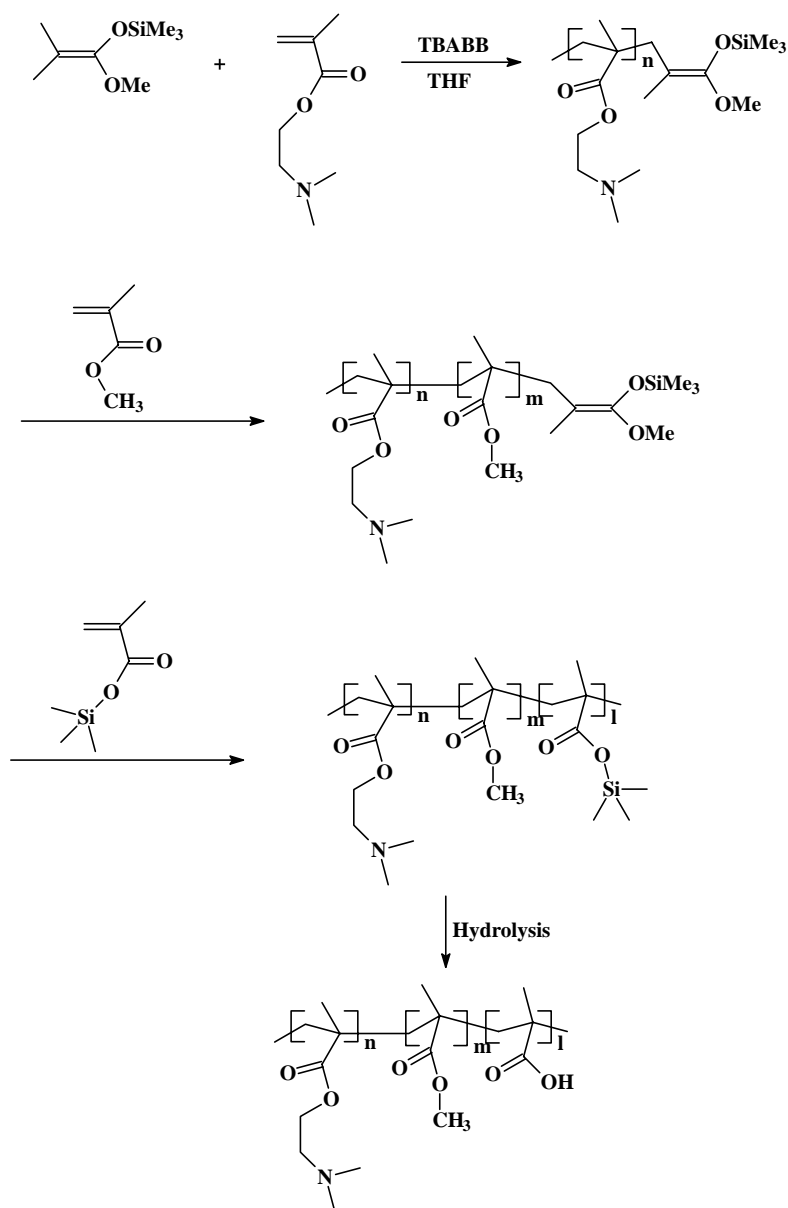
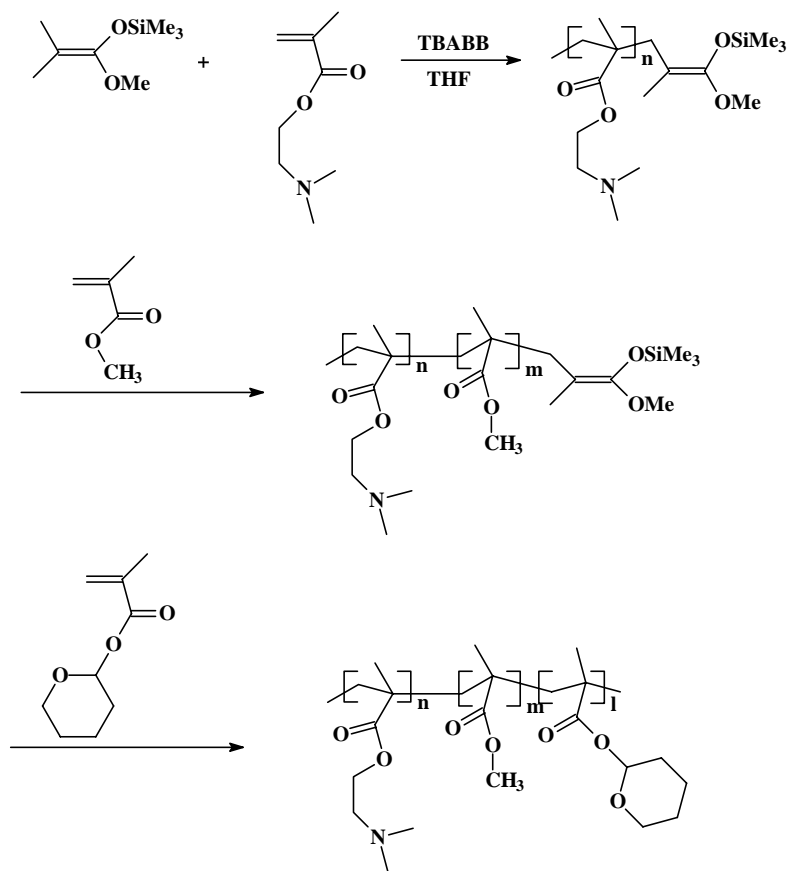
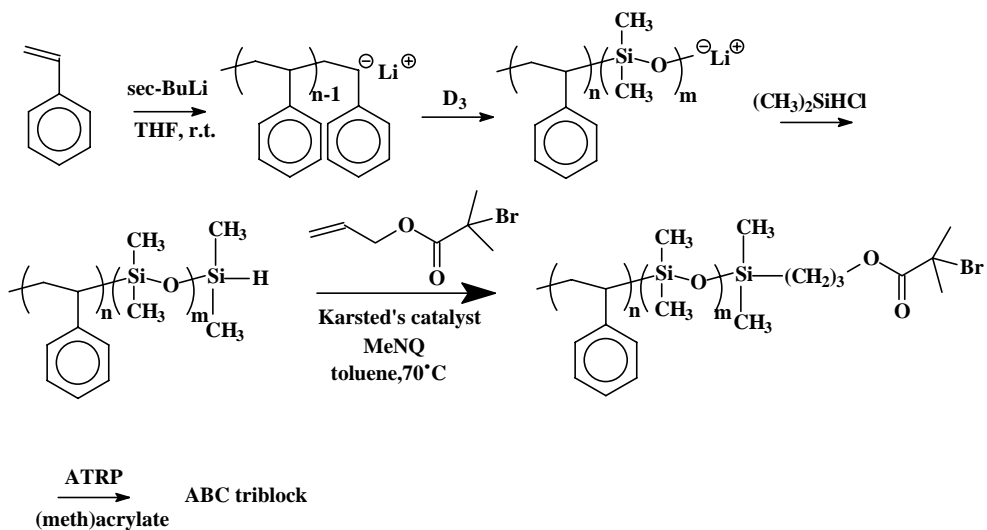


Fig. 15. Synthesis of PDMAEMA-*b*-PMMA-*b*-PMA triblock terpolymers by GTP.

acrylate blocks (Fig. 17). PS-*b*-PDMSLi living diblock copolymers were prepared anionically by sequential addition of monomers and were subsequently terminated with dimethylchlorosilane. The hydrosilyl-end functions were subjected to hydrosilylation reaction with allyl 2-bromoisobutyrate in toluene using the Karstedt catalyst [bis(1,3-divinyl-

1,1,3,3-tetramethyl-disiloxane)platinum complex] in the presence of 2-methyl-1,4-naphthoquinone, MeNQ. The 2-bromoisobutyrate end-fragment was then used for the growth of a third block by ATRP. Specifically, *n*-butyl acrylate, BuA was polymerized using CuBr/4,4'-di-*n*-nonyl-2,2'-bipyridine (*dn*Nbpy) as the catalyst/ligand system to

Fig. 16. Synthesis of PDMAEMA-*b*-PMMA-*b*-PTHMPMA triblock terpolymers by GTP.Fig. 17. Synthesis of PS-*b*-PDMS-*b*-PMEMA triblock terpolymers by anionic polymerization and ATRP.

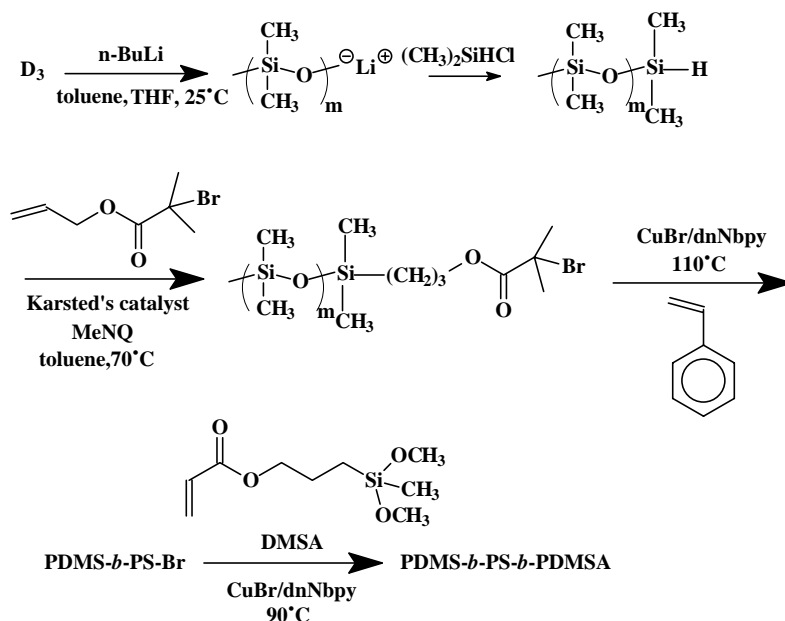


Fig. 18. Synthesis of PDMS-*b*-PS-*b*-PDMSA triblock terpolymers by anionic polymerization and ATRP.

provide PS-*b*-PDMS-*b*-PBuA triblock terpolymers. The polymerization of MMA was conducted using a mixed CuCl/CuBr catalyst and the same ligand [35]. The synthetic procedure was monitored by SEC and NMR techniques. Products of rather low molecular weight (around 10,000) and relatively narrow molecular weight distribution ($M_w/M_n = 1.2$) were obtained.

A similar procedure was adopted for the synthesis of PDMS-*b*-PS-*b*-PDMSA triblock terpolymers, where DMSA was 3-(dimethoxymethylsilyl)propyl acrylate (Fig. 18) [36]. PDMS carrying hydrosilyl functional end-groups was prepared by anionic polymerization and termination of the living polymer with dimethylchlorosilane. Hydrosilylation reaction was then performed to provide PDMS chains with 2-bromoisobutyryl bromide end-functions. Subsequent ATRP of St and DMSA with CuBr/dnNbpy provided the desired terpolymer. The molecular weight distribution of the intermediate PDMS-*b*-PS was rather broad ($M_w/M_n = 1.38$). The corresponding value for the final product was not reported. These ABC terpolymers were then grafted onto silicon wafers through the interaction with the PDMSA blocks. A remarkable change of the morphological

behavior was obtained when the brushes were treated in different solvents. After rinsing the wafers with toluene, a good solvent for both PDMS and PS blocks, the surface morphology was governed by the PS chains, due to the low PDMS content and the covalent bonding of the PDMSA blocks to the oxide layer of the wafer. The same behavior was obtained when the wafers were treated with MeOH a non-solvent for both PDMS and PS blocks. The surface morphology of the brushes was dramatically changed when they were immersed in hexane, a good solvent for PDMS and non-solvent for PS. The PS segments were collapsed allowing the PDMS chains to rise to the surface of the wafers.

2.2. Star-shaped ABC miktoarm terpolymers

2.2.1. Anionic polymerization

The term 'miktoarm' has been attributed to star polymers with three or more arms, at least two of which are molecularly and chemically different. The term mikto is coming from the Greek word μικτός, meaning mixed.

Isono et al. [37] synthesized 3-miktoarm star terpolymers of S, DMS and *t*BuMA by using the

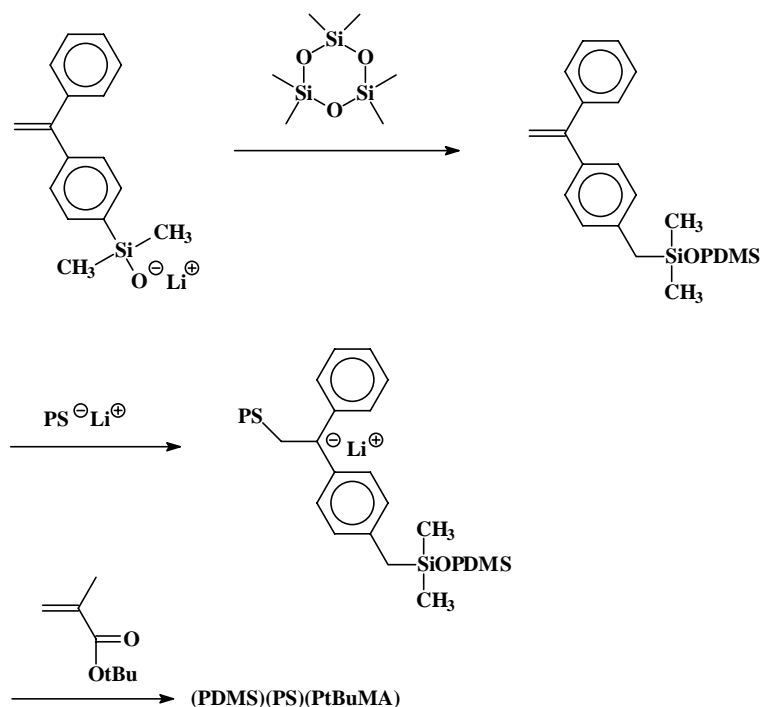


Fig. 19. Synthesis of (PDMS)(PS)(PtBuMA) miktoarm star terpolymers by anionic polymerization.

lithium salt of *p*-(dimethylhydroxy)silyl- α -phenyl styrene as the initiator for the polymerization of hexamethylcyclotrisiloxane. The vinyl terminated PDMS subsequently reacted with PSLi, and the resulting macromolecular in-center initiator was then used for the polymerization of *tert*-butyl methacrylate, to give the desired miktoarm star (Fig. 19).

ABC miktoarm stars containing PS, PI and PBd were synthesized by Hadjichristidis and co-workers [38] according to the procedure shown in Fig. 20. The first step involved the addition of living PI arms to excess SiMeCl_3 , followed by elimination of the excess SiMeCl_3 and titration of $\text{PI-Si}(\text{CH}_3)\text{Cl}_2$ with the living PSLi arms. The linking reaction was monitored by SEC. Finally, excess living PBd arms reacted with the resulting $(\text{PI})(\text{PS})\text{Si}(\text{CH}_3)\text{Cl}$ to give the miktoarm star $(\text{PS})(\text{PI})(\text{PBd})$. More recently, Hadjichristidis et al. [39] prepared 3-miktoarm stars of PS, PI and PDMS, as well as miktoarm stars of PS, PI and P2VP [40] with the same methodology. In a slightly modified procedure, the same group [41] prepared ABC miktoarm stars of PS, PI and PMMA.

The synthetic scheme involved the synthesis of the $(\text{PS})(\text{PI})\text{Si}(\text{CH}_3)\text{Cl}$ in a hydrocarbon solvent (Fig. 20), and its subsequent reaction with a dianion formed from 1,1-diphenylene and Li in THF (Fig. 21). Due to the stoichiometry used, only one of the two anions reacted with the Si–Cl group, producing a sterically hindered reactive anionic site for the polymerization of MMA at low temperatures, leading to the formation of the third arm.

The synthesis of three series of different ABC miktoarm star terpolymers was reported by Dumas and collaborators [42]. In the first and second series,

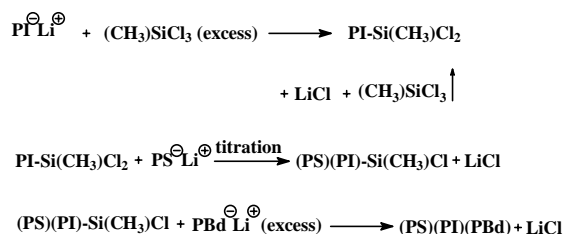


Fig. 20. Synthesis of (PS)(PI)(PBd) miktoarm star terpolymers by anionic polymerization.

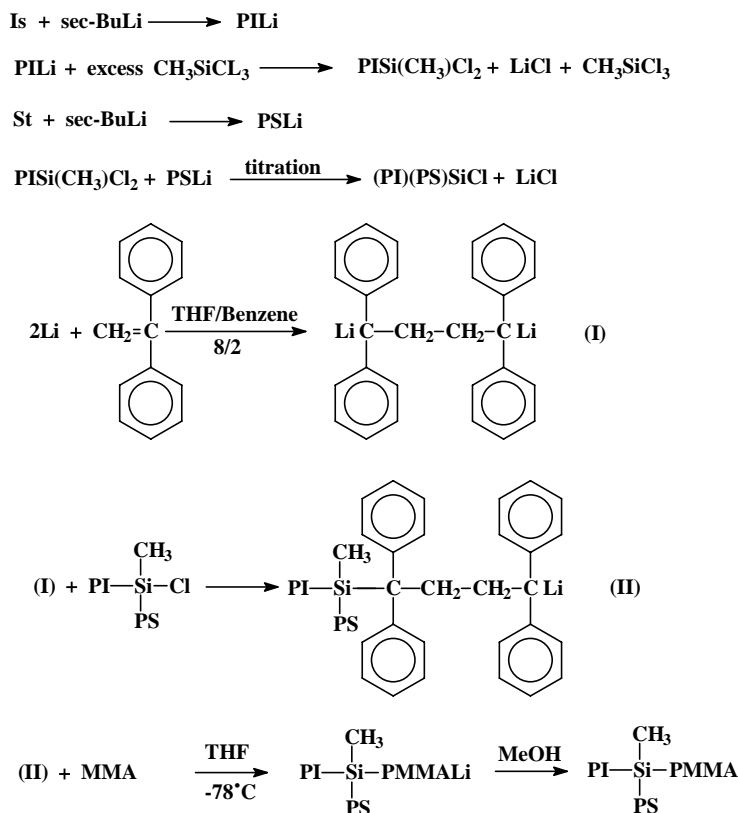


Fig. 21. Synthesis of (PS)(PI)(PMMA) miktoarm star terpolymers by anionic polymerization.

A was PS, B was PEO and C was either poly(ϵ -caprolactone) (Fig. 22) or poly(L-lactide), while in the third A was PS, B was PMMA and C was PEO. Living arm A (PS in all cases) was obtained by using cumyl potassium as the initiator, which was subsequently reacted with the double bond of (1-[4-(2-*tert*-butyldimethylsiloxy)ethyl]phenyl-1-phenylene) to give living PS end-functionalized with a protected –OH group. After deprotection of the –OH group, reaction with diphenylmethyl sodium afforded the sodium alcoholate, which served as the initiating site for the polymerization of the third arm, either ϵ -caprolactone or the L-lactide. For the synthesis of the (PS)(PMMA)(PEO) miktoarm star, the same synthetic procedure was followed, with MMA and EO instead of EO and ϵ -caprolactone. Dumas et al. [43] also synthesized a series of (PS)(*Pt*BuMA)(PEO) miktoarm star terpolymers with the same methodology. The molecular characterization indicated

relatively low polydispersity indices (~ 1.2) thus implying high degree of molecular and compositional homogeneity.

Stadler and collaborators [44] using the DPE methodology were able to synthesize (PS)(PBd)(PMMA) miktoarm terpolymers. DPE-capped living PS, formed from PSLi and DPE, reacted with bromomethyl-substituted DPE to produce a polymer with a diphenyl-substituted vinyl group at one end. PBdLi addition to the double bond led to a PS–PBd diblock copolymer with an in-center anionic living site, which was subsequently used for the polymerization of MMA to afford the ABC stars. The same synthetic approach was used for the synthesis of ABC miktoarm stars of PS, PBd, and poly(2-vinylpyridine).

In an extension of the methodology involving DPE derivatives, Hirao and collaborators [45,46] reported the preparation of chain-end and in-chain

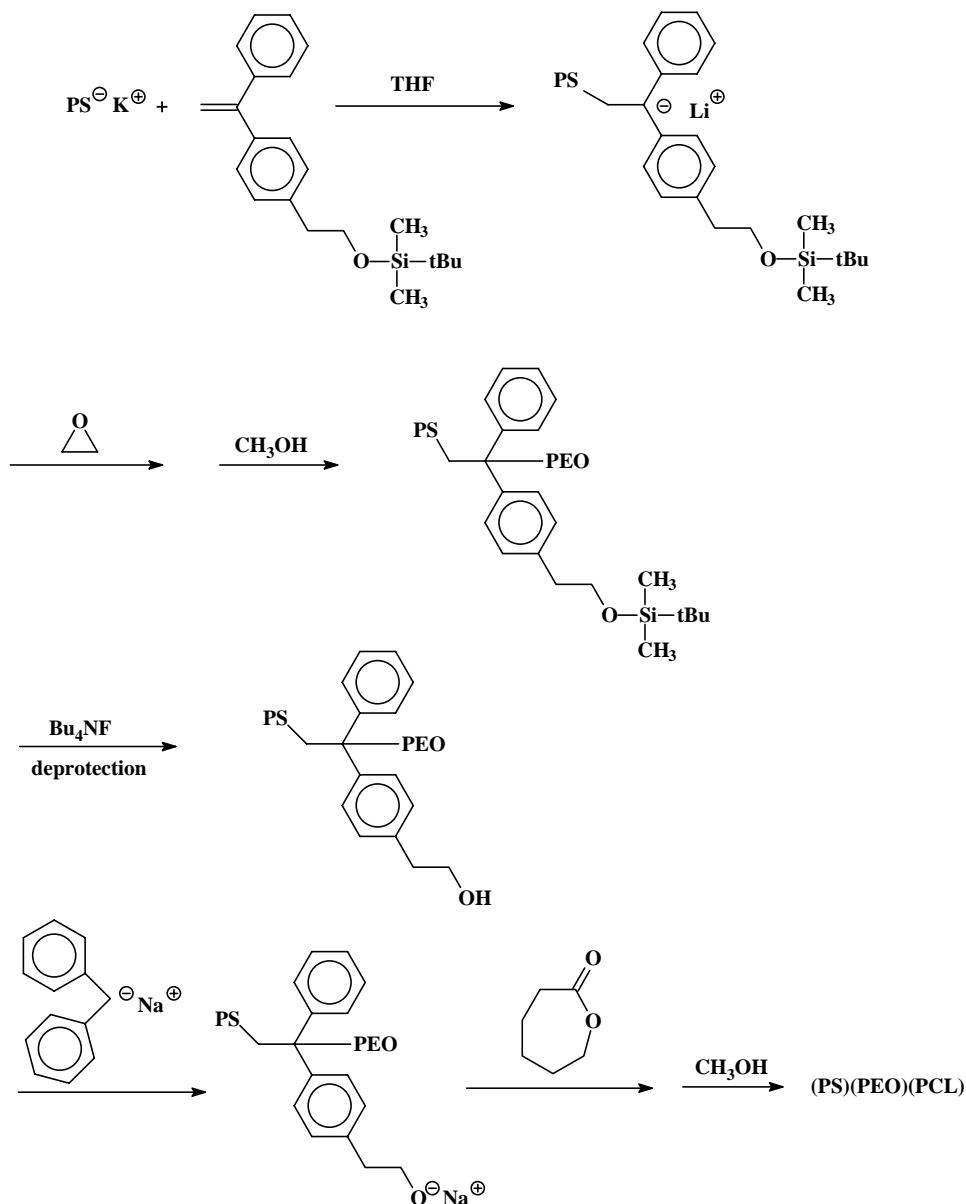


Fig. 22. Synthesis of (PS)(PEO)(PCL) miktoarm star terpolymers by anionic polymerization.

functionalized polymers with a definite number of chloromethylphenyl or bromomethylphenyl groups as well as their utilization in the synthesis of miktoarm star polymers. According to Hirao's synthetic strategy, a macro-anion is reacted with a DPE derivative with two methoxymethyl groups at the meta positions of the phenyl rings (Fig. 23). After deactivation with

methanol, the methoxymethyl groups can be converted quantitatively to chloromethyl groups (CMP) by reaction with BCl_3 . These CMP groups can serve as linking sites to other living polymeric chains. Using CMP-functionalized polystyrenes, along with appropriate DPE derivatives, a variety of miktoarm star terpolymers of the ABC_2 , ABC_4 and AB_2C_2 were

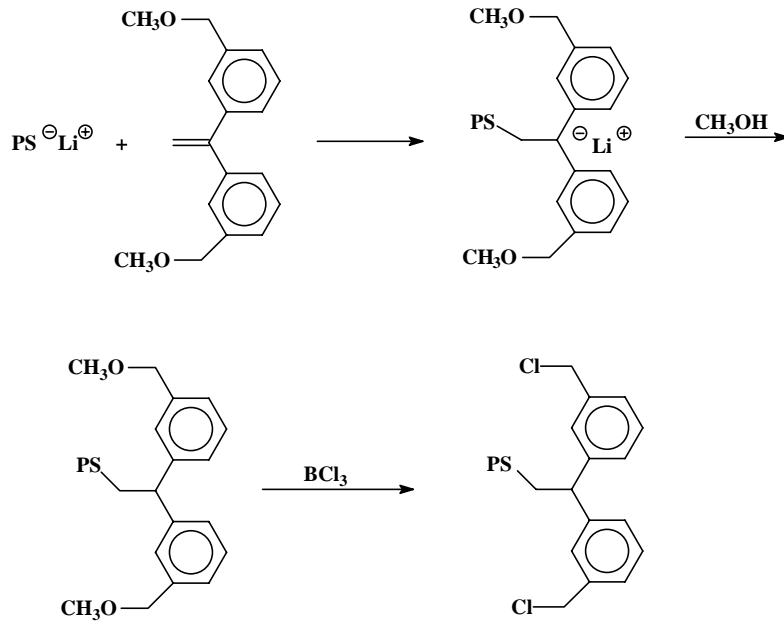


Fig. 23. Synthesis of PS chains with two chloromethylphenyl groups at the same chain end.

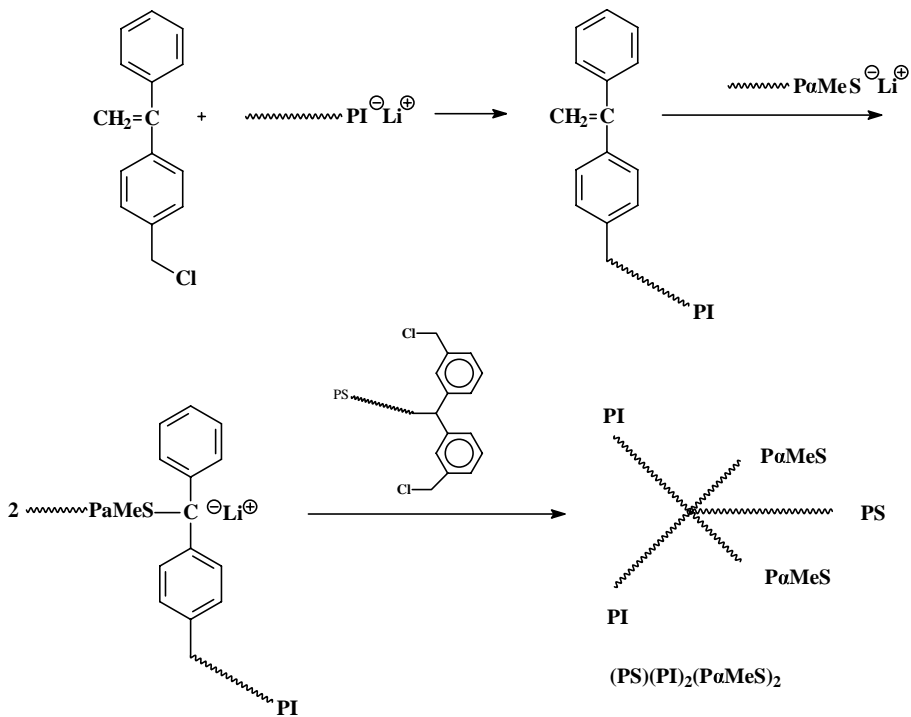


Fig. 24. Synthesis of (PS)(PI)₂(PaMeS)₂ miktoarm star terpolymers by anionic polymerization.

synthesized, where A, B and C are PS, PI and poly(α -methylstyrene) (P α MeS), respectively. The reactions used for the synthesis of AB₂C₂ are given in Fig. 24, as an example.

2.2.2. Reversible addition-fragmentation chain transfer (RAFT) polymerization

Pan et al. [47] synthesized (PS)(PMA)(PEO) and (PS)(PNIPAM)(PEO) miktoarm star terpolymers, where PNIPAM is poly(*N*-isopropylacrylamide) (Fig. 25). By using RAFT polymerization, a PS with a terminal dithio group was synthesized, which was subsequently reacted with excess maleic anhydride. The PS with terminal anhydride and dithio group, was used as the macroinitiator of the second monomer, i.e. either methyl acrylate or *N*-isopropylacrylamide. Finally, the anhydride group of maleic anhydride was reacted with the –OH group of PEGM to produce the third arm as indicated in Fig. 25. The synthesis of

the miktoarm stars was monitored by NMR spectroscopy and SEC. The polydispersity indices of the final terpolymers were between 1.12–1.18.

2.2.3. Combination of different polymerization methods

By using a combination of RAFT and ring opening polymerization (ROP), Pan et al. [48] synthesized (poly(ethylene oxide) methyl ether) (polystyrene)(poly(L-lactide)) ((MPEO)(PS)(PLLA)) 3-miktoarm star terpolymers. The synthetic approach involved the reaction of the ω -functionalized –OH group of the poly(ethylene-oxide) methyl ether with maleic anhydride under conditions where only one hydroxyl group could be esterified. The double bond of the maleic group was then reacted with dithiobenzoic acid, resulting a dithiobenzoic terminated MPEO. The second carboxyl group of the maleic anhydride was

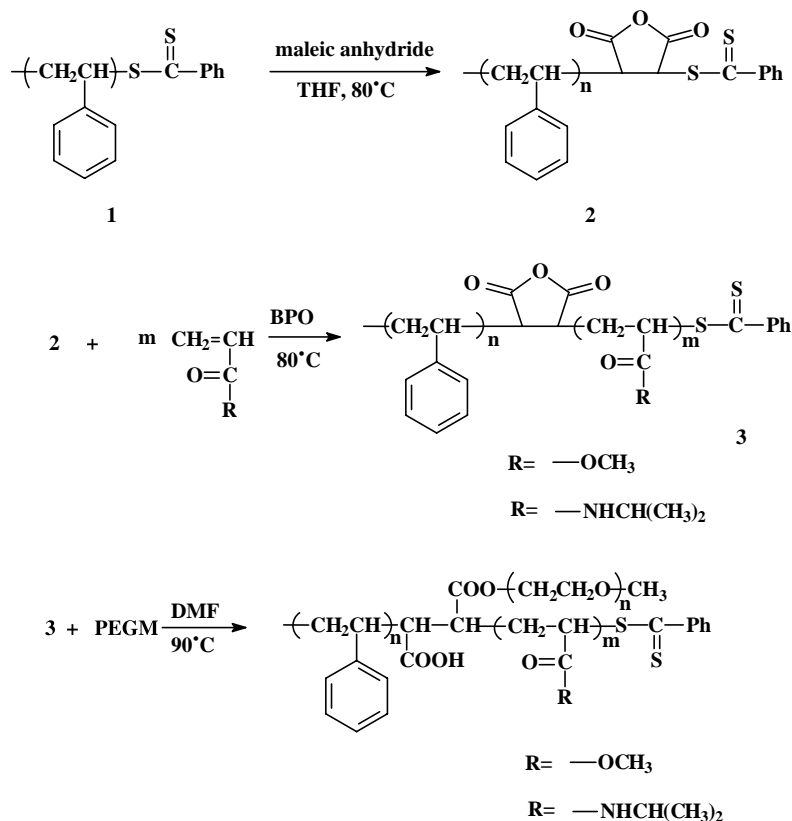


Fig. 25. Synthesis of (PS)(PMA)(PEO) and (PS)(PNIPAM)(PEO) miktoarm star terpolymers by RAFT.

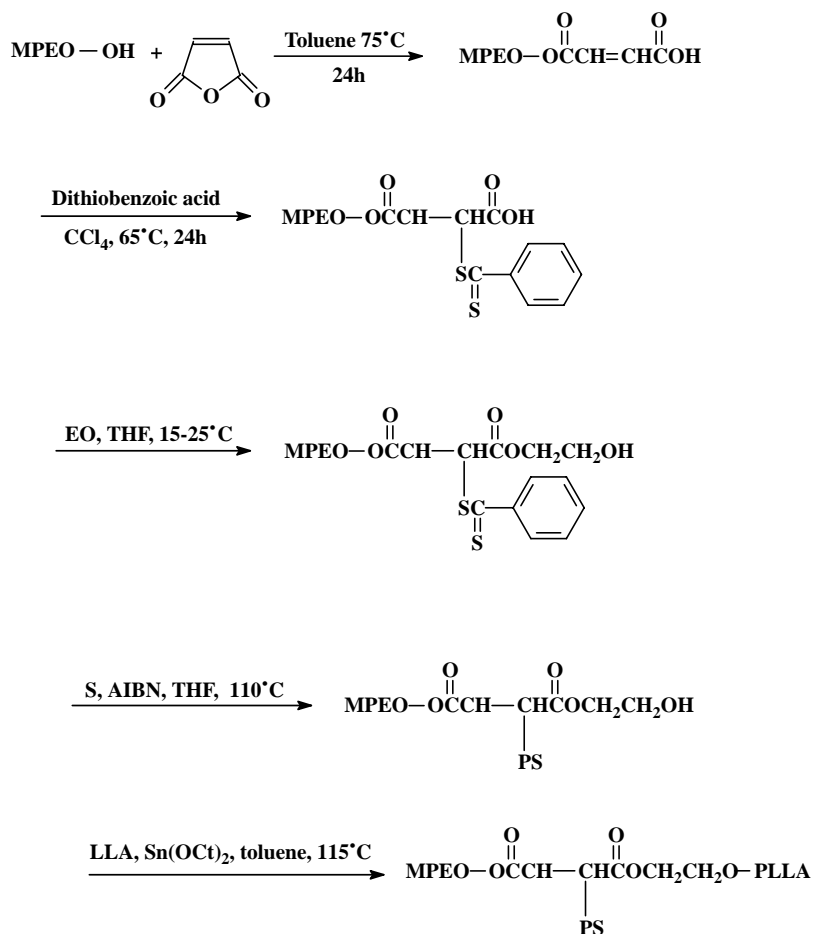


Fig. 26. Synthesis of (MPEO)(PS)(PLLA) miktoarm star terpolymers by RAFT and ROP.

then reacted with ethylene oxide, leading to the corresponding ester with a free $-\text{OH}$ group. The dithiobenzoic group of the MPEO was used for the RAFT polymerization of styrene in THF, at 110°C , and AIBN as the initiator. Finally, the $-\text{OH}$ group attached at the junction point of the diblock copolymer was used as the initiating site for the ROP of L-lactide, in the presence of $\text{Sn}(\text{Oct})_2$ in toluene at 115°C (Fig. 26). The intermediate products along with the final terpolymers were characterized by SEC and NMR spectroscopy. The polydispersity indices of the intermediate along with the final products were between 1.05 and 1.07, indicating a high degree of molecular and compositional homogeneity.

Pan et al. [49] by using a combination of RAFT and cationic ROP, synthesized a series of [poly(methyl methacrylate)][poly(1,3-dioxepane)](polystyrene) 3-miktoarm star terpolymers. The synthetic approach involved the synthesis of PS functionalized with a dithiobenzoate group, by using RAFT polymerization, and subsequent reaction of this group with hydroxyethylene cinnamate, in THF (Fig. 27). The hydroxyl group served as the initiating site for the cationic ring opening polymerization of 1,3-dioxepane in the presence of triflic acid. Finally, the diblock copolymer with the dithiobenzoate group situated between the two blocks was used for the reversible addition-fragmentation transfer polymerization of methyl methacrylate. The miktoarm star terpolymers were characterized by NMR spectroscopy and SEC.

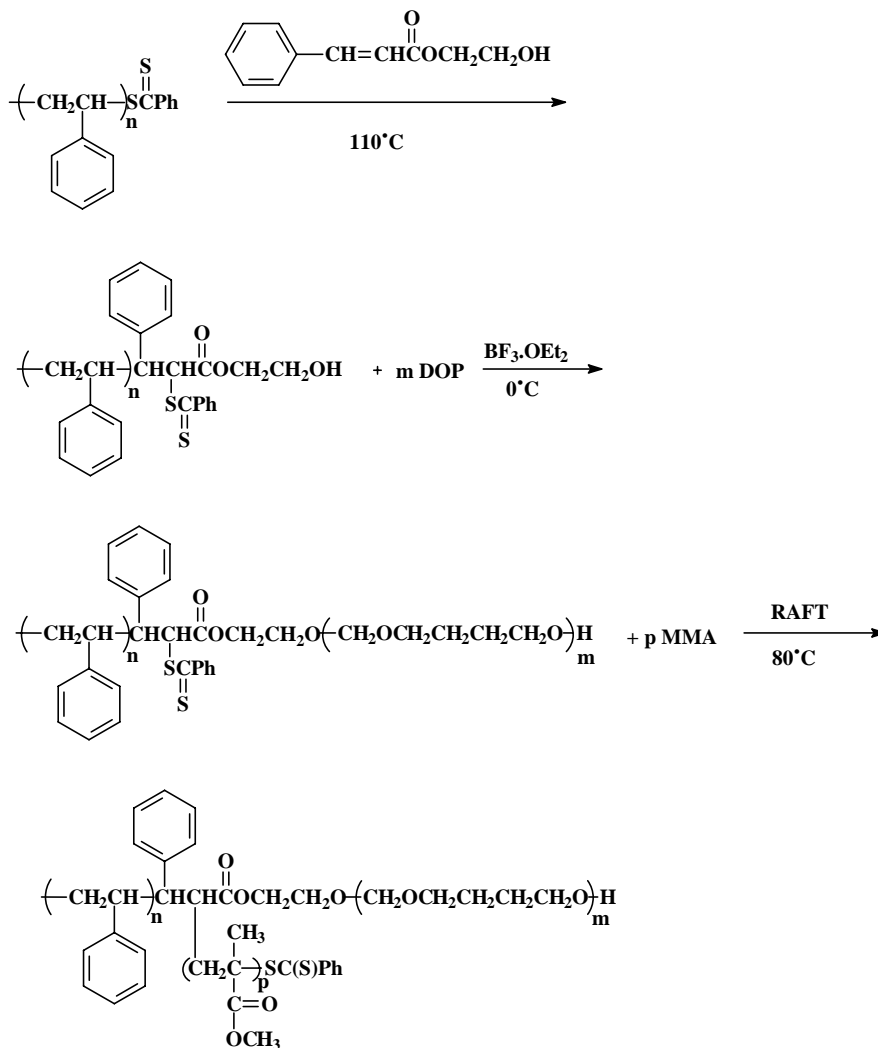


Fig. 27. Synthesis of (PMMA)(PDOP)(PS) miktoarm star terpolymers by RAFT and ROP.

Pan et al. [50] also synthesized (polytetrahydrofuran)[poly(1,3-dioxepane)] (polystyrene), (PTHF)(PDOP)(PS), 3-miktoarm stars via a combination of cationic ROP (CROP) and ATRP. The star terpolymers were synthesized by using two different functional groups, carboxylic acid and CHBr, which can be initiating sites of the two different polymerizations. These two groups were introduced at one end of the polytetrahydrofuran chain, through the reaction of $-\text{OH}$ functionalized PTHF with 2-bromosuccinic

anhydride. The $-\text{COOH}$ group was transformed to COCl group, which with AgClO_4 served to form the second arm by CROP. Finally, the remaining Br initiated the ATRP of styrene (Fig. 28). The reactions used are shown in Fig. 26. The intermediate diblocks along with the final terpolymers were characterized by NMR and SEC. The relatively large polydispersity indices of the terpolymers obtained (1.49–1.54), indicate that the final terpolymers contain some amount of unreacted diblock and PTHF precursors.

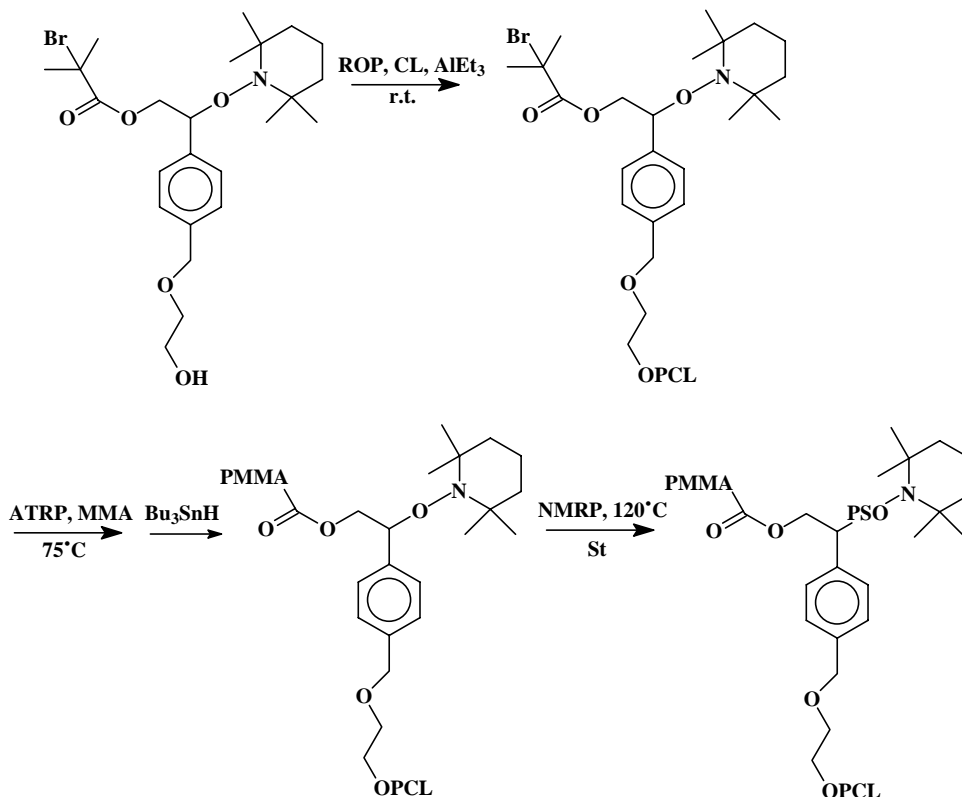


Fig. 29. Synthesis of (PS)(PMMA)(PCL) miktoarm star terpolymers by ATRP and ROP.

that the final cyclic terpolymers exhibited high molecular and compositional homogeneity.

3. Self-assembly of ABC triblock terpolymers in solution

3.1. Introduction

The self-assembly of simple diblock copolymers (AB) in solvents selective for one of the blocks has been investigated extensively for several decades. As a result a plethora of nanostructures ranging from spherical star-like core–corona micelles to crew-cut, cylindrical and compound micelles and vesicle have been identified [54–58]. The solution self-assembly of ABC triblock terpolymers has attracted the interest of investigators only in the last decade thanks to their successful synthesis. Although, less attention has been

paid to the ABC self-organization in solution than in bulk the potential for nanostructure formation in selective solvents is enormous. The presence of three different components (blocks) in the same molecule results in (i) the increase in the number of block/selective solvent combinations (especially if binary or ternary solvent systems are used in order to tune solvent selectivity), (ii) the increase of macromolecular topological isomers. i.e. macromolecular architecture, (iii) the increase in the number of possible arrangements of the different chains in the micelles due to the steric constraints and energetic/entropic requirements imposed by the presence of a third block. In linear ABC terpolymers, some, rather simple, micellar structures which have been anticipated from the solvent's selectivity towards each block include (i) mixed corona micelles, if the solvent is selective for both blocks, (ii) core–shell–corona micelles, if the solvent is selective only for one of the end blocks,

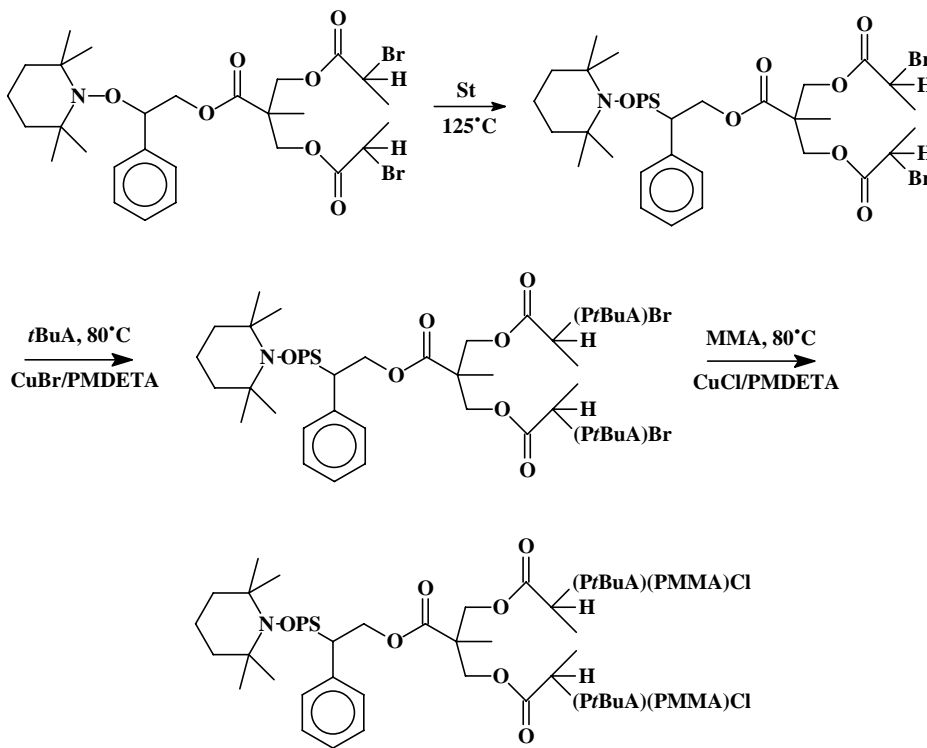


Fig. 30. Synthesis of (PS)(PtBA)₂(PMMA)₂ miktoarm star terpolymers by ATRP and NMRP.

(iii) core-inner corona-outer corona micelles, if the solvent is selective for the middle block and one of the end blocks (Fig. 32). Other more complicated and less predictable structures have also been observed, and will be discussed below.

3.2. Self-organization in organic solvents

Compared to the investigation of ABC self-assembly in aqueous media, those addressing the self-assembly in organic solvents are very few.

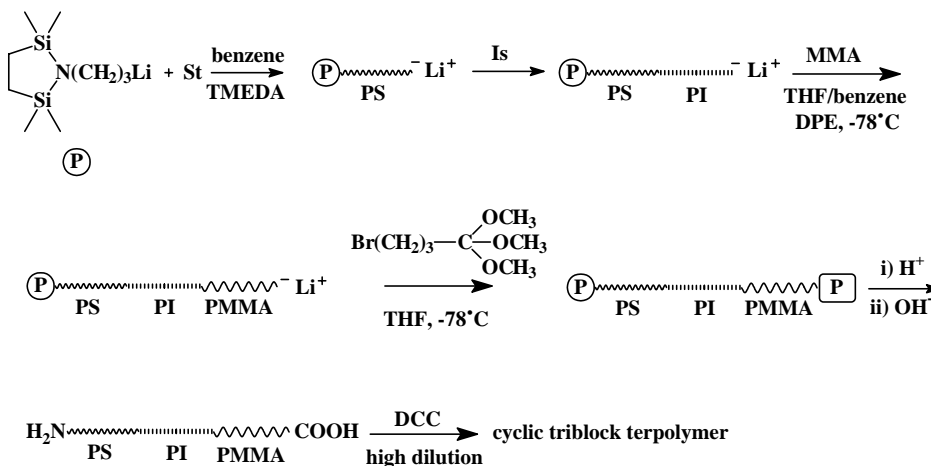


Fig. 31. Synthesis of PS-*b*-PI-*b*-PMMA cyclic terpolymers by anionic polymerization.

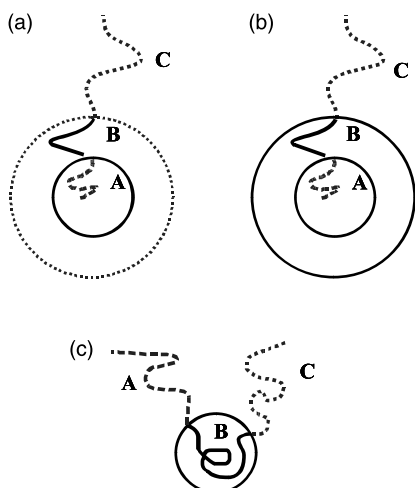


Fig. 32. Three possible spherical micellar structures from ABC triblock terpolymers (a) core-inner corona-outer corona micelles (or two layer corona micelle) in a solvent selective for blocks B and C; (b) core-shell-corona micelles in a solvent selective for block C; (c) mixed corona micelles in a solvent selective for blocks A and C. The conformation of one terpolymer chain is depicted for clarity.

Tsitsilianis and Sfika [17] studied the formation of spherical micelles from poly(styrene-*b*-2-vinylpyridine-*b*-methyl methacrylate) triblocks in toluene, a bad solvent for poly(2-vinylpyridine), by light scattering, viscometry and TEM. Mixed corona micelles were formed and were termed heteroarm star-like micelles due to their similarity to A_nB_n heteroarm (or miktoarm) star copolymers. Their aggregation number and size were found to depend mainly on the molecular characteristics of both the insoluble and soluble blocks. Comparison with the micelles formed from PS-P2VP diblock copolymer, of similar molecular characteristics, revealed that the terpolymers form micelles of lower aggregation number due to the presence of the second end block.

Poly(ferrocenylphenylphosphine-*b*-ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFP-PFS-PDMS) coil-crystalline-coil triblocks were studied in hexane, a selective solvent for PDMS by Wang and collaborators [19]. Light scattering and TEM experiments showed that the terpolymer with the shorter PFP blocks formed cylindrical micelles due to the crystallization of PFS blocks. An increase in the PFP block resulted in the suppression of PFS crystallization and the formation of spherical micelles (Fig. 33). The influence of PFS crystallization on the

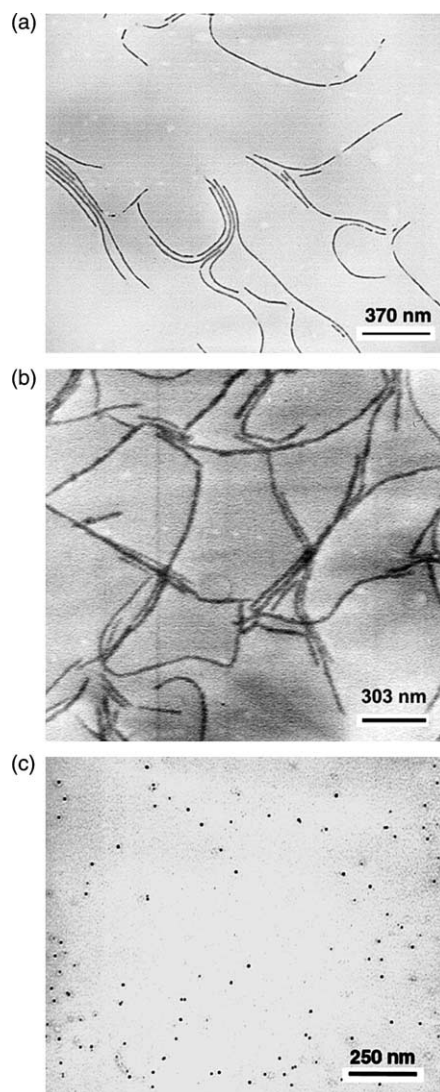


Fig. 33. TEM images from PFP_{*x*}-*b*-PFS_{*y*}-*b*-PDMS_{*z*} triblock terpolymers in hexane (*x*, *y*, *z* denote degree of polymerization). (a) PFP₁-*b*-PFS₄₀-*b*-PDMS₃₀₄, (b) PFP₆-*b*-PFS₄₅-*b*-PDMS₂₂₀, (c) PFP₁₁-*b*-PFS₅₀-*b*-PDMS₆₀₀.

shape of the triblock micelles was corroborated by SAXS measurements, confirming the existence of crystalline PFS domains only in the cylindrical micelles.

Fernyhough et al. [59] investigated the effect of solvent selectivity on the micellar characteristics of poly(styrene-*b*-isoprene-*b*-methyl methacrylate) (PS-PI-PMMA) linear triblock terpolymers in solvents

selective for the PS (DMAC) and PMMA (DMF) blocks, namely dimethylacetamide (DMAC) and dimethylformamide (DMF). Light scattering and viscosity experiments pointed to the conclusion that in DMF (non-selective for PI) spherical mixed corona micelles with high aggregation numbers and compactness were formed. The size of the micelles was controlled mainly by the molecular characteristics of the soluble blocks but the molecular weight and content of the PI insoluble block also played a role. The possibility of creating surface hetero-functionalized micelles was also considered since the triblock terpolymers used in this study had different end groups (protected amine and protected carboxyl groups) at the ends of the polystyrene and poly(methyl methacrylate) blocks.

3.3. Self-organization in aqueous media

The self-organization of triblock terpolymers in aqueous media has been studied in more detail, due to the importance of such systems for biological and technological applications and to their similarities with natural abundant macromolecular systems.

Water-soluble linear triblock terpolymers of rather low molecular weight, containing hydrophilic blocks of opposite charge have been investigated since the mid 1990s by Patrickios and co-workers as synthetic analogues for protein solution behaviour and other biological related studies [23,29,30,60]. ABCs consisting of 2-(dimethylaminoethylmethacrylate), methyl methacrylate and methacrylic acid blocks were the first to be explored [29]. Triblocks with different block sequences were compared with random terpolymers with regard to micelle formation in water. Micellization of the triblocks was found to depend on solution pH, with the hydrophobic PMMA forming part of the micellar core in all cases. Constraints imposed by the presence of two hydrophilic blocks resulted in the formation of micelles with small aggregation numbers and sizes. Random terpolymers were molecularly soluble over the entire pH range, whereas precipitation of the triblocks was observed only at the isoelectric point. At basic pH a small increase in the value of the critical micelle concentration with increasing temperature could be identified. Fluorescence measurements using pyrene as the probe showed the ability of these micelles to

solubilize hydrophobic substances. Along the same lines triblock terpolymers of methyl vinyl ether, ethyl vinyl ether and methyl tri(ethylene glycol) vinyl ether were also investigated [23]. These triblocks formed micelles in aqueous solutions containing high salt concentrations. The block sequence, under these conditions, influence the micelle size, aggregation number, micelle-unimer equilibrium and cloud points. High salt concentration also shift micelle-unimer equilibrium in favor of micelle formation.

Kriz et al. [33] studied poly(2-ethylhexyl acrylate-*b*-methyl methacrylate-*b*-acrylic acid) (PEHA-PMMA-PA) terpolymers in D_2O by NMR, SANS and light scattering. Experimental results indicated the formation of narrowly distributed spherical micelles with PEHA inner and PMMA outer core layers and PA coronas. Some intermixing between the layers was observed at the two inner-outer core and outer core–corona interfaces. About 22 mol% of the acrylic acid units were immobilized at the core–corona interface. PEHA inner cores were found to be highly swollen by small amounts of cyclohexane, a solvent selective for PEHA, thus, demonstrating the encapsulation and solubilization capabilities of these micelles.

More recently, triblock terpolymers of methyl methacrylate, 2-(dimethylamino)ethyl methacrylate and hexa(ethylene glycol) methacrylate (PMMA-PDMAEMA-PHEGMA) were found to form micelles in aqueous solutions [31]. Their sizes and cloud points were determined by the block sequence. The cloud point was found to depend on the position of the temperature sensitive PDMAEMA block. The solution properties of terpolymers based on benzyl methacrylate, 2-(dimethylamino)ethylmethacrylate and methoxyhexa(ethylene glycol)methacrylate were also studied [32]. The terpolymers were found to form micelles in dilute aqueous salt free solutions due to the presence of the hydrophobic poly(benzyl methacrylate) block. The size of the micelles depends on the sequence of the three blocks in the terpolymer. The ability of these terpolymers to act as emulsion stabilizers was also investigated.

Giebeler and Stadler [6] investigated the solution behavior of several poly(styrene-*b*-2-vinylpyridine-*b*-methacrylic acid) terpolymer samples of high molecular weight, produced by anionic polymerization and subsequent postpolymerization chemical

modification, in THF/H₂O mixtures. Potentiometric, conductometric and turbidimetric titrations indicated the presence of two equivalent points due to the presence of acidic and basic groups in the same molecule, as well as an isoelectric point. Detailed structural characterization of the supramolecular structures formed was not given.

A similar behavior was reported for triblock polyampholytes of 5-(*N,N*-dimethylamino)isoprene, styrene and methacrylic acid [15]. Dynamic light scattering and freeze-fracture TEM were used to characterize the aggregates formed by these materials. Hydrodynamic radii were in the range from 260 to 120 nm depending on the pH of the solution. TEM images and calculations based on the contour length of the chains indicate that the spherical structures observed were vesicles.

Cai and Armes, recently, studied the formation of three different core-shell micelle types from a single ABC triblock structure, poly(ethylene oxide-*b*-2-(diethylamino)ethylmethacrylate-*b*-2-(succinyloxethyl methacrylate)) (PEO-PDEA-PSEMA) [28], as a function of pH. At low pH, micellar cores were comprised of hydrogen bonded PSEMA/PEO blocks and protonated PDEA coronas. These hydrogen bonded micelles could be disrupted either by addition of methanol or by lowering the temperature of the solution. At intermediate pH, cores of an interpolyelectrolyte complex between neutralized PSEMA and PDEA blocks were formed, encapsulated in a PEO corona. Their stability was sensitive to the ionic strength of the solution due to electrostatic screening. In this case dissociation occurred above 0.15 M NaCl concentration. At higher pH values micelles having a hydrophobic PDEA core and a mixed corona of anionic PSEMA and neutral PEO chains were observed (Fig. 34).

Core-shell-corona micelles were also formed from a poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) (PS-P2VP-PEO) terpolymer in water [14]. The structure of these micelles was elucidated by light scattering in the wet state and by TEM and AFM in the dry state. Monodisperse spherical micelles were formed whose size depended on solution pH. At acidic pH (pH < 5) larger micelles with a two-layer corona were observed, due to the protonation of pyridine units. At basic pH (pH > 5) smaller two-layer core micelles were observed due to the collapse of

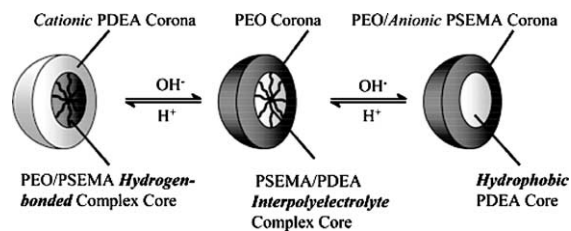


Fig. 34. Schematic representation of the types of micelles formed by PEO-PDEA-PSEMA triblock terpolymers in aqueous solution by varying pH.

the inner P2VP corona layer, as a result of pyridine deprotonation. Reproducible inter conversion of the micelles between the two states was possible through changes of pH. Isolated Au nanoparticles could be created within the micelles, after loading the P2VP shell with AuCl₄⁻ anions followed by reduction of Au.

The same group has recently shown that the morphology of the three layer PS-P2VP-PEO micelles could be tuned by changing the preparation protocol [61]. When micelles were formed in the presence of a solvent selective for PS (benzene or toluene) the micellar shape tended to change to cylindrical presumably due to the change of the volume fraction of the PS block (Fig. 35). Based on this observation and the fact that the ends of cylinders possessed a strongly spherical shape, the authors assumed that cylindrical micelles are formed by collapse of spherical micelles. This new micellar morphology was also used as a nanoreactor for the preparation of Au nanoparticles, which reside in the P2VP shell. Unfortunately, Au nanocylinders did not form.

Biodegradable-biocompatible micelles were prepared from poly(ethylene oxide-*b*-glycidol-*b*-L,L-lactide) triblocks after hydrolysis of the polyglycidol blocks [21]. These micelles bearing hydroxyl groups at the middle layer can be used in a number of biological applications due to the possibility of chemically transforming the hydroxyl groups. Their structural properties could be tuned by the molecular characteristics of the terpolymers.

The influence of chemical modification of one block on the micellar properties was investigated by Zhou et al. on poly(ethylene oxide-*b*-styrene-*b*-1,2-butadiene) terpolymers which were transformed to poly(ethylene oxide-*b*-styrene-*b*-fluorinated 1,2-butadiene) by selective fluorination of the butadiene units

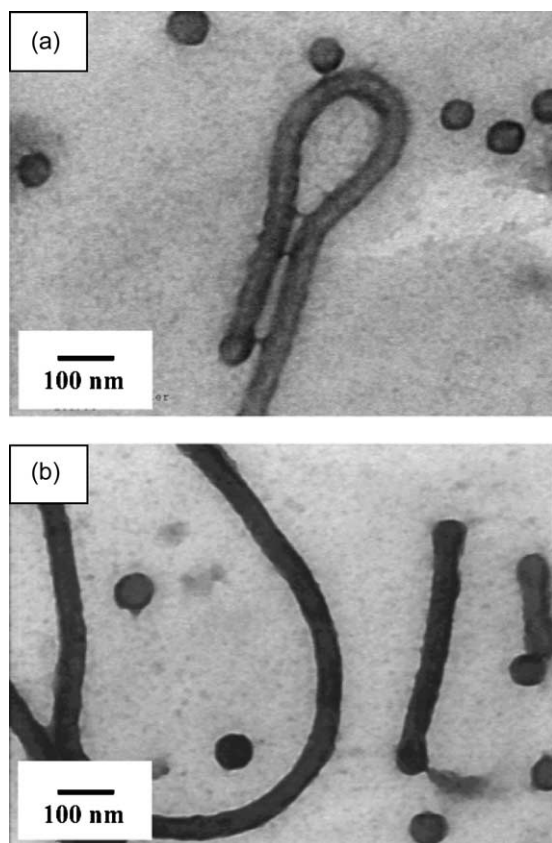


Fig. 35. TEM images of PS_x - $P2VP_y$ - PEO_z micelles prepared at pH 2 from 70/30 (wt/wt) DMF–benzene mixtures (x , y , z denote degree of polymerization). (a) PS_{200} - $P2VP_{140}$ - PEO_{590} , staining with $H_3PO_4 \cdot 12WO_4$ (P2VP is stained). (b) PS_{140} - $P2VP_{120}$ - PEO_{795} , staining with RuO_4 (P2VP and PS are stained).

[20]. The unmodified triblocks formed spherical core–corona micelles in aqueous media, whereas the fluorinated analogues formed core–shell–corona oblate elliptical micelles. This behavior was ascribed to the stronger segregation of the insoluble blocks and the increase in the hydrophobicity of the polybutadiene block in the latter case.

Aggregates with different morphologies could be obtained from an amphiphilic triblock terpolymer consisting of styrene, methyl methacrylate and acrylic acid units, by changing the preparation protocol [8]. The aggregates were formed by first dissolving the terpolymer in a common organic solvent (dioxane, THF or DMF) followed by gradual addition of water. At different water contents a variety of aggregate

morphologies including spherical, rodlike and vesicular structures were identified by TEM (Fig. 36). It was concluded that the aggregates possess a three layer inner structure, the PS being the first to collapse by water addition, followed by PMMA whereas PA remains soluble in all cases.

Recently, the preparation of polymeric vesicles from a poly(acrylic acid-*b*-styrene-*b*-4-vinyl pyridine) terpolymer was reported by Liu and Eisenberg in DMF/THF/ H_2O mixtures [62]. The vesicles could be obtained at either low or high pH. However, at intermediate pHs ($3 < pH < 11$) spherical or ellipsoidal aggregates were observed. From zeta potential measurements, it was inferred that, at low pH, protonated P4VP blocks form the outside and PA the inside part of the vesicles at low pH, whereas the opposite is true at high pH (Fig. 37). Vesicles with PA blocks outside could be reverted to vesicles with P4VP blocks outside by simple pH alteration (Figs. 38 and 39). The opposite transformation was not possible even though the vesicles were in dynamic equilibrium. In general, inversion was found to be a gradual process and assumed to proceed through whole vesicle rearrangement rather than single chain-mediated mechanism.

In another case vesicles with asymmetric layers were observed in solutions of poly(ethylene oxide-*b*-dimethylsiloxane-*b*-methyloxazoline) (PEO-PDMS-PMOXA) triblock terpolymers [34]. Fluorescence labeling of the PMOXA ends allowed the determination of the detailed structure of the vesicles. It was concluded that for the copolymer with the shorter PMOXA block PEO is located in the outside, while for terpolymers with longer PMOXA the positioning is reversed. It was suggested that the amphiphilic PEO-PDMS-PMOXA terpolymers are well suited for the preparation of asymmetric layers in aqueous media.

The rheological behavior of heterotelechelic polyelectrolytes, i.e. poly(styrene-*b*-sodium acrylate-*b*-*n*-butyl methacrylate) (PS-PNaAc-PBMA) triblock terpolymers with small hydrophobic end blocks (PS, PBMA) was investigated by Tsitsilianis et al. [11]. Even at low concentrations, transient networks were formed with functions consisting of PS and PBMA domains in contrast to those formed from PS-PNaAc-PS where the crosslinks were only PS. This was also supported by the different rheological behavior of the

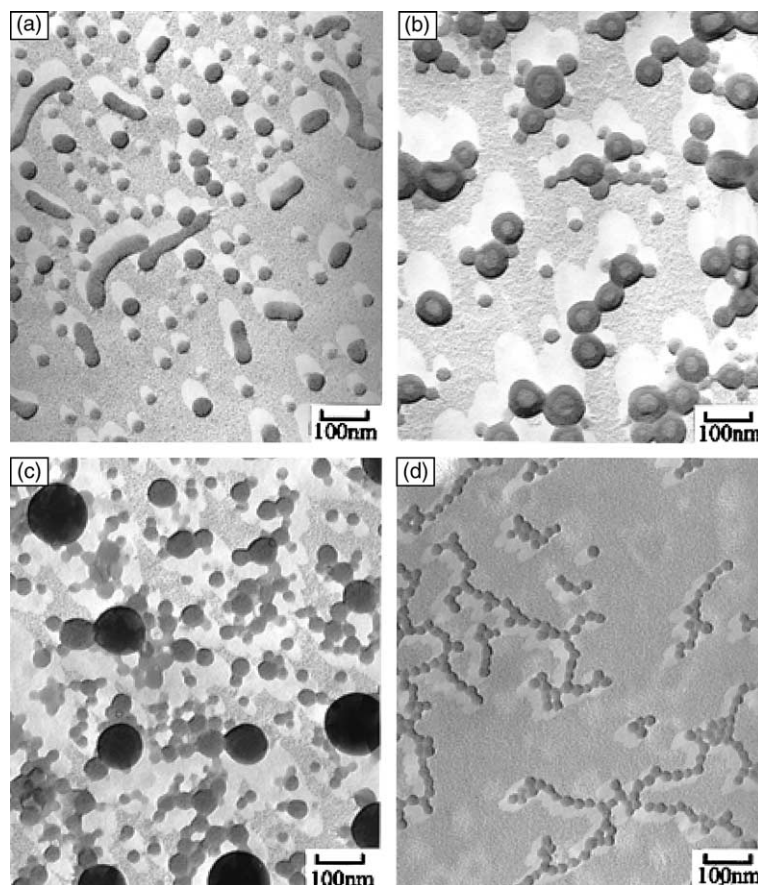


Fig. 36. TEM micrographs of aggregates formed by a PS–PMMA–PAA triblock terpolymer from solutions in different solvents and different water contents (polymer concentration is fixed at 3 wt%). (a) From a dioxane solution at 18 wt% added water. (b) From a dioxane solution at 25 wt% added water. (c) From a THF solution at 40 wt% added water. (d) From a DMF solution at 55 wt% added water.

two systems and the more pronounced association effects observed in the heterotelechelic sample.

3.4. Non-conventional nanostructures obtained through ABC self assembly in solution

Recently, ABC triblock terpolymer self-organization was used in order to facilitate the formation of several non-conventional nanostructures in solution. A few examples will be discussed below.

A triblock terpolymer, prepared by the connection of a terpyridine end-capped poly(styrene-*b*-2-vinylpyridine) diblock and a similarly end-capped poly(ethylene oxide) through complexation with ruthenium (II) cations, has shown the ability to form three layer spherical micelles in aqueous media [18]. These

micelles were shown to be pH sensitive in a manner analogous to that of micelles formed from covalently bonded PS–P2VP–PEO. Detachment of the PEO coronas could be accomplished by addition of the strong ligand hydroxyethyl-ethylenediaminetriacetic acid sodium salt (HEEDTA). This compound competes with the terpyridine groups for complexation on the ruthenium cations and replaces the terpyridine end-capped PEO chains, leading to the formation of PS–P2VP micelles with terpyridine ligands on the outside (Fig. 40).

Janus micelles were prepared by crosslinking the polybutadiene blocks of poly(styrene-*b*-butadiene-*b*-methyl methacrylate) terpolymers in the solid state [63]. The terpolymers used, formed a ‘ball at the wall’ morphology in the bulk state. After solubilization,

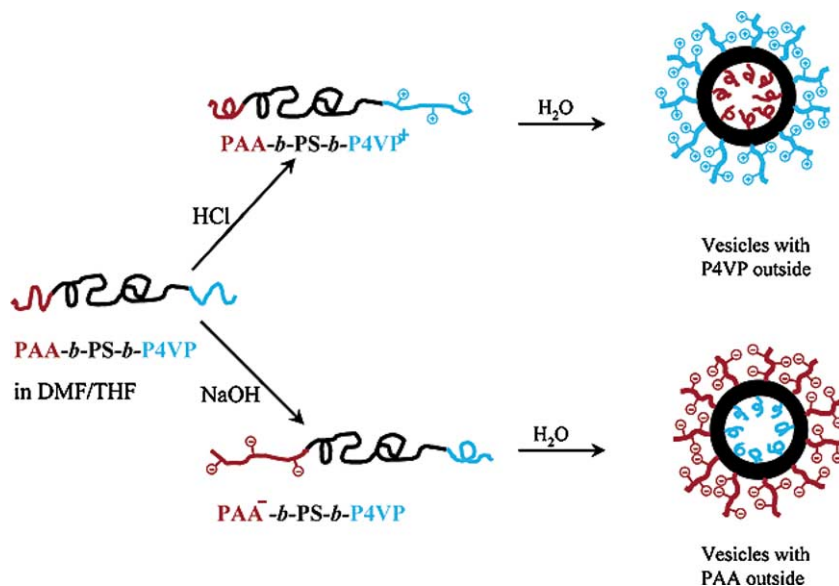


Fig. 37. Schematic representation of the preparation of the two types of vesicles from a PAA–PS–P4VP triblock terpolymer.

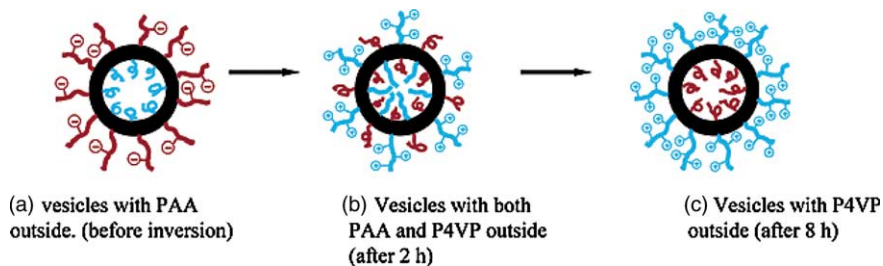


Fig. 38. Schematic representation of the inversion of vesicles formed by a PAA–PS–P4VP triblock terpolymer. At the initial state, PAA chains are outside and at the final state P2VP chains are outside.

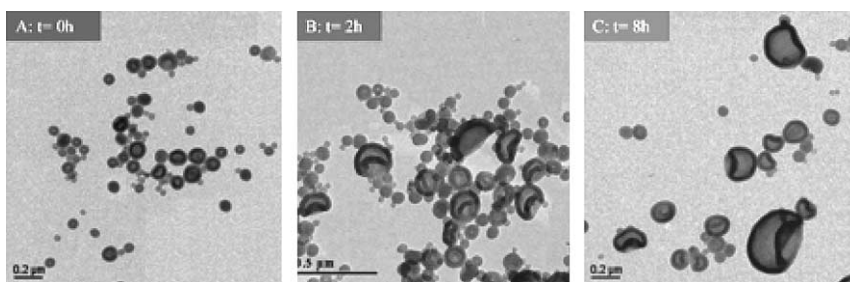


Fig. 39. TEM micrographs of the vesicles inversion starting with PAA on the outside (A), after an inversion time of 2 h (B), and after an inversion time of 8 h (C).

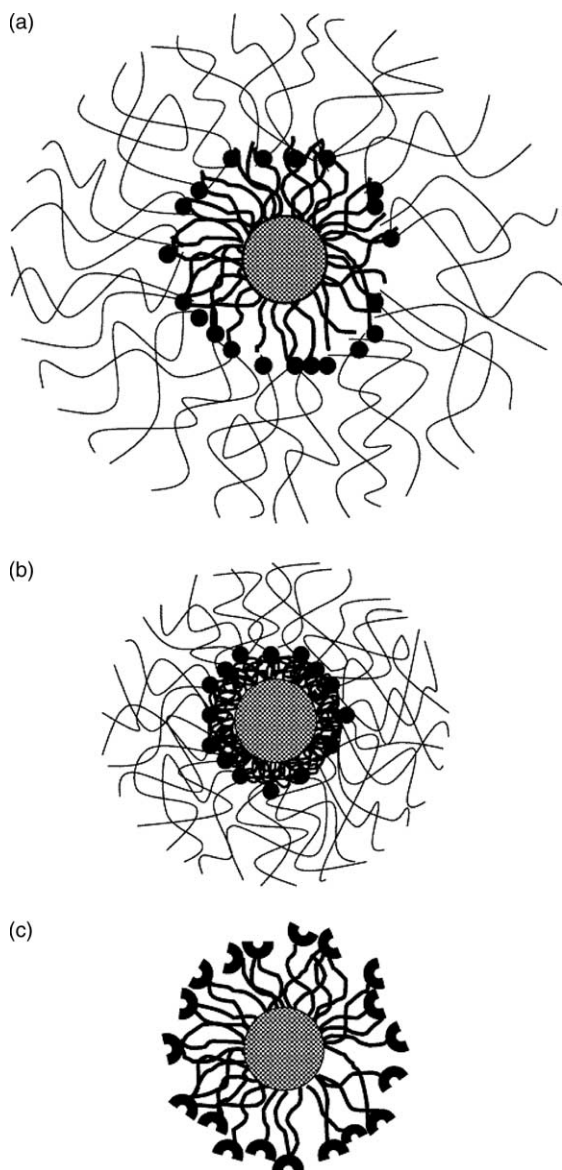


Fig. 40. Schematic representation of PS_{32} - b - $P2VP_{13}$ -[Ru]- PEO_{70} metallo-supramolecular micelles at $pH < 5$ (a), $pH > 5$ (b), and after addition of a large excess of HEEDTA (c). PS core: central sphere; P2VP chains in thick black; PEO chains in thin black; bis(terpyridine)ruthenium complex: black dots in (a) and (b); terpyridine ligand: half-circles in (c).

micelles with two chemically different hemispheres were observed in solution (Fig. 41). The same concept was used for the preparation of amphiphilic Janus micelles with polystyrene and poly(methacrylic acid) hemispheres, after alkaline hydrolysis of the PMMA

block [64]. Using a variety of experimental techniques, the authors observed that the individual micelles were found to aggregate into larger superstructures (spherical supermicelles), in salt containing aqueous solutions, whose size depended on the pH of the solution (Figs. 42 and 43). Larger spherical objects were also observed to coexist with these supermicelles in solution.

Stewart and Liu prepared hollow nanospheres using the micelles of a poly(isoprene- b -2-cinnamoyl ethyl methacrylate- b -*tert*-butyl acrylate) (PI-PCEMA-PtBA) triblock terpolymer as precursors [9]. The triblocks formed core-shell-corona micelles in THF/methanol mixtures (methanol content varied from 50 to 99%, v/v) with PI cores, PCEMA shells and PtBA coronas. The pendant double bonds of the PCEMA shells were cross-linked using UV radiation and the PI cores were removed by ozonolysis to form the desired hollow nanospheres (Fig. 44). Nanostructure formation, before and after polymer modification, was followed by dynamic light scattering, viscometry, TEM and fluorescence spectroscopy (Fig. 45).

Armes and collaborators utilized a number of triblock terpolymers, prepared by ATRP polymerization methodologies in order to prepare shell cross-linked micelles with characteristics responsive to their environment [25–27,65].

The possibility of preparing shell crosslinked (SCL) micelles at high concentration of solids (up to 10%, wt/v) has been demonstrated in two cases [25, 65], where poly(propylene oxide- b -2-(dimethylamino)ethyl methacrylate- b -oligo(ethylene glycol) methacrylate) (PPO-PDMA-POEGMA) and poly(ethylene oxide- b -2-(dimethylamino)ethyl methacrylate- b -2-(*N*-morpholino)ethyl methacrylate) (PEO-PDMA-PMEMA) micelles, in aqueous media, were used as precursors. In the micelles investigated, PPO and PMEMA formed the core, PEO and POEGMA blocks formed the outer corona and PDMA the inner corona or shell. The PDMA blocks were cross-linked with 1,2-bis(2-iodoethoxy)ethane. Due to the presence of the highly solvated PEO and POEGMA corona blocks that sterically stabilizes the association colloid structure, no appreciable intermicellar cross-linking was observed even at high concentrations of the triblock.

Shell cross-linked micelles with pH-responsive cores were, more recently, prepared by crosslinking

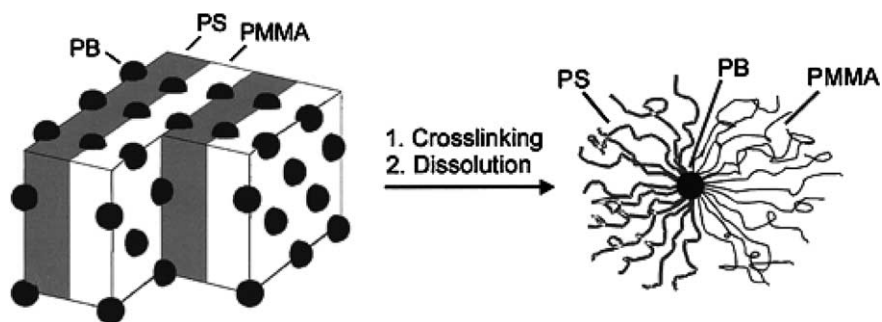


Fig. 41. Schematic representation of the preparation of Janus micelles.

the PDMA inner coronas of poly(ethylene oxide-*b*-2-(dimethylamino)ethyl methacrylate-*b*-2-(diethylamino) methacrylate) (PEO-PDMA-PDEA) triblocks [27]. These terpolymers formed micelles in basic conditions ($\text{pH} > 7.3$) with PDEA cores. The crosslinking of the PDMA blocks was achieved by selective quaternization with 1,2-bis(2-

iodoethoxy)ethane (BIEE). The amount of BIEE needed to ‘freeze’ the desired structure was found to depend on the length of the PEO outer corona block. The size of SCL micelles was independent of temperature but high swelling of the particles was observed at low pH values due to protonation and therefore increase of the hydrophilicity of the

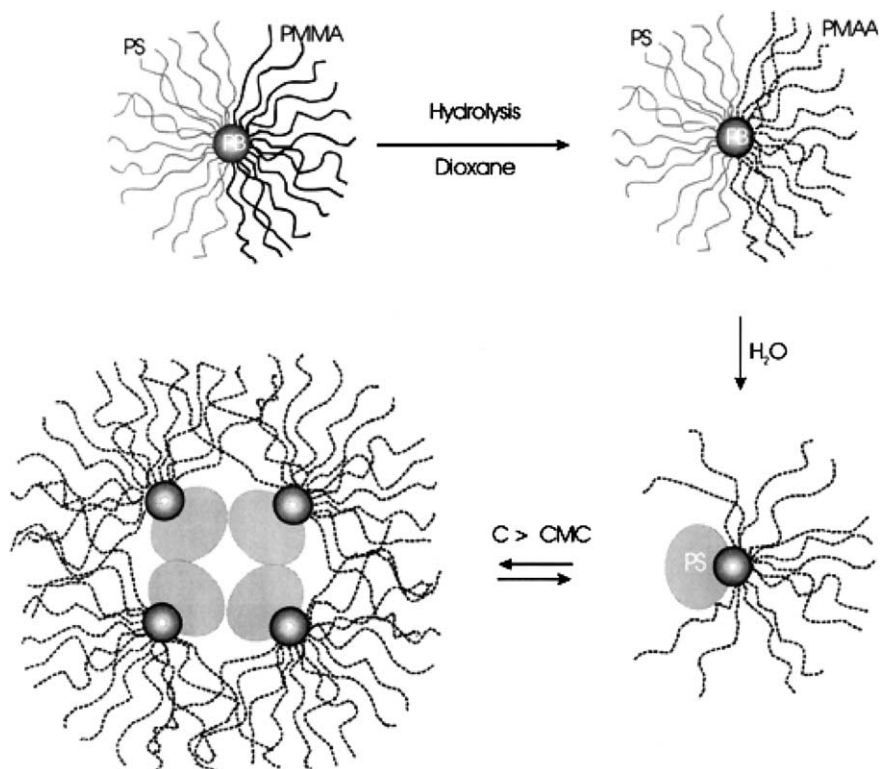


Fig. 42. Synthesis of amphiphilic Janus micelles and tentative structures in aqueous solutions.

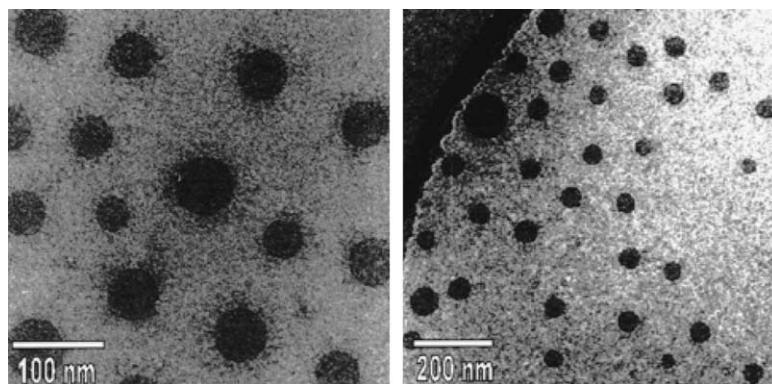


Fig. 43. TEM pictures of the Janus micelle aggregates in water plus 0.17 M NaCl.

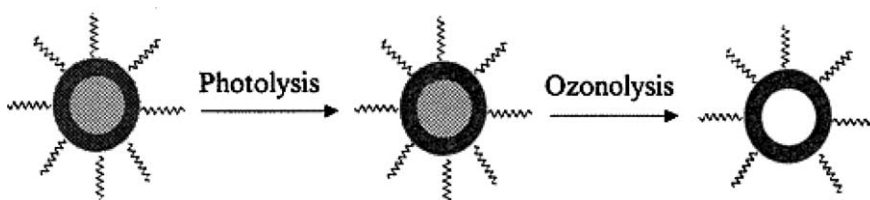


Fig. 44. Schematic representation of the preparation of hollow nanospheres from PI-PCMA-PtBA triblock terpolymer micelles.

PDEA blocks (Fig. 46). The degree of micellar swelling could be varied systematically through variation of the block lengths and the degree of crosslinking.

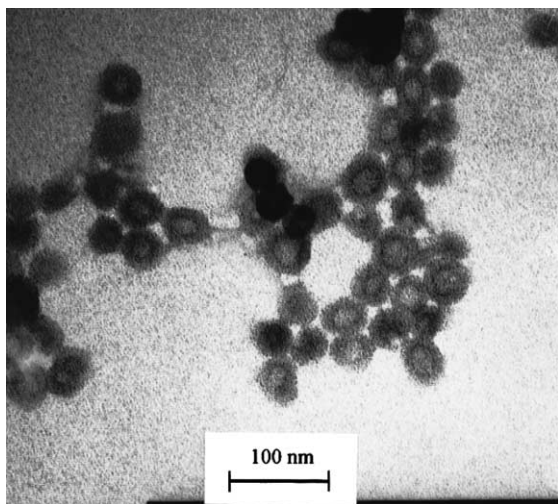


Fig. 45. TEM micrograph of hollow nanospheres prepared from PI-PCMA-PtBA triblock terpolymer micelles. The sample was stained with RuO₄.

Finally, in another study poly(ethylene oxide-*b*-glycerol monomethacrylate-*b*-2-(diethylamino)ethylmethacrylate) (PEO-PGMA-PDEA) and poly(ethylene oxide-*b*-2-hydroxyethylmethacrylate-*b*-2-(diethylamino)ethylmethacrylate) (PEO-PHEMA-PDEA) terpolymer micelles, at pH > 8, were used for the preparation of pH-responsive SCL micelles [26]. In this case, crosslinking of the inner corona

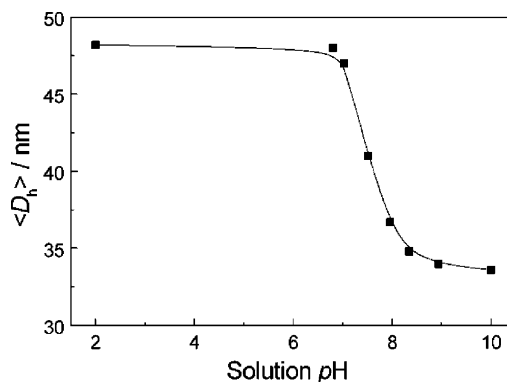


Fig. 46. Variation of average hydrodynamic diameter, $\langle D_h \rangle$, of PEO-PDMA-PDEA SCL micelles prepared at a polymer concentration of 0.50% (w/v) with a target degree of cross-linking of 30%.

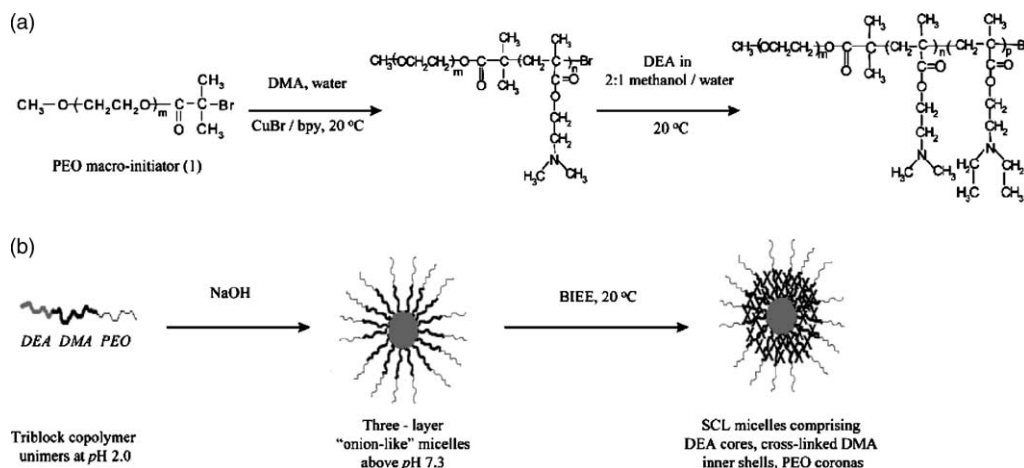


Fig. 47. Reaction scheme for the preparation of PEO–PGMA–PDEA triblock copolymers (a) and subsequent SCL micelles formation (b).

blocks (PGMA or PHEMA) containing hydroxyl groups was accomplished with vinyl sulfone (Fig. 47). The SCL micelles subsequently served as nanoreactors for the synthesis of gold nanoparticles after complexation of the PDEA blocks with AuCl_4^- precursor ions.

4. Microphase separation in the bulk

4.1. Introduction

Multiblock multicomponent polymers have the potential to generate a variety of well-defined and controlled multiphase microdomain morphologies with very small dimensions and/or provide the supramolecular structures with a mesoscopic length scale. They could, possibly, undergo order–order or order–disorder transitions leading to even more interesting structures with potential applications, e.g. multifunctional sensors, multiselective catalysts for sequential or simultaneous chemical reactions.

The variety of morphologies obtained from linear diblock and triblock copolymers, consisting of only two chemically different components, is well understood due to extensive studies of the microphase assembly of such materials. It is well known that chemically different chains exhibit repulsive interactions, leading to reduction of the conformational

entropy, since the different blocks will self-assemble into microphases. In such materials the junction points are located on one single interface (Inter Material Dividing Surface, IMDS), and the larger its thickness the less reduced is the conformational entropy. Microphase separation of binary block copolymers depends on one composition variable (volume fraction of one component) and on one Flory–Huggins interaction parameter χ_{AB} .

In the case of more complicated block copolymeric systems consisting of three or more components, more independent variables (e.g. two composition variables and three interaction parameters in the case of three component systems), which lead to a large variety of new morphologies, should be considered. In addition, the block sequence can also be changed, leading to another factor which could influence the finally observed structure. Only during the last decade, there has been information in the literature on the microphase separation of multiblock multicomponent systems, the majority of which concerns the cases of linear polymeric materials. The lack of information regarding star polymers is due to their difficult and time consuming synthesis.

It should be noted that for miktoarm star terpolymers the block sequence does not affect the morphology, as it does for the linear ABC materials, due to the existence of only one junction point from which all blocks emanate. In most cases this

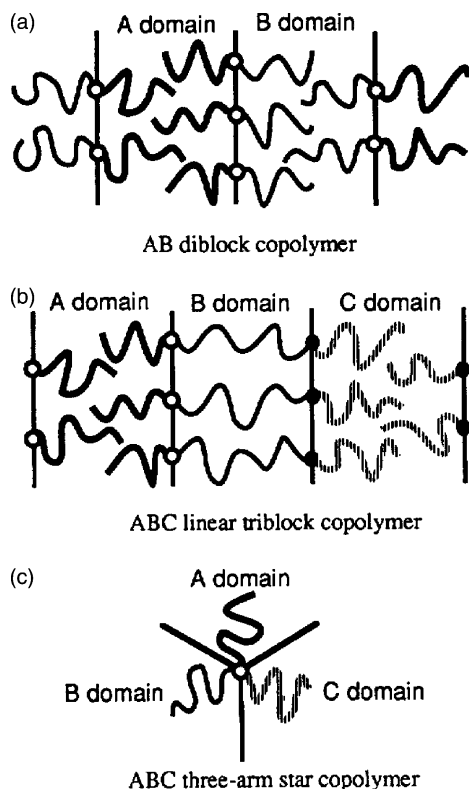


Fig. 48. Schematic illustration of linear AB and ABC co- and terpolymers as well as of ABC miktoarm stars. (a) AB diblock copolymer, junction point is located on an interface. (b) ABC triblock terpolymer, the two junction points are located on two different interfaces. (c) ABC miktoarm star, the junction point is located on a line.

constraint for the non-linear materials leads to the placement of the junction points onto lines, instead of interfaces, as exhibited in Fig. 48 [66].

There are 15 possible arrangements of the three blocks of an ABC terpolymer (Fig. 49). Many of these arrangements are very difficult or impossible to synthesize for the time being. It is of great importance to consider the formation of the microphase-separated morphology of a film resulting from the evaporation of a homogeneous solution of the simpler of these arrangements, which are the linear samples consisting of three chemically different chains and two junction points. (Fig. 49a–c).

Assuming that: (i) the three blocks are of equal degree of polymerization ($N_A = N_B = N_C$), (ii) the blocks exhibit equal binary interaction parameters

($\chi_{AB} = \chi_{BC} = \chi_{CA}$) and (iii) the solution is perfectly homogeneous, a solvent with a polymer/solvent interaction parameter matching that of the three blocks could be envisioned. This should be the true non-preferential solvent for this special triblock terpolymer, but it is more likely that such a solvent will prefer at least one of the blocks. As the solution becomes more concentrated, in reality this least solvated block will begin to experience increased self-segment interaction in order to decrease the less preferred polymer–solvent interactions, while minimizing contact with the remaining two blocks. In short, the least-solvated block will begin to phase separate from solution. All the above are schematically exhibited in Fig. 50 [67].

If this precipitating block happens to be one of the end-blocks, e.g. the A block (Fig. 50, first step), a three-phase four-layer lamellar morphology would be observed. Initially layers of the A block would be separated from mixed B and C. As the solvent continues to evaporate, B and C segments are no longer screened from one another and thus they begin to microphase separate. Two new Inter Material Dividing Surfaces (IMDS) result and all of the B mid-blocks form bridges between A and C. If the mid-block precipitates first, both bridges and loops of the mid-block could be formed as the end-blocks are initially mixed. Upon end-block microphase separation, each mid-block loop migrates to straddle an A/C interface, resulting in a checkerboard of alternating A and C domains parallel to the B interface (Fig. 50, second step). Therefore, it is really crucial to appoint thermodynamic stability on the observed morphologies for multiblock multicomponent systems.

4.2. Theory

4.2.1. Linear ABC terpolymers

Riess and collaborators [68] first mentioned the possibility of microphase separation for linear triblock terpolymers. While in the case of the diblock and triblock copolymers, only one type of morphology is possible (e.g. spheres, cylinders or lamellae) in the case of the terpolymers different features in the microphase separated state are observed (e.g. spheres within a lamellae, lamellae with spheres at the interfaces, three-phase four-layer lamellae, etc.), leading to the understanding of the complexity in

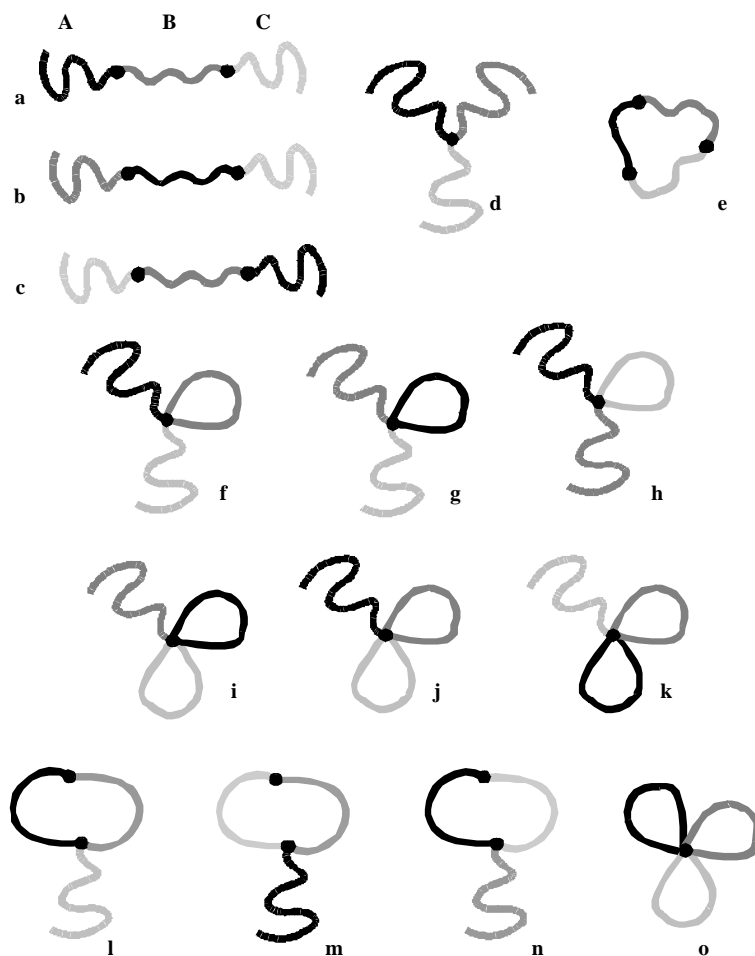


Fig. 49. Schematic presentation of all possible arrangements for an ABC terpolymer. (a–c) Linear triblock terpolymer, ABC, BAC, CBA, respectively. (d) Miktoarm star terpolymer. (e) Cyclic terpolymer. (f–h) One of the chains is cyclic (starts and ends at the junction point) and the other two linear. (i–k) One chain is linear and the two are cyclic. (l) All chains are cyclic.

the self-assembly of terpolymers. The aforementioned study only focused on the linear case since the synthesis of more complex materials (e.g. miktoarm terpolymers) was not available during the early 1980s.

Kane and Spontak [69] deployed a self-consistent field theory for AXB linear terpolymers exhibiting lamellar morphology. This theory was based on Semenov's [70] theoretical predictions for diblocks and described the periodicity L of terpolymers with an identical manner as in the case of linear diblock copolymers ($L \propto N^{2/3}$). Actually, Kane and Spontak used a self-consistent field formalism based on AB diblock and ABA triblock copolymers. In the

sequence, X denotes either a third chemically different monomer C or a random A/B segment exhibiting both A and B monomeric units. The microdomain periodicity exhibited in these materials depends on the interaction parameters of the A–C and B–C pairs and on the molecular composition.

Another important theoretical approach describing different morphologies of ABC terpolymers in the SSL was established by Zheng et al. [71] based on the work by Ohta et al. [72–74], and focused on the sequence of the blocks and on the values of their interaction parameters. The results were compared with experimentally observed structures leading to

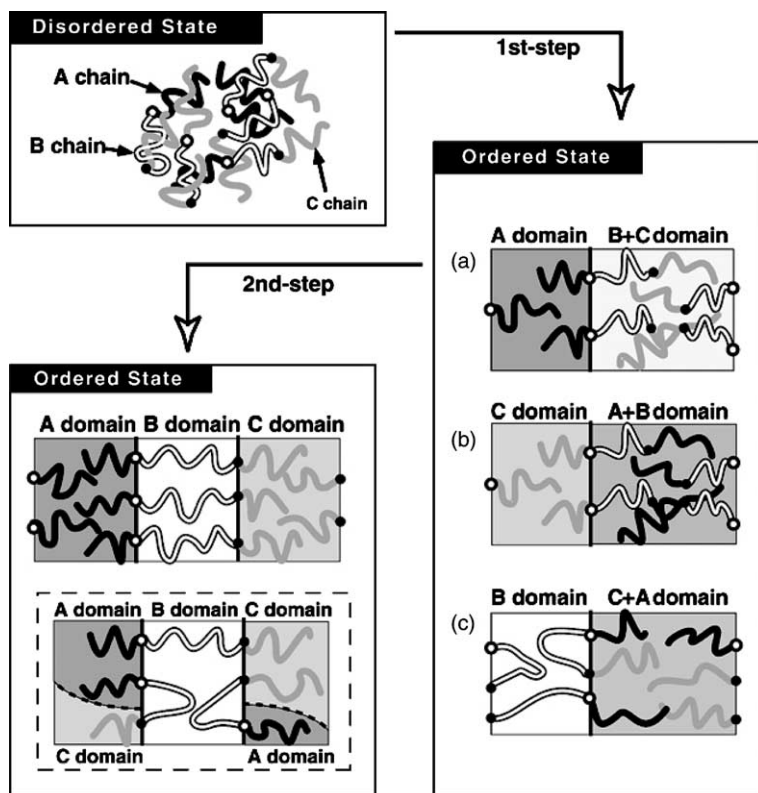


Fig. 50. Casting of the selective solvent stepwise. One block is microphase separated from the remaining two which are microphase separated from each other at the next step.

similar results and new structures, which were not at the time observed experimentally but already predicted. It should be noted that the approximation used depended on the fact that the chain conformation free energy is approximated by a Coulomb-like interaction, leading to mostly qualitatively, rather than quantitatively, correct phase diagrams.

Ohta et al. [72–74] theoretically studied the self-assembly of linear ABC terpolymers in the SSL by calculating the free energy functional in terms of localized monomer densities based on variational method for each ordered structure. One is a mean field approximation for deriving the free energy functional and the other approximation excludes non-localization for higher order coupling for the density expansion of the free energy functional.

Lyatskaya et al. [75] demonstrated that the segmental properties influence the stability of different morphologies (lamellar and cylindrical) exactly in

the same manner as for diblock copolymers [76]. Mean-field theory in the SSL for the terpolymers together with the differences in local characteristics of the segments, such as widths, persistence lengths and interfacial tension coefficients at the two interfaces were used [75]. It is of major importance to mention that this group also did a comparison between experimental results and theoretical predictions and concluded that a qualitative rather than a quantitative correlation could be made in most cases.

Fredrickson and collaborators [77] studied symmetric ABC terpolymers and concluded a more stable square lattice of A and C spheres in a B matrix when compared to the hexagonal arrangement. They also concluded that the gyroid cubic structure would be more stable than the ordered tricontinuous double diamond (OTDD) morphology for this polymer type, even though cubic structures are unstable when compared to cylindrical or lamellar morphologies.

Cubic structures, however, have demonstrated better mechanical properties from cylinders and lamellae leading to potential applications of increased interest [57].

It should be noted that Matsen and co-workers [76] simulated different projections of the gyroid leading to the major conclusion that the OTDD structure reported by Mogi et al. [78] was eventually gyroid. Monodisperse melts of symmetric ABC linear terpolymers are studied using the self-consistent field theory with the A and C blocks having the same molecular weight and the interactions A/B and B/C being approximately identical. Correspondence with other theoretical approaches leads to similar results and to the conclusion that the complex cubic phase exhibited in such materials is the gyroid morphology.

It is clear that theoretical studies [76,77] are very well acknowledged in the case of understanding the stability of complex structures and are not as misleading as experimentally observed morphologies sometimes are.

Additionally, Khokhlov and collaborators [79] investigated spherical micelles for asymmetric ABC terpolymers in the strong segregation limit, SSL. It was shown that the presence of strongly associated A blocks enhances the segregation tendency between the other two blocks. The polymeric chains are different in segments and highly incompatible. The system mainly studied in this work was a melt of BC block copolymer with strongly associative A-groups at the end of the B block. Aggregates from the A block are formed inside the B micelle, which is considered to be spherical in shape, leading to stabilized microphase separation between the B and C segments.

Modified random phase approximation theory was adopted near the order–disorder transition (ODT) regime in certain ABC and ACB linear terpolymers [80], leading to the conclusion that such theoretical approximations are very useful in the design of such materials without any prior experimental data or necessary complicated calculations. By altering the composition, triangle phase diagrams are created for four types of triblock terpolymers in terms of the relative strengths of the interaction energies between the different materials.

A very recent study by Qiu and co-workers [81] described the microphases of ABC linear triblock

terpolymers. A real space implementation of the self-consistent field theory for the material was considered in two-dimensional space. Lamellae, hexagonal lattice, core–shell hexagonal lattice, tetragonal lattice, lamellae with beads inside, lamellae with beads at the interface and hexagonal phase with beads at the interface are reported as stable for such polymeric systems. Composition and interaction parameter values are extremely crucial since their variation completely alters the trigonal phase diagram. Actually, the least complex phases (lamellae) are modified to more complex (lamellae or hexagonal with beads) as the blocks become more asymmetric in composition and the segment–segment interactions are different.

The behavior of the ABC materials by swelling the two end blocks is also reported in the literature [82]. The tricontinuous cubic structures in ABC linear terpolymers and A and/or C homopolymer blends were studied theoretically by using the Monte-Carlo lattice-simulation technique combined with the diagonal bond method (DBM). AC symmetric ABC terpolymers as ingredients of surfaces separating phases rich in A and C homopolymers were employed. The tricontinuous space consists of two struts (A- and C-filled) separated by the B-polymer region. A transition from gyroid to diamond and primitive cubic structure was observed upon addition of more homopolymer, a phase sequence noted only for surfactant systems. It should be mentioned that additional homopolymers behave as solutions in surfactants and lipid systems.

X-ray scattering was also used in order to explain cubic (P, D and G) structures formed in ABC linear terpolymers [83,84]. The approach established in these papers can be used for even more complex multicomponent systems exhibiting cubic structures. The model used interprets the X-ray diffraction patterns of terpolymers exhibiting complex multiple continuous triply periodic structures. The imminent fitting between the model described and the experimental data leads to the determination of the adopted structure, the volume fractions of the continuous phases and the width of the interfaces. Therefore, not only qualitative but also quantitative analysis can be adhered.

4.2.2. Non-linear ABC terpolymers

Theoretical approximations and morphology predictions were recently carried out by Dotera et al. [85] and by Pan et al. [86] for miktoarm star terpolymers of the ABC type. The literature concerning theoretical predictions for this complex architecture is rather limited, since the synthesis of such materials leading to morphologically three-phase structures has been developed rather recently. The combination of theory and experiment and whether they converge or not, as in the case of linear terpolymers, is of great interest. Dotera's group [85] simulated the behavior of miktoarm star terpolymers by using the Monte Carlo calculation method. This approach was already used for the microdomain structural behavior of diblock copolymers of the AB type, and the consideration which needed to be taken into account for the calculations was the addition of the C chain, at the common junction point of A and B blocks. The microphase-separated morphology of the non-linear terpolymers with arm length ratio 1:1: x , for the three different components was investigated according to the recently proposed diagonal bond method (Monte Carlo with DBM). The theoretical phase diagram of the miktoarm ABC with arm-length ratio 1:1: x and with symmetric interactions between three components is exhibited in Fig. 51.

Microdomain structures of 3-miktoarm star terpolymers in three-dimensional space were investigated by dynamic density functional theory (DDFT) as reported by Pan and co-workers [86]. Analysis of DDFT demonstrates that the junction points are restricted to lie on periodically spaced parallel lines formed by the mutual intersections of different domains at the strong segregation between distinct blocks. The structures which were taken from this approach are given in Fig. 52. The results indicate that microstructures and distributions of junction points depend not only on the architecture of the macromolecule chain but also on interaction parameters between distinct blocks.

Unfortunately, theoretical predictions for the microphase separation of cyclic triblock terpolymers have not appeared in the literature.

4.3. Experimental

4.3.1. ABC linear terpolymers

As is evident from Fig. 49, a large number of complex architectures can be imagined in the case of ABC terpolymers leading to pure or combined linear, non-linear and cyclic chains. Linear terpolymers (Fig. 49a–c) and miktoarm stars (Fig. 49d) have

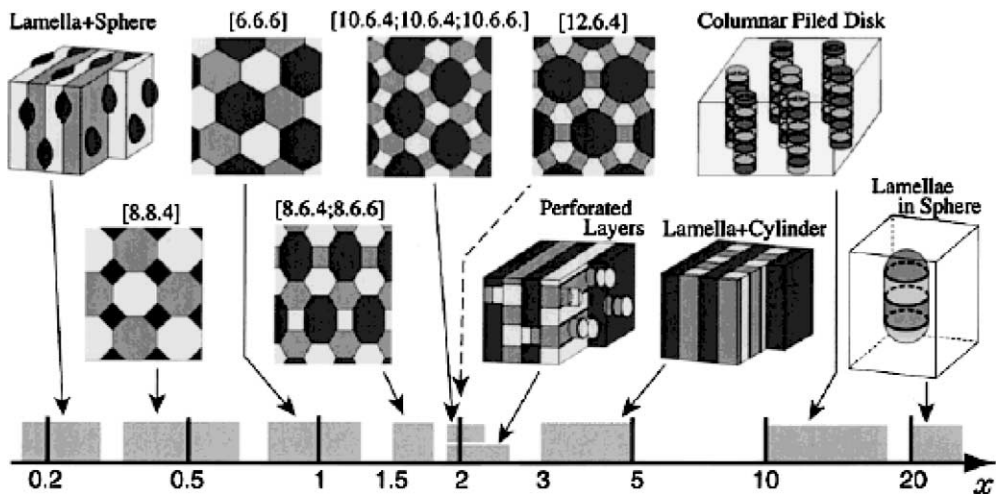


Fig. 51. Phase diagram of ABC star polymers with arm-length ratio 1:1: x , with symmetric interaction parameters. Morphologies are lamella + sphere (L+S), five cylindrical structures in sectional view, perforated layer (PL), lamella + cylinder (L+C), columnar piled disk (CPD) and lamella in sphere (L-in-S).

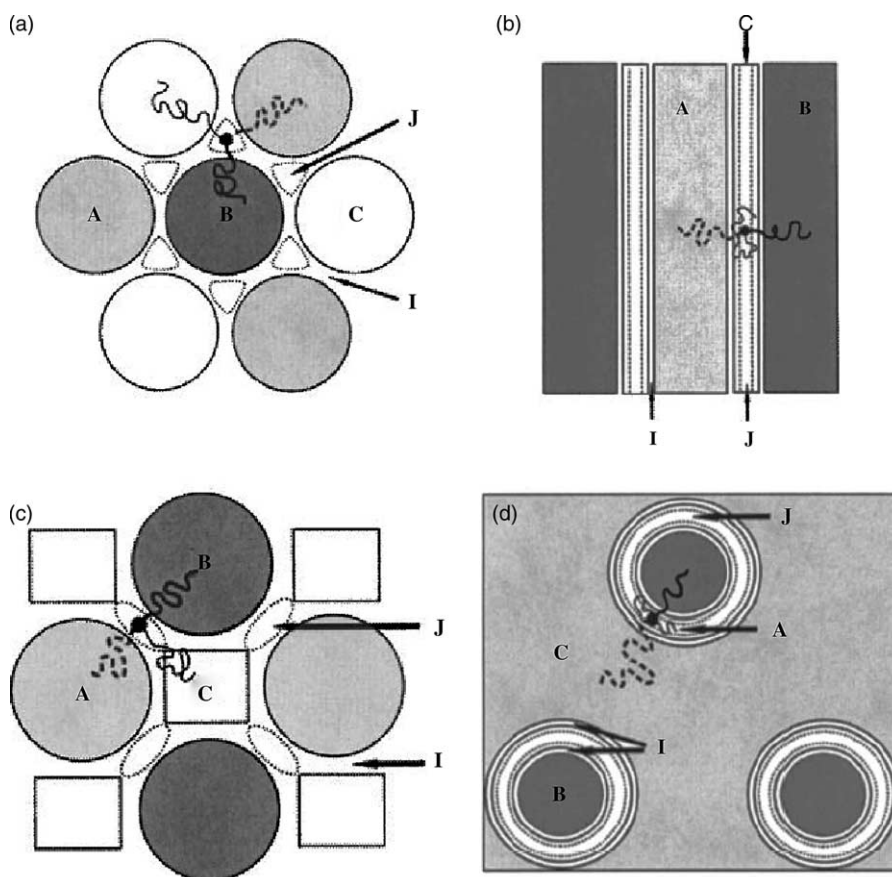


Fig. 52. Schematic illustration of theoretical approximations for ABC miktoarm terpolymers. (a) Schematic of section perpendicular to the cylinders, J is the junction region and I is the area where blocks and junctions mix. Degrees of polymerization and χ interaction parameters are equal. (b,c) Similar schematic but different presentation due to changes in the χ interaction parameters. (d) Schematic illustration perpendicular to the cylinders when the three components exhibit different degrees of polymerization as well as different χ .

been cited more often, because of the relatively simple synthesis, especially in the case of the linear sequence.

Bates and Fredrickson [87] have given a summary of the observed morphologies of ABC linear systems. These structures, for which changes in composition, molecular weight or block sequence completely alter the observed morphology of the system, are illustrated in Fig. 53.

Block sequence plays an important role in the observed morphology of linear terpolymers when the overall composition is approximately equal [78,88, 89]. The behavior, in most cases, can be understood by comparing the different interfacial tensions of the adjacent blocks. When these are similar between A/B

and B/C, then the three-phase four-layer lamellae structure is observed.

It should be noted that [89] a new type of cylindrical microdomain structure with alternating types of diene regions along the cylinder axis was recently observed for linear BSI materials. It is the first time that microphase separation and very well-ordered structures were observed for a system consisting of two dienic and a styrenic component. The major conclusion regarding such materials was that a three-component microphase-separated system occurred even when the two diene blocks were adjacent, as in the SBI sequence, leading to the conclusion that the PB:PI 1,4/3,4 diene combination

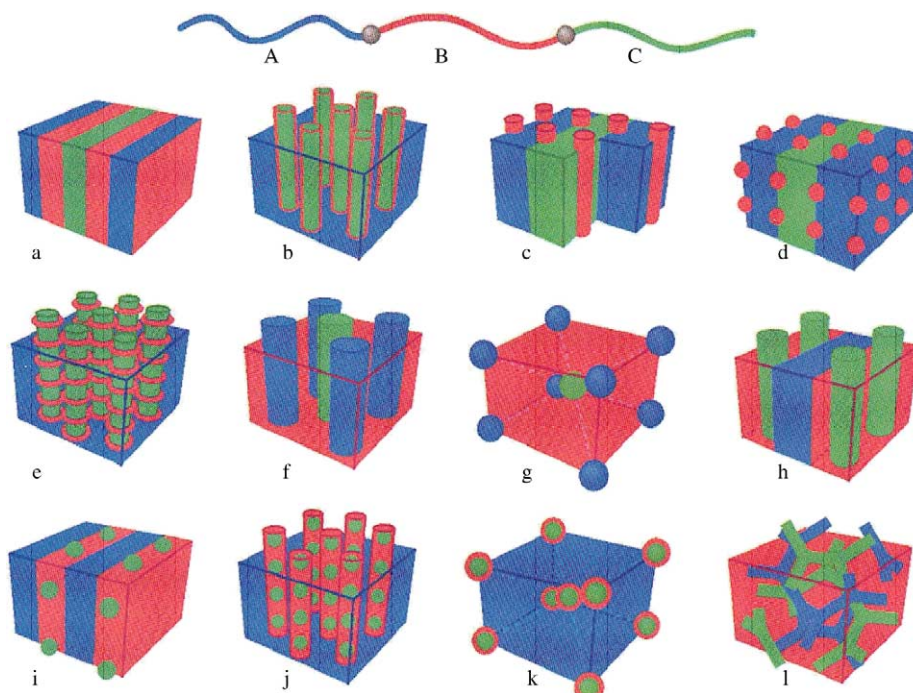


Fig. 53. Overall schematic of the most predominant morphologies observed in ABC linear terpolymers. Blocks are illustrated with blue, red and green colours corresponding to the A, B and C segments, respectively.

has a larger Flory-Huggins χ parameter than the other three possible combinations of PB:PI diene microstructures. These structures are illustrated in Fig. 54.

The aforementioned SBI and BSI materials exhibit microphase separation in contrast to previous paper by Neumann et al. [90]. These authors reported that PI-1,4 and PB-1,2 are miscible and concluded that the ABC terpolymers behave as a pseudodiblock system. The hydrogenated materials were also studied leading to different morphological observations via TEM when compared to the non-hydrogenated materials. An extensive study of diene microphase separation was reported much earlier by Cohen et al. [91,92] who investigated homopolymer and diblock/homopolymer blends of various diene microstructure combinations. Ternary blends of the two homopolymers with the diblock and binary blends of a single homopolymer with the diblock were one- or two-phase materials depending on the sample composition, the ratio, and the number of diene units in the diblock.

An extremely significant contribution to the discovery and understanding of the self-assembly of linear triblock terpolymers was made by Stadler

et collaborators. [4,5,93–97]. This group investigated linear terpolymers consisting of polystyrene, polybutadiene and poly(methyl methacrylate), leading to the emergence of a large number of very interesting morphologies. For SBM with approximately equal volume fractions for the three blocks lamellar morphology was observed. By keeping the end-block ratio equal and varying the middle block volume fraction from 0.03 to 0.3 the formation of spheres and cylinders between the lamellae of the outer blocks was established. When the volume fraction of the middle block was further increased, cylindrical or spherical domains of S and M were observed in a B matrix. The molecular weight in this case plays an important role as to whether or not the end blocks will be located on different domains or form mixed structures. As previously mentioned, the casting solvent influences the observed morphology. In the SBM sequenced terpolymer, with a 30% benzene/70% cyclohexane casting solvent, a new hexagonal structure was observed. S and M cylinders on a square lattice were expected but a hexagonally packed array of S cylinders surrounded by six M

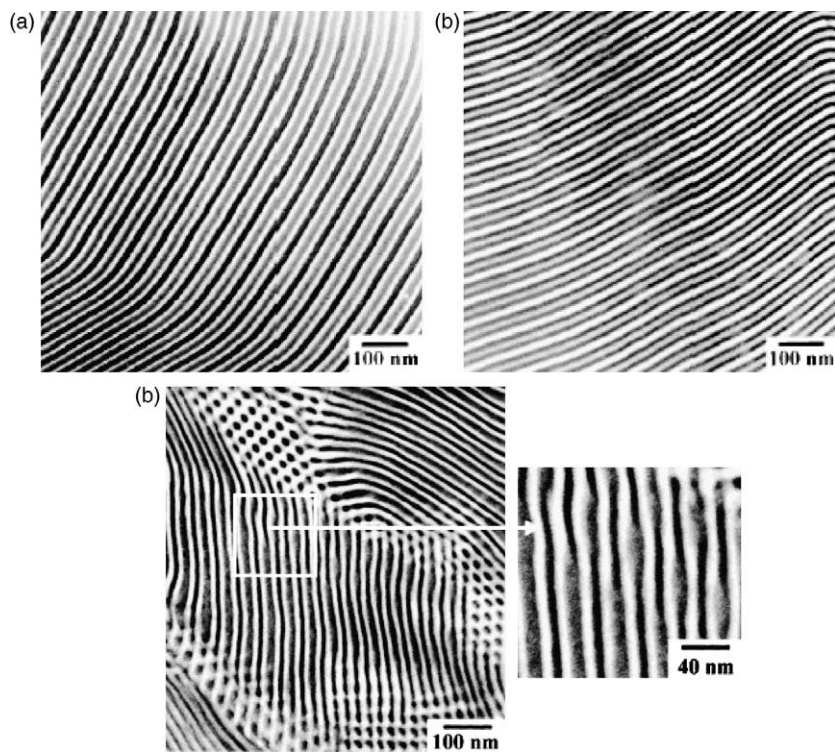


Fig. 54. (a and b) Three-phase four-layer lamellae structure for the BSI and the SBI linear terpolymers, where all blocks exhibit approximately equal volume fractions. The alternation in block sequence is evident that it does not affect the obtained morphology. (c) TEM images for a BSI linear terpolymer exhibiting cylindrical morphology. The magnified portion of the image shows alterations in the cylinder contrast along the axial direction. These alterations are antisymmetric between adjacent cylinders. White regions are PS, gray are PI and black are PB.

cylinders was found. When one of the end blocks was greatly increased to a volume fraction higher than 0.6, the observed morphologies were either concentric spheres or concentric cylinders in a matrix of the block with the higher content. The volume fraction of the middle block is significant in this case and leads finally to new unique microdomain morphologies. Among them the so-called ‘helical’ morphology is the only non-centrosymmetric microdomain structure exhibited so far in ABC linear terpolymers.

The possible conversion of one block is another possible way to alter morphology. Such an alternation was reported in the literature by Stadler and collaborators [93,98,99], where the B block was hydrogenated to poly(ethylene-*co*-butylene) block. This change can be explained by the change in the interfacial tension between S/B, EB/M when compared to those of S/EB and EB/M, leading to induced curvature of the interface between the

endblocks. Similar findings were obtained when the B block was modified by the use of different transition metal complexes.

A unique structure known as the ‘knitting pattern’ [100–102] was observed by hydrogenation of the polybutadiene block of a symmetric SBM with almost 27% B. The corresponding SBM terpolymer exhibits a lamellar morphology. The ‘knitting pattern’ is located between the lamellar morphology and that where the middle block forms a cylinder at the lamellar interface between the end blocks. The ‘knitting pattern’ is obtained when the film is cast from chloroform and the lamellar structure when a toluene solution is used. Such an effect from the casting solvent was not indicated in other SBM samples. Changing the sequence from SBM to BSM alters the obtained morphology for the same reason as that of the ISP and SIP case due to increased dissimilarities between the interfacial block tensions.

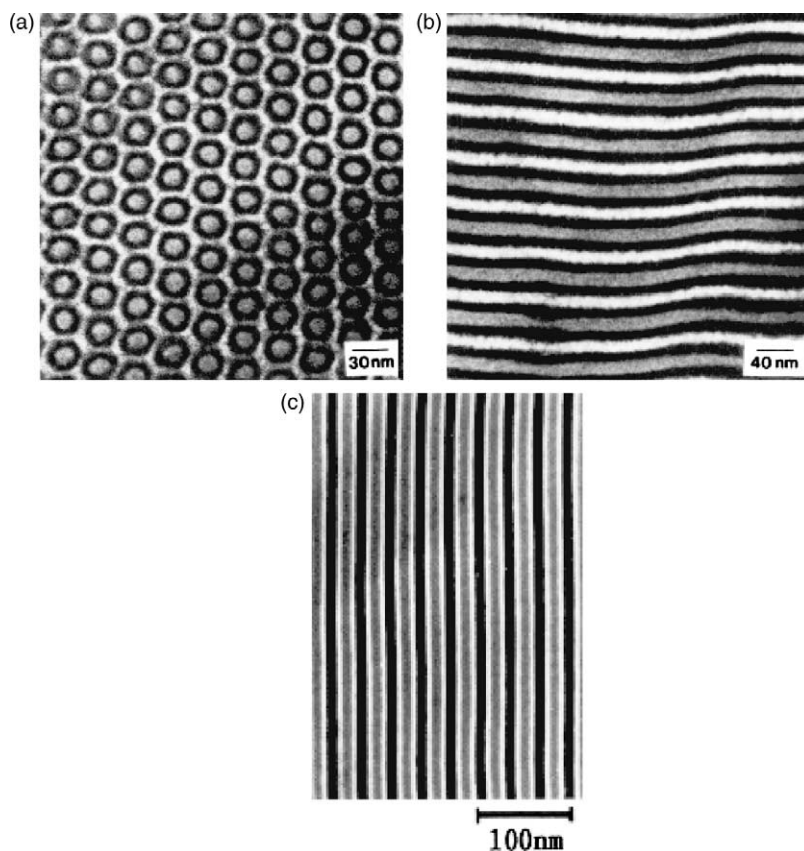


Fig. 55. (a) Axial TEM projection of hexagonally packed structural units, exhibiting concentric cylinders, for the SIP sequence. The darkest regions correspond to the OsO_4 stained PI domains, while the grey regions are CH_3I stained P2VP domains. (b) Transverse TEM projection. The light, grey, and dark regions correspond to projections through the PS matrix, the P2VP core, and the PI annulus, respectively (adopted from Ref. [23], Fig. 2). (c) Three-phase four-layer lamellae which is exhibited from the ISP sequence.

While the material polyisoprene-*b*-polystyrene-*b*-poly(vinylpyridine) (ISP) with approximately equal block volume fractions exhibits the three-phase four-layer lamellae [1], the terpolymer polystyrene-*b*-polyisoprene-*b*-poly(vinylpyridine) [88] (SIP) forms hexagonally packed core shell cylinders (Fig. 55). It should be noted that in the case of the SIP materials the PI component was mainly 1,4- in microstructure, while in the ISP the microstructure was completely different: $\sim 60\%$ 3,4 and $\sim 40\%$ 1,2.

In the case of the SIP materials, the PI component was mostly (90%) 1,4 in microstructure, while in the ISP the microstructure was completely different, being $\sim 60\%$ 3,4 and $\sim 40\%$ 1,2. Such observation leads to the fact that the aforementioned materials do not contain perfectly identical segments. It has been

reported that there is immiscibility [89] between different dienes (PI: $\sim 60\%$ 3,4 and PB: $\sim 92\%$ 1,4). Therefore, both the monomer sequence and the χ parameter between the SI and IP in the two sequences are different, leading to different structures for approximately identical volume fractions.

SIP and ISP materials were previously studied by Matsushita and collaborators [78,2], where the OTDD (Ordered Tricontinuous Double Diamond) structure was obtained and thoroughly evaluated. This structure was obtained even when the block sequence was altered. At that time this structure was unique, but a reevaluation paper from Thomas et al. [103] led to the currently held conclusions that the double diamond structure is really rare and the double Gyroid is most prominent in the case of diblock copolymeric materials. Taking into

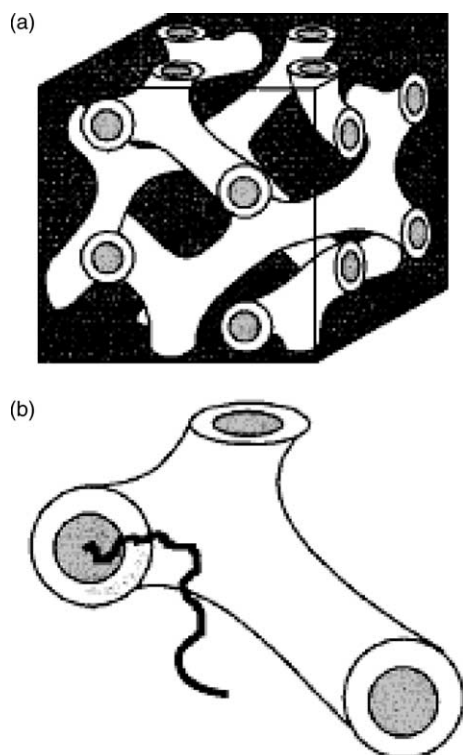


Fig. 56. (a) Schematic representation of the core-shell gyroid unit cell. (b) Illustration of the topological arrangement of the blocks in the matrix and the networks.

consideration the theoretical predictions by Matsen and co-workers [76] and Fredrickson and collaborators [77] concerning the OTDD structure, it can be concluded that the Gyroid cubic structures are more favorable than the Diamond ones.

The substitution of PI with PBd ($\sim 90\%$ 1,2) led to the existence of a new type of three-dimensional cubic structure which was proven by transmission electron microscopy and computer simulations for a linear SBV triblock copolymer where S is polystyrene, B is poly(1,2-butadiene), and V is poly(2-vinylpyridine) [104]. This structure is identified as the core-shell gyroid morphology and a schematic representation is given in Fig. 56. However, this morphology was only found as a minority structure in addition to lamellae, and therefore it should be assumed that it may not be the equilibrium morphology for such materials.

Abetz and co-workers have also studied the morphologies obtained from PS-*b*-PB-*b*-poly(*tert*-butyl methacrylate) [105] and the corresponding

chemically modified PS-*b*-PB-*b*-poly(methacrylic acid) [106]. Initially, the study [105] was aimed at exploring the microphase separation in different solvents (THF and chloroform), which led to very distinct differences in the resulting structures. Such differences can be attributed to the altered swelling behavior of the respective blocks in the solvents, and thus the casted films do not reach an equilibrium structure even though long-term stability is exhibited.

The microphase structural change from the unmodified to the modified material [106] is very clear, and reveals that the interaction parameter and therefore the miscibility between the blocks and the solvent are completely altered. The chemical modification of one block from *tert*-butyl methacrylate to acrylic acid plays a significant role in the selectivity of the solvent, whereas the miscibility change with the other two blocks is not that important. The swelling behaviour is also altered, especially in the acrylic acid terpolymers and seems to play the major role in determining the finally observed morphology.

The morphological behaviour of thermally treated PS-*b*-PB-*b*-poly(ϵ -caprolactone) was recently investigated by Balsamo et al. [107,108]. This group found that annealing at high temperatures can influence the obtained morphology, and a transition from lamellar-cylindrical (lc) to a cylindrical-ring (cr) structure is obtained within the same copolymer (Fig. 57). Long-range order of the samples was also observed depending on the composition. It should be noted that the self-assembly together with the presence or lack of spherulites in the bulk indicate the grapple between the crystallization and the microphase separation, especially when the composition of the crystalline block (PCL) is enhanced. Finally, the differences in the observed structures were straightforward with regard to the thermal properties and behaviour of the terpolymers.

The microphase separation and phase behavior for an ABC (SIO) consisting of crystalline (PEO), glassy (PS) and rubbery (PI) blocks with different block sequences was also investigated by Bates and collaborators [109–112]. Addition of PEO in a symmetric PS-*b*-PI diblock copolymer was studied [109] leading to the formation of different final triblock terpolymers varying only in the amount of added PEO. The molecular characteristics of the

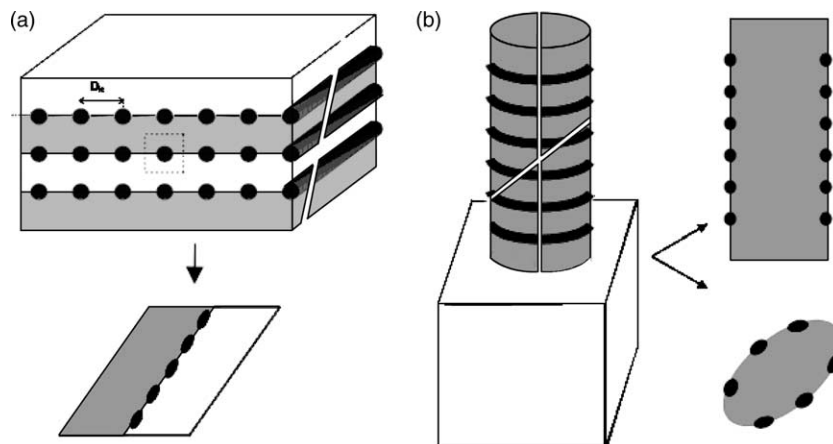


Fig. 57. Schematic illustration of the (a) lamellar-cylindrical (lc) and (b) cylindrical-ring (cr) structure for the PS-*b*-PB-*b*-PCL. Black regions are PB, grey are PS and white are PCL.

parent diblock were chosen in such a way in order for the final terpolymer to undergo ODT at experimentally accessible temperatures. The formation of two- and three-domain lamellar structures, hexagonally packed core-shell cylinders, and pentacontinuous core-shell gyroid morphology were observed.

The investigation of doped terpolymers (SIO) with salt was reported [110], by keeping the PS and PI volume fractions constant and varying that of the PEO block doped with the salt. The result was that morphologies exhibited in the neat material (core-shell gyroid and semi-perforated lamellae) were replaced by the core-shell cylindrical morphology in the doped material.

The same group evaluated the role of the sequence of the blocks in linear PS-PI-PEO and PI-PS-PEO triblock copolymers when $f_{PI}=f_{PS}$ and $0 < f_{PEO} < 0.33$ near the order-disorder transition [111]. Altering the sequence from PS-PI-PEO to PI-PS-PEO has a very distinct effect on the microphase separation between the two- (PS-*b*-PI) and three-domain (PS-*b*-PI-*b*-PEO) lamellae limits. Even though four-ordered structures separate the LAM₂ and LAM₃ states in PS-PI-PEO, only one (new) ordered morphology is included in the composition space between these limiting states in PI-PS-PEO, exhibiting *Fddd* space group symmetry. This structure was found to exist for a wide composition range of PEO ($0.12 < f_{PEO} < 0.25$). It also seems that the structure consists of crystallographic elements thoroughly different from

the core-shell gyroid topology, leading to a new non-cubic network structure, and constructed from two parts of perforated layer (PL) and one part gyroid (G).

The same group has evaluated [112] the roles of block sequencing and lithium perchlorate doping on the phase behavior of poly(styrene-*b*-isoprene-*b*-ethylene oxide) and poly(isoprene-*b*-styrene-*b*-ethylene oxide) triblock copolymers along the $f_I=f_S$ compositional length from a parent diblock copolymer to the symmetric $f_I=f_S=f_O$ triblock copolymer. In the ISO system, lithium doping led to an increase in segregation strength as shown by the increase in order-disorder transition temperatures and domain spacings. However, the melting temperature reduction for a given domain size is greater in the ISO relative to the SIO triblock copolymers.

Bates' group also investigated the morphological behaviour of other linear ABC terpolymers, such as PI-*b*-PS-*b*-poly(dimethylsiloxane) (ISD) [10]. The ISD terpolymer studied has equal volume fractions of PS and PI (0.40 and 0.41, respectively), and the volume fraction of the PD is approximately half (0.19). It was found that the material obtained the core-shell gyroid structure with *la3d* space-group symmetry (Fig. 58).

It should be noted that the same group also studied the morphology transition of such SID materials when swelling occurred with the addition of homopolystyrene and homopoly(dimethylsiloxane) [113]. The molecular weights of the homopolymers were very

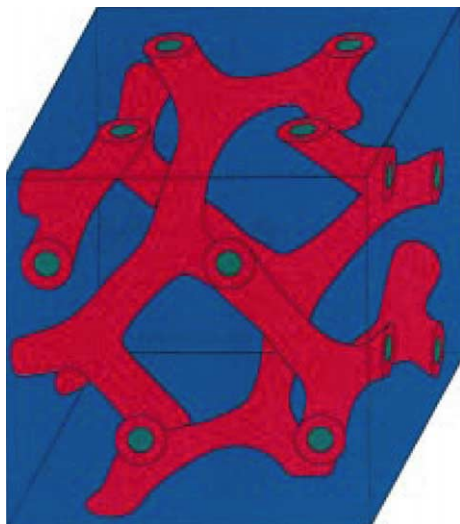


Fig. 58. Schematic illustration of the core-in-shell gyroid structure associated with the poly(isoprene-*b*-styrene-*b*-dimethylsiloxane) (ISD) triblock copolymer; blue, red, and green regions correspond to I, S, and D domains, respectively.

low in order to ensure complete mixing. From the complex ordered microstructure of the neat material, transitions are exhibited to core-shell cylinders and core-shell gyroid, depending on the percentage of the homopolymers.

Finally, the study of PI, PS and poly(methyl vinyl ether) (PMVE) terpolymer is also reported [67]. The microphase separation in this material is carried out in two steps. When casted from toluene the TEM images exhibit a lamellae two-phase PI/(PS/PMVE) system. Addition of only a drop of water as observed by PTA staining, caused the PS and PMVE to microphase separate within the already formed lamellar phases (Fig. 59). Water is a selective solvent for PMVE, and probably lowered the T_{ODT} between PS and PMVE.

4.3.2. ABC non-linear terpolymers

In contrast to the large variety of studies regarding ABC linear terpolymers, relevant morphological investigations of ABC non-linear terpolymers are

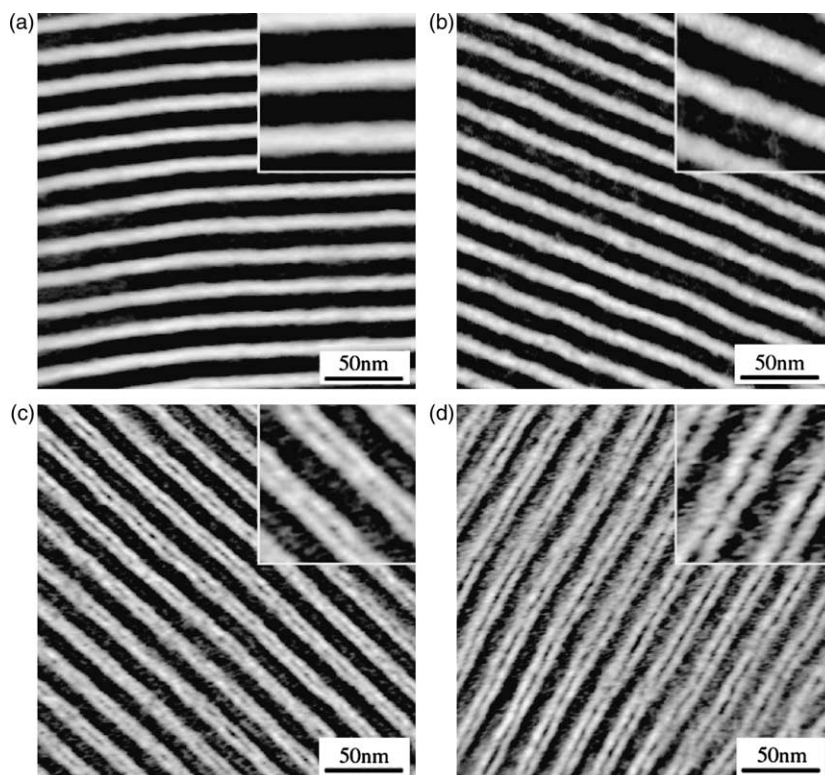


Fig. 59. TEM images for the ISV sequenced terpolymers, obtained first from staining with OsO_4 and then by PTA. (a) 0 min with PTA, (b) 30 min with PTA, (c) 45 min with PTA, (d) 60 min with PTA. Inset images are given in each case to better understand the observed structures.

very limited. This is due to the fact that such materials are very difficult to synthesize. Regarding the cyclic triblock terpolymers experimental data have not been reported in the literature. The materials most often studied are the miktoarm stars (Fig. 47d).

The first morphological characterization of a miktoarm terpolymer, consisting of PS, PI and PB was reported in the literature by Hadjichristidis and collaborators [114]. Actually, they were the first group to synthesize such materials by using controlled chlorosilane chemistry. Unfortunately, the TEM images exhibited a two-phase system, hexagonally close packed white cylinders of PS in a black matrix, leading to the conclusion that the two polydienes were completely mixed due to their very low χ interaction parameter.

Okamoto and co-workers [66] investigated miktoarm stars of A: polystyrene, PS; B: poly(*tert*-butyl methacrylate), PtBMA; C: poly(dimethylsiloxane), PDMS. They were the first to obtain microphase separation of all three components, where each microdomain forms a three-dimensionally continuous network, resulting in an ordered tricontinuous microdomain structure. The volume fractions of the blocks were approximately equal. The final obtained structures were either hexagonal columns or lozenge-shaped columns of each microdomain, completely different from what the authors expected (Fig. 60).

The morphological study of another set of ABC miktoarm star terpolymers, which three incompatible

components was reported by the Hadjichristidis' group [115,116]. The materials consisted of PS, PI and PMMA. PS and PMMA are highly incompatible towards PI and weakly incompatible between each other. This difference in the interaction parameters and the complex architecture of the material allow the molecule to 'choose' which arms directly interact for the microphase separation. In the first paper [115], both distinct three-phase microdomain structures and junctions lie on the PI–PS interface causing partial mixing between the PS and PMMA segments. The second paper [116] provides direct evidence that the SIM material adopts a structure where all the junction points are confined on lines (Fig. 61). This latter conclusion is of major importance and has already been verified theoretically by Pan and co-workers [86]. In this case, the experimental data have preceded the theoretical predictions and are in good quantitative and qualitative agreement.

The same group synthesized and morphologically studied miktoarm star terpolymers of PS, PI and P2VP [poly(2-vinylpyridine)] [40]. It was observed that this material exhibited similarities with the SIM terpolymers, and the junction points were again confined to lines instead of interfaces.

Abetz and collaborators [117] also made major contributions to the understanding of ABC miktoarm star terpolymer microphase separation. The materials synthesized were identical with those of the Hadjichristidis' group [40], with a difference only in the polydiene: PB was used by Abetz and PI by

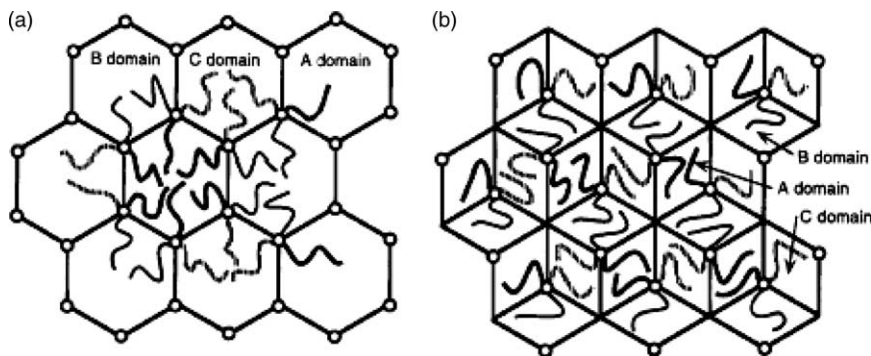


Fig. 60. Probable morphological structures for ABC materials exhibiting equal volume fractions. (a) Each chain consists of a hexagonal column. (b) Each microdomain consists of a lozenge-shaped columns. In both case the junction points are located on lines perpendicular to the paper.

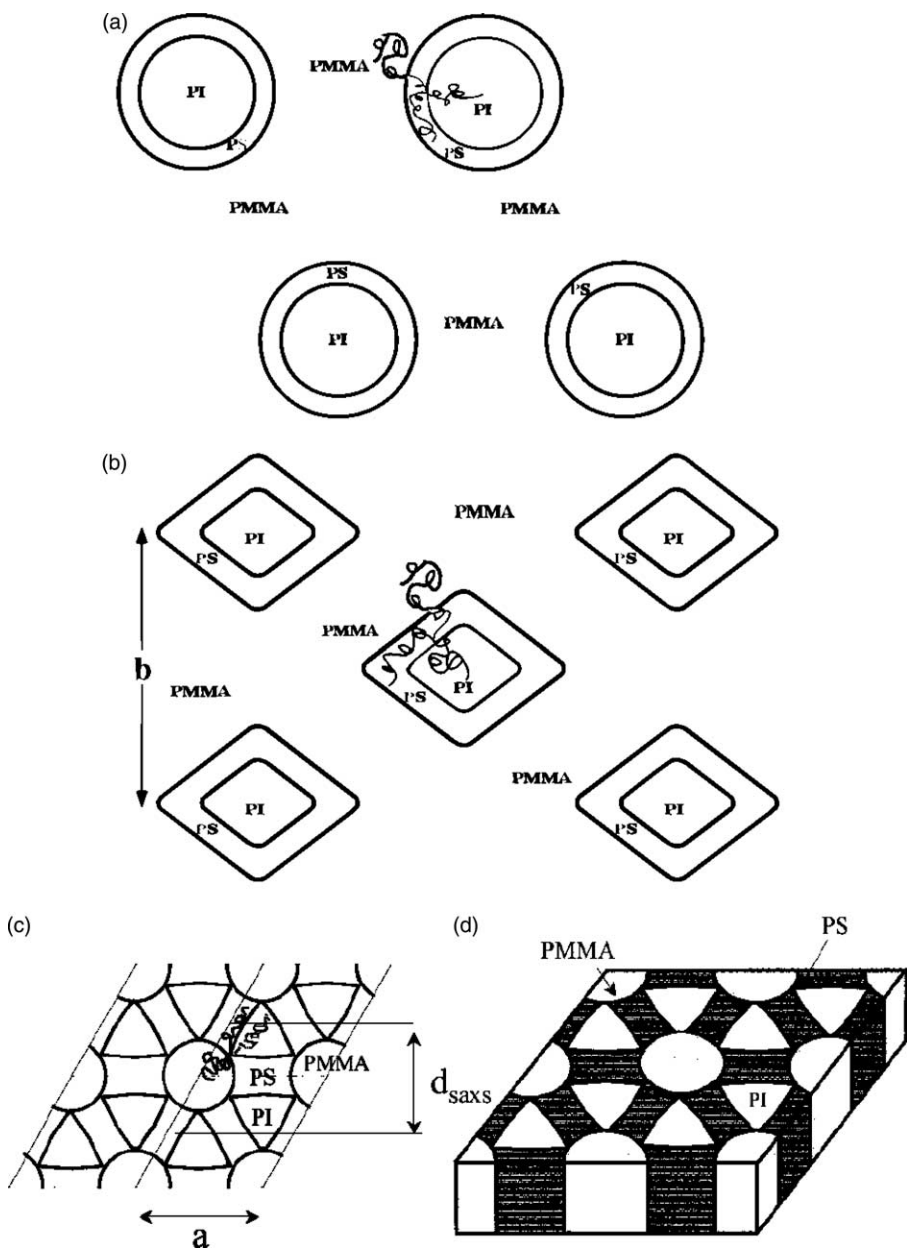


Fig. 61. Schematic presentations of the morphologies for the SIM materials. (a) Hexagonally packed PI cylinders with a concentric PS annulus in a PMMA matrix. The junction points are distributed on the PS–PI interface. (b) Concentric rhombhedral morphology. The junction points are distributed again on the PS–PI interface. (c and d) Representative chain conformation and perspective exhibiting the junction points which are residing on lines where the three different microdomains intersect, respectively.

Hadjichristidis. A large series of SBV materials were examined in order to distinguish the effect of volume fraction on the obtained morphology. For lower P2VP content, the system exhibited tetragonal or hexagonal

morphologies, and when the ϕ_{P2VP} increased to 50–60% hexagonal structure was obtained. Such morphologies indicate the confinement to lines for the junction points.

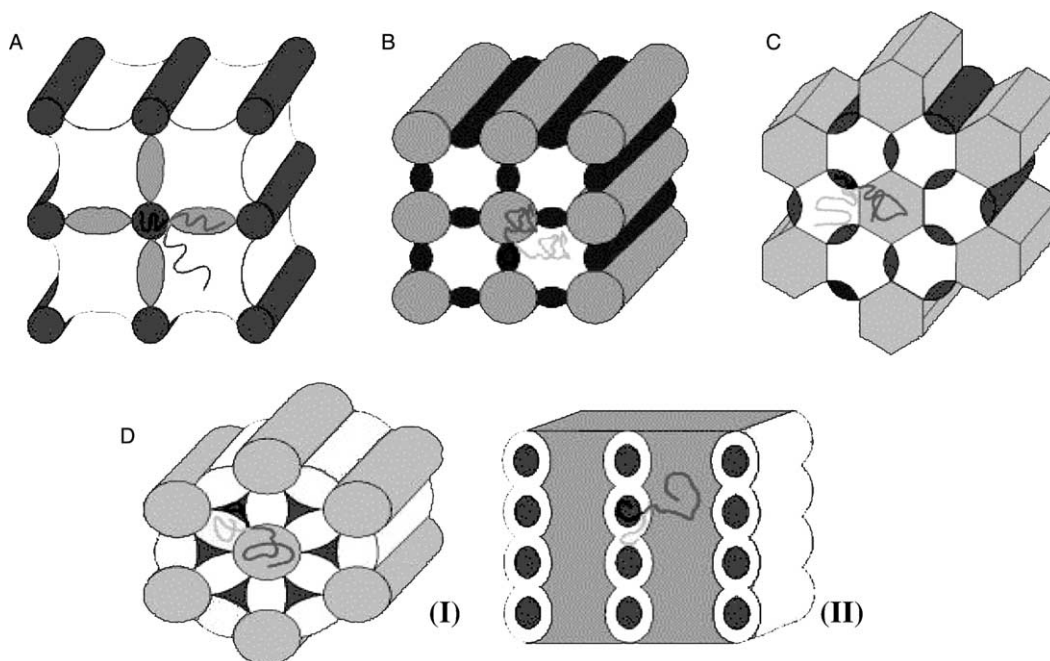


Fig. 62. Schematic illustration of the morphologies obtained for (PS)(PI)(P2VP) miktoarm star terpolymers. White regions are PS, grey are P2VP and dark grey are the PB regions. (A) PS and PB form a tetragonal lattice of cylinders and P2VP forms small domains between the two other phases. (B) PS cylinders are surrounded by four P2VP, and PB is located in such a manner in order to face four P2VP cylinders. (C) The hexagonally shaped P2VP cylinders are surrounded by six PS cylinders along the surface and by six PB cylinders along the edges. (D) The structures (I) and (II) coexist in all observations by TEM. (D I) The PB domains share three interfaces with PS domains, while the PS domains have only two PB domains in their environment. (D II) P2VP and PS lamellae are indicated and PB cylinders are contained by the PS lamellae domains.

Lamellar morphologies were obtained when ϕ_{PS} was smaller than the ϕ_{PB} , despite the value of ϕ_{P2VP} , due to larger incompatibility between the PBd and P2VP segments. The junction points in these materials are not confined to lines but to interfaces (Fig. 62).

Finally, the morphological characterization of an ABC miktoarm terpolymer consisting of PS, PI and PDMS was recently reported and identified by a method different from conventional TEM [118]. A combination of three-dimensional electron tomography and Energy-Filtering TEM were adopted. Only one of the three components has contrast under TEM investigation when the specimen is stained with OsO_4 . Zero loss images ($\Delta E=0$) with the EF-TEM exhibit unique resolution and contrast when compared with corresponding images from conventional TEM, since the energy filter eliminates the inelastically scattered electrons causing chromatic aberration. Electron tomography can very clearly distinguish

nanostructures in real space and together with EF-TEM can provide the complete identification of the three-dimensional microdomain structure for the complex material (Fig. 63).

Unfortunately, experimental results on the morphological behavior of cyclic triblock terpolymers have not appeared in the literature.

5. Future perspectives

Recent developments in synthetic capabilities and understanding of the parameters that lead to living polymerizations have allowed for the synthesis of more complex structures including more than three different blocks in the same molecule. There are relatively few examples in this area. Nevertheless, these materials are expected to have very interesting properties both in solution and in bulk.

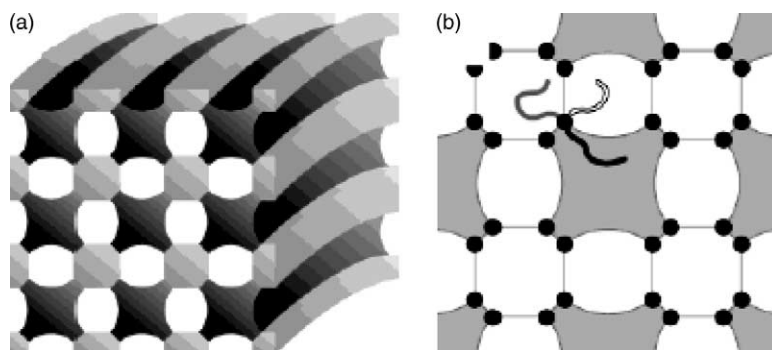


Fig. 63. (a) Schematic presentation of the model for the (PI)(PS)(PDMS) miktoarm star terpolymer, consisting of dark (PI), grey (PDMS) and white (PS) cylinders with specific shapes. (b) Presentation of the confinement to lines (filled circles).

Benzyl potassium was successfully employed as anionic initiator for the synthesis of PS-*b*-PI-*b*-P2VP-*b*-PEO tetrablock quarterpolymer and PS-*b*-PI-*b*-P2VP-*b*-*t*BuMA-*b*-PEO pentablock quintopolymer [13,119].

Multiblock copolymeric structures containing poly(1,3-cyclohexadiene), PCHD, blocks were also synthesized with *s*-BuLi as the initiator and either tetramethylene ethylenediamine, TMEDA or 1,4-diazabicyclo[2,2,2]octane, DABCO, as the additive leading to the synthesis of PS-*b*-PBd-*b*-PI-*b*-PCHD tetrablock quaterpolymers [120].

Linear ABCD quaterpolymer consisting of PS, PI, PDMS and P2VP blocks were prepared by Hadjichristidis' group, and the microphase separation was reported by Hasegawa et al. [121]. The synthesis was carried out by anionic polymerization, sequential addition of monomers and the use of 2-(chloromethylphenyl)ethyldimethyl chlorosilane as a specific heterofunctional linking agent. The PI, PDMS, and P2VP domains form triple coaxial cylinders with a hexagonal shape packed in a hexagonal array in the PS microphase, to form the honeycomb shaped matrix (Fig. 64). The potential applications of such systems include multifunctional sensors and multiselective catalysts for sequential or simultaneous chemical reactions of various kinds.

A 4-miktoarm star quaterpolymer was synthesized using the chlorosilane approach similar to the one adopted for the synthesis of the 3-miktoarm stars (PS) (PI)(PBd), consisting of four different arms, namely PS, poly(4-methyl styrene), P4MeS, PI and PBd [122].

Other ABC triblock terpolymers and more complex structures containing less common blocks, such as polypeptides or polyisocyanates can be prepared opening new horizons in the field of polymer science.

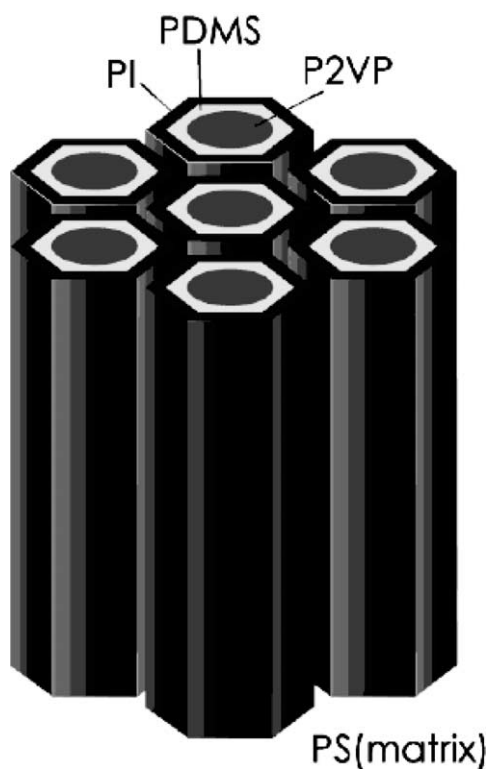


Fig. 64. Schematic illustration of the model for the hexagonal triple coaxial cylinder structure observed in PS-*b*-PI-*b*-PDMS-*b*-P2VP. White (PS), dark (PI), light grey (PDMS) and dark grey (P2VP) regions are indicated.

6. Conclusions

Advancements in synthetic polymer chemistry have allowed a wide range of ABC type triblock terpolymers to be synthesized by all living polymerization methods and their combinations. In most cases, these blocks are thermodynamically incompatible, giving rise to a rich variety of morphological microstructures both in bulk and in solution. A broad range of fundamental issues associated with understanding of self-assembly processes and the factors that control phase behavior, developments in molecular and structural characterization as well as elucidation of the response of block copolymers to external fields are under continuous investigation. At present the synthetic capabilities are more powerful than the theoretical and experimental studies employed to understand the properties of such macromolecular systems. It is anticipated that a better understanding of the structure–property relationships for these materials will lead to impressive new polymers with numerous applications. It is synthetically possible to prepare complex linear and non-linear block copolymers consisting of more than three different blocks. This development opens new horizons in the field of polymer physics generating a much wider range of microdomain structures in both bulk and solution.

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