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Processes for obtaining linear block copolymers

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Abstract. The advantages and disadvantages of modern methods of synthesis of linear block copolymers using identical and different mechanisms of monomer polymerisation are considered. The attention is focussed on the synthesis of block copolymers with a controlled molecular structure and narrow molecular-mass distribution. The matrix effects that appear in block copolymerisation due to chemical complementarity of the blocks are considered. The bibliography includes 393 references.

I. Introduction

Block type copolymers include a broad spectrum of heteropolymer compounds comprised of two (A, B), three (A, B, C) and more components. There are linear block copolymers, graft copolymers, star-like block copolymers and block copolymers of complex molecular architecture.[1] During the last fifteen years the synthesis of block copolymers has been considered in reviews and monographs (see, *e.g.*, Refs 2 – 11). This is due to considerable interest of researchers in such compounds and the development of new polymerisation techniques (first of all, controlled, or 'pseudoliving', radical polymerisation [12]) that open new possibilities for macromolecular design. Block copolymers are widely used in nanotechnologies;[13 – 19] therefore, obtaining of almost monodisperse products with specified length and position of particular blocks requires improvement of relevant synthetic procedures.

Various methods of synthesis of linear di-, three- and multiblock copolymers of the types A-b-B, A-b-B-b-A, B-b-A-b-B, A-b-B-b-C, $[A\text{-}b\text{-}B]_n$, $[A\text{-}b\text{-}B\text{-}b\text{-}C]_n$ and gradient (tapered) block copolymers of the A-b-(B-co-A)-b-B type are available at the moment. All of them can be divided into three main groups, namely, (i) sequential polymerisation of monomers by the same mechanism; (ii) monomer polymerisation by some mechanism; and (iii) interaction between reactive end groups of oligomers.

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This review concerns the first two groups of the methods of synthesis of linear block copolymers and manifestations of the matrix effects in block copolymerisation, where the first block already formed and the growing second block in the macromolecules of di- or triblock copolymers are chemically complementary. In each case we begin with a brief survey of the corresponding polymerisation mechanism and provide references to comprehensive sources.

II. Sequential polymerisation of monomers by the same mechanism

One-stage (or one-pot) synthesis of linear block copolymers is the most preferable method. The approach involves sequential introduction of different monomers into the reaction without changing external conditions (temperature, solvent, *etc.*) and leads to copolymers of necessary composition, with the desired block lengths and narrow molecular mass distribution (MMD). This can be done provided a correct choice of monomers using the 'living' ionic, ion-coordinative and 'pseudoliving' radical polymerisation.

1. Homogeneous and microheterogeneous radical polymerisation

Sequential free radical polymerisation was the first method used for the synthesis of linear block copolymers. A PMMA-b-PS block copolymer [PMMA is poly(methyl methacrylate) and PS is polystyrene] was synthesised in the early 1940s by adding styrene to PMMA macroradicals.[20] The technique was then used for preparation of various block copolymers of the A-b-B and A-b-B-b-A types.[21] The mechanism, advantages and drawbacks of free radical polymerisation are well known.[22, 23] The advantages of this block copolymer synthesis were found to be simplicity of practical implementation, high reaction rate and versatility, a great choice of the monomer pairs and weak dependence on the solvent nature and a presence of impurities.[22, 23] However, poor controllability of the process owing to its high rate and various chain termination reactions leads to broad MMD and compositional inhomogeneity of resulting block copolymers and to the presence of homopolymer impurities. This makes the method unpromising compared to other techniques.

At the same time the advantages of the process (see above) still attract the attention of researchers, as indicated by studies of so-called 'micellar' radical polymerisation.[24 – 27] At present, this technique is used only in aqueous medium for the synthesis of multiblock copolymers from polyacrylamide (PAA) or

polyacrylic acid (PAAc) and their hydrophobically modified derivatives. However, the one-stage synthesis and some degree of self-control in the system allow one to hope for progress of research in this field. Since only a few reviews of the method are available,[24, 27] we will dwell on it in more detail.

The main idea of 'micellar' polymerisation, as applied to the synthesis of block copolymers rather than random ones from a mixture of monomers in the presence of radical initiators, is to separate the chemically different monomers is such a fashion that the system be characterised by microheterogeneity and no phase separation. This can be done using a mixture of amphiphilic monomers in water in the presence of surfactants (surfactant concentration should be higher than the critical micelle concentration).[24–31] The mechanism of 'micellar' polymerisation is shown in Fig. 1. One (soluble) monomer is dissolved in the reaction medium and the other (insoluble) monomer is present in the hydrophobic core of surfactant micelles. The introduction of a soluble initiator (potassium or ammonium persulfate) causes polymerisation of the hydrophilic monomer and the hydrophilic block is thus formed. If the growing chain 'meets' a surfactant micelle, polymerisation of the hydrophobic monomer occurs and the hydrophobic block is formed. A multiblock copolymer is a final product.

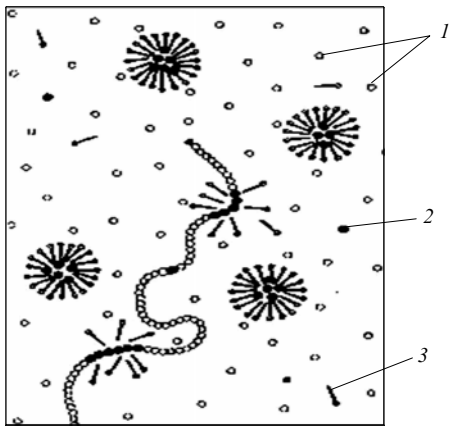
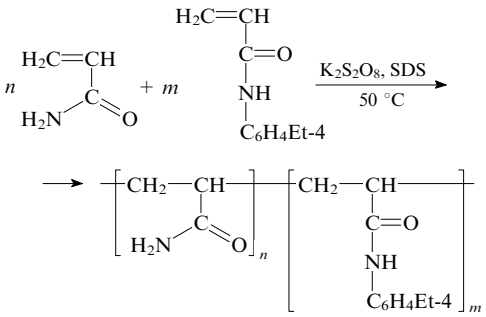


Figure 1. Schematic representation of micellar radical polymerisation.[32] Hydrophilic monomer molecules (*1*), hydrophobic monomer molecules (*2*) and surfactant micelles (*3*).

The authors of the pioneering studies (see, *e.g.*, Ref. 33) assumed that copolymers thus synthesised are comprised of randomly distributed hydrophilic and hydrophobic monomers. However, the properties of these copolymers were different from those of the random copolymers synthesised from the same monomers in a common solvent; therefore, a microblock structure of the copolymers was proposed.[30] This hypothesis was confirmed by the results of fluorescence studies of the copolymers containing acrylamide derivatives with styryl or pyrenyl groups as hydrophobic co-monomers.[34, 35] These studies revealed one of the basic regularities of 'micellar' polymerisation, namely, the higher the hydrophobic monomer to surfactant ratio the longer the hydrophobic blocks.[24] The structure of micelles was determined. It was shown that the hydrophilic fragments of hydrophobic monomers are located in the hydrophilic 'corona', which also contains a small amount of hydrophilic monomers.[24, 34] Hence, it was assumed that chain propagation through addition of hydrophobic monomers begins proceeds in the hydrophilic 'corona' of micelles.

Kinetic studies[32, 36] of the reaction of acrylamide with *N*-(4-ethylphenyl)acrylamide in the presence of sodium dodecyl sulfate (SDS) as surfactant revealed some additional features of 'micellar' polymerisation.



Solubilisation of hydrophobic monomers into micelles does not reduce their accessibility to the growing chains formed in the aqueous medium. Hydrophobic monomers are more rapidly added to the propagating chain in the initial steps of the process (the larger the hydrophobic monomer : surfactant ratio the higher the addition rate). This effect was explained by migration of the hydrophobic monomers between micelles that occurs three orders of magnitude faster than the addition of these monomers to the PAA$^{\bullet}$ radical. As a result, during polymerisation of the hydrophobic monomer in one micelle the delivery of this monomer from other micelles is also possible. Therefore, in the initial stages of the process the number of monomer units in the hydrophobic blocks, which determines the lengths of such blocks, can be larger than the average number of hydrophobic monomers in the micelle. As the monomer in the micelles is consumed, the hydrophobic blocks become shorter. The major distinction between 'micellar' polymerisation and conventional emulsion polymerisation consists in the high surfactant to hydrophobic monomer ratio (from 15 : 1 to 70 : 1 by mass, see Ref. 32).

Pioneering studies on 'micellar' polymerisation were carried out using pairs of monomers with hydrophilic acrylamide (AAm) and hydrophobic *N*-mono-substituted AAm. In addition to *N*-(4-ethylphenyl)acrylamide (see the reaction shown above), *N*-benzylacrylamide[37] and *N*-octyl-, *N*-decyl- and *N*-dodecylacrylamide were used as hydrophobic co-monomers.[38] The hydrophilic/hydrophobic balance in the system was changed using not only insoluble *N*-(n-decyl)acrylamide or *N*-[4-(n-butyl)phenyl]acrylamide and soluble AAm, but also ionogenic monomers, such as sodium acrylate, sodium 3-acrylamido-3-methylbutanoate and sodium 2-acrylamido-2-methylpropanesulfonate.[39, 40] Therefore, multiblock copolymers comprised blocks built of random copolymers of AAm with ionogenic co-monomers. Recently, alkyl methacrylates[41] and *N*,*N*-dialkyl acrylamides[42, 43] with growing hydrocarbon 'tails' have been used as hydrophobic monomers. Surfactants used in 'micellar' polymerisation include not only anionic SDS and sodium hexadecyl sulfate,[32, 41–43] but also cationic surfactants, *e.g.*, hexadecyltrimethylammonium bromide.[37]

2. 'Living' anionic polymerisation

Sequential 'living' anionic polymerisation is the most widely used method of synthesis of linear block copolymers of specified composition, molecular masses of constituent blocks and narrow MMD. Generally, 'living' polymerisation involves no chain termination and chain transfer stages, *i.e.*, the rate constants for these reactions are equal to zero ($k_t = 0$, $k_{tr} = 0$, see Refs 22, 23, 44 and 45). However, the 'living' mechanism is also retained if k_t and k_{tr} are much lower than the rate constant for chain propagation in accordance with the following criteria[46]

$$\frac{k_p}{k_t} \geqslant \frac{\ln([M]_0/[M]_\infty)}{[I]_0},$$

$$\frac{k_p}{k_{tr}} \geqslant 10\frac{[M]_0}{[I]_0} \sim 10\,\overline{P}_n\,.$$

Here $[M]_0$ and $[I]_0$ are the initial concentrations of the monomer and initiator, respectively; $[M]_\infty$ is the concentration of monomer at the end of polymerisation and $\overline{P}_n$ is the degree of polymerisation .

These relations represent two important conditions for 'livingness' of the system and obtaining of polymers with predictable structure and molecular mass. The third conditions is fast initiation of the process.[22] Exactly in this case the polymer chains are formed and grow simultaneously and the degree of polymerisation rises linearly with the monomer conversion (q)

$$\overline{P}_n = \frac{q[M]_0}{f_i[I]_0},$$

where f_i is the efficiency of initiation. In actual experiments, the condition $k_i = \infty$ (k_i is the rate constant for initiation) is not necessary for control of the molecular mass of a polymer; it is sufficient that inequality $k_i \geqslant k_p$ be valid.[46] Obtaining a narrow MMD requires that the following additional conditions be met: (i) equal activity of the growing chains or fast exchange between their active sites; (ii) irreversible chain growth (rate constant for chain propagation should be much higher than the rate constant for depolymerisation). Under these conditions the MMD of the polymer depends only on the degree of polymerisation (according to the Poisson distribution) and the M_w/M_n ratio (*i.e.*, polydispersity index) near to unity.

The 'livingness' of a system may be determined provided that individual or relative rate constants for chain growth, chain termination and chain transfer are known.[47,48] These principles of retention of the 'living' mechanism mainly concern ionic processes characterised by long lifetimes of active species (this makes it possible to create the fast initiation mode) and by the absence of bimolecular chain termination reactions. Practical implementation of controlled, or 'pseudoliving', radical polymerisation is based on other principles (see below Sections II.5–II.7).

The mechanism of anionic polymerisation and the problems related to the activity of monomers, stability of macroradicals, choice of initiators, solvents and temperature have been subjects of intensive research and discussion.[22,23,44,46,49] We remind that anionic polymerisation assumes a nucleophilic attack of carbanion on the double bond of the monomer. Therefore, the monomer which has the most electrophilic double bond and provides greater stabilisation of the negative charge is the most reactive. The nucleophilicity of initiator should be high enough to initiate the process, but not too high to preclude the occurrence of side reactions. The formal criterion for sufficiently high nucleophilicity of the initiator is as follows: the pK_a of corresponding conjugate acid is equal to or higher than the pK_a value of the macroanion.[22,50] Different forms of active species, namely, ion pairs, separated ion pairs and free ion pairs are in equilibrium. The rate of anionic polymerisation (k_p^-) in the free ion regime increases dramatically[44]

$$k_p^- \approx 10^5\, k_p^{\pm}.$$

To reduce this parameter and thus obtain a narrower MMD, lithium chloride is introduced into the system (this salt shifts the equilibrium from free ions to ion pairs).[46,51,52]

$$\sim R^- + Li^+ \rightleftharpoons \sim R^-\ Li^+ \xrightarrow{LiCl}$$

$$\longrightarrow \sim R^-\ Li^+ \cdot LiCl \overset{LiCl}{\rightleftharpoons} \sim R^-\ Li^+ \cdot 2\,LiCl$$

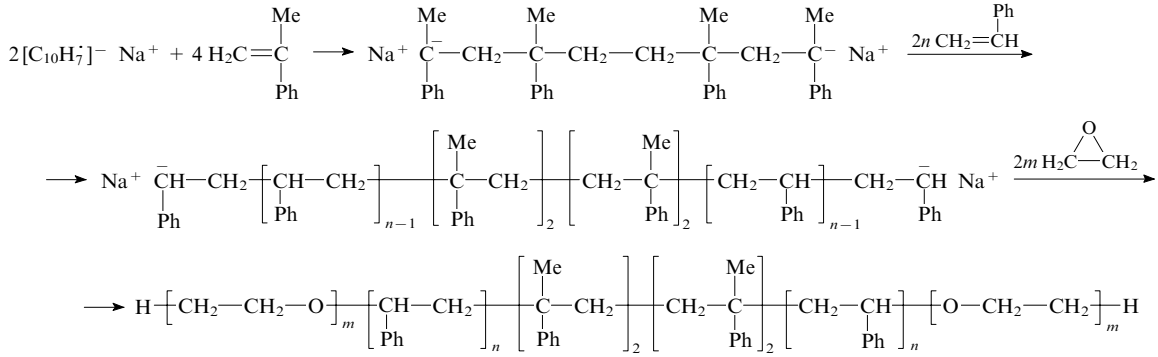
Solvents used in anionic polymerisation processes include hydrocarbons and ethers. Protic and halogen-containing solvents that favour chain transfer or termination are not used. The 'living' anionic polymerisation requires pure reagents, inert atmosphere and correct choice of temperature conditions. Polymerisation of nonpolar monomers in nonpolar solvents is well controllable at moderate positive temperatures (from 0 to 50 °C). Anionic polymerisation of polar monomers in polar solvents occurs at much higher rates, being controllable at low temperatures (as rule, −78 °C). Chain termination is most often attained by adding methanol.

To obtain a copolymer of specified composition, particular block lengths and narrow MMD by 'living' anionic polymerisation, some additional problems should be solved. The main problem is the relative reactivity of monomers, which determines the possibility or impossibility of initiation of polymerisation of the second (and then third) monomer by macroanions formed in the polymerisation of the first (and the second) monomer.[22,44,46] To this end, a series of monomers with increasing (electrophilic) reactivity are chosen. The process begins with polymerisation of the least reactive monomer that produces the most reactive macroanion; then increasingly more reactive monomers are added. The second problem is the side reactions occurring upon nucleophilic attack of macroanions on other reactive groups of the second (or third) monomer rather than the double bond. This is true for polymerisation of polar monomers containing hydroxyl, carbonyl, ester, amino and other groups.[22,46] To prevent the process, the 'living' ends of a preceding block are protected by monomers with bulky groups in α-position (α-methylstyrene, α-diphenylethylene, *etc.*). In addition, only protected derivatives of common functional monomers, in particular, (meth)acrylic acids are employed instead of ordinary functional monomers.[9,53,54] The protective groups include *tert*-butyl, trimethylsilyl, benzyl, alkoxyalkyl and other groups that are removed by polymer-analogous transformations of the block copolymer.[9] Sequential anionic polymerisation requires a correct choice of reaction conditions (solvent and temperature) to avoid a heterogeneous process. This is particularly important in the synthesis of block copolymers with thermodynamically incompatible blocks. In this connection we will now consider particular syntheses of block copolymers.

a. Binary nonpolar/nonpolar block copolymers

Nonpolar monomers (styrene, dienes, *etc.*) and their macroanions formed in nonpolar solvents show almost identical reactivity in anionic polymerisation. The similarity of nucleophilicities of the styrene and diene macroanions is confirmed by almost equal pK_a values of conjugate acids (40–42 for styrenes and 43 for dienes).[46] Therefore, the order in which monomers are introduced is of no concern for the synthesis of corresponding di-, tri- and multiblock copolymers. Copolymers with nonpolar blocks were among the first copolymers synthesised.[55–57] Among them, copolymers based on polystyrene (PS) and polybutadiene (PB) are best known. These are the first representatives of thermoplastic elastomers[58] that can absorb radiation.[59] Di-, tri- and multiblock copolymers of predictable structure and narrow MMD were synthesised by sequential addition of styrene (St) and butadiene (B) (or *vice versa*) in nonpolar solvents (hexane, benzene, *etc.*) in the presence of initiators (organolithium compounds). Moreover, by sequentially introducing (i) one monomer, (ii) an equivalent mixture of two monomers and (iii) the other monomer into the reaction one can obtain the so-called gradient triblock copolymers.[60–62] Here, the PS and PB blocks are separated by a 'mixed' block characterised by a compositional gradient (transition from pure PS to pure PB) owing to the features of copolymerisation of the monomers.

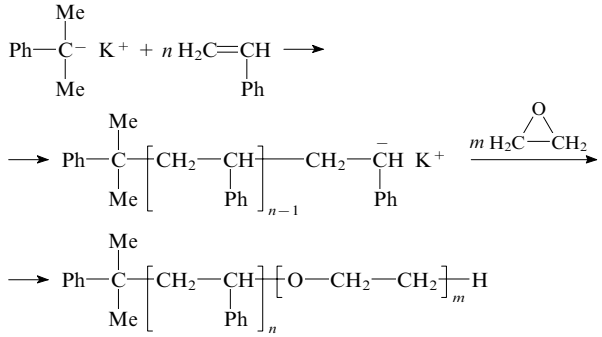
Scheme 1



b. Binary nonpolar/polar block copolymers

Polar monomers are much more reactive than nonpolar ones in anionic polymerisation in contrast to the reactivity ratio of corresponding macroanions. Therefore, anionic polymerisation of polar and nonpolar monomers only leads to two types of block copolymers, namely, A-b-B and B-b-A-b-B (A is the hydrophobic block, which is formed first). Multiblock copolymers based on such pairs of monomers are synthesised using other techniques, *e.g.*, by the reaction between the end functional groups.

The block copolymers in question first of all include amphiphilic block copolymers based on nonpolar PS, PB and polyisoprene (PI) and on polar poly(ethylene oxide) (PEO). When comparing the nucleophilicities of the St and ethylene oxide (EO) macroanions using the pK_a values of conjugate acids (41–42 and 16–18, respectively),[46] it is clear that sequential polymerisation of St and EO should develop very actively. The authors of Ref. 63 were among the first to obtain a PS-b-PEO diblock copolymer by sequential introduction of St and EO into the reactor in the presence of cumyl potassium as initiator.



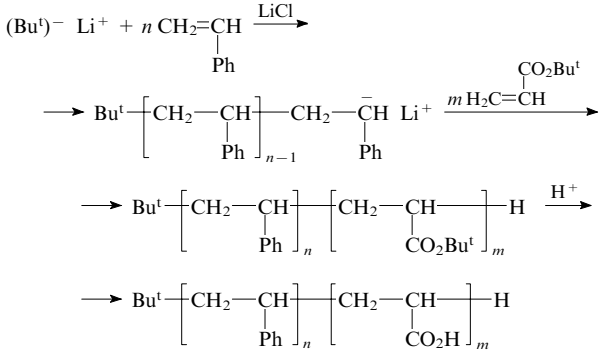
This copolymer was also synthesised using toluene as solvent and 1-phenylethyl potassium as initiator.[64] Polymerisation of the first block was carried out at 10 °C. The kinetic curves showed an induction period of about 1 h, which reduced as the temperature increased and upon introduction of tetrahydrofuran (THF). Polymerisation of the second block was conducted at a higher temperature (30 °C); as a result, the EO conversion increased to 92%. To study the self-assembly of block copolymers into micelles, PS-b-PEO copolymers containing intermediate units bearing pyrene, anthracene and phenathrene groups were synthesised.[65,66] To improve the controllability of sequential polymerisation of St and EO, in the 1990s it was proposed to carry out the process in a polar solvent (THF) at low temperatures (−78 °C).[67,68]

PEO-b-PS-b-PEO triblock copolymers were first prepared using sodium naphthalene as initiator and THF as solvent.[69] An analogous initiator (potassium naphthalene) was used in polymerisation of styrene and ethylene oxide.[70] However, in a series of other works [64,71,72] the dimeric or tetrameric adducts of sodium (potassium) naphthalene with α-methylstyrene were applied as initiators (Scheme 1). It was found that the reactivities of metal naphthalenes in block copolymerisation decrease as follows: potassium naphthalene > sodium naphthalene > lithium naphthalene. The last-named compound is a very poor initiator for the block copolymerisation of styrene and ethylene oxide.[64]

Di- and triblock copolymers based on polydienes and PEO were synthesised by the same method using mono- and bifunctional organopotassium initiators. In this case the lithium initiator was inefficient. For instance, a PB-b-PEO copolymer was obtained in a polar medium (THF) in the presence of cumyl potassium as initiator,[73] while a PEO-b-PI-b-PEO triblock copolymer was synthesised by sequential polymerisation of isoprene and EO in THF with potassium naphthalene as initiator.[74] Polymerisation of the first block was carried out at −40 °C for 6 h and that of the second block was performed at 25 °C for 3 days. Raising the temperature was due to low solubility of PEO in THF.

The copolymers in question also include copolymers with PS, PB or PE (polyethylene) nonpolar blocks and polar blocks of polyalkyl (meth)acrylates and products of their hydrolysis [PAAc and polymethacrylic acid (PMAAc) or their salts]. Note that methacrylates treated as conjugate acids with respect to macroanions formed from them are characterised by pK_a values of 27–28,[46] which is much lower than the pK_a values of styrene and dienes. Therefore, macroanions based on alkyl(meth) acrylates are incapable of initiating anionic polymerisation of nonpolar monomers. The first syntheses of di- and triblock copolymers based on PS and poly(*tert*-butyl acrylate) (PTBA) were reported in the 1990s.[75] Sequential anionic polymerisation was conducted in THF in the presence of LiCl at −78 °C.

Scheme 2



The block copolymer precursors were then hydrolysed in toluene at 80 °C in the presence of *p*-toluenesulfonic acid as catalyst to obtain the PS-b-PAAc and PAAc-b-PS-b-PAAc polyacid blocks. The synthesis of PS-b-PAAc and PS-b-PMAAc copolymers with controlled molecular structure and narrow MMD following Scheme 2 was simultaneously

reported by three research groups.[68, 76, 77] The side reactions characteristic of 'living' PS chains in the polymerisation of (meth)acrylates were avoided by 'capping' the ends of macroanions by 1,1-diphenylethylene [76, 77] or α-methylstyrene.[68] This synthetic procedure is used to change the hydrophilic/hydrophobic balance in block copolymers; this is a basic technique in the design of micellar structures sensitive to the pH value of the medium and to salt additives.[78, 79] The lengths of the PS and PAAc blocks varied over a rather wide range, but the polydispersity index of the block copolymers was low ($M_w/M_n = 1.05-1.21$).[80] An alternative procedure of PTBA transformation into PAAc involves prolonged (more than 10 h) hydrolysis in dioxane at 100 °C in the presence of HCl.[79] PAAc or PMAAc can also be converted to polyacrylates or polymethacrylates by adding alkali.[79]

PE-b-PMAAc and PMAAc-b-PE-b-PMAAc block copolymers were synthesised by sequential anionic polymerisation involving two polymer-analogous reactions.[81] First, anionic polymerisation of butadiene and *tert*-butyl methacrylate (TBMA) in the presence of mono- or bifunctional initiators resulted in PB-b-PTBMA and PTBMA-b-PB-b-PTBMA copolymers. This was followed by hydrogenation of PB using Wilkinson's catalyst and hydrolysis of PTBMA.

Sequential anionic polymerisation of styrene and alkoxyethyl methacrylates, namely, 1-(ethoxy)ethyl methacrylate (EEMA) and 1-(*tert*-butoxy)ethyl methacrylate (TBEMA), was carried out not only at −78 °C and −35 °C, but also at 0 °C.[82] A well-controlled process resulted in PS-b-PEEMA and PS-b-PTBEMA copolymers of predictable molecular architecture.

Yet another group of copolymers belonging to this class comprises diblock copolymers based on PS or poly(*tert*-butylstyrene) (PTBS) and cationic polyelectrolytes, namely, poly(2-vinylpyridine) (P2VP), poly(4-vinylpyridine) (P4VP), poly[5-(*N*,*N*-diethylamino)isoprene] and their quaternised derivatives. They are of interest as stabilisers of colloidal dispersions;[83] however, the attention was focussed on their micellar structures [84, 85] and films showing microphase separation.[86] It should be noted that the pK_a values of 2-vinylpyridine and 4-vinylpyridine treated as conjugate acids with respect to corresponding macroanions are much lower (29 and 26, respectively) than the pK_a values of styrene and dienes.[46] Therefore, polyvinylpyridine macroanions cannot initiate polymerisation of the nonpolar monomers mentioned above. A typical synthetic route to PS-b-P2VP, PS-b-P4VP and PTBS-b-P2VP assumes sequential introduction of nonpolar and polar monomers in THF, the presence of n-butyllithium or *sec*-butyllithium as initiator and a low temperature (−78 °C).[86, 87] Yet another initiator, namely, an adduct of *sec*-butyllithium with 1-methylstyrene, was used [84] to obtain block copolymers with $M_w/M_n = 1.13-1.14$. When needed, the polyvinylpyridine block was treated with methyl iodide in ethanol, which resulted in a strong cationic polyelectrolyte.[84]

Basic monomers, namely, 5-(*N*,*N*-dialkylamino)isoprenes, have been synthesised quite recently.[88, 89] Two new amphiphilic block copolymers having poly[5-(*N*,*N*-diethylamino)-isoprene] (PDEAI) blocks, PS-b-PDEAI and PDEAI-b-PS-b-PDEAI, were prepared and studied.[90–92] The procedure for the synthesis of the triblock copolymer consisting of sequential introduction of diethylaminoisoprene, styrene and again diethylaminoisoprene [91] points to almost equal reactivities of the monomers. The polymerisation was carried out in benzene at 10 °C using *sec*-butyllithium as initiator. The copolymers had narrow MMDs ($M_w/M_n = 1.2-1.4$, $M_n = 1.36\times10^4-2.68\times10^4$).[91, 92] Quaternisation of the copolymers with dimethyl sulfate gave copolymers having strong cationic polyelectrolyte blocks.

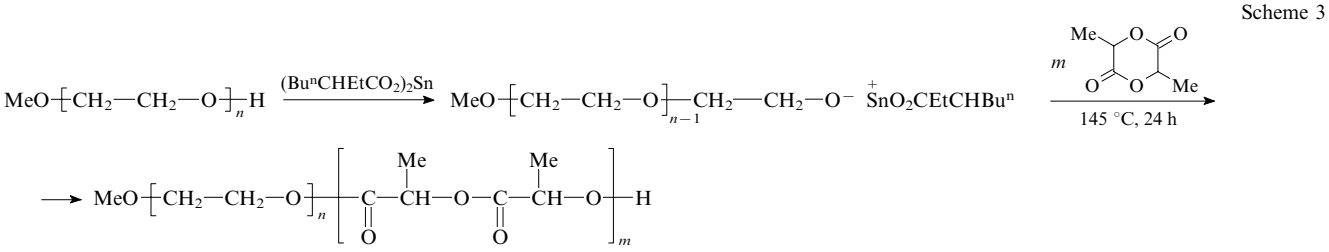
c. Binary polar/polar block copolymers

This group comprises block copolymers based on PEO and poly[alkyl (meth)acrylates]. Comparison of the pK_a values of alkyl (meth)acrylates and oxiranes showed that alkyl (meth)-acrylate macroanions should be more reactive than PEO macroanions. Indeed, 'living' poly[alkyl (meth)acrylates] readily initiate the polymerisation of EO.[93] However, when using methyl methacrylate (MMA), one can obtain inhomogeneous PMMA-b-PEO copolymers due to side reactions between the 'living' end groups of PEO and the methyl ester groups of PMMA. The monomers can also be introduced in the reverse order. For instance, efficient polymerisation of MMA in THF using PEO disodium alkoxide was reported.[94] This was explained by the fact that the nucleophilicity of the macrodianions is higher than that of the anions at one chain end. Sequential anionic polymerisation of EO and MMA faces two problems.[95] One of them consists in low solubility of PEO in THF. To avoid the formation of a heterogeneous system, polymerisation of the second block should be carried out at $T > 20$ °C. Under these conditions for polymerisation of MMA the chain termination and chain transfer reactions seem to be unavoidable. The second problem is transesterification between the PEO macroanion and MMA. It was found that by protecting the ester groups of (meth)acrylates with *tert*-butyl groups it is possible to preclude the formation of side products and to obtain copolymers with a desired structure and narrow MMD irrespective of the order of introduction of the monomers. In particular, polymerisation of EO and TBMA in THF at room temperature using cumyl potassium as initiator led not only to diblock copolymers characterised by narrower MMD ($M_w/M_n = 1.4-1.7$) compared to the polymerisation of EO and MMA, but also to multiblock copolymers.[96] Analogously, sequential anionic polymerisation of the same monomers was used for the synthesis of all possible di- and triblock copolymers, that is, PEO-b-PTBMA, PTBMA-b-PEO, PEO-b-PTBMA-b-PEO and PTBMA-b-PEO-b-PTBMA [97] with diphenylmethyl potassium and potassium naphthalene as initiators. The synthetic procedure involved polymerisation of TBA at −78 °C; after introduction of ethylene oxide the temperature was raised to 35 °C. Analysis of the reaction products by gel-permeation chromatography and by NMR and IR spectroscopies revealed no side processes and no homopolymers. Quantitative hydrolysis of *tert*-butyl ester groups of PTBMA led to formation of new block copolymers containing PMAAc.

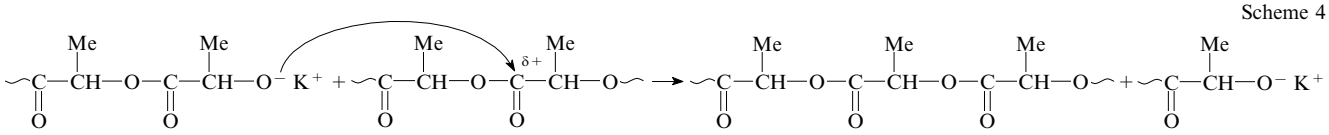
The known non-ionogenic di- and triblock copolymers based on hydrophilic PEO and hydrophobic poly(propylene oxide) (PPO) should be pointed out. They are produced on a large-scale basis under the trademarks 'Proxanols', 'Pluronics' and 'Poloxamers' mainly by sequential anionic polymerisation.[22] These amphiphilic block copolymers can form micelles [98] and complexes with many organic substances [99, 100] including pharmaceuticals.[101]

A quite interesting group of copolymers is built of PEO and cationic P2VP or P4VP blocks. There are few studies on the synthesis of such compounds, although their micelle-forming properties in aqueous solutions have been a subject of intensive research.[102] Since 2-vinylpyridine and 4-vinylpyridine (VP) are characterised by much higher pK_a values than oxiranes (29 and 26 *vs.* 16–18, respectively),[46] one can assume that PVP macroanions will be more reactive than PEO macroanions. This requires that the basic monomer be polymerised first. This order of introduction of the monomers was used in the synthesis of P2VP-b-PEO diblock copolymer.[102, 103] The polymerisation was carried out in THF at −78 °C with cumyl potassium/18-crown-6 ether complex as initiator.[103] In spite of a narrow MMD of the P2VP blocks, not all 'living' P2VP chain ends initiated the polymerisation of EO. As a result, the

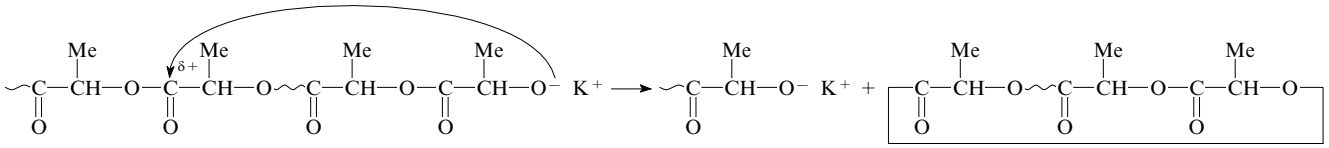
Scheme 3



Scheme 4



Scheme 5



reaction product contained up to 30 mass% of P2VP homopolymer.

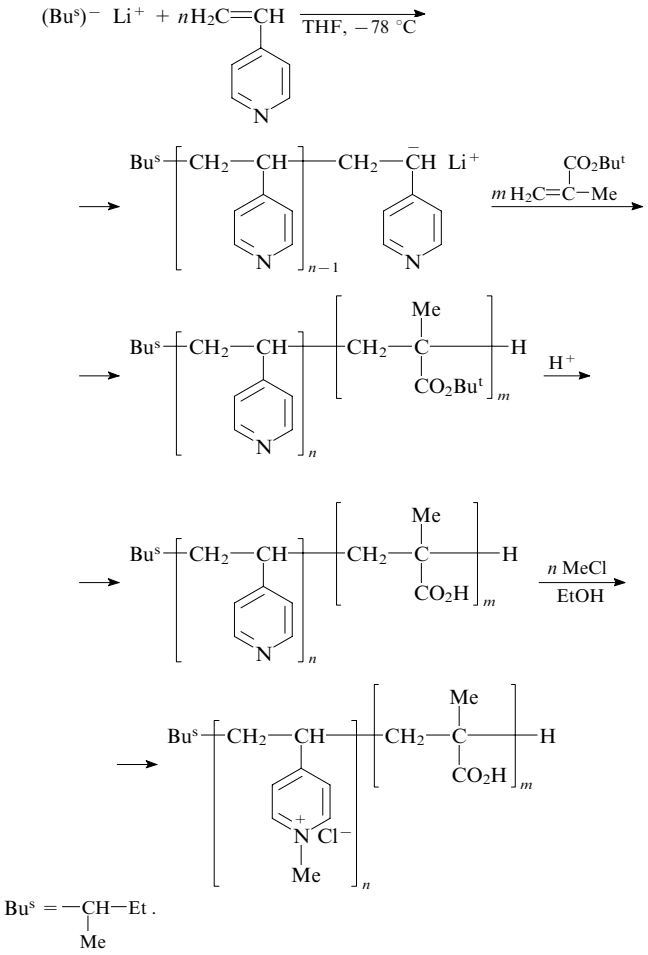
Recently, there has been search for new polar hydrophobic polymer blocks to obtain micelle-forming biocompatible and biodegradable materials by copolymerisation with PEO. One of such polymers is poly(ε-caprolactone) (PCL). Copolymers PEO-b-PCL that were synthesised and studied recently [104, 105] are promising for the design of macromolecular therapeutic systems.[106] It should be noted that among the monomers listed in Ref. 46, lactones have the lowest pK_a values in the range from 6 to 8, *i.e.*, their macroanions have the lowest nucleophilicity. Yet another biodegradable hydrophobic polymer is poly-L(or DL)-lactide (PL),[107] which is also widely used as a constituent of block copolymers. For instance, copolymers PEO-b-PL and PL-b-PEO-b-PL were synthesised and studied.[108, 109] However, the synthetic procedure did not involve sequential anionic polymerisation; macroinitiators based on commercially available polyethylene glycol (PEG) ($M_n = 4 \times 10^3$) or PEG monomethyl ether (PEGME, $M_n = 5 \times 10^3$) were employed. The hydroxyl groups of PEG or PEGME were activated by metallic potassium (in THF) [108] or tin 2-ethylhexanoate,[109] converted to mono- or bifunctional initiators and then anionic ring-opening polymerisation of DL- or L-lactide (Scheme 3) was carried out.

Copolymers PEO-b-PL and PL-b-PEO-b-PL were characterised by M_n of $(5.8-19.2) \times 10^3$ and $(6.0-17.4) \times 10^3$, respectively.[109] Analogous triblock copolymers [108] had similar molecular masses; however, the MMD was broad ($M_w/M_n = 3.04-4.21$) due to intermolecular (Scheme 4) and intramolecular (Scheme 5) re-esterification reactions during the polymerisation of D,L-lactide.

By combining sequential anionic polymerisation and polymer-analogous transformations it is possible to form copolymers containing anionic PAAc or PMAAc blocks and nonionogenic thermally sensitive *N*-mono- or *N*,*N*-dialkyl-substituted acrylamide blocks.[9] They are called the double stimuli-responsive copolymers, because the state of the polyacid blocks is determined by the pH value, while the state of the substituted PAA blocks is governed by temperature. The first stage involved block copolymerisation of protected *tert*-butyl acrylate (TBA) with *N*,*N*-diethylacrylamide (DEAA)[9] initiated by a mixture of diphenylhexyl lithium with LiCl. The polymerisation of the first block was followed by introducing triethylaluminium into the system. In the second stage the PTBA-b-PDEAA copolymer was hydrolysed to obtain the PAAc-b-PDEAA copolymer. A similar technique was used for the synthesis of PTBMA-b-PDMAA copolymers [PDMAA is poly(*N*,*N*-dimethylacrylamide)] with different block lengths.[110] First, *tert*-butyl methacrylate was polymerised under the action of an oligostyryllithium adduct with 1,1-diphenylethylene in the presence of LiCl ($T = -30$ °C). Then, the active centres were modified with an excess of diethylzinc at -40 °C, the temperature was reduced to -78 °C, *N*,*N*-dimethylacrylamide was introduced and the process continued. Block copolymers thus obtained had $M_n = 3.7 \times 10^4$ ($M_w/M_n = 1.33$) and 1.542×10^5 ($M_w/M_n = 1.28$) and contained 48.7 mass % and 14.3 mass % of PDMAA, respectively.

Amphoteric block copolymers, or copolyampholytes, containing acid (PAAc or PMAAc) and basic {poly[*p*-(*N*,*N*-dimethylamino)styrene] (PDAS), PVP and poly[2-(dimethylamino)alkyl methacrylates]} blocks occupy a special position. They are synthesised by sequential anionic polymerisation of the basic monomers and protected alkyl (meth)acrylates followed by acid hydrolysis of the polyester blocks. Amphoteric diblock copolymers P2VP-b-PMAAc and P2VP-b-PAAc were first obtained [111] by sequential polymerisation of 2-VP and trimethylsilyl methacrylate (TMSMA) or TBA followed by hydrolysis of the protected ester groups. A P4VP-b-PMAAc copolymer synthesised in a similar fashion was converted to poly(4-vinyl-1-methylpyridinium chloride)-b-PMAAc copolymer by quaternisation of pyridine groups (Scheme 6).[112, 113] When obtaining the PTMSMA-b-PDAS and PTBMA-b-PDMAEMA copolymers {PDMAEMA is poly[2-(dimethylamino)ethyl methacrylate]},[114, 115] the order of introduction of the acid and basic monomers was reversed. Therefore, the macroanions formed by the basic monomers and protected alkyl (meth)acrylates have similar nucleophilicities. Note that the PTBMA-b-PDMAEMA copolymer [115] had a desired molecular mass ($M_{n\,exp} = 5.4 \times 10^3$ from gel-permeation chromatography data, *cf.* $M_{n\,theor} = 5.5 \times 10^3$) and a narrow MMD ($M_w/M_n = 1.08$). The initiation efficiency of the polymerisation of 2-(dimethylamino)ethyl methacrylate by PTBMA macroanions was $f_i = 0.92$. Copolyampholytes PMAAc-b-PDMAEMA were also synthesised and studied.[116–118] A similar synthesis of the di- and triblock copolymers A-b-B, A-b-B-b-A and B-b-A-b-B with poly[2-(dimethylamino)alkyl methacrylate] (alkyl = ethyl, propyl and 1-ethylmethyl) groups as the A component and sodium polymethacrylate as the B component was reported.[119] Polymerisation was carried out in THF at -78 °C with diphenylmethyllithium as initiator and LiCl as regulator.

Scheme 6



d. Nonpolar/polar block terpolymers

One of the first reviews concerning the synthesis of linear block terpolymers by sequential anionic polymerisation was reported in 1980.[120] In the last decade, considerable advances in the design of A-b-B-b-C copolymers with controlled molecular structures were made using this technique. As previously, the key factor in the design of the synthetic procedure is the relative reactivity of monomers and their macroanions.

A few studies on the synthesis of A-b-B-b-C-terpolymers containing two nonpolar blocks have been reported so far. Recently, PS-b-PB-b-PMAAc terpolymers were obtained by hydrolysing PS-b-PB-b-PTBMA terpolymers synthesised by sequential polymerisation of St, butadiene and TBMA.[121] It was found that the presence of a polar (ionogenic) and two nonpolar blocks ('hard' PS and 'soft' PB) in the sane macromolecule leads to a specific morphology of triblock copolymer films, which is different from that of diblock copolymer films. To study the morphology of terpolymers with two nonpolar blocks, a PB-b-PS-b-PEO terpolymer was synthesised by sequential polymerisation with *sec*-butyllithium as initiator.[122] Hydrogenation of the PB block in the presence of Wilkinson's catalyst gave a PE-b-PS-b-PEO terpolymer with two crystallisable end blocks.

Terpolymers having one nonpolar PS or PB block are of much greater interest. The simplest task is to synthesise terpolymers with a side nonpolar block, which in this case is polymerised first and its highly reactive 'living' chain end initiates the polymerisation of a broad spectrum of polar monomers. This method was employed to obtain a PS-b-PMMA-b-PTBA terpolymer.[123] The polymerisation of St in cyclohexane was initiated by *sec*-butyllithium. Once formed, the PS block was 'capped' with α-methylstyrene to avoid side reactions in the polymerisation of MMA. Then, the third monomer was added. Subsequent hydrolysis of TBA units with *p*-toluenesulfonic acid in toluene (at 100 °C for 5 h) afforded the PS-b-PMMA-b-PAAc terpolymer. It was shown that no hydrolysis of MMA units occurs in the polymer-analogous reaction. This polymerisation scheme was implemented in the synthesis of PS-b-PMMA-b-PEEMA terpolymer[82] with MAAc protected by 1-(ethoxy)ethyl groups as the third monomer. It was possible to introduce the second and third monomers in any order and thus to change the position of the PMAAc ionogenic block formed upon hydrolysis of the protected units. Terpolymers thus obtained had desired compositions and narrow MMDs. PS-b-PMAAc-b-PMMA terpolymers with central ionogenic block and similar chemical structure were also synthesised.[124] The ability of the A-b-B-b-C terpolymers comprised of one nonpolar, one polar hydrophobic and one polar hydrophilic (ionogenic) block to form specific micellar structures in aqueous and non-aqueous media attracts the attention of researchers. Such block copolymers may be used as nanoreactors and nanocontainers.[13, 14, 17, 18]

Recently, the synthesis of terpolymers with one nonpolar and two polar hydrophilic blocks by sequential anionic polymerisation has been part of research on novel micellar structures. A number of studies in this field concern the synthesis and investigation of PS-b-P2VP-b-PEO terpolymers with the polybasic central block.[125–129] Monitoring of changes in the molecular masses and MMDs of the blocks in the course and after the synthesis by gel-permeation chromatography and ^{1}H NMR spectroscopy gave $M_{n\,PS} = 2 \times 10^4$ ($M_w/M_n = 1.07$), $M_{n\,P2VP} = 1.4 \times 10^4$ and $M_{n\,PEO} = 2.6 \times 10^4$, the polydispersity index of the terpolymer was 1.1 (Ref. 128). The terpolymers formed specific core–shell–corona aqueous micelles.[127, 130]

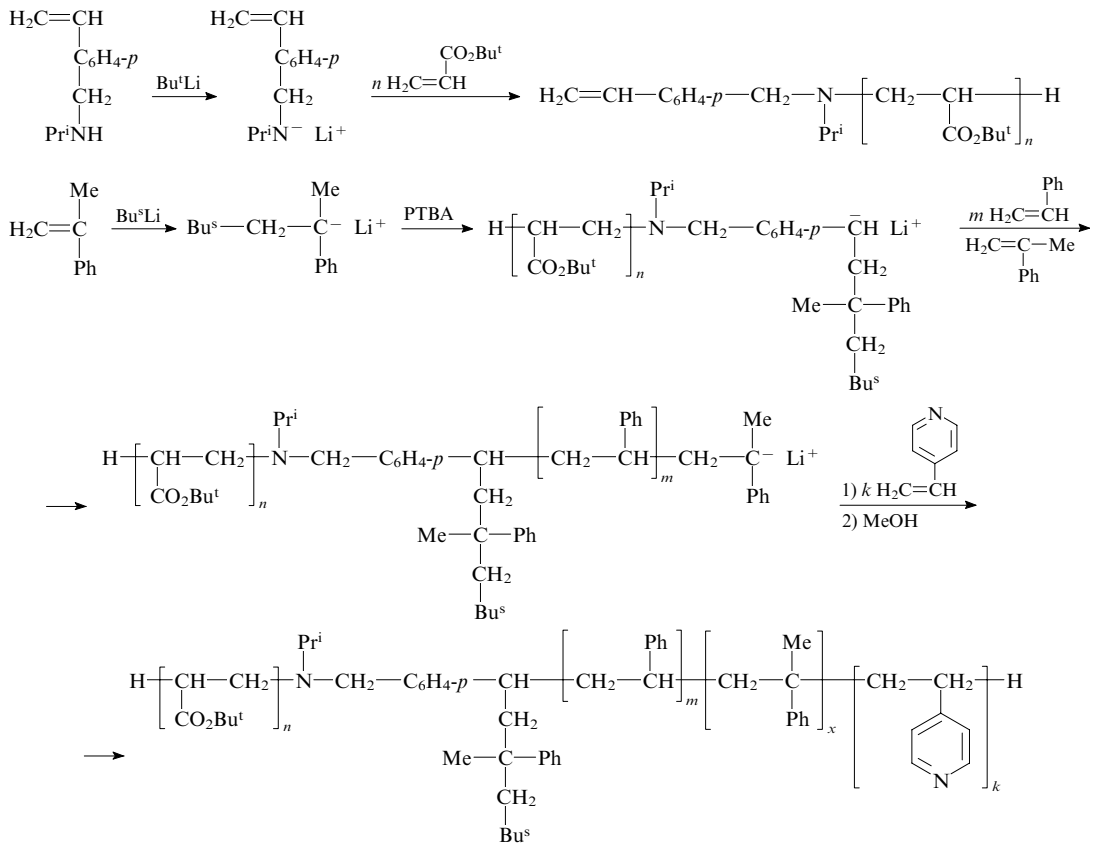
A series of studies is devoted to the synthesis of ampholytic block terpolymers. The PS-b-P2VP(P4VP)-b-PMAAc block copolyampholytes were prepared by conventional technique.[131] Sequential polymerisation of St, VP and protected MA gave a precursor of terpolymer and subsequent acid hydrolysis of the protected units resulted in the copolyampholyte. Attempts to synthesise a triblock copolyampholyte with the nonpolar central PS block were reported.[132, 133] This is a severe problem because P2VP (or P4VP) and protected polymethacrylate macroanions cannot initiate the polymerisation of St. To overcome the difficulty, 5-(*N*,*N*-dimethylamino)isoprene (DMAI) was used instead of 2-VP (or 4-VP).[132] The reactivity of DMAI in anionic polymerisation is similar to that of St; therefore, no bifunctional initiator was used in the synthesis of the PDMAI-b-PS-b-PMAAc terpolymer with the central PS block. Sequential polymerisation of the necessary monomers in the reactor afforded a precursor, PDMAI-b-PS-b-PTBMA terpolymer, which was hydrolysed to obtain the PDMAI-b-PS-b-PMAAc copolyampholyte. Another procedure was employed for the synthesis of a copolyampholyte with the side P4VP block.[133] In the first stage, a PTBA-based macromonomer with the terminal double bond was prepared. Then, initiation of the macromonomer and anionic polymerisation of St and P4VP (Scheme 7) were carried out.

The process was performed in THF at −78 °C using an adduct of *sec*-butyllithium with α-methylstyrene as initiator in the presence of LiCl. The copolyampholyte samples were characterised by narrow MMD ($M_w/M_n = 1.09–1.11$, $M_n = 5.26 \times 10^4 – 9.86 \times 10^4$).

e. Polar block terpolymers

Presently, a few terpolymers formed by various methacrylates are available. The monomers used are similar in reactivity; therefore, by varying the order of their introduction one can form hydrophilic and hydrophobic blocks at necessary positions. In particular, terpolymers comprised of

Scheme 7



x is the number of molecules of the capping agent (α-methylstyrene) added.

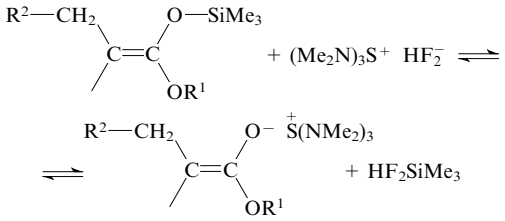
poly[2-(perfluorobutyl)ethyl methacrylate], PTBMA and poly[2-(trimethylsilyloxy)ethyl methacrylate] (PTMSOEMA) were synthesised; the monomers were introduced in different order.[134] Poly[2-(hydroxy)ethyl methacrylate] blocks were prepared by selective hydrolysis of protected PTMSOEMA units. The microphase structure of terpolymer films was studied.[135]

3. Anionic group transfer polymerisation

Anionic group transfer polymerisation (GTP) discovered in 1983 (Ref. 136) is widely used for the synthesis of di- and triblock copolymers based on polyacrylates and polymethacrylates at room temperature or at somewhat higher temperatures. The key condition for practical implementation of a sequential process is to use monomers with similar reactivities. Opinions differ on the mechanism of this kind of polymerisation.[22,23,137–139] Researchers who proposed the GTP technique explained the 'living' mechanism of the polymerisation of methacrylates in the presence of initiators (*O*-silyl ketene ketals) and catalysts [strong nucleophiles, *e.g.*, HF_2^- with tris(dimethylamino)sulfonium or tetrabutylammonium counterions] by the formation of intermediate eight-membered ring accompanied by transfer of the trimethylsilyl group.[22,46] This is the so-called associative mechanism.

However, more recently yet another (dissociative) mechanism was proposed with allowance for a lower rate of the process compared to the classical anionic polymerisation of methacrylates, a narrower MMD of polymers and nearly identical stereochemical structure of polymers synthesised by both methods (instead of predominant isotacticity expected for GTP).[140,141] It assumes that GTP occurs as anionic polymerisation in which a small amount of enolate anions is in equilibrium with the vast majority of silyl ketene ketal end groups.[46]

Scheme 8



Owing to this equilibrium the lifetime of the enolate anions is shortened, which favours retardation of GTP compared to the classical anionic polymerisation. The equilibrium (see Scheme 8) and its shift towards a particular type of active centres also provides an explanation for the lower polydispersity of GTP products. Since here the role of counter-ions is played by tris(dimethylamino)sulfonium or tetrabutylammonium cations, solvent-stabilised free anions should act as the chain growth centres.

At present, GTP is treated as classic anionic polymerisation controlled by reversible chain termination (dissociative mechanism) and/or degenerate chain transfer.[46] Note that direct group transfer polymerisation of AAc and MAAc is also impossible; the PAAc and PMAAc blocks are prepared by GTP of corresponding protected derivatives followed by removal of the protective groups using relevant chemical reactions.[9] Now we will consider some examples of the GTP-synthesis of block copolymers.

a. Binary block copolymers

Amphiphilic diblock copolymers PMMA-b-PMAAc were synthesised [142] using GTP and a polymer-analogous reaction. Sequential polymerisation of MMA and benzyl methacrylate (BMA) was followed by hydrolysis of the protected units. Diblock copolymers PMMA-b-PAAc were prepared in a

similar fashion to study the micelle-forming properties.[143] The AAc units were protected with *tert*-butyl groups. Triblock copolymer PTBMA-b-PMMA-b-PTBMA was synthesised from the same monomers (MMA and TBMA) by the GTP method.[144] The copolymer with the central hydrophobic block surrounded by hydrophilic blocks was isolated upon hydrolysis of PTBMA.

New diblock copolymers with various basic blocks were synthesised by sequential GTP of 2-(imidazol-1-yl)ethyl methacrylate and DMAEMA at 25 °C using the 1-methoxy-1-trimethylsiloxy-2-methylpropene – tetrabutylammonium benzoate system as initiator.[145] The basic block containing imidazole groups showed high catalytic activity in the hydrolysis of *p*-nitrophenyl acetate. Two more copolymers with the basic blocks, namely, PDMAEMA-b-PDEAEMA {PDEAEMA is poly[2-(ethylamino)ethyl methacrylate]} and PDEAEMA-b-PMEMA {PMEMA is poly[2-(morpholino)ethyl methacrylate]} were obtained by the GTP technique.[146, 147]

Diblock copolyampholytes containing PDMAEMA and PMAAc were synthesised by the same method using protected benzyl methacrylate monomer[148] and tetrahydropyranyl methacrylate (THFMA).[149] In the latter case, poly-THFMA blocks were readily hydrolysed at room temperature.

b. Block terpolymers

Model block terpolymers poly[(2-ethylhexyl) acrylate]-b-PMMA-b-PAAc with gradually increasing hydrophilicity of the blocks were synthesised by sequential polymerisation of 2-ethylhexyl acrylate with MMA and TBA followed by hydrolysis of the PTBA block.[150] The GTP technique was used for the synthesis of not only diblock, but also triblock copolyampholytes containing two unlikely charged blocks (PDMAEMA and PMAAc) and a hydrophobic PMMA block.[148] The position of the hydrophobic block strongly affected the micelle-forming properties of the copolyampholytes.[151] Triblock copolyampholytes containing the same polymeric components were also obtained using THFMA as the protected monomer and all possible types of introduction of the monomers.[152] Polymerisation was followed by hydrolysis of the PTHFMA block in a weak acid medium.

4. 'Living' cationic polymerisation

'Living' cationic polymerisation makes the design of the chemical structure of block copolymers more versatile, because there exist monomers (isobutylene, alkyl vinyl ethers, *etc.*) that are better polymerised by the cationic mechanism.[22, 23, 44, 45] Specific features of cationic polymerisation and the stages, kinetics and conditions for carrying out the process have been well documented;[22, 45, 46] because of this, we will only dwell on the key steps. Cationic polymerisation represents a sequential addition of monomers possessing the properties of nucleophiles and capable of stabilising the positive charge to carbocations.[22, 23, 45] The development of the process requires that the double bond be the most nucleophilic fragment of the monomer molecule. Traditionally used initiators of 'living' cationic polymerisation include protic acids and products of the interaction of Lewis acids with water, alcohols, ethers and alkyl halides. High reactivity of carbocations predetermines a high rate of chain growth, which makes the process poorly controllable. In addition, β-H atoms become highly mobile; therefore, chain transfer by abstraction of β-protons from the growing carbocations is a typical side reaction occurring in the course of cationic polymerisation of α-olefins.[46] However, the side reactions can be suppressed by carrying out polymerisation at low temperatures in hydrocarbons and in chlorine- and nitrogen-containing solvents.[153] Protic solvents and amines that favour chain transfer and chain termination should not be used.

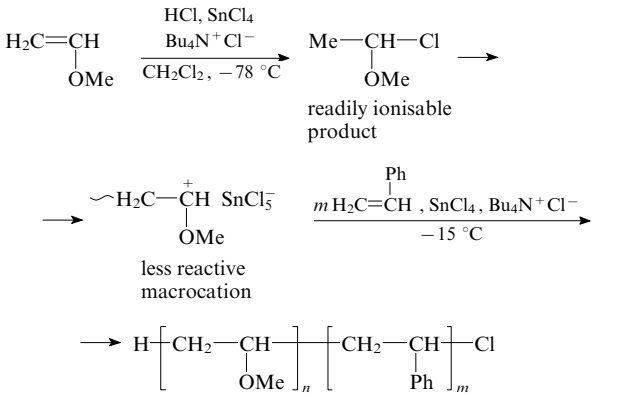
In cationic polymerisation the active centres include the contact and free ion pairs that coexist in equilibrium. The solvent separated ion pairs are not involved in polymerisation processes.[46] The reactivities of ion pairs and free ions in cationic polymerisation are almost equal ($k_p^{\pm} \approx k_p^{+}$), but these species have different lifetimes.[154, 155] This leads to products of higher polydispersity compared to anionic polymerisation products. An important condition for providing the 'livingness' of the process is reduction of the polymerisation rate. This is achieved by shift of the equilibrium between the active centres towards the contact ion pairs. The growth centres are 'deactivated' by introducing salts (containing the same counterion as the active centre)[156] and nucleophiles (Nu)[46] that interact with carbocations and form stable ion pairs.

$$\sim R^+\ An^- \rightleftharpoons \sim R^+ + An^- \overset{Nu}{\rightleftharpoons}$$
$$\rightleftharpoons \sim R{-}Nu^+\ An^-.$$

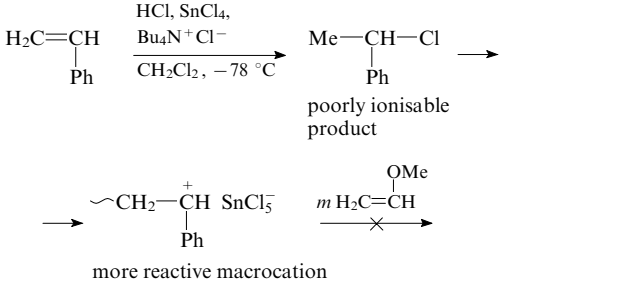
Binding of carbocations to salts or nucleophiles under fast exchange between the active and 'sleeping' centres causes the rate of the process and the polydispersity of macrochains to decrease. Yet another important condition is the reversible character of chain termination. In cationic polymerisation, in the absence of impurities and chain termination agents, the chain growth is mainly ceased owing to collapse of the ion pair,[46] namely, formation of a covalent bond between the carbocation and counterion (or its fragment[22]). However, in some cases the reaction is reversible due to, *e.g.*, the addition of halide ions from the $SnCl_5^-$, $SbCl_6^-$, $SnBr_5^-$, BCl_4^- and BBr_4^- counterions. In such systems, one can hope for controllable character of polymerisation.

The design of a sequential chain in the synthesis of block copolymers using cationic polymerisation has a number of specific features. In particular, the most reactive (most nucleophilic) monomer is most often polymerised first (Scheme 9). This favours fast and quantitative initiation. The polymerisation of the more reactive monomer requires a lower temperature. To activate the polymerisation of the other (less reactive) monomer, the temperature and/or concentration of the co-initiator is increased (Scheme 10).[46]

Scheme 9



Scheme 10



Numerous examples of the synthesis of the A-b-B, A-b-B-b-A, B-b-A-b-B and A-b-B-b-C copolymers by sequential cationic polymerisation are available in the literature. In the early studies, sequential polymerisation of THF and 3,3-bis(chloromethyl)oxetane was carried out.[157] More recently, poly(*p*-methoxystyrene)-b-poly(isobutyl vinyl ether) diblock copolymers were prepared.[158] Now we will consider the synthesis of particular block copolymers.

a. Binary nonpolar block copolymers

Studies [159–162] on the synthesis of block copolymers by sequential cationic polymerisation revealed the possibility of introducing the monomers in the reversed order starting from the less reactive monomer provided that the first block is 'capped' with a readily ionisable monomer that cannot be polymerised. This technique was used to obtain almost monodisperse ($M_w/M_n < 1.1$) di- and triblock copolymers containing polyisobutylene (PIB) and poly(1-methylstyrene) (PMS) or other styrene derivatives. Initially, HCl and $TiCl_4$ were used as initiator and co-initiator, respectively. The polymerisation of IB was followed by 'capping' the PIB block with 1,1-diphenylethylene and deactivation of the first Lewis acid ($TiCl_4$) with titanium isopropoxide or butoxide [$Ti(OR)_4$]. Then, the second Lewis acid ($SnBr_4$) was added and the styrene derivative was polymerised. The efficiency of polymerisation initiation of the second monomer approached 100%. At the same time a study on the synthesis of PS-b-PMS-b-PS copolymers from styrene and *p*-methylstyrene (*p*-MS) characterised by similar reactivities using a bifunctional initiator showed that the resulting triblock copolymer had a narrower MMD ($M_w/M_n = 1.15$) if the more reactive *p*-MS was polymerised first.[163] When styrene was polymerised first, the product was characterised by $M_w/M_n = 1.34$.

Sequential cationic polymerisation was used for the synthesis of PS-b-PIB-b-PS triblock copolymers with nonpolar components, which possessed the properties of thermoelastic elastomers.[164–168]

b. Binary nonpolar/polar block copolymers

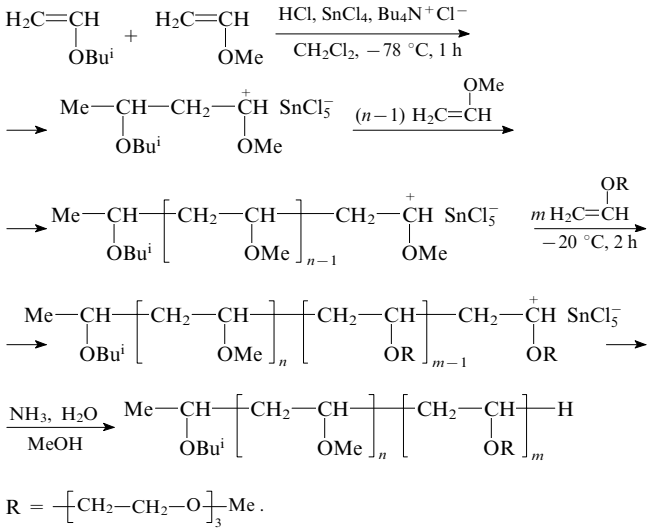
Syntheses of block copolymers based on PS, PMS or PB (nonpolar blocks) and on various poly(vinyl ethers) (polar blocks) have been reported. Cationic polymerisation of the following pairs of monomers was studied: *p*-MS–isobutyl vinyl ether (IBVE),[169] St–methyl vinyl ether (MVE), St–chloroethyl vinyl ether (CEVE)[170] and α-MS–CEVE.[171] The best results (narrower MMD) were obtained where more reactive monomers, namely, IBVE and MVE, were polymerised first. The technique was used to obtain [170] a PMVE-b-PS copolymer with controlled molecular structure and a polydispersity index of 1.33, although the temperature and the Lewis acid concentration were increased in the second stage (see Scheme 9). Polymerisations of the less reactive monomers in the first stage led to mixtures of block copolymers with homopolymers formed by the more reactive monomers in second stage.[169, 170] Since α-MS and CEVE had almost identical reactivities, their block copolymerisation could be performed in any order.[171]

Sequential cationic polymerisation starting with the less reactive monomer was employed for the synthesis of PIB-b-PMVE copolymers with a very narrow MMD ($M_w/M_n < 1.1$).[172]

c. Binary polar/polar block copolymers

Typical representatives of this group are diblock copolymers based on various polyethers. Copolymers PMVE-b-PCVE [poly(cetyl vinyl ether)] having two polyether blocks ($M_n < 3.5 \times 10^3$), a narrow MMD and controllable composition were obtained [173] using a HI/ZnI_2 mixture as initiator in the early stage of research in this field.[173] Sequential cationic polymerisation starting from the most nucleophilic monomer was employed for the synthesis of diblock copolymers comprised of poly(isobutyl vinyl ether) and poly(*p*-metoxystyrene) (PMOS),[169] PMVE and PMOS [174] and poly[*p*-(*tert*-butoxy)-styrene] (PTBOS) and PIBVE.[169] Copolymers PMVE-b-PMTEGVE (PMTEGVE is poly(methyltriethylene glycol vinyl ether) were prepared in a similar fashion (Scheme 11) [175] using an adduct of HCl with isobutyl vinyl ether and $SnCl_4$ as initiating system. The addition of tetrabutylammonium chloride enhanced the 'livingness' of the system. Seven samples of copolymers were obtained in a yield of 99 mass % (no homopolymers). They had molecular masses ($M_n = 1.58 \times 10^3 - 1.40 \times 10^4$) similar to theoretical values and narrow MMDs ($M_w/M_n = 1.14 - 1.29$).

Scheme 11



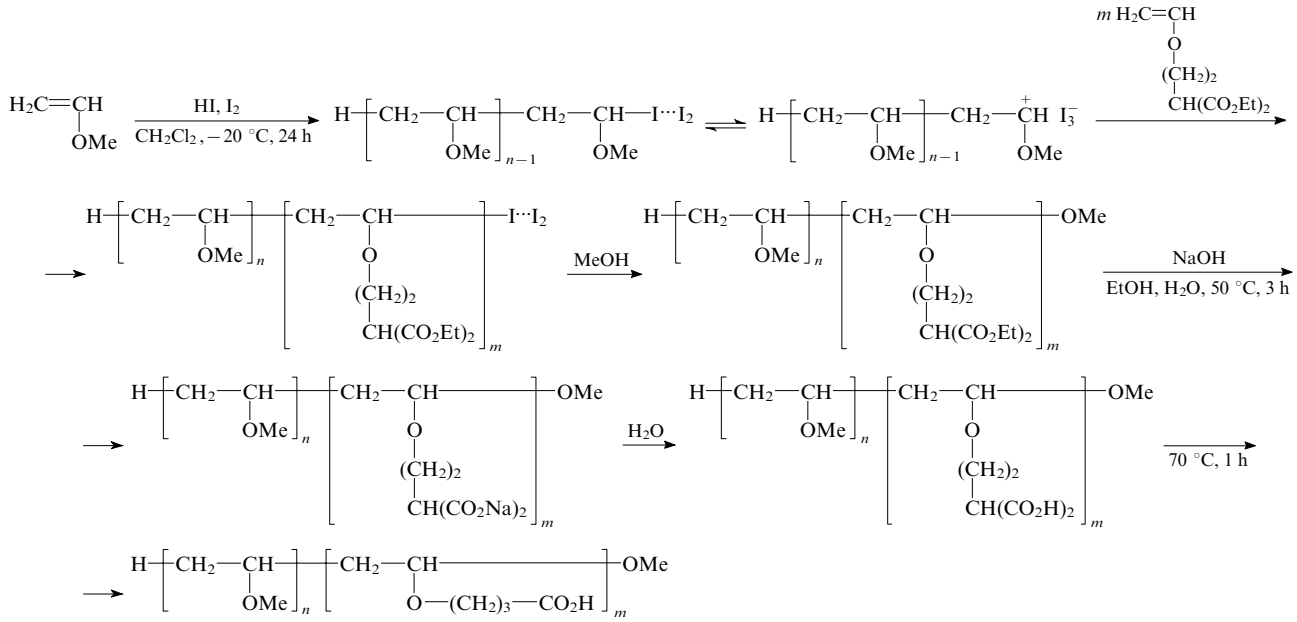
Sequential cationic polymerisation of MVE and ethyl [2-(vinyloxy)ethyl]malonate (EVOEM) to prepare PMVE-b-PVOBA diblock copolymers [PVOBA is poly(vinyloxy-4-butanoic acid)] (Scheme 12) was reported.[176] Polymerisation of the first block of variable length was followed by introduction of a constant amount of the second monomer and the process was continued. The diblock copolymers thus obtained were involved in two polymer-analogous reactions, namely, alkaline hydrolysis followed by decarboxylation after dialysis. According to size exclusion chromatography and ^1H NMR spectroscopy data, five specimens of PMVE-b-PVOBA were characterised by variation of the molecular mass of the first block over a wide range ($M_n = 5.86 \times 10^3 - 3.55 \times 10^4$) and by small variations of the molecular mass of the second block [$M_n = (4.94 - 6.37) \times 10^3$]. The copolymers had narrow MMDs ($M_w/M_n = 1.1 - 1.3$) and served as efficient stabilisers of aqueous and organic iron oxide dispersions.

This polymerisation technique also appeared to be efficient in the synthesis of diblock copolymers based on poly(2-ethyl-2-oxazoline) and poly(L-lactide).[177] Such copolymers attract increasing interest of researchers because they contain two biocompatible blocks.

d. Block terpolymers

The search for new methods of control of the micellar and microphase structures of copolymers predetermines an increase in the number of components in block copolymers, which in turn requires improvement of synthetic procedures. 'Living' cationic polymerisation, which is also employed in this case, is of limited use compared to 'living' anionic polymerisation. Among the small range of block terpolymers synthesised by this method, mention may be made of model triblock copolymers based on poly(ethyl vinyl ether) (PEVE), PMVE

Scheme 12

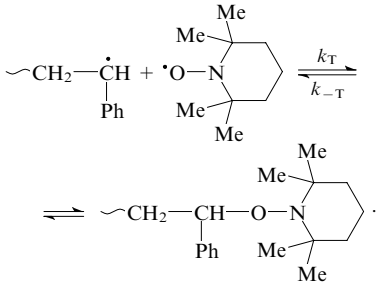


and PMTEGVE containing an equal number of each type of monomer units ($N = 20$).[178] These terpolymers attract the attention of researchers owing to combination of a water-insoluble (PEVE), poorly water-soluble (PMTEGVE) and readily water-soluble (PMVE) blocks in the same macromolecule. Interestingly, the terpolymer dissolved in water (less than 1 mass %) possessed the micelle-forming properties only upon addition of a low-molecular-mass salt.

5. 'Pseudoliving' radical polymerisation involving stable radicals

A fundamental problem in polymer chemistry is to develop methods of controlled radical synthesis of polymers. This problem was solved by the end of the XXth century. At present, there are three commonly accepted types of 'pseudoliving' radical process. These are the stable free radical polymerisation (SFRP), atom transfer radical polymerisation (ATRP) and reversible addition–fragmentation transfer (RAFT) radical polymerisation. Mention may also be made of the molecular design *via* interchange to xanthates (MADIX). At the same time all the methods are based on common principles that allow one to carry out a controlled 'pseudoliving' radical process. From the standpoint of control, the drawbacks of free radical polymerisation include (i) high reactivity of radicals and, as a consequence, a very high rate of the process and (ii) bimolecular chain termination reactions. Therefore, it was proposed to 'divide' the overall polymerisation process into a large number of 'short-term' stages by choosing such reversible chain termination reactions (SFRP and ATRP) or chain transfer reactions (RAFT and MADIX) that their equilibrium constants be rather low and provide a long 'sleep' period. Thus, the main idea of 'pseudoliving' radical polymerisation is to provide conditions for reversible chain termination (inhibition) or chain transfer provided that these reversible reactions are faster than the recombination reaction ($k_{in(tr)} \gg k_r$).[23, 179–183] Reversible chain termination or chain transfer reactions characterised by low equilibrium constants play the role of a 'valve' that 'opens' the polymerisation process and 'closes' it upon adding a few monomer units. The characteristic features of a 'pseudoliving' radical process include a linear dependence of the molecular mass of the polymer on the monomer conversion and a narrow MMD.[22, 180–184] The kinetic laws of various types of 'pseudoliving' polymerisation have been comprehensively treated in reviews.[185, 186] An original method of determination of the kinetic parameters of controlled radical processes by linearising the polymer chain length distribution was proposed.[187] Presently, all types of 'pseudoliving' polymerisation are widely used in the synthesis of block copolymers; therefore, we will consider the key features of each type separately.

Otsu and Yoshita [188] were the first to report the significance of reversible chain termination in radical polymerisation. In the mid-1980s, the SFRP technique was developed.[189, 190] The best results were obtained for the polymerisation and copolymerisation of St-based monomers. Reversibility of the process was maintained by the chain termination reaction involving the growing chains and stable nitroxides [*e.g.*, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)], which became reversible at $T > 100$ °C.



The equilibrium constant for C–O bond cleavage in the polymeric alkoxyamine formed is [23, 191]

$$K = \frac{k_{-T}}{k_T} = 2.1 \times 10^{-11} \text{ mol litre}^{-1}.$$

Here k_T and k_{-T} are the rate constants for chain termination and re-initiation (TEMPO addition and elimination), respectively. In the presence of TEMPO a controlled radical polymerisation of St is thermally initiated using a conventional radical initiator (*e.g.*, benzoyl peroxide) and low-molecular-mass alkoxyamines (AOA) that are products of the interaction of the initiator, TEMPO and (in some cases) monomer molecule.[23, 179, 180] The rate of 'pseudoliving' polymerisation of St in the presence of AOA obeys the first-order equation with respect to the monomer concentration

$$-\frac{d[M]}{dt} = k_p K\beta[M],$$

where K is the equilibrium constant and $\beta = [AOA]/[T^{\bullet}]$ is the alkoxyamine : TEMPO concentration ratio (this ratio is a constant for a steady-state process).[23, 179] In addition, up to $q \sim 90\%$ the process is characterised by a linear dependence of the molecular mass on conversion and by narrow MMD ($1.05 < M_w/M_n < 1.2$)

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + \frac{2}{tk_{-T}}.$$

A feature of 'pseudoliving' polymerisation of styrene is alternation of short ($\sim 10^{-4}-10^{-3}$ s) addition steps of some monomer molecules to the growing chains and long (~ 40 min) 'sleep' periods. In the late stages of SFRP polymerisation the rate of the process decreased and the polydispersity of the product increased because of the decomposition of the polymeric alkoxyamine due to disproportionation reaction between the nitroxide radical and the growing macroradical resulting in hydroxyamine and the polymer with the double bond at the chain end.[186]

In addition to TEMPO, stable radicals *N*,*N*-di(*tert*-butyl)-*N*-oxyl (DBN), *N*-(*tert*-butyl)-*N*-(isopropylphenyl)methyl-*N*-oxyl (TIPNO), *N*-(*tert*-butyl)-*N*-(*tert*-butyldiethylphosphonyl)methyl-*N*-oxyl (DEPN), *etc*. were also used in the SFRP processes.[185, 186] The structure of the nitroxide radical strongly affects the kinetic parameters of the SFRP process. In particular, the more sterically hindered the nitroxide the easier the C—O bond cleavage in alkoxyamines and the higher the rate constants for their dissociation (k_{-T}) and the equilibrium constants (K). For instance, the polymerisation of styrene in the presence of DEPN was characterised by an equilibrium constant K of 6×10^{-9} mol litre^{-1} (see Refs 185 and 192), which is two orders of magnitude higher than in the case of TEMPO. This makes it possible to reduce the temperature of the SFRP process.[186]

SFRP of acrylic monomers (especially methacrylates) in the presence of TEMPO is complicated by the accumulation of nitroxide in the system, which slow down or even prvent the polymerisation.[9] The degree of control and the rate of polymerisation of these monomers considerably increase in the presence of sterically hindered nitroxide compounds, such as TIPNO, DBN and DEPN. The reason is a higher dissociation rate of the corresponding alkoxyamines compared to that of the TEMPO-based ones.[185, 186] In addition, a kinetic study of SFRP of *tert*-butyl acrylate in the presence of DBN showed that the rate of the process increases upon addition of a radical initiator dicumyl peroxide.[193] No significant MMD broadening occurs in this case. In addition, polymerisation of n-butyl acrylate under the action of DEPN occurred even without decomposition of polymeric alkoxyamine and was well controlled.[192] At the same time the polymerisation of methacrylates was poorly controlled even using sterically hindered nitroxides because polymeric alkoxyamines tend to undergo disproportionation involving abstraction of a proton from α-methyl group.[186, 194]

Recently, an interesting avenue of research on *in situ* formation of nitroxide radicals in the polymerisation system emerged.[195, 196] High-molecular-mass spin adducts are formed in the reactions of chain growth radicals with nitrones and nitroso compounds,[197–202] triazines,[203] sterically hindered secondary amines,[204] a nitrogen monoxide/nitrogen dioxide mixture [196] and other compounds. Controlled syntheses of PS, PMMA, poly(vinyl chloride) (PVC), poly(*N*-vinylpirrolidone) (PVPD) and copolymers of VPD with MMA in the presence of these stable radicals were carried out at low temperatures (50–120 °C) and at rather high rates.[196–199, 205] However, inhomogeneous structure of the *in situ* formed nitroxides was reported.[196]

A new interesting approach to involvement of inactive monomers (MMA and vinyl acetate (VA) in controlled SFRP process by copolymerisation with an active monomer (St) was proposed.[194, 206] Yet another procedure for practical implementation of a 'pseudoliving' SFRP process in the presence of an alternative stable radical, namely, a product of oxidation of alkyl-9-borobicyclo[3.3.1]nonane, will be considered below (see Section III.1).

a. Binary nonpolar block copolymers

Pioneering studies on SFRP of styrene and its derivatives (under the action of benzoyl peroxide in the presence of TEMPO) aimed at preparing block copolymers date back to the early 1990s.[184, 207–210] The method was used for the synthesis of A-b-B and A-b-B–b-A type block copolymers.[211–214] More recently, SFRP was also employed in the synthesis of copolymers with polar blocks.

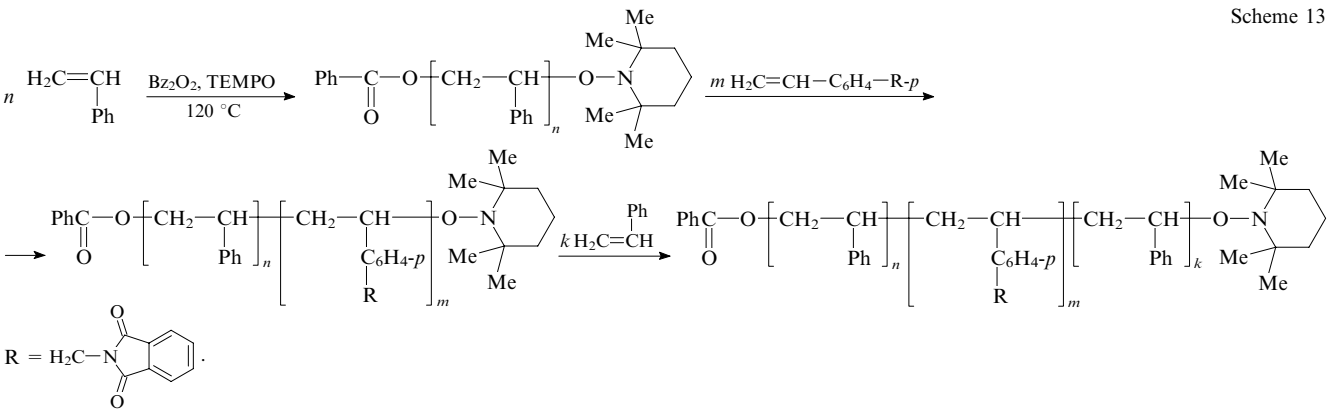
b. Binary nonpolar/polar block copolymers

Quite interesting copolymers PS-b-PPhIMS {PPhIMS is poly-[*p*-(phthalimidomethyl)styrene]} and PS-b-PPhIMS-b-PS were prepared by the SFRP method.[215] Initially, the polymerisation of styrene under the action of benzoyl peroxide in the presence of TEMPO resulted in PS bearing a nitroxide end group. Then it was used as macroinitiator of the polymerisation of PhIMS, and diblock copolymers with the same end group were thus synthesised. The third, PS, block was obtained using the diblock copolymer as macroinitiator (Scheme 13).

The molecular masses of the PS blocks increased in proportion to conversion and the M_w/M_n ratio was 1.15–1.25. The number-average molecular masses, M_n, of the copolymers varied between 1.9×10^4 and 3×10^4. Under the action of hydrazine the phthalimide groups were converted to amino groups and thus di- and triblock copolymers containing basic poly[*p*-(aminomethyl)styrene] blocks were prepared.

Diblock copolymers containing the first PS block and PMMA, poly(ethyl methacrylate) (PEMA), poly(butyl meth-

Scheme 13



acrylate) (PBMA), poly(octyl methacrylate) (POMA), PDMAEMA, poly(vinyl acetate) (PVA) and PDMAA as the second block were synthesised analogously using the same initiator (benzoyl peroxide) in the presence of TEMPO radical at higher temperature ($T = 130$ °C).[216] The copolymers were thoroughly characterised by gel permeation chromatography and ^{1}H NMR spectroscopy. The first stage involved the synthesis of PS blocks with nitroxide group ($M_n = 5\times10^2 - 2.6\times10^3$), which played the role of macroinitiators in the next step. In all cases, except the polymerisation of DMAEMA and VA, the diblock copolymers were obtained in high yields, the molecular masses increased in proportion to conversion and the polydispersity was $M_w/M_n = 1.2-1.5$. The end nitroxide groups were detected for all the copolymers. Interestingly, an earlier attempt[217] to attain controlled homopolymerisation of DMAA in the presence of TEMPO also failed. Controlled homo- and block copolymerisation of this monomer is only possible in the presence of sterically hindered nitroxides TIPNO.[218] (Co)polymers thus obtained were characterised by $M_n = 4\times10^3 - 4.8\times10^4$ and a narrow MMD ($M_w/M_n = 1.10-1.21$).

It should be noted that the polydispersity indices of the diblock copolymers obtained by SFRP of PS and poly(meth)acrylates are much higher than those of the identical copolymers synthesised by sequential anionic polymerisation. This is quite natural because the efficiency of nitroxide-bearing PS in SFRP of acrylates is low ($f_i < 0.6$ at 125 °C), being even lower for the polymerisation of methacrylates ($f_i < 0.4$).[210] Therefore, such diblock copolymers have a broader MMD.

Nitroxide-controlled radical polymerisation was successfully used for the synthesis of diblock copolymers from sodium poly(styrene sulfonate) (PSSNa) and polyvinylnaphthalene[219] and a copolymer with PS blocks and alternating copolymer of St with maleic anhydride (MA).[220] *N*-(*tert*-Butyl)-*N*-(2-methyl-1-phenylpropyl)-*o*-(1-phenylethyl)hydroxyamine was used instead of TEMPO and the poly(St-alt-MA)-b-PS copolymer was synthesised in one step.[220] Styrene and MA were taken in a 9 : 1 ratio; the process began with alternating copolymerisation of styrene with MA, which was followed by homopolymerisation of excess styrene upon consumption of MA. A linear increase in M_n with conversion and a narrow MMD ($M_w/M_n \leqslant 1.2$) were observed.

c. Binary polar/polar block copolymers

Only few studies on the synthesis of polar/polar block copolymers using the SFRP technique have been reported so far. In particular, a PTBA-b-PDMAA diblock copolymer was obtained by the SFRP method; subsequent hydrolysis of TBA units afforded PAAc blocks.[218] Studies[221–223] carried out to selectively modify the microphase structure of polymer films were based on an original idea. Block copolymers containing protected poly(*p*-hydroxystyrene) blocks were synthesised by the SFRP method in the presence of alkoxyamine. To this end, *p*-acetoxystyrene (AOS), *p*-(*tert*-butoxy)styrene (TBOS), *p*-[di(*tert*-butyl)methylsiloxy]styrene and *p*-(tetrahydropyranyloxy)styrene (THPOS) were used. The main goal was not only to improve the polymerisation process using protected monomers, but also to selectively remove the protective groups from particular blocks of the copolymers by a chemical or thermal method, thus affecting the microphase structure of polymer films. In particular, the protective groups were removed from the PAOS blocks by treatment of the films with hydrazine hydrate and from the PTHPOS blocks by heat treatment.

6. Controlled atom transfer radical polymerisation

Controlled atom transfer radical polymerisation (ATRP) is an alternative to 'pseudoliving' radical polymerisation. The method developed by two independent research groups in the mid-1990s[224–229] differs from the SFRP technique in that chain growth is controlled by a reversible termination redox reaction. The growing chain reversibly interacts with a metal (copper[224,226] or ruthenium[227,228]) halide fragment of a complex with an organic base, donates an electron to the metal and adds the halogen atom. In the case of a copper catalyst the equilibrium is as follows:

$$\sim CH_2-\underset{\displaystyle X}{\overset{\displaystyle \cdot}{C}}H + Cu^{II}Hal_2\cdot L \underset{k_{Cu^I}}{\overset{k_{Cu^{II}}}{\rightleftharpoons}} \sim CH_2-\underset{\displaystyle X}{CH}-Hal + Cu^{I}Hal\cdot L\,. \quad (1)$$

Hal = Cl or Br, L is organic ligand; X is substituent.

Since in the course of polymerisation the halogen atom is transferred along the chain, this 'pseudoliving' mechanism was named ATRP. The equilibrium constant for chain growth activation is[23,181]

$$K = \frac{k_{Cu^I}}{k_{Cu^{II}}} = \frac{[M_n^{\cdot}][Cu^{II}]}{[M_nHal][Cu^{I}]}\,,$$

where $[M_n^{\cdot}]$ and $[M_nHal]$ are the concentrations of the 'living' and 'sleeping' radicals. The polymerisation is initiated by low-molecular-mass organic compounds containing a mobile halogen atom, *e.g.*, 1-phenylethyl halides. Most often, complex-forming organic ligands include 2,2′-bipyridyl and its derivatives, namely, 4,4′-di-(hept-1-yl)-2,2′-bipyridyl; 4,4′-di(non-5-yl)-2,2′-bipyridyl (DNBP) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, *N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetraamine, *etc.*[181,186] The reversible termination mode is attained at high temperatures ($T > 100$ °C). However, lower-temperature ATRP were also reported. For instance, the ATRP of styrene, MA and MMA in the presence of $Cu^ICl(Br)$ complexes with sterically hindered DNBP was carried out at 90 °C; the corresponding equilibrium constants K being rather high, namely, $(1-2)\times10^{-8}$ (Ref. 230), 1.2×10^{-9} (Ref. 231) and 7×10^{-7} (Ref. 232). With nickel and rhodium halide complexes with triphenylphosphine [$NiBr_2(PPh_3)_2$ and $RhBr(PPh_3)_3$] as catalysts the temperature of the ATRP polymerisation of MMA was reduced to 75 °C[233] with retention of MM control and a narrow MMD of PMMA.

The ATRP method has been well documented in monographs and research communications[12,181,186,234–237] that provide comprehensive treatment of the mechanism of this process and criteria for the choice of each component of the system (monomer, initiator, transition metal, organic ligands and solvent). When carrying out an ATRP process, the initiator, regulator, solvent and other conditions should be chosen for each monomer in such a fashion that the equilibrium constant ($K = 10^{-8\pm2}$) and the rate constant for deactivation of radicals ($k_{da} = 10^{7\pm1}$ litre mol^{-1} s^{-1}) be optimum [for reaction (1) $k_{da} = k_{Cu^I}$].[238] The method does its best in the polymerisation of St- and (meth)acrylate-based monomers, but can also be used for polymerisation of acrylamide, (meth)acrylamides and dienes.[238] It should be noted that ATRP polymerisation can be performed not only in organic solvents (most studies),[232,239–241] but also in the bulk,[242] in emulsion,[243] in suspension[244] and even in aqueous solutions.[245,246] However, an attempt to use this approach for polymerisation of (meth)acrylamides failed;[247] the process was poorly controlled and the resulting polymers were characterised by a broad MMD. Similar results were obtained for ATRP of DMAA, which led to $M_w/M_n > 1.6$ for the resulting PDMAA.[248,249] It was shown that ATRP requires the use of protected acid monomers that cannot be coordinated to the

transition metal and thus poison the catalyst.[9] In addition, the best catalytic systems are obtained using protonated basic ligands, because this precludes strong complexation with the metal.

In contrast to 'living' anionic polymerisation the ATRP technique is quite tolerant to the nature of monomers and solvents. This makes it possible to synthesise the A-b-B-b-A, B-b-A-b-B and A-b-B-b-C type copolymers from polar and nonpolar monomers starting in any order. Each ATRP synthesised polymer has a mobile halogen atom at the chain end. Therefore, it can act as macroinitiator of polymerisation of other monomers under the action of the same catalytic system. Some examples of the use of ATRP for the synthesis of binary and ternary block copolymers are presented below.

a. Binary nonpolar/polar block copolymers

In this group the most popular objects of synthetic studies are di- and triblock copolymers of PS with protected poly(meth)-acrylates. As mentioned above, the (meth)acrylic monomers are protected to prevent the poisoning of catalyst. Di- and triblock copolymers of PS with poly(butyl acrylate) (PBA) of well-defined molecular structure were obtained.[250] Similar PBA-b-PS copolymers were synthesised in a water–hexane–Brij98 dispersion.[251] The process was initiated by ethyl-2-bromoisobutyrate and a complex of CuBr with DNBP was used for reversible termination. The block copolymers thus obtained were characterised by $M_n = 1 \times 10^4 - 4 \times 10^4$ and $M_w/M_n = 1.12 - 1.25$. Amphiphilic di- and triblock copolymers of PS with PAAc were obtained as follows:[252–256] di- or triblock precursors (with PTBA) were synthesised by ATRP and subsequent acid hydrolysis of the TBA units gave the PAAc blocks. Studies[252,253] were carried out using methyl 2-bromopropionate as initiator and a complex of CuBr with PDMETA as catalyst. A 'pseudoliving' mechanism of the process with a linear increase in M_n depending on conversion was observed at 60 °C only in polar solvent (acetone).

A similar scheme was also used to obtain block copolymers of PS with PMAAc in other studies;[257,258] however, the protected monomer was *p*-nitrophenyl methacrylate in the former study and TBMA in the latter.

Examples of successful use of ATRP in the synthesis of highly hydrophobic diblock copolymers based on PS and polyfluorinated polyalkoxystyrenes have been reported.[259,260] First, polyfluorinated monomers, namely, 2,3,5,6-tetrafluoro-4-(2,2,3,3,3-pentafluoropropoxy)styrene [TF(F_5)S] and 2,3,5,6-tetrafluoro-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctoxy)styrene [TF(F_{15})S] were synthesised and their ability to undergo controlled ATRP was checked and confirmed.[260] The products synthesised were characterised by a narrow MMD ($M_w/M_n \leqslant 1.3$). Oligomers with $M_n = 6.5 \times 10^3$ were then used as macroinitiators of the polymerisation of styrene, which resulted in A-b-B type copolymers [poly-TF(F_5)S-b-PS and polyTF(F_{15})S-b-PS] of well-defined molecular structure and narrow MMD. In addition, the polymerisation in a xylene solution (owing to poor solubility of the fluorinated blocks) was performed using the reverse order of introduction of the monomers and led to B-b-A type copolymers characterised by $M_{n\,PS}$ of 4×10^3 and 9.7×10^3, PS content of 36 and 90 mol.%, respectively, and $M_w/M_n \leqslant 1.37$.

An ATRP synthesised diblock copolymer of poly(4-fluorostyrene) (PFS) and poly(methyl acrylate) (PMA) was converted to PFS-b–PAAc amphiphilic copolymer by hydrolysis of the PMA blocks and used for the synthesis of micellar nanoparticles with cross-linked 'corona' comprised of the PAAc blocks.[261]

b. Binary polar/polar block copolymers

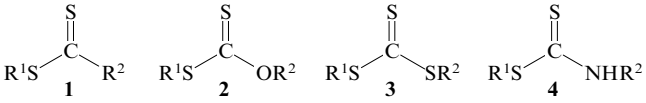
ATRP was used for preparation of amphiphilic diblock copolymers containing hydrophobic PMA or PMMA blocks. A block copolymer precursor synthesised by sequential polymerisation of MMA with TBMA was selectively hydrolysed,[262] which resulted in PMMA-b-PMAAc copolymer. This scheme was also employed in the synthesis of amphiphilic diblock copolymer PAAc-b-PMA[263] with TBA as the protected monomer in the first stage. The micelle-forming properties of the copolymers were the most interesting.

c. Block terpolymers

In recent years, the ATRP method has been used for the synthesis of copolymers containing three chemically different blocks (terpolymers). For instance, not only diblock copolymers, but also terpolymers of composition PTBA-b-PS-b-PMA were synthesised in the study mentioned above.[263] Sequential introduction of TBA, PS and PMA faced no problems, unlike the case of 'living' anionic polymerisation (see Section II.2). The ATRP polymerisation of TBA, MA and styrene led to a PTBA-b-PMA-b-PS terpolymer, which was converted to the PAAc-b-PMA-b-PS terpolymer with increasing block hydrophobicities by hydrolysis of the PTBA block.[252] The micelle-forming properties of these compounds and the possibility of nanoparticle formation with a chemically cross-linked 'corona' was studied.

7. 'Pseudoliving' radical polymerisation with reversible chain transfer

The third type of 'pseudoliving' radical polymerisation, namely, reversible addition–fragmentation chain transfer (RAFT) polymerisation was developed in the 1998–1999s.[264–267] It is characterised by the lowest sensitivity to the nature of monomers, solvents and external polymerisation conditions. The method was even used for controlled synthesis of PAAc ($M_w/M_n = 1.23$) using unprotected AAc [$T = 60$ °C, dimethylformamide (DMF) as solvent and azobis(isobutyronitrile) (AIBN) as initiator].[264] A feature of the RAFT polymerisation is the presence of dithioester chain transfer agents (CTA) of the general structure **1**–**4**



which readily react with either the initiator radical (*e.g.*, AIBN) or the growing polymer chain, thus forming a new CTA, or with the macroCTA, and the reactive radical $(R^1)^{\bullet}$, which reinitiates the polymerisation:

initiation

$$\mathrm{I{-}I} \xrightarrow{k_d} 2\,\mathrm{I}^{\bullet}, \qquad \mathrm{I}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{I{-}M}^{\bullet}, \tag{2}$$

where k_d is the rate constant for decomposition of the initiator;

chain growth

$$\mathrm{I{-}M}^{\bullet} + (n-1)\,\mathrm{M} \longrightarrow \mathrm{I{-}M}_n^{\bullet}; \tag{3}$$

addition–fragmentation reaction

$$\mathrm{I{-}M}_n^{\bullet} + \mathrm{S{=}C(R^2){-}S{-}R^1} \underset{k_{-ad}}{\overset{k_{ad}}{\rightleftharpoons}} \mathrm{I{-}M}_n\mathrm{{-}S{-}\dot{C}(R^2){-}S{-}R^1} \underset{k_{\beta}}{\overset{k_{-\beta}}{\rightleftharpoons}} \mathrm{I{-}M}_n\mathrm{{-}S{-}\dot{C}(R^2){=}S} + (\mathrm{R}^1)^{\bullet}; \tag{4}$$

where k_{ad} and k_{-ad} are the rate constants for addition of (macro)CTA molecules to the growing chains and for elimination of the (macro)CTA molecules, respectively, and k_β and $k_{-\beta}$ are the rate constants for addition of $(R^1)^\bullet$ radicals to the macroCTA molecules and for their fragmentation, respectively;

re-initiation/chain growth

$$(R^1)^\bullet + m\,M \longrightarrow R^1{-}M_m^\bullet; \qquad (5)$$

chain alignment(degenerative chain transfer)

$$R^1{-}M_m^\bullet + S{=}C(R^2){-}S{-}M_n{-}I \underset{k_{-ad}}{\overset{k_{ad}}{\rightleftharpoons}} R^1{-}M_m{-}S{-}\dot{C}(R^2){-}S{-}M_n{-}I \underset{k_{-ad}}{\overset{k_{ad}}{\rightleftharpoons}} R^1{-}M_m{-}S{-}C(R^2){=}S + I{-}M_n^\bullet. \qquad (6)$$

'Pseudoliving' polymerisation mode provides a reversible chain transfer.[264, 265, 268] Reversible (degenerative) chain transfer occurs until the MMs of the growing chains become almost equal to one another, thus providing a narrow MMD.

The rate constant for degenerative chain transfer, *i.e.*, the rate constant for radical exchange in the CTA molecules [stage (6)], is defined as follows:

$$C_{ex} = \frac{k_{ex}}{k_p} = 0.5\frac{k_{ad}}{k_p},$$

where k_{ex} and k_p are the rate constant for degenerative chain transfer and the rate constant for chain growth, respectively.[185, 186] At $C_{ex} \geqslant 100$ and at low conversions, the starting CTA is completely transformed into macroCTA following reaction (4) and then the macroCTA participates in degenerative chain transfer following reaction (6). The highest C_{ex} values are characteristic of the RAFT polymerisation of n-alkyl acrylates, they are somewhat lower for the polymerisation of styrene and even more lower for that of MMA.[269] For instance, the polymerisation of styrene ($T = 40$ °C) and MMA ($T = 60$ °C) under the action of macroCTA (polystyryl dithiobenzoate) was characterised by $C_{ex} = 6000 \pm 2000$ and 140, respectively.[270] The existence of radical intermediates [see stages (4) and (6)] in the RAFT polymerisation of styrene, n-butyl acrylate (nBA), *N*-vinylpyrrolidone, VA and other monomers was proved by EPR spectroscopy.[271, 272] No proof was obtained only for MMA owing to high k_{-ad} value.[271] The first CTAs used in the synthesis of PAAc were 1-phenylethyl dithiobenzoate [264] and 1-cyanoethyl-2-pyrrolidone-1-carbodithioate.[273]

Practical implementation of a RAFT process requires that the rates of radical addition to the C=S double bond and subsequent abstraction of reactive radicals be higher than the chain propagation rate. Therefore, the choice of the R^1 and R^2 radicals in the CTA molecule matters. To provide fast radical addition to CTA, the R^2 substituent should act as stabiliser. Usually, this role is played by the phenyl group.[268] Rapid abstraction of the R^1 radical requires that R^1 have a rather long lifetime, be active in the re-initiation reaction and be surrounded by bulky groups to avoid recombination. With allowance for these requirements, good results were obtained using a tertiary radical of 4-cyanopentanoic acid.[268, 273, 274] By appropriately choosing the R^2 substituent one can also eliminate the well-known effect of a strong decrease in the chain propagation rate in the presence of RAFT agents.[186, 267]

Yet another reaction proposed [275] to control radical polymerisation processes is the reaction of chain transfer to dithiocarbonates (xanthates) of general formula represented by structure **2**. This type of controlled radical polymerisation was named the 'molecular design *via* interchange to xanthates' (MADIX). Among other CTAs used for reversible chain transfer, mention may be made of trithiocarbonates **3** and dithiocarbamates **4**.[273, 276–278] For instance, dibenzyl and bis(1-phenylethyl) trithiocarbonates provided well-controlled polymerisation of AAc [279] and benzyl and cumyl dithiocarbamates provided well-controlled polymerisation of *N*-isopropylacrylamide.[277]

The number-average MM of a polymer obtained by RAFT polymerisation is given by [280]

$$\bar{M}_n = q\frac{M_M[M]_0}{[CTA]_0 + 2f_i[I]_0(1 - e^{-k_d t})} + M_{CTA},$$

where M_M and M_{CTA} are, respectively, the molecular masses of the monomer and CTA, and $[M]_0$ and $[CTA]_0$ are the initial concentrations of the corresponding reactants. For an ideal RAFT process the number of polymer chains emerged from the initiator molecules should be minimum. In this case the second term in the denominator becomes small compared to $[CTA]_0$. In addition, the parameter M_{CTA} can be neglected at a high molecular mass of the polymer. Therefore, in most studies on RAFT polymerisation the value $\bar{P}_n$ was estimated from the relationship

$$\bar{P}_n = q\frac{[M]_0}{[CTA]_0}.$$

Once synthesised, polymers contain dithioester, xanthate, trithiocarbonate or dithiocarbamate end groups, which permits continuation of controlled radical polymerisation of other monomers to obtain linear block copolymers. The method allows one to carry out controlled synthesis of anionic and cationic polyelectrolytes and polyelectrolyte block copolymers in aqueous medium. Below we present some examples of the synthesis of block copolymers using different versions of the technique. All of them concern diblock copolymers containing at least one polar block.

a. Nonpolar/polar diblock copolymers

These block copolymers were synthesised by the RAFT method. For instance, a PS-b-PEA [PEA is poly(ethyl acrylate)] copolymer was obtained by the MADIX technique in emulsion.[281] By hydrolysis of the ethyl acrylate units it was converted to amphiphilic copolymer PS-b-PAAc. A PS-b-PEA copolymer ($M_{n\,PS} = 2 \times 10^3$, $M_{n\,PEA} = 1.95 \times 10^4$; $M_w/M_n \sim 2.0$) was synthesised in a similar fashion and the effect of the degree of hydrolysis of PEA on the character of the micelle-forming properties of the diblock copolymer in aqueous medium was studied.[282] A series of poly(St-alt-MA)-b-PS copolymers with variable length of both blocks [$M_n = (3.11 - 3.52) \times 10^4$] and narrow MMD ($M_w/M_n = 1.09 - 1.16$) was synthesised by the RAFT method.[283]

b. Polar (including ionogenic) block copolymers

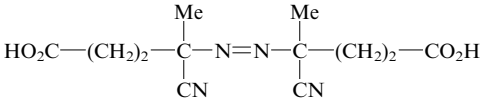
The RAFT method was used for the synthesis of diblock copolymers involving PAAc and PMAAc, namely, PBA-b-PAAc, PMMA-b-PMAAc and PBMA-b-PMAAc, where PBMA is poly(benzyl methacrylate).[265] The polymerisation was carried in DMF with 1-phenylethyl dithiobenzoate as CTA. The copolymers obtained were characterised by low polydispersity. More recently, block copolymers of PAAc with poly(*N*-isopropylacrylamide) (PAAc-b-PIPAA) were synthesised using 1-cyanoethyl 2-pyrrolidone-1-carbodithioate as

CTA.[273] The first block to synthesise was PAAc, which then played the role of macroCTA in the polymerisation of *N*-isopropylacrylamide. Diblock copolymers with the same components were also obtained with benzyl and cumyl dithiocarbamates as CTA.[277] The presence of dithiocarbamate groups at the end is important for subsequent transformation to thiols and conjugation with proteins or pharmaceuticals.

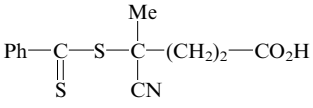
In some studies on the synthesis of polar block copolymers by 'pseudoliving' RAFT polymerisation (see above) and in most related studies to be considered below it was pointed that the best results (narrower MMD) can be obtained if the more rigid block is synthesised first. This indicates an important role of the conformation of the first block in the initiation and growth of the second block. For instance, amphiphilic block copolymers PAAc-b-PTBA with well-controlled molecular structure were obtained by polymerisation of acrylic acid followed by the polymerisation of TBA using trithiocarbonate or xanthate as CTA.[284] The synthetic route to the block copolymers based on poly(meth)acrylonitrile (PMAN and PMA) involving the RAFT polymerisation starting with the rigid block (PMAN) was patented.[285] Chain-transfer agents of general formula R—S—C(=S)Z (R is a mobile group capable of easy elimination by the radical mechanism and Z is a hydrogen or halogen atom or a low-molecular-mass or polymer group) were proposed for the synthesis of linear block copolymers.

Block copolymers having two hydrophilic blocks, PAA and PAAc, were synthesised by the MADIX method using mono- or bifunctional xanthates as CTA.[286] The A-b-B and A-b-B-b-A type copolymers were characterised by $M_w/M_n \leqslant 1.5$.

Interesting studies on the synthesis of polyelectrolyte block copolymers using an improved RAFT technique are available.[268, 287] The polymerisation was initiated by 4,4′-azobis(4-cyanopentanoic) acid (ABCPA) (**5**), which gave the same tertiary radicals of 4-cyanopentanoic acid upon thermal decomposition as those formed upon abstraction from the CTA molecule [4-cyanopentanoic acid dithiobenzoate (CPADTB) (**6**)] in the course of chain transfer reactions.



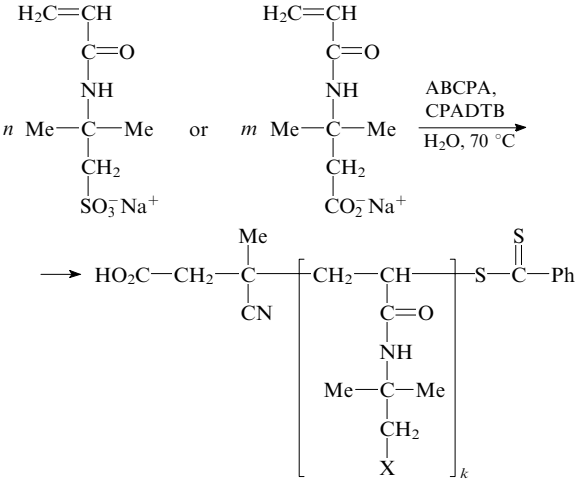
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6

This methodology was employed for controlled synthesis of three diblock copolymers containing various polyanionic or polycationic blocks in aqueous solution *via* RAFT. These were PSSNa-b-PVBNa based on poly(sodium 4-styrenesulfonate) and poly(sodium 4-vinyl benzoate), PVTMAC-b-PDMVBA based on poly(vinyltrimethylammonium chloride) and poly(*N*,*N*-dimethylvinylbenzylamine) and PNaAAMPS-b-PNaAAMB based on poly(sodium 2-acrylamido-2-methylpropane sulfonate) and poly(sodium 3-acrylamido-3-methyl butanoate). The first two copolymers were obtained in two steps.[268] The first step (sealed tubes, 70 °C, 8 h) afforded almost monodisperse PSSNa and PVTMAC containing dithioester end groups. The molecular masses of the blocks monotonically increased with conversion. In the second stage (reactor, 70 °C, inert atmosphere, 24 h) both blocks played the role of the macroCTA in 'pseudoliving' radical polymerisation of sodium vinyl benzoate and *N*,*N*-dimethylvinylbenzylamine. The copolymer containing polyanionic blocks was characterised by $M_n = 1.86 \times 10^4$ and $M_w/M_n = 1.18$ while the copolymer with polycationic blocks had $M_n = 5.1 \times 10^4$ and $M_w/M_n = 1.37$.

The third copolymer, PNaAAMPS-b-PNaAAMB, was synthesised from *N*-substituted acrylamides in two stages using the same reactor [287]



X = $SO_3^-Na^+$ or $CO_2^-Na^+$, $k = (n + m)$ or $(m + n)$.

The monomers were introduced in different order and the overall polymerisation processes were studied, because the polymerisation of acrylamide monomers by the SFRP and ATRP methods is problematic (see above). The polymerisation of the first block (PNaAAMPS or PNaAAMB) was accompanied by a linear increase in M_n with increasing conversion, the reaction being first-order with respect to the monomer concentration; the first-order rate plot showed an induction period ($\sim$1 h). This was attributed [287] to the slow initiation by the initiator used. Unlike the SFRP and ATRP methods for which the polydispersity of products usually decreases with conversion, here the polydispersity M_w/M_n somewhat increased with conversion but remained below 1.3. Because of high viscosities of strong polyelectrolytes in aqueous solutions (this can reduce the reaction rate) in the second stage of polymerisation the concentration of the second monomer was halved. Simultaneously, the duration of the polymerisation of the second block was doubled. The molecular masses M_n of the PNaAAMPS-b-PNaAAMB and PNaAAMB-b-PNaAAMPS copolymers (6.97×10^4 and 5.79×10^4, respectively) were in excellent agreement with the theoretical values; the polydispersities M_w/M_n were also low (1.14 and 1.16, respectively).

c. Multiblock copolymers

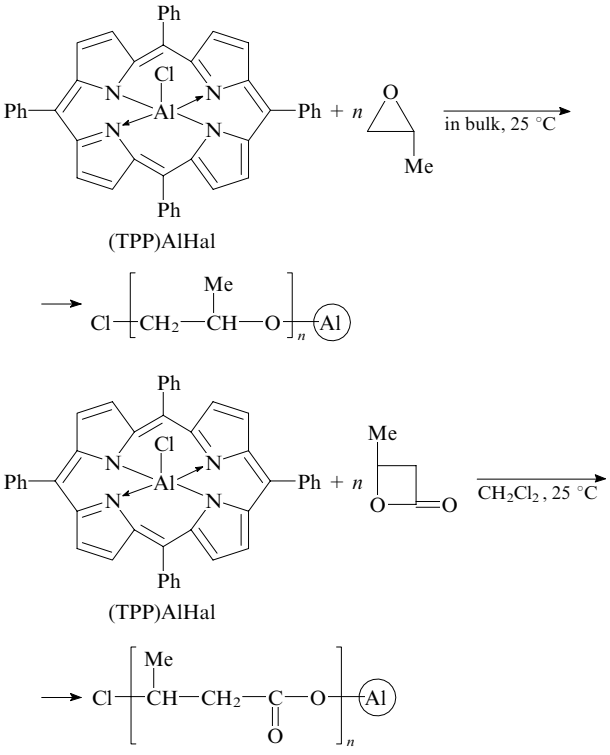
Prospects for the synthesis of block polyelectrolytes in aqueous solutions offered by the RAFT and MADIX methods are clouded by some circumstances. First, most CTAs are insoluble in water. Second, the synthesis of copolymers containing only one polyelectrolyte block often causes an abrupt increase in the medium viscosity. This complicates the RAFT polymerisation of tri- and multiblock copolymers or makes the process impossible. Therefore, now considerable attention is paid to industrial implementation of this polymerisation technique. In particular, prospects for the synthesis of homopolymers and copolymers using emulsion/miniemulsion RAFT polymerisation technique were studied.[288–292] The advantages of the RAFT process under conditions of emulsion/miniemulsion polymerisation compared to the same process in a homo-

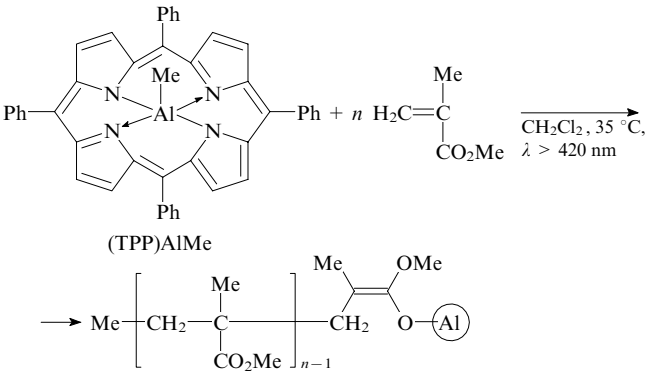
geneous medium consist in a higher chain propagation rate (due to segregation of radicals) and a better processability of products owing to low viscosity in solution at high polymer content. To improve the process, it was proposed to use a train of continuous tank reactors instead of a single reactor.[293] This allows one to achieve higher monomer conversions in smaller reaction volumes and to obtain narrow-MMD multiblock copolymers of specified architecture. Taking the synthesis of gradient multiblock copolymers of St with n-butyl acrylate as an example, it was shown that the composition and length of any block can easily be varied by varying the temperature, flow rate in the reactor train and the injection point. The polymerisation was carried out at 72–77 °C with $Na_2S_2O_8$ as initiator, 1-phenylethyl phenyldithioacetate as CTA and SDS as emulsifier).

8. Other methods

Now we will dwell on yet another, rarely used, method of 'living' polymerisation, namely, sequential anion-coordination polymerisation in the presence of metalloporphyrins, which permits the synthesis of certain block copolymers of specified molecular architecture. It has been comprehensively treated in a review[46] and concerns controlled room-temperature, ring-opening polymerisation of oxiranes, β-lactones, δ-valerolactones, ε-caprolactones, D-lactide, methacrylates and methacrylonitrile. The role of polymerisation initiators and nanoreactors, where a next monomer molecule is added to a growing chain by the anion-coordination mechanism, is played by (5,10,15,20-tetraphenylporphyrinato)aluminium chlorides, (5,10,15,20-tetraphenylporphyrinato)(methyl)aluminium and (5,10,15,20-tetraphenylporphyrinato)(methoxy)aluminium.[46] The growth centres include aluminium alkoxides for the polymerisation of oxiranes, δ-valerolactones, ε-caprolactones and D-lactide; aluminium carboxylate for the polymerisation of β-lactones and aluminium enolate for the polymerisation of methacrylates (see the processes shown in Scheme 14).

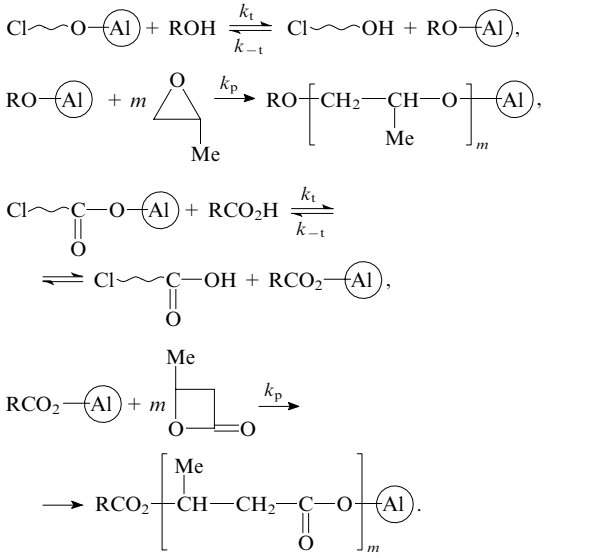
Scheme 14





Reversible chain termination reactions of the alcohol or carboxylic acid protons (for the polymerisation of oxiranes and lactones) represent important elements of control of the polymerisation of heterocyclic compounds (see the first and third processes in Scheme 15).[46, 294]

Scheme 15



The reversible chain termination reactions are much faster compared to chain propagation, namely, $k_t/k_p = 10$ (Ref. 294). Therefore, the polydispersity index of polymers remains very low ($M_w/M_n \approx 1.1$). The number-average degree of polymerisation in these processes is given by the ratio[46]

$$\overline{P}_n = q\frac{[M]_0}{[(TPP)AlHal] + [H]},$$

where [H] is the concentration of the compound containing a mobile proton (alcohol or acid). Owing to fast reversible chain termination by the alcohol or acid protons these processes take a few days or weeks until complete consumption of the heterocyclic compounds.[46] However, they can be accelerated by introducing sterically hindered Lewis acids, *e.g.*, methylaluminium bis[2,6-di(*tert*-butyl)-4-methylphenolate].[295]

Unlike heterocyclic compounds, (TPP)AlHal do not initiate the polymerisation of methacrylates and methacrylonitrile. Polymerisation of these monomers in the presence of (TPP)AlMe is only possible upon irradiation of the system with visible light (see the last reaction in Scheme 14). These slow processes can also be accelerated by introducing solid Lewis acids, such as methylaluminium bis[2,6-di(*tert*-butyl)phenolate], triphenylphosphine and organoboron compounds.[46] The Lewis acids are coordinated by the monomer carbonyl groups and enhance their electrophilicity. Successful polymerisation of non-irrradiated methacrylates can be performed using more

nucleophilic porphyrins, such as (propylthio)- and (phenylthio)(5,10,15,20-tetraphenylporphyrinato)aluminium with methylaluminium bis[2,6-di(*tert*-butyl)-4-methylphenolate].[46] In these processes the degree of polymerisation (up to $P_n = 300$) is determined by the ratio

$$P_n = \frac{q[M]_0}{[I]_0},$$

and the MMD is very narrow ($M_w/M_n = 1.05-1.2$).[46]

Aluminium porphyrinates were used in the synthesis of diblock copolymers from two oxiranes,[296,297] two β-lactones,[298] β-lactone and oxirane.[298] In the last (mixed) case, β-lactone was polymerised first because aluminium carboxylate at the chain end initiated the polymerisation of oxiranes, whereas the corresponding aluminium alkoxide was incapable of initiating the polymerisation of β-lactone. Diblock copolymers were also obtained by sequential polymerisation of EO and ε-caprolactone,[83] propylene oxide and D-lactide[299] and various methacrylates.[300] It should be noted that, in contrast to carbochain polymers, products of polymerisation of heterocycles (in particular, polyethers and polyesters) possess a unique ability to undergo biodegradation.[301] Therefore, considerable attention has been paid recently to the design of block copolymers containing these specific blocks.[104-109]

III. Combination of different mechanisms of monomer polymerisation

This Section concerns alternative methods of synthesis of block copolymers. Common to all of them is the involvement of different polymerisation techniques in the course of synthesis. This strategy of synthesis of block copolymers is called multimode polymerisation.[9] The new avenue of research began with a study [302] whose authors reported for the first time a transition from 'living' cationic polymerisation of THF to 'living' anionic polymerisation of St. Short after this publication the subject has attracted considerable attention of researchers.[303,304] The major impetus to the development of multimode polymerisation techniques came from the need of the synthesis of copolymers from blocks of different chemical nature that are difficult or hard to synthesise by sequential polymerisation of monomers by the same mechanism. The idea of using polymeric products of large-scale synthesis for preparation of block copolymers also played its role. At present, three strategies of multimode polymerisation of linear block copolymers are developed. These are (i) formation of macroinitiators for radical, ionic or other types of polymerisation at the ends of ready polymers; (ii) combination of various mechanisms of controlled ('living' ionic and 'pseudoliving' radical) polymerisation and (iii) use of bifunctional initiators. Consider now each strategy in more detail.

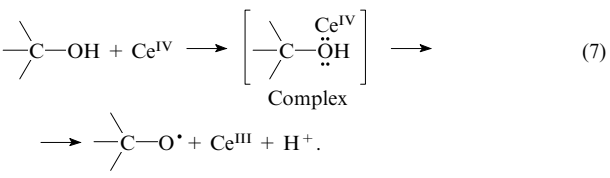
1. Formation of macroinitiators based on ready blocks

Transformation of the end groups of polymers into macroinitiators of polymerisation requires that they bear active groups of particular chemical nature. In some polymers, such groups are formed in the course of synthesis. An example is provided by PEG containing active hydroxyl groups at the chain ends. In other polymers, especially in practically important polyolefins [PE, polypropylene (PP), PS, poly(4-methylpent-1-ene), *etc.*] the formation of active groups occurs during the synthesis or follows it.[8,305]

a. Macroinitiators based on poly(ethylene glycol)

The use of the OH groups of PEG and PEGME to obtain macroinitiators of radical polymerisation and prepare A-b-B, A-b-B-b-A and B-b-A-b-B block copolymers has been a subject of considerable literature (see, *e.g.*, Refs 306-310). These problems have been treated in most detail in a review.[6] There are two main methods of conversion of PEG into macroinitiators. One of them involves direct 'activation' of the OH groups of PEG in the presence of other monomers followed by synthesis of block copolymers. The other technique involves modification of the end groups of PEG, their 'activation' in the presence of monomers and synthesis of di- or triblock copolymers. Now we will consider some examples.

Direct activation of PEG is possible in a redox reaction of formation/breakup of complexes between hydroxyl groups and mixed-valence metal ions (Co^{III}, Ce^{IV}, Mn^{III}, *etc.*).[311] The mechanism of a reaction of isolated OH groups with a Ce^{IV} salt is as follows:[311,312]



(7)

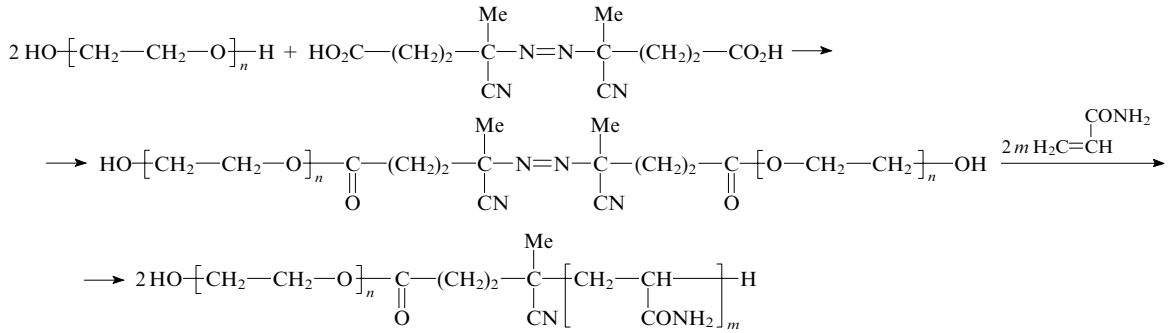
The lifetime of the intermediate complex varies from tens of seconds to a few hours depending on the structure of the hydroxyl-containing compound.[312]

Novitskaya and Konkin [306] were the first who used reaction (7) for the synthesis of PAN-b-PEO-b-PAN copolymers (PAN is polyacrylonitrile). The starting PEG had a molecular mass of 4.4×10^3. The PEO content in the resulting triblock copolymer varied from 12% to 20 % by mass. More recently, this technique was employed for the synthesis of PAA-b-PEO-b-PAA, PEO-b-PIPAA, PIPAA-b-PEO-b-PIPAA and PAAc-b-PEO-b-PAAc copolymers with variable molecular mass of the PEO block.[307,308] A PMMA-b-PEO-b-PMMA copolymer was synthesised in a similar fashion in the presence of Mn^{III}.[309]

Yet another method was used for modification of the hydroxyl groups of PEG and formation of thermal macroinitiators, which form free radicals upon a change in temperature. In particular, the reaction of PEG with 4,4-azobis(4-cyanopentanoic acid) gave a polyazo ester, which was used in the synthesis of PEO-b-PAA diblock copolymers (Scheme 16).[310]

The same thermal macroinitiator was obtained as intermediate product in the synthesis of the PEO-b-PS, PEO-b-PMA, PEO-b-PMMA, PEO-b-PVA and PEO-b-PAN copoly-

Scheme 16



mers.[313] The reactivities of monomers were compared at the same macroinitiator concentration under identical conditions (60 °C, 24 h). The rates of polymerisation of MA and MMA were higher and, therefore, higher q values and molecular masses of blocks were observed in these cases (q 80% – 85% for MA and MMA *vs.* at most 20% for styrene). This macroinitiator was also obtained [314] by the interaction of PEG with 4,4-azobis(4-cyanopentanoic acid) anhydride. Then, it was thermally 'activated' in the presence of styrene and the PEO-b-PS copolymer was obtained.

A macroinitiator with ester end groups was synthesised in the reaction of PEG (M_n = 400) with azobis(cyanopentanoic) acid chloride in the presence of benzoyl chloride or acetyl chloride (Scheme 17) [315] and used in the polymerisation of St to obtain a liquid block copolymer PEO-b-PS with $M_n = 2.2 \times 10^4 - 2.9 \times 10^4$.

Yet another polyazo ester was synthesised by the interaction of PEG with AIBN in acidic medium (Scheme 18).[316] Its heating in aqueous acrylonitrile solution caused the formation of polydisperse PEO-b-PAN block copolymer (maximum yield 40 mass % at 85 °C) containing a soluble (6% – 12% of PAN) and insoluble (86% – 92% of PAN) fractions.

A more complex method [317] of synthesis of PEG-based macroinitiators of styrene polymerisation involves [317] the formation of macroazocarbamate in the reaction of PEG with aliphatic diisocyanate and then with 4,4-azobis(4-cyanopentan-1-ol). Heat treatment of the macroazocarbamate in the presence of styrene led to PEO-b-PS copolymer (Scheme 19).

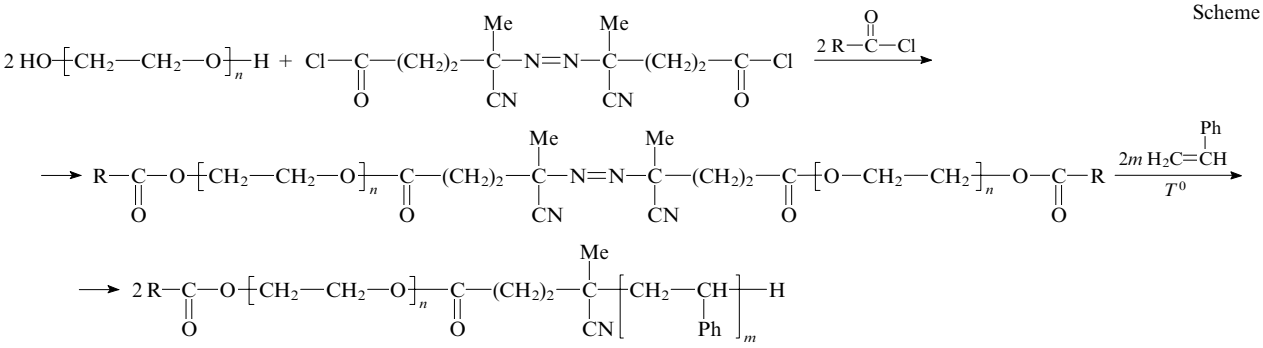
Macrodiazocarbamate was synthesised analogously using isophorone diisocyanate and initiated polymerisation of MMA.[318] The final product, a PMMA-b-PEO-b-PMMA copolymer, had $M_w = (2-7) \times 10^5$.

Yet another type of modification of the OH groups of PEG to obtain a PS-b-PEO-b-PS triblock copolymers is shown in Scheme 20.[319, 320] PEG was mixed with isophorone diisocyanate and then with dihydroperoxides of general formula HOO–R–OOH or with monoperoxide Bu^{t}OOH. This resulted in yet another thermal macroinitiator, PEO diperoxycarbamate. The final triblock copolymer had a broad MMD and contained the homopolymer due to occurrence of the chain transfer reaction.[319]

Direct 'activation' of the OH groups of a PEG-based polyazo ester in the interaction with Ce^{IV} or Mn^{III} followed by thermal initiation was used [321] for the synthesis of PMMA-b-PEO-b-PMMA and PMMA-b-PEO-b-PS block copolymers (Scheme 21). A bifunctional polyazo ester was treated with Ce^{IV} or Mn^{III} salts in MMA solution at room temperature. The resulting tetrablock copolymer with the central azo group was heated in the presence of styrene or MMA.

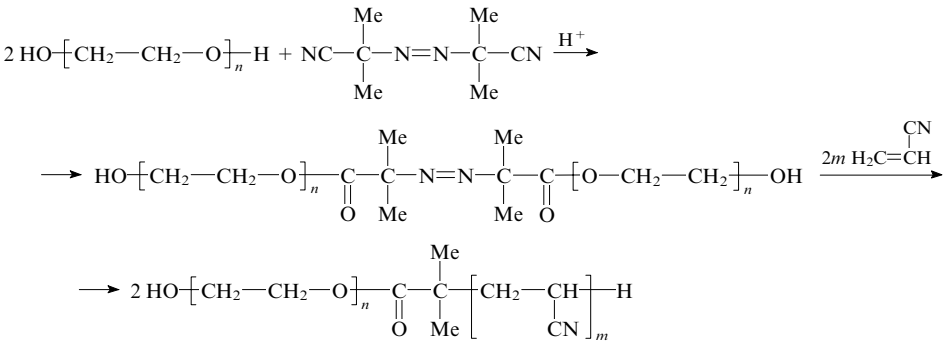
Of course, the block copolymers obtained by radical polymerisation of monomers under the action of PEG-based macroinitiators had broader MMDs compared to the block

Scheme 17

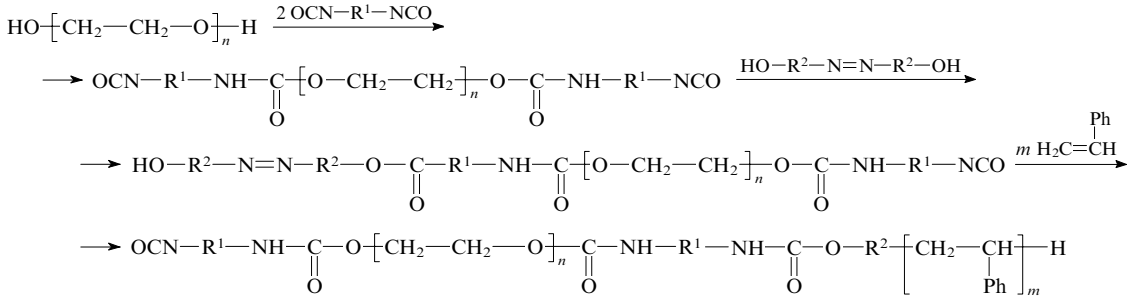


R = Ph or Me.

Scheme 18

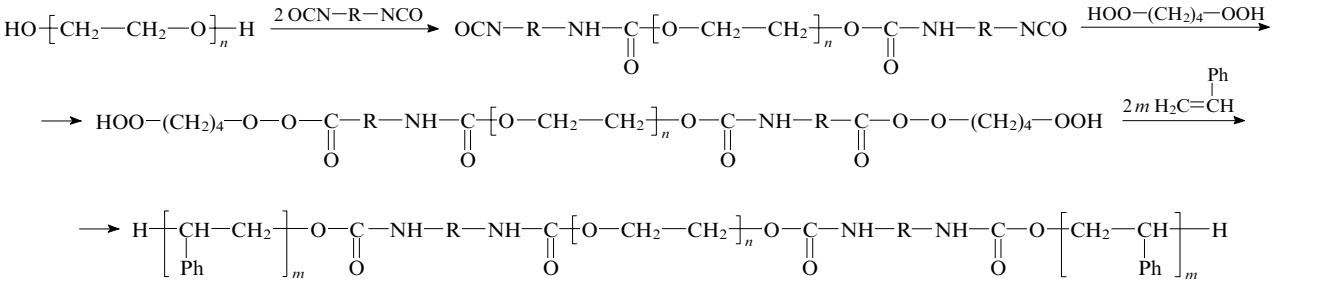


Scheme 19



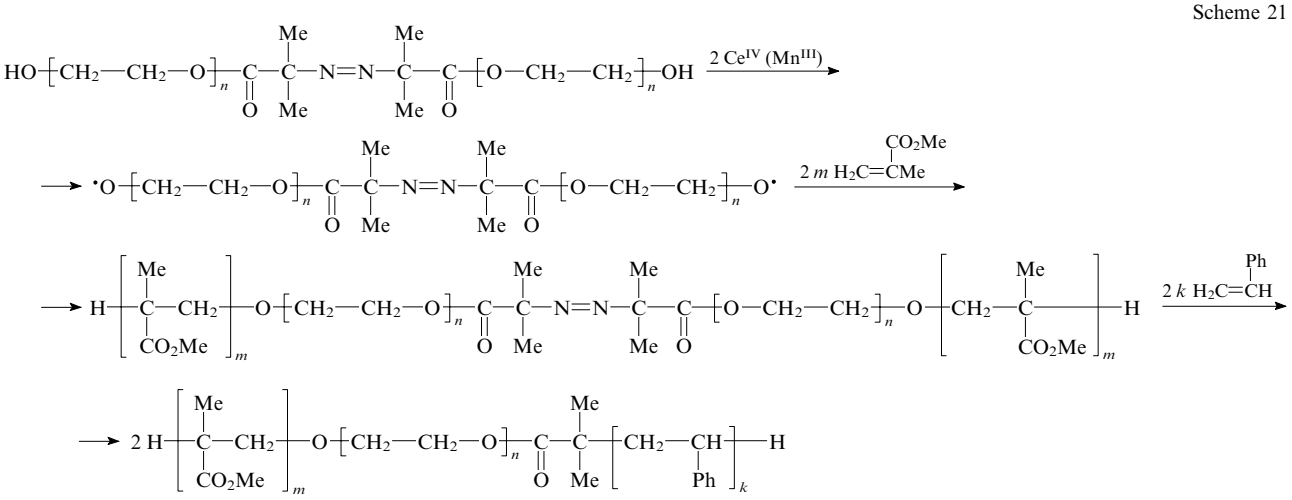
R^1 = Alk, R^2 = $-(CH_2)_3-CMe-CN$.

Scheme 20



R = CH(Me)–CH$_2$–C(=O)–CH$_2$–CH(Me).

Scheme 21



copolymers obtained by controlled sequential polymerisation. Nevertheless, in the former case the number of partners for PEG was larger.

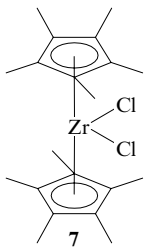
Recently, various transformations of PEG into mono- and bifunctional macroinitiators of anionic ring-opening polymerisation of lactones and lactides to synthesise biodegradable block copolymers [108, 109] (see Section II.2) and studies on the formation of PEG-based macroinitiators of controlled radical polymerisation were reported. For instance, the bromo derivatives of PEG and random copolymers of ethylene glycol and propylene glycol [poly(EG-co-PG)] were used in ATRP of 2,3,4,5,6-pentafluorostyrene (PFSt).[322, 323] PEG chains ($M_n = 2 \times 10^3 - 1 \times 10^4$) and poly(EG-co-PG) ($M_n \sim 1 \times 10^3$, EG content 74 mass %) were converted into macroinitiators by esterification of OH groups with bromoisobutanoic acid bromide. ^{1}H NMR spectroscopy studies confirmed the limiting degree of functionalisation of the end groups ($F_n = 1$). The ATRP of PFSt at both ends of polyethers afforded triblock copolymers PPFSt-b-PEG-b-PPFSt and PPFSt-b-P(EG-co-PG)-b-PPFSt. The molecular masses of the central blocks increased by 15%–84 % by mass and the polydispersity index M_w/M_n was less than 1.22. The triblock copolymers formed films with well-defined microphase separation and complexes with Li^+ salts.

A unique synthesis of diblock polyelectrolyte PEO-b-P(NaMA) by ATRP in aqueous solution was reported.[324] The polymerisation of NaMA performed with a PEG bromo derivative as macroinitiator and the Cu^{I}Br–2,2′-bipyridyl system as catalyst resulted in a high yield of narrow-MMD copolymer. A feature of the synthesis consisted in an optimal pH value (pH 8–9) that allowed one to maintain a balance between the possible reduction of P(NaMA) chain propagation rate at too high pH and competing protonation of 2,2′-bipyridyl at too low pH.

b. Macroinitiators based on polyolefins

Polyolefins are polymeric materials produced on a large-scale basis. Due to the lack of polar groups they are poorly compatible with inorganic fillers, polar polymers, glass fibre, pigments and metals. An efficient method of improving the compatibility of polyolefins with other materials is the synthesis of polyolefin-based block copolymers containing polar blocks. Therefore, in the last decade researchers undertook considerable efforts to develop methods of functionalisation of polyolefins. These methods were most comprehensively treated in reviews.[8, 305] In the text below we present the most promising techniques used for the synthesis of linear block copolymers. In this connection we will first dwell on the synthesis of polyolefins.

At present, stereoregular polyolefins are synthesised on a large scale using ionic-coordination polymerisation in the presence of heterogeneous or homogeneous Ziegler–Natta catalysts [*e.g.*, $TiCl_3 + AlR_nCl_{3-n}$ ($n = 1-3$) on $MgCl_2$ powder].[22, 305] The mechanism of the process is well known.[22, 23] Recently, new homogeneous metallocene and post-metallocene catalysts have been widely used in the field. The major components of the metallocene catalysts are sandwich complexes of Group IV transition metals (Ti, Zr or Hf) with two cyclopentadienyl ligands (**7**). In some cases ligands may be linked by bridging groups involving carbon or silicon atoms.[305]



7

Cp_2ZrCl_2 (Cp = η-C_5H_5)
Complex with unsubstituted ligands

$Cp^*_2ZrCl_2$ (Cp^* = η-C_5Me_5)
Complex with substituted ligands

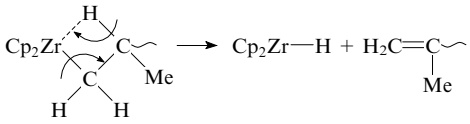
Active co-catalyst of metallocenes is methylalumoxane (MAO) of general formula $-[Al(Me)-O]_n-$ with a molecular mass of 8×10^2 to 1.5×10^3 (Ref 305), which is formed upon partial hydrolysis of trimethylaluminium. The post-metallocene catalysts may contain unsubstituted and substituted indene (Ind) or fluorene (Flu) ligands, in particular, $(Ind)_2ZrCl_2$ and $(Flu)_2ZrCl_2$, instead of cyclopentadienyls.[305] The ability of the ligands to donate electrons to the transition metal increases in the order Cp < Ind < Flu.[325] By varying the electronic and steric effects by changing the ligand structure one can control the polymerisation, stereoregularity and the MM of polyolefins, as well as modify their end groups.

To prepare macroinitiators, the end groups of homo- or copolyolefins are functionalised in the course of metallocene-catalysed synthesis of these compounds (to make the products cheaper) using two main procedures involving formation of (i) unsaturated end groups to be chemically modified and (ii) end groups capable of directly initiating block copolymerisation when activated.

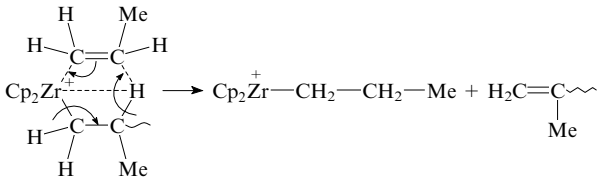
The formation of terminal double bonds in polyolefins is due to transfer of β-H atoms or β-alkyl groups (if exist), which occur in the active centres of chain growth (see the reactions shown in Scheme 22) and reduce the molecular mass of the polymer.[8, 305] The first type of transfer resulting in metal hydrides and alkenes (first reaction) was observed in the active centres of neutral or positively charged alkylmetallocenes.[305] The second type of transfer (second reaction) was detected in the polymerisation of propylene on heterogeneous metallocene catalysts and in the copolymerisation of propylene with ethylene on Cp_2ZrCl_2 + MAO.[305] Transfer of β-alkyl (methyl) groups to the transition metal (third reaction) was observed in a study of propylene oligomerisation with Cp^*_2LaMe as catalyst.[326]

Scheme 22

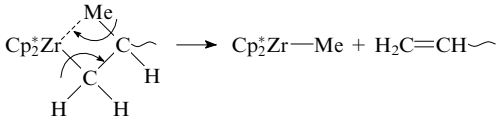
β-*H transfer to transition metal*



β-*H transfer to monomer*



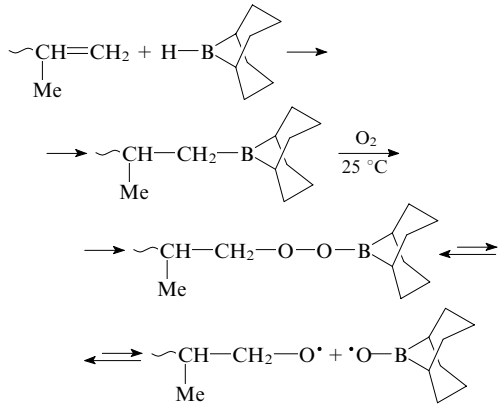
β-*Alkyl transfer to transition metal*



The transfer reactions can be controlled with ease by varying the metallocene structure (electronic and steric factors) and conditions of polymerisation (temperature and pressure).[305] The more readily the ligands donate electrons to the metal the lower (i) the thermodynamic affinity of the metal to the β-proton in the growing chain and (ii) the probability of β-proton transfer. A similar effect can be attained by increasing the volume and number of substituents in the ligands, because this is accompanied by an increase in steric hindrances to the orientation of a single polymer chain (see the first process in Scheme 22) or to that of a polymer chain and a monomer molecule (see the second process in Scheme 22) in the active centre that are necessary for β-proton transfer. In addition, reduction of the pressure and temperature causes the transfer rate to decrease; at $T < -20$ °C, the chain transfer reactions can be suppressed at all.

Further modification of unsaturated polyolefin end groups can be done in various fashions.[305] One of the most promising methods is to form macroinitiators by, *e.g.*, quantitative ($F_n = 1$) hydroboronation of unsaturated end groups using 9-borabicyclo[3.3.1]nonane (9-BBN) (Scheme 23). Alkylborane groups thus obtained are readily oxidised at room temperature and form two radicals.[305]

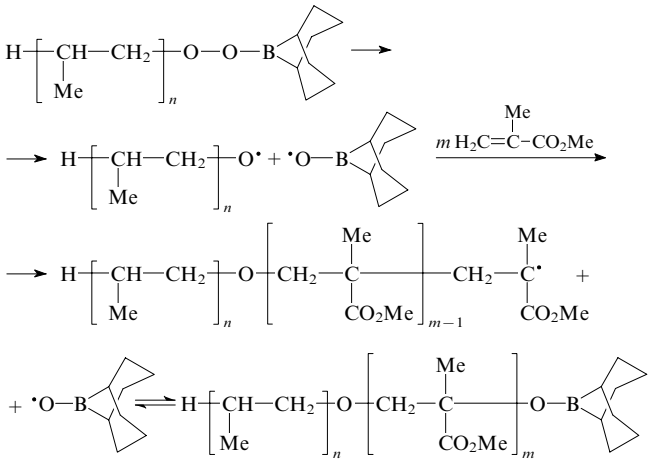
Scheme 23



The alkoxyl radical is reactive and readily initiates the polymerisation of α-olefins. The borinate radical is more stable, being incapable of initiating polymerisation. In fact, alkyl-9-BBN peroxide, which is in equilibrium with the reactive (C−O•) and stable (B−O•) radicals, forms an initiating and control system, which can maintain the 'pseudoliving' character of radical polymerisation [326] and is similar to alkoxyamines based on the TEMPO stable radicals in the mechanism of action.

This method of formation of macroinitiators at the ends of unsatured polyolefins was first used for the synthesis of the following diblock copolymers: PP-b-PMMA and PP-b-PEMA,[327] PP-b-PBA, PP-b-PS and PP-b-PVA [328] and PP-b-poly(St-alt-MA).[329] For the first copolymer the 'pseudoliving' polymerisation of MMA is described by Scheme 24.

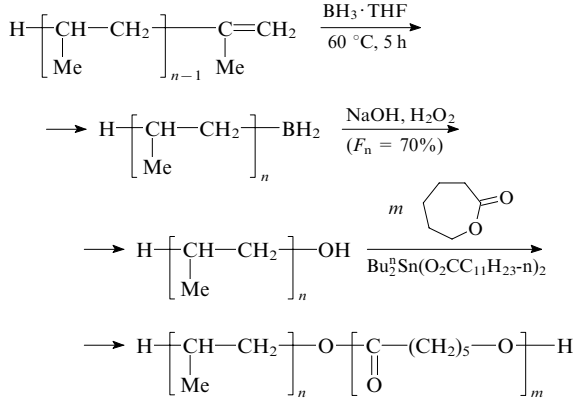
Scheme 24



In this step, the molecular mass of the polymer increased from 1.3×10^4 (for the starting PP) to 2.9×10^4 (for the PP-b-PMMA copolymer) and the polydispersity index varied insignificantly, from 1.5 to 1.7 (Ref. 327). High efficiency of the initiation with alkylborane groups ($f_i = 1$) was pointed.

Hydroboronation of unsatured polyolefins (isotactic PP) followed by oxidation of the product (Scheme 25) was used to form hydroxyl end groups.[330] Quantitative addition of the borane groups to the double bonds was characterised by lower oxidation efficiency (final value $F_n = 0.7$). The modified PP was activated by dibutyl tin dilaurate [$Bu^n_2Sn(O_2CC_{11}H_{23}$-n)$_2$] and used as macroinitiator of anionic ring-opening polymerisation of ε-caprolactone.[331,332] Based on PP with $M_n = 1.0 \times 10^3$, a PP-b-PCL copolymer with $M_n = 4.6 \times 10^3$ (see Ref. 332) was obtained; the monomer conversion was 70%.

Scheme 25

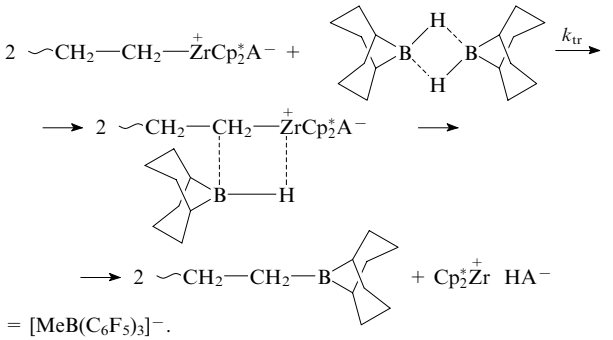


A more complex procedure for conversion of unsaturated polyolefins to macroinitiators by hydroboronation (Scheme 26) was also reported.[333] Treatment of isotactic PP ($M_n = 2.2 \times 10^3$) with a borane/dimethyl sulfide complex led to replacement of all protons by PP chains. Subsequent addition of an organomagnesium reagent resulted in quantitative yield of a macroinitiator of 'living' anionic polymerisation, which was used for the synthesis of PP-b-PMMA block copolymer ($M_n = 2.5 \times 10^3 - 3 \times 10^3$). The 'living' mechanism of polymerisation of the PMMA blocks was confirmed by a linear increase in their molecular mass with time.

Consider two recently developed methods of *in situ* formation of active end groups in polyolefins in the course of metallocene-catalysed synthesis.[8] They are based on the reaction of chain transfer to specific chain transfer agents (CTA) that do not affect the chain propagation rate. One method uses 9-BBN, while the other uses *p*-methylstyrene as CTA.

In situ modification of polyolefin end groups with 9-BBN appeared to be a complicated task. A proton of the 9-BBN group can be exchanged with ease with alkyl groups of metal alkyls and simultaneously react with unsaturated α-olefins. Therefore, polymerisation of olefins on metallocene catalysts can involve not only chain transfer to 9-BBN, but also side exchange reactions (between borane and aluminium alkyl groups of MAO) and hydroboronation of monomers. Nevertheless, these problems were solved and the side reactions avoided.[8,305] It was shown that the 9-BBN molecules form stable dimers in the conventional nonpolar solvents (hexane, toluene) used for carrying out metallocene-catalysed polymerisation and do not react with olefins. In this case, a perfluoroborate co-initiator, which does not react with most alkylboranes, was used instead of MAO. This made it possible to develop a rather efficient polymerisation process (Scheme 27) resulting in polyolefins bearing one 9-BBN end group.

Scheme 27



$A^- = [MeB(C_6F_5)_3]^-$.

A narrow-MMD polymer was obtained [334] by the polymerisation of ethylene in the presence of 9-BBN on the $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ and $[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$ catalysts. A linear dependence of P_n(PE) on the monomer: 9-BBN concentration ratio was established:

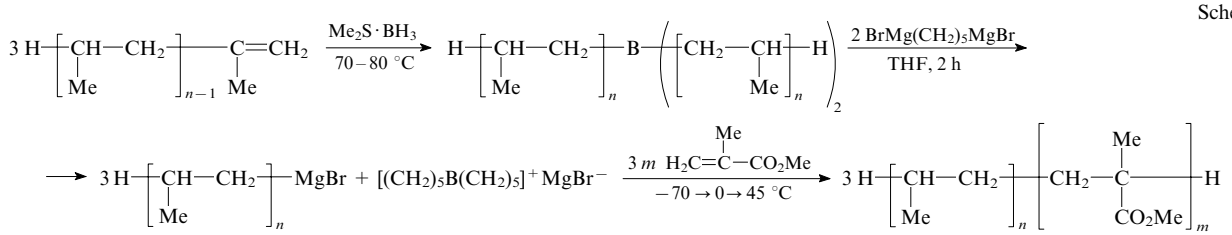
$$P_n = \frac{k_p[M]}{k_{tr}[CTA]}.$$

The k_p/k_{tr} ratio determined from the slope of the straight line thus obtained equals 75. The presence of borane end groups in PE was confirmed by NMR spectroscopy. 9-BBN was used as CTA in the synthesis of syndiotactic PS on $[Cp^*_2TiMe_2]^+$. $[MeB(C_6F_5)_3]^-$ catalyst.[335] As the 9-BBN concentration increased, the molecular mass of PS decreased. 9-BBN has almost no effect on the stereotacticity of PS; however, the catalyst activity reduced, which was explained by competitive coordination of St and 9-BBN to the catalyst.

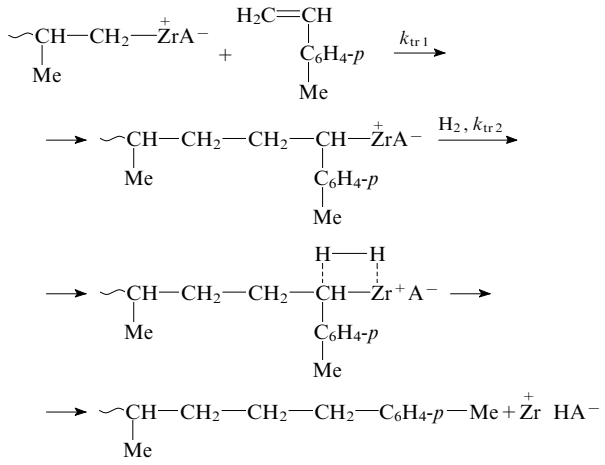
Borane-modified PE and PS were used as macroinitiators of controlled radical polymerisation of MMA and benzyl methacrylate.[334–336] The macroinitiators were 'activated' using the known oxidation reaction of alkyl-9-BBN (see Scheme 23). The kinetics of MMA polymerisation ($T = 25$ °C) under the action of oxidised PE chains (PE: $M_n = 1.94 \times 10^4$ and 4.27×10^4; $M_w/M_n = 2.1$ and 2.2, respectively) was studied.[334] The linear increase in the molecular mass of PMMA with time confirmed the 'pseudoliving' mechanism of radical polymerisation. The resulting PE-b-PMMA copolymers had $M_n = 9.03 \times 10^4$ and 9.76×10^4 and similar MMDs ($M_w/M_n = 2.0$ and 2.9). An analogous picture was observed in a study [335] of MMA and BMA polymerisation under the action of oxidised PS ($M_n = 1.5 \times 10^4$, $M_w/M_n = 2.2$). The molecular masses of the PMMA and PBMA blocks linearly increased with time, which indicated correctness of the polymerisation mechanism proposed. After 24 h, the PS-b-PMMA and PS-b-PBMA copolymers were characterised by M_n of 2.9×10^4 and 3.33×10^4, respectively.

Yet another example of efficient CTA is provided by *p*-methylstyrene.[8] Introduction of this compound and molec-

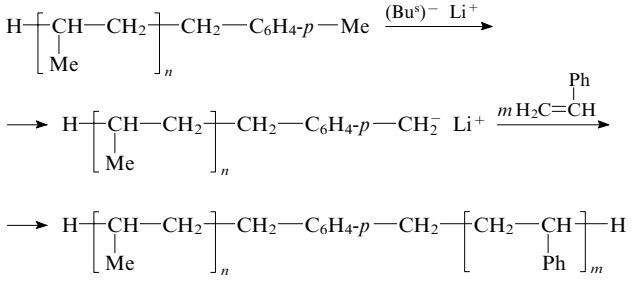
Scheme 26



ular hydrogen in metallocene-catalysed polymerisation of olefins led to chain termination and formation of terminal *p*-methylphenyl groups. To make the reaction mechanism efficient and avoid the copolymerisation of olefins with MS, it was proposed to use a sterically hindered metallocene catalyst with bridging ligands. For instance, the problem of chain transfer to MS in the propylene polymerisation in toluene ($T = 30$ °C) was solved using the *rac*-Me_2Si[2-Me-4-Ph(Ind)]$_2ZrCl_2$ + MAO system as catalyst.[337] Owing to steric hindrances in the active centre, one *p*-MS molecule added to PP and after that, the polymerisations of all monomers ceased. To cleave the Zr–C bonds and restore the Zr–H bonds responsible for continuation of the polymerisation cycle, hydrogen was added.



The terminal character of *p*-methylphenyl groups was confirmed by ^1H and ^{13}C NMR spectroscopies and by the involvement of PP in 'living' anionic polymerisation of styrene.[337] The *p*-methylphenyl groups were 'activated' using the metallation reaction.



The modified PP was suspended in cyclohexane in the presence of excess Bu^sLi at room temperature for 5 h. The product was filtered off and used in the polymerisation of styrene. An increase in the molecular mass of PS with time confirmed the 'living' mechanism of polymerisation. Two samples of the PP-b-PS copolymer with $M_n = 5.4 \times 10^4$ and 1.175×10^5 ($M_w/M_n = 2.34$ and 2.25) were prepared (*cf.* $M_n = 2.59 \times 10^4$ and $M_w/M_n = 2.3$ for the initial modified PP).

The last-named two methods of functionalisation of polyolefins and formation of macroinitiators seem to be the best. They provide a convenient transition from metallocene catalysed polymerisation of the first block to controlled radical or ionic polymerisation of the second block. This offers prospects for attachment of blocks of different chemical nature to the polyolefin blocks and for the design of copolymers of specified molecular structure.

c. Macroinitiators based on another polymers

Polydimethylsiloxane (PDMS) containing flexible hydrophobic chains is produced on a large-scale basis and attracts considerable interest of researchers as a component of block copolymers. The compound is widely used as macroinitiator of polymerisation of various monomers in both the native (with silanol end groups) and end-group-modified forms. Remind that usually PDMS is synthesised on a large-scale basis by anionic polymerisation of cyclic dimethylsiloxanes accompanied by partial polycondensation.[22] The modification of SiOH groups in PDMS can be best exemplified by the etherification reaction. PDMS containing one or two silyl ketene acetal groups was used as macroinitiator of GTP of (meth)acrylic acids protected with *tert*-butyl or dimethylsilyl groups.[338–340] The initiation efficiency was low and therefore the di- and triblock copolymers contained an impurity of the starting PDMS.[338] Hydrolysis of the protected blocks gave amphiphilic copolymers of PDMS and PAAc (or PMAAc) of the A-b-B and B-b-A-b-B types. The copolymers possessed the properties of a surfactant and stabilised the polymerisation dispersions even in supercritical carbon dioxide.[339, 340] PDMS was also used as macroinitiator of 'pseudoliving' radical polymerisation.[341, 342] To this end, halogen derivatives of PDMS were first obtained and the 'pseudoliving' ATRP was carried out.

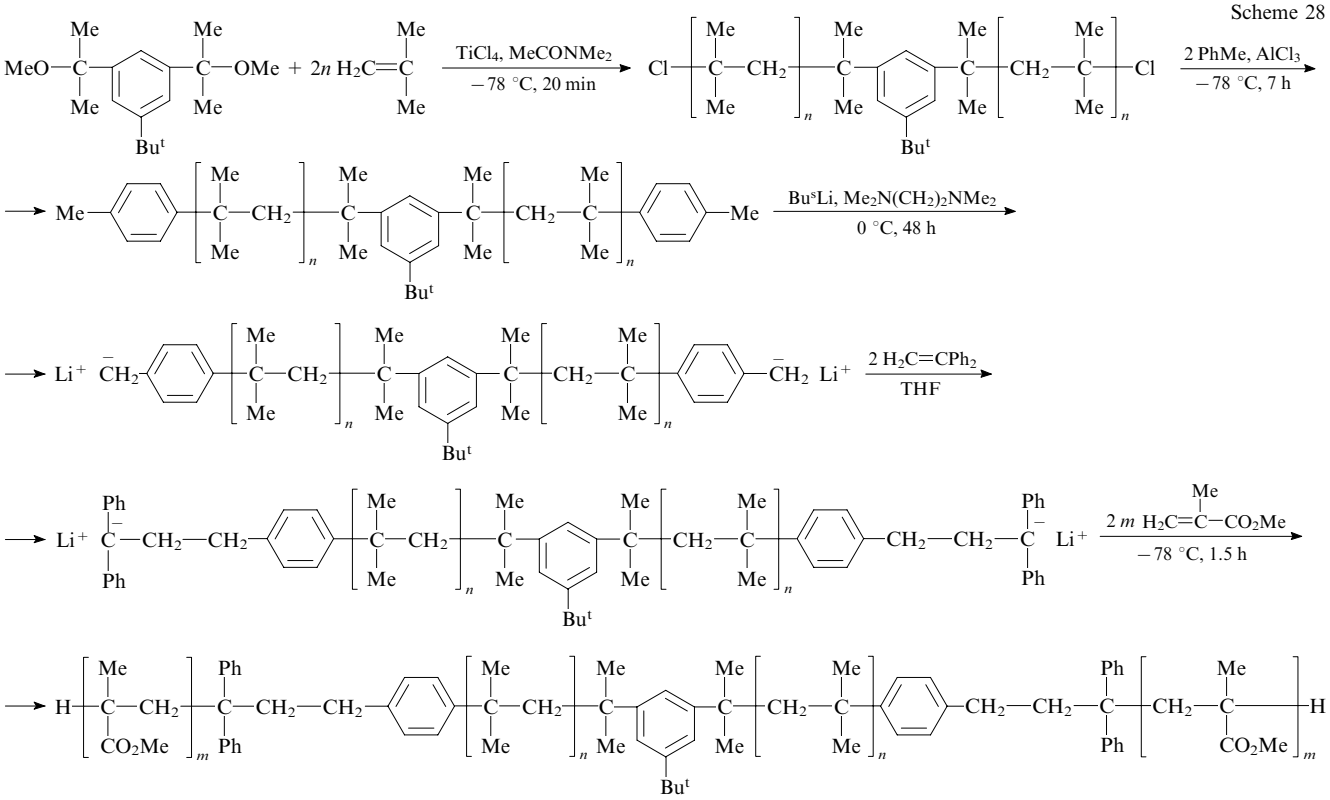
Recently, yet another method of formation of macroinitiators of radical polymerisation was developed. This is ultrasonic destruction of polymer chains in the presence of monomers. The technique is of particular importance for the synthesis of block copolymers based on natural polymers, *e.g.*, chitosan {poly[β(1–4)-2-amino-2-deoxy-D-glucose]} belonging to polysaccharides.[343] Chitosan is a cationic polyelectrolyte characterised by high reactivity and sorption capacity and also radiation resistance. Ultrasonic destruction of chitosan ($M_v = 1.44 \times 10^5$, frequency 22 kHz, electric current 40 mA, $T = 0$ °C) in an acetic acid solution in the presence of VPD, AA, acrylonitrile and DMAEMA salt causes the formation of block copolymers containing almost no homopolymers.[343] Only in the case of AAm did the final product contain about 2 mass % of PAA. Clearly, the products of synthesis should be polydisperse with respect to molecular mass and composition. Indeed, ultrasonic destruction of polymers takes some time to complete; the limiting value of the molecular mass is attained at the end of this time interval.[344] For chitosan, the limiting molecular mass is 2×10^3 after 15–20 min.[343] As a result, in the initial step of ultrasonic destruction the macroradicals initiating the polymerisation of monomers are longer than in, *e.g.*, 20 min; this is the reason for polydispersity of the product.

2. Combination of 'living' cationic and 'living' anionic polymerisation

Synthetic procedures involving a combination of several types of 'living' ionic and/or 'pseudoliving' radical polymerisation open new prospects for the design of block copolymers; however, this requires considerable experimental efforts. The main problem consists in quantitative conversion of one type of active centres into another type of polymerisation centres. Studies on conversion of 'living' carbocations into 'living' carbanions began in the early 1990s.[345–353] They were aimed at obtaining block copolymers of nonpolar PIB (elastomer highly resistant to external factors) with rigid poly(meth)acrylate, poly(meth)acrylic acid, polyacrylamide and polyester polar blocks. A number of methods of modification of PIB macrocations were proposed.

Cationic polymerisation of IB was initiated with bifunctional cumyl ether, namely, 1,3-bis(1-methoxyisopropyl)-5-(*tert*-butyl)benzene in the presence of dimethylacetamide and $TiCl_4$.[348, 349] Therefore, the polymerisation carried out in a methyl chloride–n-hexane mixture [40 : 60 (vol.%)] with heating in the last step immediately gave a dichloro derivative of

Scheme 28



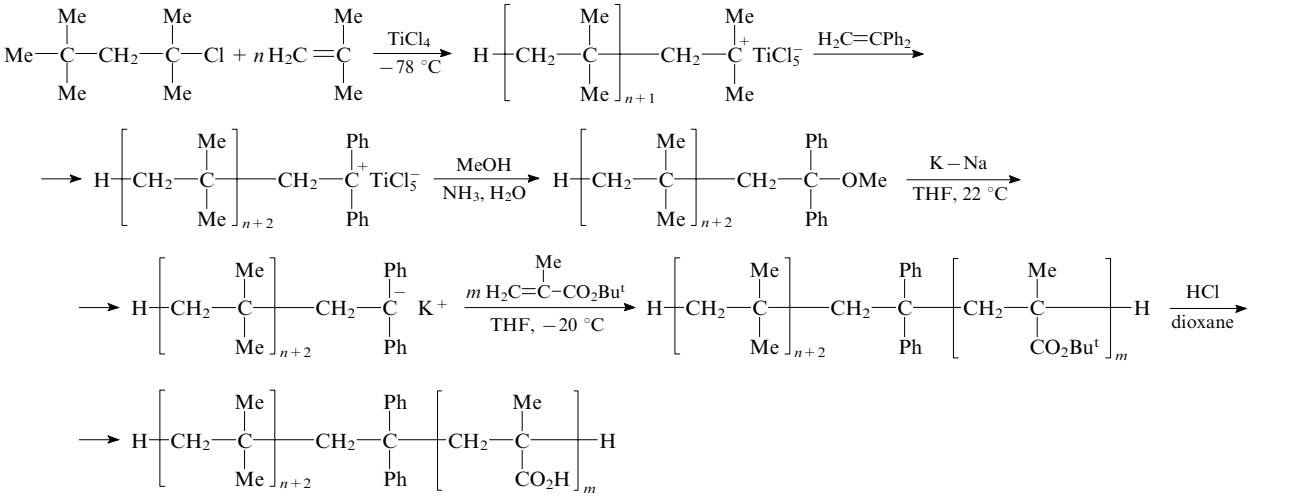
PIB (Scheme 28),[22] Cl—PIB—Cl, which had the expected molecular mass and showed a narrow MMD ($M_n = 6.1 \times 10^4$, $M_w/M_n = 1.15$). In the second stage it was used in the toluene alkylation according to Friedel–Crafts and a ditolyl derivative of PIB was obtained ($F_n = 1$).

In the third stage, MePh—PIB—PhMe was transformed into a 'living' polydianion by the reaction of *sec*-butyllithium (in n-hexane) in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) followed by the reaction with 1,1-diphenylethylene in THF. Then, the monomer (MMA) was introduced, the temperature was reduced and PMMA-b-PIB-b-PMMA copolymers were obtained (see Scheme 28). The copolymers were characterised by $M_{n\,PMMA} = 7 \times 10^3 - 1.65 \times 10^4$ and a narrow MMD ($M_w/M_n = 1.23 - 1.30$) and contained almost no homopolymers.[349] The PMMA blocks showed a high stereoregularity (content of syndiotactic units was about 75%).

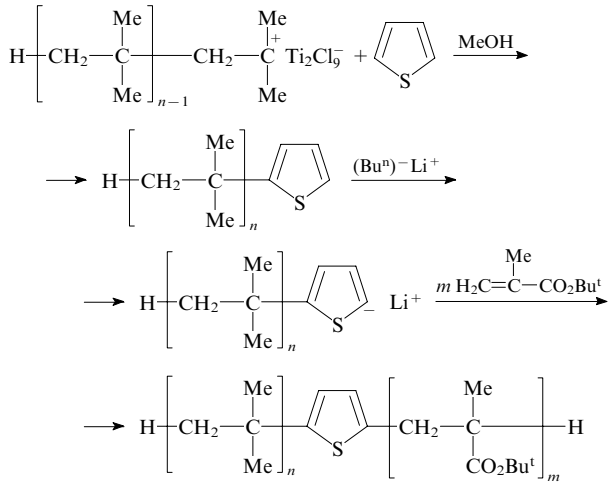
A simpler procedure for quantitative conversion of PIB macrocations to macroanions was also proposed.[9,354–356] In the first step cationic polymerisation of IB in a MeCl–n-hexane mixture was initiated by $TiCl_4$ with 2,4,4-trimethyl-2-chloropentane (Scheme 29). 'Living' PIB chains were 'capped' with diphenylethylene, terminated with methanol and diphenylmethoxyl terminal fragments were thus obtained. In the second step they were quantitatively converted to carbanions by the reaction of methoxy groups with alkali metals. Then, the polar monomer (TBMA) was introduced, the temperature was reduced and 'living' anionic polymerisation was carried out. This resulted in PIB-b-PTBMA copolymers with controlled molecular mass and a narrow MMD; subsequent hydrolysis gave a block polyacid PIB-b-PMAAc (see Scheme 29).

Yet another method of transformation of PIB macrocations into macroanions to obtain PIB-b-PTBMA

Scheme 29



Scheme 30



(Scheme 30)[9] differs from the technique considered above in that (i) macrocations are 'capped' with thiophene in the last step of IB polymerisation and (ii) thiophenelithium derivative of PIB ($F_n = 1$) should be synthesised to initiate anionic polymerisation of polar monomers, such as TBMA.

3. Combination of 'living' anionic and 'pseudoliving' radical polymerisation

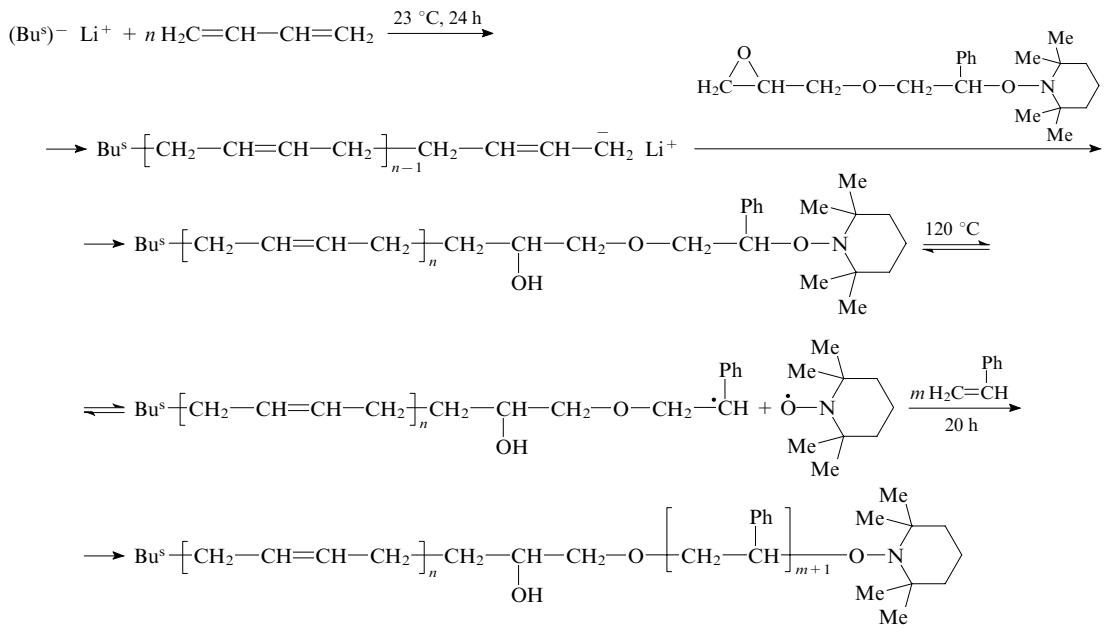
The discovery of various types of 'pseudoliving' radical polymerisation was followed by intensive use of these techniques in multimode polymerisation. The most promising method of synthesis of block copolymers with controlled molecular structure and low polydispersity is a combination of controlled radical polymerisation and 'living' ionic polymerisation.[181] At the same time, attempts to obtain, *e.g.*, PS-b-PBA, PS-b-PMMA and PS-b-PI copolymers with rather broad MMDs by 'pseudoliving' polymerisation (SFRP) following the free radical process have also been reported.[357]

A specific feature of the multimode process involving a 'pseudoliving' (radical mechanism) and a 'living' (ionic mechanism) polymerisation consists in performing the ionic polymerisation first. The reason is not only the higher temperatures of controlled radical processes, but also easier conversion of ionic active centres into the groups necessary for initiation and control of 'pseudoliving' radical polymerisation. These groups are different for different types of polymerisation, namely, nitroxides for SFRP, mobile halogen atoms for ATRP, dithioester groups for RAFT and dithiocarbonate (or trithiocarbonate and trithiocarbamate) groups for MADIX.

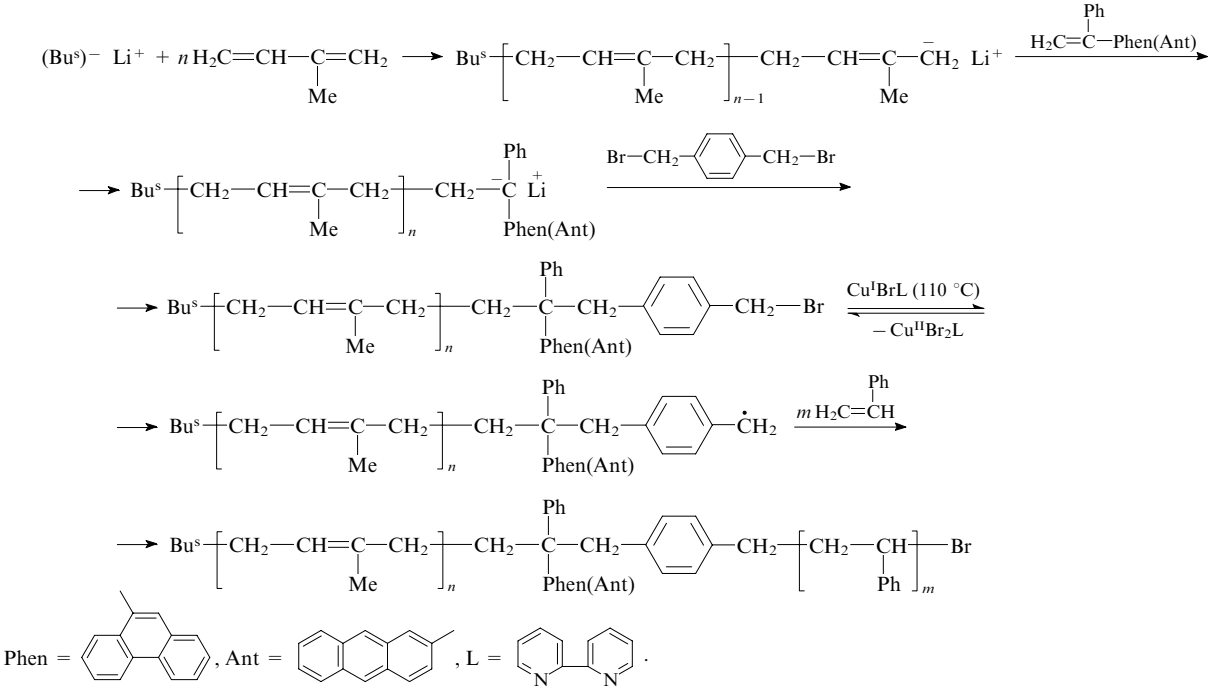
There are strong proofs of the synthesis of linear block copolymers of well-defined structure and narrow MMD by combining 'living' anionic polymerisation with SFRP or ATRP. A PB-b-PS copolymer was synthesised using anionic polymerisation followed by SFRP.[358,359] The process (see Scheme 31) began with 'living' anionic polymerisation of butadiene in cyclohexane. Termination of PB macroanions to change the polymerisation mechanism was done with an epoxy-functionalised alkoxyamine, namely, 2,2,6,6-tetramethyl-1-(2-glycidyloxy-1-phenylethoxy)piperidine.[358] The nitroxide-'capped' PB block had $M_n = 3.84 \times 10^3$ (this is in agreement with the calculated values) and a narrow MMD ($M_w/M_n = 1.02$). High degree of functionalisation of PB ($F_n > 0.95$) was established by ^{1}H NMR spectroscopy. In the second stage, the nitroxide-'capped' PB served a macroinitiator of 'pseudoliving' polymerisation (SFRP) of styrene in the bulk (see Scheme 31) with the initiation efficiency $f_i = 1$. After 20 h, styrene conversion was 65%. The PB-b-PS copolymer was characterised by $M_n = 1.74 \times 10^4$, which was in agreement with the calculated value ($M_n = 1.5 \times 10^4$), and a low polydispersity index ($M_w/M_n = 1.22$).

Considerable literature devoted to combination of 'living' anionic polymerisation with ATRP is available. Now we will dwell on some typical examples. Nonpolar block copolymers PI-b-PS were synthesised using a multimode process involving anionic polymerisation and ATRP.[360] The synthesis involved not only the polymerisation of particular blocks and transformation of active centres, but also the formation of fluorescent phenanthryl or anthryl linkers between the blocks (Scheme 32) to study the structure and properties of the copolymers. The polymerisation of isoprene in cyclohexane was followed by sequential addition of 1-(9-phenanthryl)- or 1-(2-anthryl)-1-phenylethylene and α,α′-dibromo-*p*-xylene to 'living' PI. The product was isolated and used in 'pseudoliving' radical polymerisation of styrene in the presence of the CuBr–2.2′-bipyridyl system (see Scheme 32). Gel-permeation chromatography and NMR studies revealed good agreement between the experimental [$M_n = (5-45) \times 10^3$] and calculated

Scheme 31



Scheme 32



molecular mass and a low polydispersity ($M_w/M_n = 1.1-1.2$) of the PI-b-PS copolymers.

A combination of 'living' anionic polymerisation with ATRP was used[361] for preparation of PS-b-P2VP block copolymer containing nonpolar and polar (polybasic) blocks. Anionic polymerisation of St (first stage) in benzene was initiated by Bu^{s}Li and followed by modification of the PS chain ends to 'cap' them with mobile chlorine atoms (Scheme 33). The product was isolated and dissolved in toluene. The catalyst ($Cu^ICl-2,2'$-bipyridyl) was introduced followed by the second monomer (2VP) and the mixture was heated to 120 °C. Gel-permeation chromatography and NMR data showed that the molecular mass of PS-b-PVP was insignificantly different from the calculated MM and that the MMD was also narrow ($M_w/M_n = 1.05-1.14$).

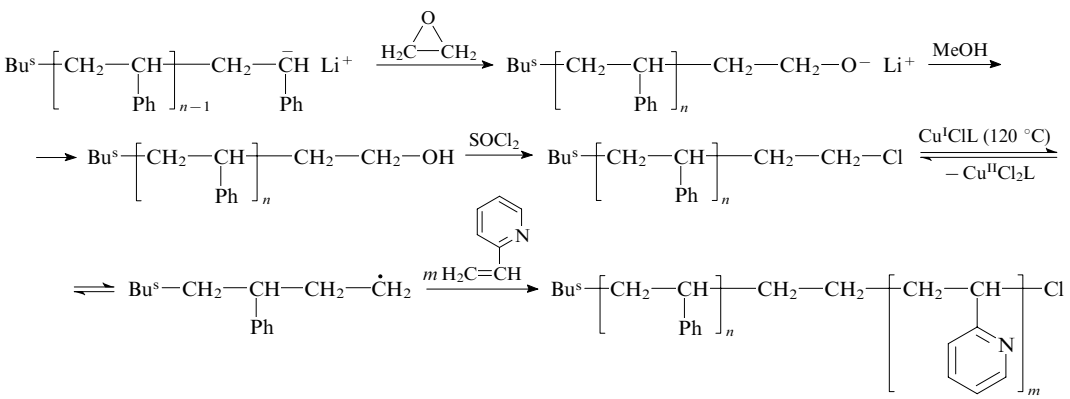
A combination of anionic ring-opening polymerisation with ATRP was used in the synthesis of diblock copolymers containing polar non-ionogenic and polyacid blocks. In particular, anionic ring-opening polymerisation of ε-caprolactone (similar to the process shown in Scheme 3) followed by ATRP of TBA resulted in a precursor (PCL-b-PTBA copolymer). Subsequent hydrolysis of the PTBA blocks (see the process in Scheme 6) gave a PCL-b-PAAc copolymer.[362] As another example, copolymers PEO-b-PTBA were synthesised by anionic ring-opening polymerisation of EO followed by modification of the OH groups of PEG with α-halo esters and subsequent ATRP of TBA.[363] The resulting copolymers were then converted to PEO-b-PAAc.

Since 'living' ionic and 'pseudoliving' radical polymerisations themselves allow one to synthesise a broad range of binary and ternary block copolymers, combination of the techniques offers additional prospects for the design of block copolymers. In this connection, noteworthy is a study[364] on the synthesis of PDMS-b-PS-b-PDMOMSPA terpolymers {PDMOMSPA is poly[3-(dimethoxymethylsilyl)propyl acrylate]}. An appropriately chosen multimode process involved anionic ring-opening polymerisation of cyclic dimethylsiloxane, transformation of the SiOH groups of PDMS into 2-bromoisobutylsilyl groups and two consecutive ATRPs of styrene and 3-dimethoxymethylsilylpropyl acrylate. The resulting terpolymer was characterised by high affinity to the surface of the silicon plate where it formed a 'brush'-like layer.

4. Combination of 'living' cationic and 'pseudoliving' mechanisms

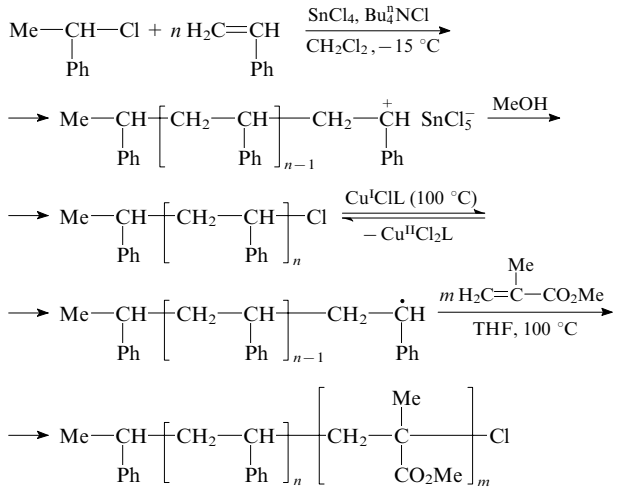
Controlled synthesis of block copolymers using 'living' cationic and 'pseudoliving' radical (ATRP) polymerisation was first reported in 1997.[365] Earlier, 'living' cationic polymerisation to obtain poly(vinyl ethers) was combined with free radical polymerisation of methacrylonitrile[366] and benzyl

Scheme 33



methacrylate.[367] The lack of control in the second stage led to polydisperse final products containing homopolymers. The authors of study [365] synthesised the PS-b-PS, PS-b-PMA and PS-b-PMMA copolymers (with two nonpolar blocks and with nonpolar and polar blocks) of controlled structure and narrow MMD. 'Living' cationic polymerisation of St was carried out using the $SnCl_4$ – 1-phenylethyl chloride initiating system in the presence of Bu^n_4NCl as nucleophile (Scheme 34).

Scheme 34



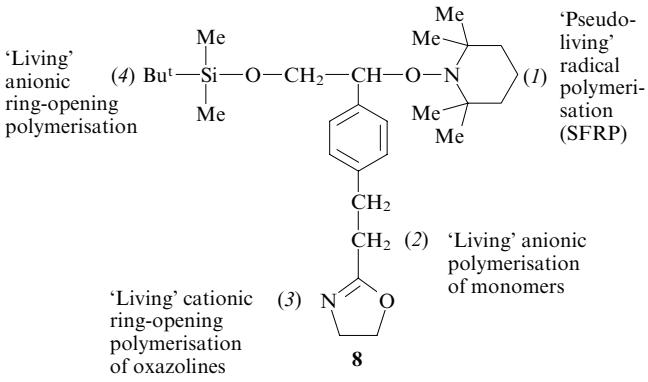
The chloro derivative of PS, isolated upon reprecipitation in methanol ($M_n = 2.1 \times 10^3$, $M_w/M_n = 1.17$), served as a macroinitiator of ATRP of styrene, MA and MMA in toluene using the Cu^ICl – 4,4′-di(non-5-yl)-2,2′-bipyridyl catalytic system. The molecular masses of the PS-b-PS, PS-b-PMA and PS-b-PMMA copolymers ($M_n = 5.08 \times 10^3$, 6.33×10^3 and 1.109×10^4, respectively) were in agreement with the calculated values (at $f_i = 1$). This means that the unmodified chloro derivative of PS is a highly efficient macroinitiator of ATRP of styrene and (meth)acrylates. The polydispersity indices of the copolymers were also low ($M_w/M_n = 1.10$, 1.20 and 1.57, respectively).

An important advantage made by the authors of study [365] is the one-pot polymersation of, *e.g.*, the PS-b-PMA copolymers. To this end, the chloro derivative of PS was deactivated by methyl methacrylate introduced at −15 °C. Then the temperature was increased and the solvent, the Lewis acid and the ester were distilled off, a solution of the catalytic system in toluene and the monomer were added, the temperature was raised to 100 °C and ATRP of methyl methacrylate was carried out. One-pot multimode process resulted in the PS-b-PMA copolymer characterised by almost the same parameters ($M_n = 6.3 \times 10^3$, $M_w/M_n = 1.21$) as the copolymer obtained *via* isolation of intermediate product.

Similar syntheses of PS-b-PIB-b-PS and PAOS-b-PIB-b-PAOS copolymers [PAOS is poly(*p*-acetoxystyrene)] containing three nonpolar blocks, as well as one nonpolar and two polar blocks, were reported.[368] Here, 'living' PIB chains propagating along both directions were 'capped' with styrene at both ends. This resulted in a dichloro derivative of PIB, which efficiently initiated ATRP of various monomers (styrene and AOS). This combination of polymerisation processes was also used for the synthesis of block copolymers of PIB with PMAAc.[369] 'Living' cationic polymerisation led to monochloro and dichloro derivatives of PIB, while ATRP of protected MAAc monomers in the presence of the $Cu^ICl(Cu^IBr)$ – *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine catalytic system followed by acid hydrolysis gave di- and triblock copolymers PIB-b-PMAAc and PMAAc-b-PIB-b-PMAAc. The molecular masses of the blocks varied as follows: $M_{n\,PIB} = 2.8 \times 10^3 - 5.6 \times 10^4$ and $M_{n\,PMAAc} = 4.3 \times 10^2 - 1.72 \times 10^3$. Thus, the authors reached the main goal, namely, they synthesised model block copolymers of variable length of the elastomeric and rigid ionic blocks. The mechanical and rheological properties of the block copolymers were determined by aggregation of macrocoils governed by hydrogen and ionic bonds.[370]

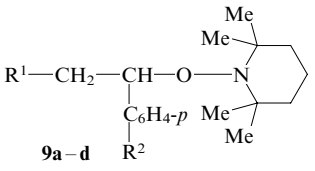
5. Application of bifunctional initiators

Design of selective multifunctional initiators is a new promising approach to implementation of multimode (including one-pot) polymerisation processes. Only a few studies on the subject are available at the moment; however, researchers point to great prospects for this strategy of synthesis of block copolymers. Unlike a simple combination of various polymerisation mechanisms, here the main advantage consists in the possibility of carrying out sequential and concurrent multimode processes that do not include additional chain end functionalisation stages. Puts and Sogah [371–374] pioneered in formulating the problem and doing research in this field. Initially, the global challenge was to design a universal initiator capable of initiating the most important types of controlled polymerisation processes.[371] It was assumed that corresponding functional groups of the initiator will act independently. Puts and Sogah greatly succeeded in solving the problem posed. They synthesised a multifunctional initiator 1-[(*tert*-butyl)dimethylsiloxy]-2-{4-[2-(4,5-dihydrooxazol-2-yl)ethyl]-phenyl}-2-(2,2,6,6-tetramethyl-1-piperidineoxy)ethane (**8**).



The compound was designed to allow for the following: (i) alkyl adducts of nitroxides (*1*) can initiate a SFRP process; (ii) C−H bonds (*2*) in α-position to the oxazoline group can form carbanions and initiate 'living' anionic polymerisation;[375] (iii) oxazoline ring (*3*) can be a monomer in cationic ring-opening polymerisation;[376] (iv) neutral oxazolines are stable to free radicals and ionic reactions; (v) oxazolines are good protective groups for carboxylic acids and can be readily removed;[377] (vi) alkylsiloxy group (*4*) can initiate anionic ring-opening polymerisation of heterocycles;[378] (vii) by removal of oxazoline protection from CO_2H groups (*3*) and *tert*-butyldimethylsilyl protection from OH groups (*4*) the polymerisation centres can be converted into polycondensation centres.[379] Thus, initiator **8** includes four polymerisation centres and allows one to obtain linear, graft and star-like block copolymers. Since only a [poly(2-oxazoline)-g-PS] graft copolymer was synthesised using this initiator,[371] analysis of the synthetic procedure goes beyond the scope of this review.

Then, the multifunctional initiators **9a**–**d** and tribromoethanol (**10**) were proposed.[372–374] Using some of them, not only one-pot, but also concurrent multimode syntheses of linear block copolymers were developed. Consider these results in more detail. A bifunctional initiator 1-hydroxy-2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethane containing a nitroxide and an OH group (**9a**) was used [374] for the synthesis of A-b-B and B-b-A copolymers from poly(ε-caprolactone)



$R^1 = Bu^tMe_2SiO$, $R^2 = CH_2Cl$ (**a**);
$R^1 = OH$, $R^2 = CH_2Cl$ (**b**);
$R^1 = PhCO_2$, $R^2 = CH_2Cl$ (**c**);
$R^1 = OH$, $R^2 = H$ (**d**).

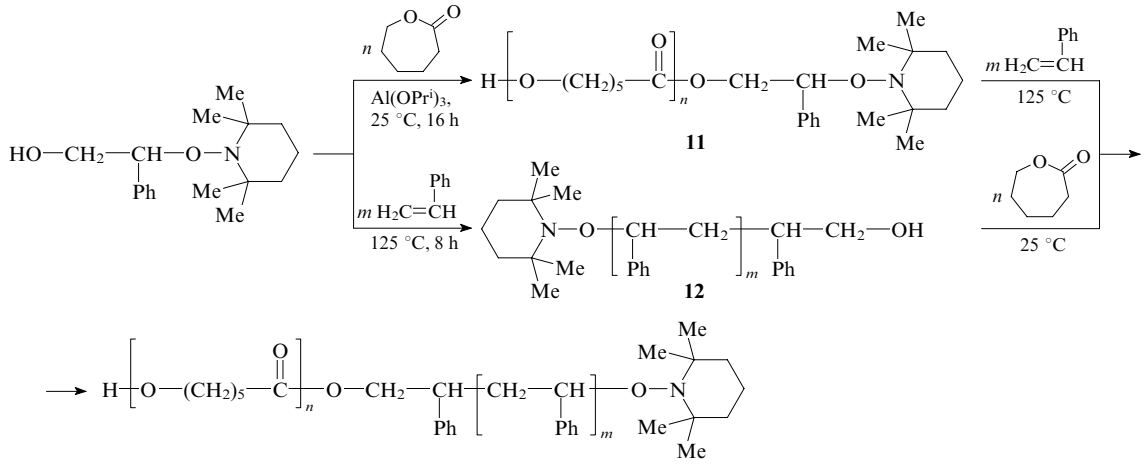
9a–d

and PS. The role of the order in which the multimode process is carried out (anionic polymerisation of ε-caprolactone (CL) followed by 'pseudoliving' SFRP of styrene, or *vice versa*) and the relative reactivities of nitroxide radicals attached to the initiator and to the PCL chain end in the polymerisation of styrene was studied. Anionic ring-opening polymerisation of CL under the action of the OH groups of the initiator in the presence of catalyst $Al(OPr^i)_3$ readily occurred in toluene at 25 °C. However, the nitroxide group of initiator initiated bulk SFRP of styrene only at a high temperature (T = 125 °C). Due to significant differences between polymerisation conditions various multimode processes (Scheme 35) involving isolation of intermediate products (**11** or **12**) could be performed with ease. There was no need for additional chain end modification steps. Gel-permeation chromatography and ^{1}H NMR studies revealed full control of the MM of the PCL and PS blocks (linear increase in MM with monomer conversion) irrespective of the order in which they were synthesised; the MMDs of particular blocks and the whole copolymer also remained narrow (M_w/M_n = 1.07–1.4). It was found that the nitroxide radicals at he PCL chains are more reactive than those attached to initiator; this manifested itself in acceleration of the polymerisation of styrene in the presence of macroinitiator **11** compared with the homopolymerisation of styrene under the action of the unmodified initiator. In addition, the molecular mass of PS in the block copolymer was controlled up to high values ($M_n = 1.5 \times 10^5$). The authors provided no explanation for this effect, but the assumption of a change in the medium polarity in the presence of PCL as the sole factor affecting the system under study was ruled out (SFRP of styrene with covalently nonbonded PCL of various molecular mass showed no acceleration of the polymerisation process).

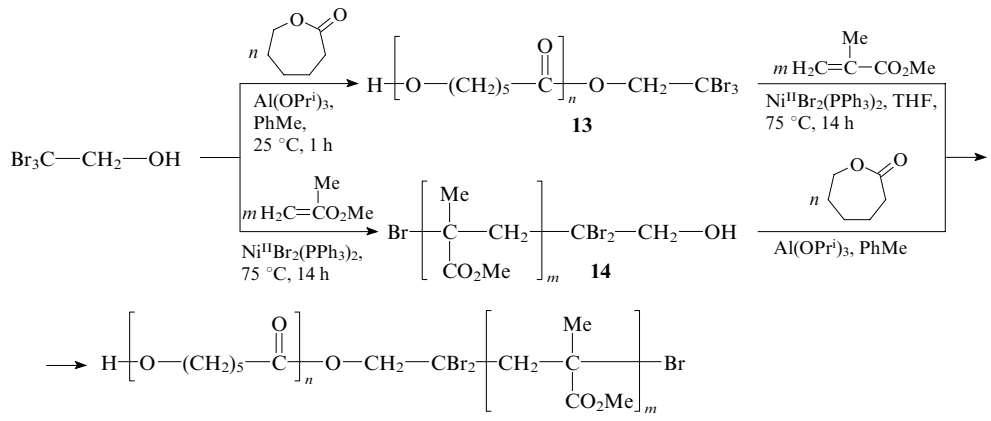
The activity of a simpler commercially available and cheap bifunctional initiator **10** in another multimode process involving 'living' anionic polymerisation and ATRP was checked.[374] First, high efficiency of the initiator in (i) anionic ring-opening polymerisation of ε-caprolactone [in toluene in the presence of catalytic amounts of $Al(OPr^i)_3$]; (ii) ATRP of styrene (in toluene with Cu^ICl–2,2′-bipyridyl as catalyst); and (iii) ATRP of MMA in THF in the presence of $NiBr_2(PPh_3)_2$ or $RhBr(PPh_3)_3$ complexes was proved. Then, multimode synthesis of A-b-B and B-b-A copolymers based on PS (or PMMA) and PCL were carried out using the reverse strategy, where polymerisation of CL was followed by polymerisation of styrene (MMA) (see example in Scheme 36). According to ^{1}H NMR data, macroinitiators **13** and **14** and hydroxyl-terminated PS showed high efficiency in polymerisation of the second block (f_i = 1). This excluded additional chain-end functionalisation stages from the synthetic procedure. The molecular masses of the PS, PMMA and PCL blocks in the copolymers were in agreement with the calculated values. The polydispersities of particular blocks and the copolymer were also low (M_w/M_n = 1.21 and 1.17 for PS-b-PCL with $M_{n\,PS} = 2.25 \times 10^3$ and $M_{n\,PS\text{-}b\text{-}PCL} = 4.45 \times 10^4$, respectively). Taking into account the fact that one end of the diblock copolymer obtained after ATRP of the second block contained chlorine atoms capable of initiating ATRP of the third block, a PCL-b-PBA-b-PMMA copolymer of specified molecular structure was synthesised.[374]

The possibility of concurrent multimode synthesis of diblock copolymers using bifunctional initiators was first

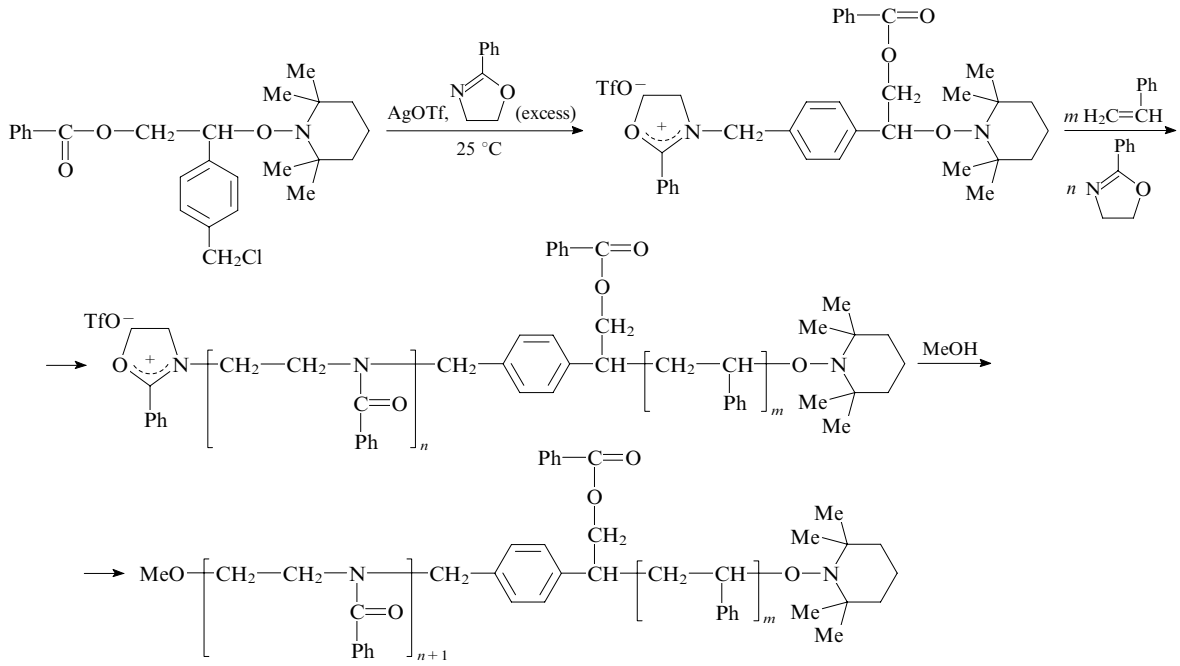
Scheme 35



Scheme 36



Scheme 37



reported by Sogah and co-workers.[373] Using 1-benzoyl-2-[4-(chloromethyl)phenyl]-2-(2,2,6,6-tetramethyl-1-piperidineoxy)-ethane (**9c**) as initiator, the authors carried out concurrent 'pseudoliving' SFRP of styrene and 'living' cationic polymerisation of 2-phenyl-2-oxazoline (PhOx) (Scheme 37). This unique synthesis was performed in the bulk as follows. The reactor was charged with anhydrous initiator and anhydrous silver triflate (silver trifluoromethaneulfonate, AgOTf), purged with an inert gas, an excess PhOx was added at 25 °C; this resulted in a cationic derivative of the initiator in excess of the monomer. Then, styrene was introduced, the temperature was raised to 125 °C and polymerisation was carried out for 44 h. The rigid block copolymer was cooled, dissolved in CH_2Cl_2 and methanol was added to convert the charged phenyloxazoline group of PPhOx-b-PS to methyl ether group. The AgCl precipitate was filtered off. The PPhOx-b-PS diblock copolymers were characterised by $P_{n\,PPhOx}$ ranging from 29 to 198. The copolymers contained almost no homopolymers (according to gel-permeation chromatography and ^1H NMR spectroscopy data) and had a narrow MMD (M_w/M_n = 1.27 – 1.40). Subsequent hydrolysis of the oxazoline units led to copolymers of PEI-b-PS with linear polyethyleneimine (PEI).

Questions posed by Sogah and co-workers.[373] remain unanswered as yet. In particular, the authors confirmed the formation of block copolymers, but gave no proofs of concurrent character of 'living' cationic and 'pseudoliving' SFRP polymerisation throughout the whole 44 h. An unambiguous answer can be obtained by investigating the kinetics and mechanisms of this and other multimode processes. At the moment, it should be emphasised that this study opens a new avenue of research on polymer synthesis, which involves concurrent and competing polymerisation processes.

IV. Matrix effects in block copolymerisation processes

Now we will consider yet another important aspect, which was ignored for long in studies on the synthesis and properties of block copolymers. Most studies on the subject concern block copolymers whose components are thermodynamically imcompatible or show a limited compatibility; macromolecules of such components form 'supercrystal' structures in the bulk [15, 19, 380, 381] and various micellar and vesicular structures in solution.[1, 7, 9, 13, 382] However, block copolymers with highly compatible, chemically complementary components are also of considerable interest. Such components can form a system of co-operative noncovalent bonds between blocks, namely, electrostatic bonds, as in ampholytic (or zwitter-ionic) block copolymers,[112, 113] or hydrogen bonds, as in the block and graft copolymers synthesised from non-ionogenic polymers and polyacids.[6, 383] This type of block copolymers is treated as intramolecular polymer complexes (IntraPC). They can be used as binders in biothechnology and medicine, membranes, as flocculants and drag reducing agents in the case of turbulent flow.[384] Taking into account specific properties of the block and graft copolymers that form IntraPC, the formation of a system of noncovalent bonds between the components in the course of synthesis was hypothesised (in other words, the case in point is manifestation of matrix effects that are well known for polymerisation of monomers in the presence of chemically complementary polymer chains, matrices, in the block and graft copolymerisation).[385] The fruitfulness of this hypothesis was first confirmed in the kinetic studies of the synthesis of starch-g-PAA and PVS-g-PAA graft copolymers. Namely, it was shown that the rate of graft copolymerisation of PAA with starch [386] and PVS [387] substantially increases compared to the rate of homopolymerisation of acrylamide under identical conditions. These results were considered in a review.[384]

Since investigations of the matrix phenomena in block copolymerisation processes are in the early stage of development, we will dwell on them in more detail. Studies [388, 389] concern the kinetics of radical block copolymerisation of PAA with different-MM PEG whose terminal groups were activated in the reaction of OH groups with Ce^{IV} ions [see reaction (7)]. Block copolymerisation was carried out in aqueous solution at 25 °C. For comparison, homopolymerisation of AAm initiated with ethanol instead of PEG was performed under similar conditions. Chemical complementarity of PAA and PEG was preliminarily confirmed in the complexation studies of covalently nonbonded polymers [390] and a system of H-bonds in the resulting InterPC [391] in water.

The results of dilatometric studies are presented in Fig. 2. All kinetic curves show an induction period. The authors believed that it is governed by the 'lifetime' of the intermediate complex formed by Ce^{IV} ions with the OH groups of PEG. The rate of block copolymerisation of PAA with the lowest-molecular-mass sample (PEG1) and the yield of the PAA-b-

Table 1. Kinetic parameters of block copolymerisation of PAA with PEG of different molecular mass and homopolymerisation of AA.

Polymer	$10^{-4} M_{v\,PEG}$	τ /min	$10^5 V_p^{20}$ /mol dm^{-3} s^{-1}	$10^5 V_p^{40}$ /mol dm^{-3} s^{-1}	$10^5 V_p^{60}$ /mol dm^{-3} s^{-1}	q (%)
PAA	–	15.5	1.6	1.02	–	53.5
TBC1	0.1	168.0	0.6 [a]	–	–	14.2
TBC3	0.6	54.9	5.76	5.62	0.16	63.4
TBC4	1.5	31.4	4.62	4.19	0.34	69.5
TBC5	4.0	25.0	15.5	7.92	2.87	80.3

Note. τ_0 is the induction period; V_p^{20}, V_p^{40}, V_p^{60} are the block copolymerisation rates at a monomer conversion, q, of 20%, 40% and 60%, respectively; and q is the monomer conversion after 20 h.
[a] Listed is the value for V_p^{10}.

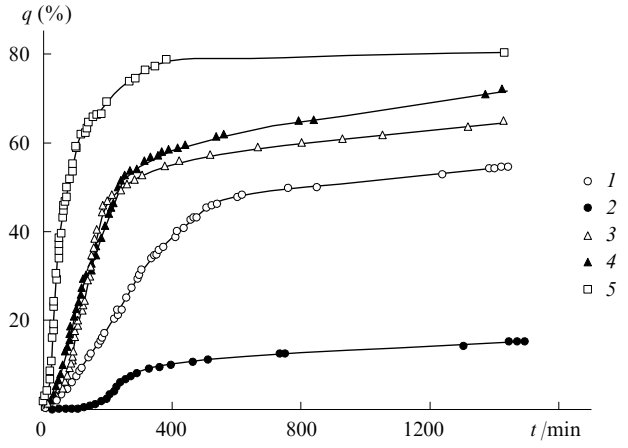


Figure 2. Conversion for homopolymerisation of AA (*1*) and block copolymerisation of PAA with PEG with a molecular mass of 1×10^3 (*2*), 6×10^3 (*3*), 1.5×10^4 (*4*) and 4×10^4 (*5*) at 25 °C plotted *vs*. time.

PEO-b-PAA1 triblock copolymer (TBC1) were very low, whereas the induction period τ_0 was very long compared to τ_0 for homopolymerisation of AAm (see Fig. 2, curves *1* and *2*). Another situation was observed in block copolymerisation of PAA with longer-chain PEG ($M_v > 1 \times 10^3$). Namely, the induction period shortened and the copolymerisation rate and the yield of the final product increased (curves *3*–*5*). This is quantitatively characterised by the data listed in Table 1.

Significant acceleration of the block copolymerisation and an increase in AAm conversion in the synthesis of the TBC3, TBC4 and TBC5 copolymers compared to the synthesis of PAA points to a positive kinetic matrix effect due to the interaction of the PEO blocks (matrices) with the growing daughter PAA blocks that are covalently bonded through a system of hydrogen bonds (see Fig. 2).[388, 389] The effect became more pronounced with elongation of the PEG block. Indeed, a change in $M_{v\,PEG}$ from 6×10^3 to 4×10^4 caused the rate of block copolymerisation (V_p^{20}) to increase by an order of magnitude compared to the homopolymerisation rate of AAm (see Tabl. 1). This is consistent with the well-known increase in the energy of the interaction between partners and stability of the polycomplex with elongation of polymer chains. Unlike similar matrix processes that occur in water due to formation of a system of H-bonds between the covalently nonbonded matrix and the daughter chain and lead to high compaction of InterPC,[392] matrix block copolymerisation of PAA with PEO resulted in water-soluble IntraPC. This is a manifestation of the effect of the third hydrophilic block (PAA), which prevented high hydrophobisation and compaction of macroglobules.

A characteristic feature of the PAA-b-PEO-b-PAA triblock copolymers is a nearly linear increase in the molecular mass of the PAA blocks (from 4.5×10^4 to 9.07×10^5) with an increase in the molecular mass of the PEO central block.[388, 389] It was established that the interblock interaction strongly affects both the synthesis and the molecular structure of the block copolymers.

Yet another type of matrix effects was observed [393] in a comparative study of the RAFT polymerisation of monomer mixtures, namely, *N*,*N*-dimethylacrylamide (DMAA) and 2-(*N*-butyl perfluorooctanefluorosulfonamido)ethyl acrylate (BPFOFSAEA), in the presence of both low-molecular-mass CTA (3-benzylsulfonylthiocarbonylpropionic acid) and a macroCTA obtained by etherification of the low-molecular-mass CTA with PDMS ($M_n = 1.8 \times 10^4$). Polymerisation was carried out under identical conditions at 60 °C. The DMAA content was constant and the content of the second monomer was varied; azobis(isobutyronitrile) was used as initiator. α,α,α-Trifluorotoluene was chosen as the common solvent with allowance for high hydrophobicity of macroCTA. RAFT polymerisation of a mixture of monomers resulted in poly-(DMAA-co-BPFOFSAEA) copolymer in the presence of the low-molecular-mass CTA and in poly(DMAA-co-BPFOFSAEA)-b-PDMS-b-poly(DMAA-co-BPFOFSAEA) copolymer in the presence of the macroCTA. In both cases the RAFT process showed some common features, namely, a linear increase in the molecular mass of the polymers with conversion and narrow MMDs for all products (M_w/M_n = 1.12–1.26). However, the compositions of the side blocks in the triblock copolymers were basically different from the compositions of the copolymers obtained in the presence of the low-molecular-mass CTA. Namely, the triblock copolymers contained a large excess of BPFOFSAEA. In fact, the hydrophobic matrix (PDMS block) 'selected' the most hydrophobic monomer (BPFOFSAEA) from the mixture, to which it has a higher thermodynamic affinity, this is the reason for the effect observed. Shortening of the induction period in the kinetic curves for the RAFT polymerisation in the presence of macroCTA was also pointed out.

* * *

In this review we considered new methods of synthesis of block copolymers and new aspects of the investigations of the regularities of polymerisation processes. with allowance for chemical complementarity of the blocks formed. This may be useful for further research in this field.

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