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Radical-initiated controlled synthesis of homo- and copolymers based on acrylonitrile

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Data on the controlled synthesis of polyacrylonitrile and acrylonitrile copolymers with other (meth)acrylic and vinyl monomers upon radical initiation and metal complex catalysis are analyzed. Primary attention is given to the use of metal complexes for the synthesis of acrylonitrile-based (co)polymers with defined molecular weight and polydispersity in living mode by atom transfer radical polymerization. The prospects for using known methods of controlled synthesis of macromolecules for the preparation of acrylonitrile homo- and copolymers as carbon fibre precursors are estimated. The major array of published data analyzed in the review refers to the last decade.
The bibliography includes 175 references.

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I. Introduction

Polymers refer to the most important modern structural materials. During the last two decades, the growth rate of world consumption of polymer materials has far exceeded the growth rate of the worldwide manufacture of industrial products. Currently, much attention is given to the synthesis of polymers with specified properties and behaviour. A special place among such polymer materials is occupied by carbon fibre reinforced plastics — remarkable structural materials of high practical, including strategic, value. The main precursor used to produce high-quality carbon fibre for manufacturing carbon fibre reinforced plastics is polyacrylonitrile (PAN) and copolymers based on acrylonitrile (AN) and other acrylic and vinyl monomers containing functional groups and strictly specified molecular-weight characteristics including low polydispersity.[1–3] Therefore, for targeted synthesis of polyacrylonitrile and its derivatives as precursors of high quality carbon fibre, of high importance is the use of controlled, or living radical polymerization. In recent years, numerous publications including original scientific papers and patents have dealt with the application of controlled synthesis techniques for homo- and copolymerization of acrylonitrile. Analysis of these data is the main subject of this review.

Detailed analysis of published data on the synthesis of homo- and copolymers based on acrylonitrile indicates that no reviews on this topic have appeared in the last decade in either Russian or public foreign editions. Therefore, the presented review will be of interest both for specialists in the synthetic chemistry of polymers and radical polymerization and for engineering chemists engaged in materials science and metal complex catalysis of polymerization processes.

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II. Controlled radical polymerization as the most effective method for the synthesis of functional polymers with specified molecular weight characteristics and properties

Currently, radical polymerization is the key method for the synthesis of polymers in industry.[4,5] In recent years, more than a half of polymers obtained all over the world have been synthesized upon radical initiation. The major advantages of radical polymerization include high rate and good reproducibility, adaptability and the possibility to obtain high-molecular-weight polymers even at early process stages, as well as the broad range of monomers able to polymerize in the presence of radical species and some other practically significant features. Meanwhile, radical polymerization has a number of considerable drawbacks, first of all, those brought about by high reactivity of free radicals, which are directly involved in the elementary steps of polymerization including macromolecular chain initiation, propagation, transfer and termination. Often, this results in self-acceleration of polymerization and spontaneous uncontrolled growth of the polymer molecular-weight (MW) and substantial broadening of molecular weight distribution (MWD), which finally has adverse effect on the properties and behaviour of synthesized polymers and often complicates their further processing.

The indicated drawbacks of radical-initiated polymerization are fully inherent in the synthesis of polyacrylonitrile, which, moreover, is bulk polymerized *via* a heterogeneous process without being dissolved in the monomer.[6,7] This is why it is virtually impossible to obtain acrylonitrile-based homo- and copolymers with a strictly specified molecular weight and narrow MWD by classical bulk or solution radical polymerization. As a rule, PAN prepared by thermal or photochemical polymerization using traditional radical initiators (peroxides or azo compounds) has broad MWD ($M_w/M_n > 3$). Furthermore, it is often poorly soluble in some organic solvents, which is caused by the formation of cross-linked macromolecular structures. As a result, this polymer is virtually unsuitable for the manufacture of high-strength carbon fibre complying with challenges of modern materials science. Therefore, the use of controlled radical polymerization techniques is especially important for the synthesis of narrow-MWD polyacrylonitrile and its derivatives as precursors of high-quality carbon fibre meeting the strength requirements of chemical engineers. It is the use of these processes that can provide linear PAN with narrow MWD ($M_w/M_n < 1.5$), which would be suitable as a precursor for the manufacture of carbon threads and modern carbon fibre reinforced plastics for special purposes.

The conditions of controlled/living radical polymerization and the key process mechanisms have been described in detail in some recent reviews of Russian and foreign researchers[8–17] and in subject collections of papers.[18] It is noteworthy that the term 'living polymerization' was first used by Szwarc[19,20] to describe the anionic polymerization in which only reversible chain termination upon the reaction of the growing chain with the counter-ion was possible, while irreversible chain termination steps were virtually missing.

The living radical polymerization implies also the presence of reversible chain termination in which the chain is repeatedly terminated ('dies') and is revived again. However, in this case, unlike the truly termination-free ionic polymerization,[19,20] apart from the reversible chain termination, competing irreversible chain termination is possible, resulting in gradual damping of the polymerization. Therefore, this process does not fully comply with the definition of a living process. It is not by chance that reactions of this type are called in the literature 'living', 'pseudo-living', 'quasi-living', 'controlled' polymerization and so on. The IUPAC initially recommended the term 'controlled/living' radical polymerization[21] (CLRP) as describing most fully the regularities of the synthesis of macromolecules under these conditions. Later, this term was replaced by 'reversible deactivation radical polymerization'.[22] In the Russian literature, the term controlled radical polymerization is used most often.

The key distinction of the controlled radical polymerization from the conventional radical polymerization is that the quadratic chain termination (irreversible reaction between two growing macroradicals) is replaced by reversible deactivation of the propagation radical upon the reaction with initiator fragments or a special additive introduced into the polymerization system.[8–15] The controlled/living polymerization is accompanied by a linear increase in the molecular weight and a decrease in the polydispersity index following an increase in the conversion. This is attributable to the fact that with simultaneous initiation in the absence of irreversible chain termination, fast exchange takes place between the active and dormant radical centres, which finally results in the parallel propagation of chains throughout the polymerization process.

All techniques for conducting controlled polymerization can be classified into three main types according to the nature of the terminating agent:

— dissociation–recombination processes involving free radicals [stable free radical polymerization (SFRP)];[8,12,15,16]

— degenerate transfer (DT) or reversible addition–fragmentation chain transfer (RAFT);[17,23]

— atom transfer radical polymerization (ATRP).[9,14,24,25]

In the controlled radical polymerization carried out by the dissociation–recombination mechanism, the mediators include stable radicals, most often, nitroxides and some transition metal complexes (organometallic-mediated radical polymerization).[10,13,26] It is noteworthy that processes of this type can be controlled by both paramagnetic and diamagnetic metal complexes, which are not radical species.

Reversible additional–fragmentation polymerization was discovered by Rizzardo and co-workers.[23,27,28] In this case, the main factor determining the controlled/living polymerization mode is repeated chain transfer involving the active additives introduced into the system, for example, aromatic and aliphatic dithioesters and their analogues.

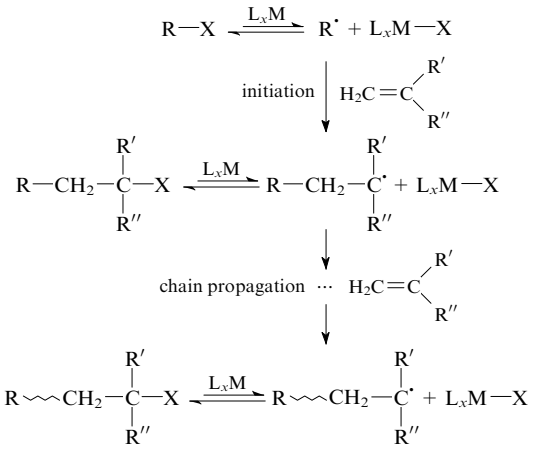
The latest achievements in the field of DT and SFRP controlled/living radical polymerization were surveyed in reviews[8,11] and in a collection of papers.[29]

The controlled atom transfer radical polymerization concept appeared owing to independent investigations of

Sawamoto's [9, 25, 30, 31] and Matyjaszewski's [14, 24, 32] research groups. In their studies, they actually proceeded from radical addition of carbon tetrachloride to the alkene double bond discovered by Kharash *et al.*[33] and extended its scope to obtain a broad range of high-molecular-weight compounds.

This reaction is catalyzed by complexes of transition metals in a lower oxidation state of the formula ML_x (where M is a transition metal, L are organic ligands). They reversibly react with alkyl halides (RX) with halogen atom transfer to the metal complex giving rise to alkyl radicals, which are able to initiate polymerization in the system (Scheme 1).

Scheme 1



R〰 is fragment of the polymer chain

Conducting this reaction in the monomer medium allows fragment-to-fragment chain growth, *i.e.*, the radical polymerization can proceed in the controlled/living mode. A very important role in the efficiency of the controlled process is played by the metal atom and its ligand environment and the conditions of synthesis of homo- and copolymers.

III. The use of atom transfer radical polymerization in the controlled/living synthesis of homo- and copolymers based on acrylonitrile and other acrylic monomers

Currently, several methods are known for conducting polymerization in the presence of transition metals. Among these, ATRP and reverse ATRP have been studied in most detail.[9, 14] In the former case, the reaction is initiated by alkyl halide or another compound containing a labile carbon–halogen bond and is catalyzed by a transition metal complex containing metal in a lower oxidation state. Upon the reaction between these compounds, the halogen atom is transferred to the metal, which thus transforms to a higher oxidation state, and a free radical initiating the polymerization is formed (see Scheme 1). The latter case implies the use of a traditional radical initiator and a metal complex containing metal in a higher oxidation state. In this case, the opposite sequence of transformations occurs: first, the decomposition of the initiator generates reactive radicals, which initiate polymer chain propagation upon reaction with the monomer. Subsequently, the controlled character of the process is maintained by the reversible reaction between the growing macroradical and the transition metal complex with metal in a higher oxidation state similarly to Scheme 1.

Currently, a highly important trend of the development of methods for polymer synthesis by atom transfer polymerization is invention of more active catalysts, which markedly shorten the reaction time and make it possible to decrease the concentration of the metal complexes used. This trend has been dictated, on the one hand, by environmental considerations related to the need to reduce the environmental emissions of toxic wastes from the polymer synthesis, in particular transition metals, and, on the other hand, economical aspects, *i.e.*, decreasing the expenditures related to the cost of catalysts and the subsequent purification of the polymer from the catalyst.

The development of new approaches to ATRP, which have been actively pursued in recent years, is aimed at overcoming these shortcomings. These methods are based on either simultaneous normal and reverse initiation, which simplifies the precatalyst treatment procedure, or involve the use of hybrid and bimetallic systems developed to enhance the degree of control with the use of economically attractive and environmentally friendly catalysts and systems using organic reducing agents to substantially decrease the required amount of the catalyst.

The simultaneous reverse and normal initiation (SR&NI) concept [33, 34] implies the use of initiation compositions comprising a classical radical initiator (*e.g.*, azobisisobutyronitrile, AIBN) and an ATRP initiator containing a labile carbon–halogen bond.

A limitation of the simultaneous reverse and normal initiation in the ATRP consists, first of all, in the fact that this approach is unsuitable for the preparation of pure block copolymers, as the presence of a radical initiator inevitably results in the formation of a homopolymer in the system. This drawback can be eliminated by using single electron transfer for the primary reduction of the precatalyst and its conversion to the active state. This idea has been further developed in the approach called activators generated by electron transfer (AGET).[35] In this case, the transition metal occurring in a higher oxidized state is reduced by using reducing agents that cannot initiate new chains: zerovalent copper,[36, 37] tin 2-ethylhexanoate [$Sn(EH)_2$],[38] ascorbic acid [39] and so on.

As noted above, the distinction of the controlled/living radical polymerization from the true living polymerization, which proceeds by an ionic mechanism,[19, 20] is the possibility of bimolecular chain termination reaction. This side process results in the metal in a higher oxidation state being accumulated in the system, which retards the polymerization. This drawback can be overcome and the metal complex can be reduced to a lower oxidation state of the metal in two ways: by adding either a radical initiator or a special reducing agent.

The first approach is considered in the literature under the name 'initiators for continuous activator regeneration' (ICAR).[40] In this approach, free radicals are generated slowly and continuously upon the decomposition of a conventional radical initiator throughout the whole polymerization process and permanently reduce and regenerate the catalyst, which is accumulated in the system.

The above-considered method for the generation of lower oxidation state metal complexes *via* the reaction

with reducing agents can also serve for regeneration of the inactive form of the catalyst, which is accumulated during standard ATRP. This approach has been called 'activators regenerated by electron transfer' (ARGET).[41] An important advantage of this method is the possibility of using very low catalyst concentrations with a rather large excess of a reducing agent. As the reducing agents in the ARGET technique, the same compounds as in AGET are used.

Yet another original and rather promising method for increasing the efficiency of atom transfer polymerization proposed by Matyjaszewski and co-workers[42,43] implies the use of electrical current to accelerate the reversible reduction of the metal from a higher to a lower oxidation state. This process is called e-ATRP. Actually, the controlled/living polymer synthesis can be performed at a rather high rate in an electrochemical cell in the presence of a metal-containing catalyst and initiator without additional introduction of activating additives.

Analysis of published data unambiguously indicates that currently the controlled atom transfer synthesis of polymers in the presence of metal complexes is the most actively developing area of CLRP and a fairly promising method for the preparation of macromolecules with specified molecular-weight characteristics and properties. Most often, these reactions are catalyzed by compounds of copper[4,24,30,31,44–46] or ruthenium[25,30,31] and also by iron,[47–49] nickel[50,51] and some other transition metals.[52]

III.1. Copper-containing catalysts in the controlled/living synthesis of polymers based on acrylonitrile

It is well known[24,53] that compounds of copper as a metal that can rather easily and, what is more important, reversibly change the oxidation state are among the most active components of catalyst systems for controlled atom transfer radical polymerization and are widely used for the synthesis of narrow-MWD polymers based on (meth)-acrylic monomers. The first works on the controlled/living synthesis of PAN involving copper compounds date back to the late 20th century: Matyjaszewski *et al.*[54,55] used copper chloride and bromide in combination with 2,2′-bipyridine (bipy) to prepare polyacrylonitrile in the ethylene carbonate medium. The authors obtained narrow-polydispersity polyacrylonitrile ($M_w/M_n \approx 1.2$); however, the conversion was rather low ($< 40\%$ in 23 h) and the resulting polymer had relatively low molecular weight, which was somewhat higher than the theoretically calculated value. The polymerization is described by first-order kinetics but the time dependence of the logarithm of the ratio of the initial to current monomer concentration [$\ln([M_0]/[M])$] is not linear, which is known[14] to indicate variation of the number of reaction centres in the course of polymerization.

Matyjaszewski *et al.*[55] performed successful synthesis of narrow-MWD ($M_w/M_n < 1.5$) polyacrylonitrile with a specified molecular weight at 30 kDa by controlled/living ATRP. The authors used a catalyst system based on copper(I) halides CuX (X = Cl, Br) and bipyridine in combination with 2-halopropionitriles as initiators. A replacement of halogen in the initiator (bromine by chlorine) retards the process and results in the formation of a polymer with a higher polydispersity index. Note that the nature of the used solvent or the absence of a solvent affects the reaction rate and the degree of control of the MWD. Meanwhile, the presented protocol of ATRP in the temperature range of 45–65 °C is not so effective for acrylonitrile as for other vinyl monomers, for example, methyl methacrylate (MMA) or other esters of unsaturated carboxylic acids, which give much higher polymer yields and lower polydispersity under similar conditions.[56]

The lack of solubility of the formed PAN in the initial monomer brings about heterogeneity of the system, which leads to loss of the process control. Therefore, the authors studied the possibility of performing polymerization in various solvents. The best results were achieved in ethylene or propylene carbonate.[55]

More recent studies of Wang and co-workers (see, for example, Ref. 57) were concerned with reverse atom transfer radical polymerization (reverse ATRP) using the system involving $CuCl_2$ and bipy. As the primary source of free radicals, they used an iniferter based on a substituted ethane derivative — diethyl 2,3-diphenyl-2,3-dicyanosuccinate (DCDPS). This compound was first used[57] as the initiator in atom transfer polymerization in combination with systems based on copper complexes. A twofold excess of bipyridine with respect to $CuCl_2$ gives not only a better control of the MW and MWD values but also ensures a fairly high reaction rate. As was to be expected, the polymerization rate considerably increased with temperature, and the apparent activation energy for acrylonitrile polymerization in this system was found to be 57.4 kJ mol^{-1}. Since the resulting polymers had chlorine atoms at the chain ends, they were used as macroinitiators for the PAN synthesis in the presence of the copper(I) chloride and bipy-based catalyst system by ATRP in a DMF solution. The linear dependence of the molecular weight on the conversion and successful post-polymerization unambiguously confirm the living nature of the reverse ATRP in the presence of copper(II) chloride.

Similar results were also obtained for 1,1,2,2-tetraphenylethane-1,2-diol (TPED) as the initiator for ATRP polymerization of acrylonitrile using the $CuCl_2$–bipy complex as the catalyst.[58] It was shown that the $CuCl_2$: bipy ratio of 1 : 2 is sufficient for the successful polymerization. This provides a good control over the molecular weights and polydispersity indices of the resulting polymers and fairly high polymerization rate. It was found experimentally that the polymerization rate increases with temperature, and the apparent activation energy for acrylonitrile polymerization involving the above-mentioned catalyst system is 53.2 kJ mol^{-1}. The polymers thus obtained were also successfully used as macroinitiators for polymerization and chain elongation in the presence of the CuCl–bipy catalyst system by the usual ATRP mechanism.

As noted above, the modern efficient variants of ATRP are based on the addition of reducing agents able to transform the catalyst into the reduced state. An advantage of these methods (ARGET, AGET or ICAR)[31,38–40,55] is the possibility to perform polymerization at higher rates with rather low catalyst concentrations, which is important from the standpoint of saving the catalyst and decrease in the expenses for the subsequent polymer purification from catalyst remainder.

By using ARGET ATRP process, Matyjaszewski and co-workers[59] performed the controlled synthesis of polyacrylonitrile with the system comprising $CuCl_2$–tris(2-pyridylmethyl)amine (TPMA) and tin ethylhexanoate or glucose as the reducing agent. The proposed

systems were suitable for performing polymerization of acrylonitrile at 40–65 °C in the presence of 75 or 25 ppm of the Cu catalyst. It is noteworthy that a decrease in the catalyst concentration under these conditions resulted in higher degree of control over the process reflected in a decrease in the polymer polydispersity index. This fact allowed for conducting the process up to ~70% conversion and for preparing polymers with MM ≈ 300 kDa. Yet another important advantage of the cited paper is that the authors established the possibility to decrease the polymerization temperature down to 40 °C. A temperature decrease resulted in some retardation of the process; however, it also suppressed side reactions, which finally provided a polymer with a molecular weight of 160 kDa and a polydispersity index of 1.18. However, the time it took to reach this conversion was ~300 h. The proposed system is suitable for polyacrylonitrile synthesis both in DMSO and in ethylene carbonate.

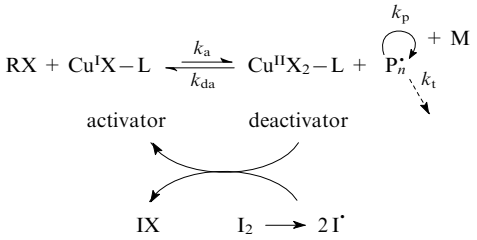
A complexing ligand can also be used as the reactive reducing agent transforming Cu^{II} to Cu^{I}; examples include hexamethyltriethylenetetramine (HMTETA),[60] pentamethyldiethylenetriamine (PMDTA)[60] or tris(2-dimethylaminoethyl)amine (Me_6-TREN).[61] The proposed systems can perform the CLRP of acrylonitrile in DMF or DMSO, giving rise to narrow-MWD polymers. The molecular weights of the obtained polyacrylonitrile vary from 7 to 40 kDa depending on the conversion, which is somewhat higher than the theoretically calculated values. The polydispersity index does not exceed 1.5. The successful experiments on chain extension by post-polymerization of a second portion of the monomer unambiguously confirm the controlled/living type of polymerization. It is worth noting that high monomer conversions are achieved in ~10 h, which is quite acceptable for the industrial use of these systems. The controlled/living AGET ATRP of acrylonitrile using HMTETA as both a ligand and a reducing agent led to a higher conversion and a lower polydispersity of the polymer as compared with a similar process involving PMDTA under the same experimental conditions. As the HMTETA content in the system increased, polymerization was accelerated and the molecular-weight distribution became wider. Note that polymerization in the presence of Me_6-TREN afforded polymers with a relatively low molecular weight despite the use of a 10-fold excess of the ligand over copper halide.

These systems were used to study the solvent effect on the CLRP parameters for acrylonitrile in DMF, toluene, xylene, acetonitrile and cyclohexanone. Comparative analysis demonstrated that among the considered solvents, DMF is preferred as it is most polar and can dissolve both the catalyst and the resulting polymer. As a consequence, the polymerization rate in DMF is much higher than in acetonitrile, cyclohexane, toluene or xylene. The apparent activation energy for acrylonitrile polymerization is 45.7 kJ mol^{-1}. The structure of the resulting polymer was studied by NMR spectroscopy, and the terminal groups able to initiate polymerization were detected. The living nature of the polymerization was confirmed by the synthesis of block copolymers of acrylonitrile with methyl methacrylate. Previously, similar systems based on copper halides and *N*,*N*,*N*′,*N*′-tetra[(2-pyridyl)methyl]ethylenediamine were successfully employed for activating styrene and methyl methacrylate polymerization.[62]

Aminodiacetic acid can serve as the ligand with copper(II) bromide.[63] In this case, commercially available carbon tetrachloride can be used as the halogen-containing initiator of the controlled polymerization of acrylonitrile. The process follows the AGET ATRP mechanism and the ascorbic acid is used to reduce Cu^{II} to Cu^{I}. The synthesis is carried out in DMF. Polymerization occurs in the controlled/living mode, as indicated by polymerization kinetics data and by a linear increase in the number-average molecular weight with monomer conversion. However, this is accompanied by an increase in the polydispersity index, which unambiguously attests to a decrease in the extent of control over the process. An NMR examination revealed chlorine atoms at the ends of the polymer chain and thus confirmed the participation of carbon tetrachloride in the initiation step of acrylonitrile polymerization.

An efficient method for the synthesis of polyacrylonitrile was proposed by Liu *et al.*,[64] who presented data on the PAN synthesis by atom transfer radical polymerization with a classical radical initiator. Copper(II) bromide complexes with bipy, PMDTA and tris(2-aminoethyl)amine (TREN) served as catalysts. Ethyl 2-bromoisobutyrate was used as the organic halogen initiator, while AIBN was chosen as the free radical initiator for continuous initiation. According to the assumed mechanism of the polymerization, the radicals resulting from AIBN decomposition react with $CuBr_2$ to reduce Cu^{II} to Cu^{I}. The copper(I) complex thus formed initiates polymerization by the ATRP mechanism. The radicals formed from AIBN make up for the active sites lost upon irreversible chain termination (Scheme 2).

Scheme 2



k_a, k_{da}, k_p k_t are rate constants of activation, deactivation, chain propagation and chain termination, respectively; I_2 is radical initiator; M is monomer

The effects of concentrations of the ligand, catalyst and radical initiator and the reaction temperature on the polymerization kinetics, polymer molecular weight and polydispersity index were studied in detail. The best control over the process is achieved with bipy as the ligand. The polymerization was found to proceed in the controlled/living fashion even when the catalyst concentration was only 50 ppm relative to the monomer. This is evident from the first-order kinetics of the polymerization with respect to the monomer, a linear increase in the molecular weight with conversion and a low polydispersity index. It was found that the resulting polymer can function as a macroinitiator for post-polymerization of acrylonitrile.

An original example of controlled/living radical polymerization of acrylonitrile at a very high rate has been reported.[65] The authors proposed using a copper dibromide- and AIBN-based system as a source of primary free radicals initiating the synthesis of macromolecules. After 40 min, the monomer conversion was already >80%. The polydispersity index of polyacrylonitrile was in the range from 1.14 to 1.38; however, the polymer MW did not exceed 10 kDa. Polymerization had typical features of a living process — first-order kinetics with respect to the monomer, a linear increase in the number-average molecular weight with conversion and a relatively low polydispersity of the synthesized samples. The researchers comprehensively studied the effects of various experimental factors, including initiator and catalyst concentrations and reaction temperature on the polymerization kinetics and MWD of the polymer. By NMR spectroscopy, the presence of active sites at the end of the polymer chain was demonstrated; they account for post-polymerization and unambiguously confirm the living mechanism of the polymerization.

Yet another fairly efficient method for conducting controlled/living radical polymerization of acrylonitrile that can be performed by low concentrations of copper(II) bromide was proposed by Zhang and Liu.[66] This method also involves the ICAR ATRP approach. 2,2′-Azobis(2,4-dimethylvaleronitrile) served as the source of free radicals and the $CuBr_2$ complex with Me_6-TREN was chosen as the catalyst. The authors synthesized polyacrylonitrile with monomer conversion of up to 98% under exceptionally mild conditions (at a temperature of 30–45 °C). The molar ratio of the copper catalyst to AN was 1 : 20 000. The effects of initiator and catalyst concentrations, their ratio and the reaction temperature on the polymerization kinetics and sample polydispersity were studied in detail. The Chinese researchers were able to obtain a polymer with a polydispersity index of ~1.08, which is a unique result for polyacrylonitrile.

A method for the synthesis of polyacrylonitrile by living radical polymerization in DMF using CCl_4 as the initiator and the $CuCl_2$- and hexamethylenetetramine (HMTA)-based catalyst system has been reported.[67] In order to increase the polymerization rate, AIBN was used as an additional source of free radicals. Polymerization proceeded in the controlled/living fashion and followed a first-order kinetics with respect to the monomer. A linear increase in the molecular weight with the monomer conversion and relatively low polydispersity of the synthesized samples were observed. It is noteworthy that the high polymerization rate and narrow MWD were retained even when $CuCl_2$ was used in a concentration of <50 ppm. At higher temperature, the polymerization rate increased and MWD broadened. Modified polyacrylonitrile containing an amidoxime group obtained under these conditions was successfully used to extract Ag^I ions from aqueous solutions of silver salts.

The ARGET and ICAR concepts noted above are based on the use of a copper(II) complex as the catalyst precursor, which is reduced under the action of donating additives or radical initiators. Not only copper halides but also oxides are suitable as catalyst precursors; copper oxide-based systems proved to be efficient in the CLRP of acrylates and styrene.[68] By using oxides, it is possible to generate the true metal complex catalyst directly in the system during polymerization (*in situ*) and thus reduce the contribution of side processes. Combining initiators of various classes and mono- and divalent copper derivatives opens up prospects for the control of polymer characteristics.[69] Indeed, in the presence of Cu_2O–bipy (at 100 °C), it is possible to obtain polyacrylonitrile with narrow MWD; an increase in the amount of the catalyst results in a decrease in the process rate and an increase in the polymer MW. The use of bi- and tridentate ligands in combination with Cu_2O does not increase the system catalytic activity. The use of phenoxybenzene-4,4′-disulfonyl chloride as the initiator resulted in the synthesis [70] of dendrite copolymers of acrylonitrile in an ATRP process (Cu_2O–bipy). As noted above, copper complexes are extensively demanded in radical polymerization as they are readily accessible, easy to prepare (actually, by mixing copper halide with the ligand) and have high catalytic action.

Tetramethylethylenediamine (TMEDA) was found to be suitable as a ligand to copper oxide.[71] This polydentate ligand was chosen for its high complexation ability towards the copper oxide Cu_2O and transfer of the oxide to the liquid phase for conducting the polymer synthesis under homogeneous conditions. The proposed catalyst system based on Cu_2O–TMEDA provides PAN with the MW of ~30 kDa and a low polydispersity index (<1.3). It is noteworthy that despite the narrow MWD of the resulting polymers, the molecular weights determined experimentally are somewhat higher than the theoretical values.

The use of metals in zero oxidation state in the presence of various ligands is a fairly ingenious and efficient method for conducting atom transfer polymerization.[72–77] In particular, for living radical polymerization of acrylonitrile, Cu^0 combined with ethyl 2-bromoisobutyrate was proposed as the ATRP initiator with bipy as the ligand.[72–74] The polymerization was carried out in DMSO under mild temperature conditions (25 °C). The monomer conversion was >90% over a period of 13 h. The synthesis of PAN under these conditions bears all features of a controlled/living process including the increase in the number-average molecular weight with increase in the conversion and the absence of a gel effect. The considered systems can be used for the synthesis of block copolymers based on MMA and styrene, which also confirms the living mechanism of polymerization.

The above-listed systems make it possible to prepare narrow-MWD polyacrylonitrile upon polymerization in DMSO even at room temperature. Widely used bromine compounds and commercially available carbon tetrachloride are both suitable as initiators in this reaction. The proposed systems run the polymerization up to 80%–90% monomer conversion over periods of 20–80 h depending on the particular system applied. The PAN samples thus formed had MW values from 10 to 200 kDa and narrow MWD (polydispersity index of ⩽1.5). The authors assume that the process occurs by the SET-LRP mechanism (involving single-electron transfer) based on disproportionation of the copper(I) complex into Cu^0 and a compound of Cu^{II}, which acts as the deactivator of polymerization.[74] NMR spectroscopy showed the presence of the ethyl 2-bromoisobutyrate moiety at the end of the polymer chain. Copolymerization of acrylonitrile

with styrene was carried out by a similar procedure to give copolymers with a low polydispersity index (<1.4).

The solvent plays an important role in the polymerization of acrylonitrile by the considered mechanism. Indeed, the maximum monomer conversion depends on the amount of DMSO.[73] At low content of the solvent, the polymer precipitates; therefore, the activation of the polymerization upon reaction with the catalyst becomes impossible and the limiting possible conversion does not exceed 50%. An increase in the concentration of the solvent induces homogenization of the system and then the process can be conducted up to high conversion. The proposed systems based on zerovalent copper can be used to prepare acrylonitrile – styrene copolymers having important practical applications.

The single electron transfer living radical polymerization (SET-LRP) was applied to synthesize PAN.[75] The reaction was catalyzed by copper (Cu^0) powder in the presence of HMTA as the ligand. Carbon tetrachloride was used as the initiator. Polymerization was carried out in DMF or in a mixed solvent. The living polymerization mechanism is indicated by the linear increase in the molecular weight with the increase in the monomer conversion and narrow MWD. An increase in the ligand concentration in the system results in a higher monomer conversion over the same period of time; in the absence of the ligand, polymerization virtually does not occur. In the authors' opinion, this is attributable to the fact that the presence of the ligand promotes dissolution of copper and increases the copper(I) disproportionation rate. Generally, polymerization rate increases with increase in the amount of the catalyst in the Cu^0–HMTA system. The addition of $CuCl_2$ to the system favours better control of the MWD and decreases the polydispersity index. It is of interest that water being a polar solvent boosts the polymerization rate.

Compositions based on zerovalent copper can be used not only for acrylonitrile homopolymerization but also for the synthesis of acrylonitrile-based copolymers. For instance, Yu *et al.*[76] studied characteristic features of the radical copolymerization of vinyl acetate (VA) and acrylonitrile in the presence of zerovalent copper. Polymerization was carried out at 25 °C in DMSO in the presence of 2,2′-bipyridine as the ligand. At low concentrations of vinyl acetate, copolymerization proceeded in the controlled/living fashion and at a fairly high rate. As the vinyl acetate concentration increased, the polymerization rate substantially decreased and the polydispersity indices of the obtained samples simultaneously increased. The composition and structure of copolymers was confirmed by IR and NMR spectroscopy and differential scanning calorimetry (DSC). The relative activities of VA and AN calculated from experimental data are 0.003 and 1.605, respectively. Actually this is the first example of using zerovalent copper for radical copolymerization of acrylonitrile. It was shown in separate experiments that vinyl acetate cannot undergo radical-initiated homopolymerization catalyzed by Cu^0.

An original binary catalyst system based on $CuBr_2$ and Zn^0 has been proposed[77] for radical polymerization of acrylonitrile. Polymerization efficiently proceeds at room temperature even in the presence of 10 to 50 ppm of the catalyst system. The process displays all the key features of living radical polymerization, as indicated by the first-order kinetics, a linear increase in the number-average molecular weight with increase in the conversion and a low polydispersity index of the resulting samples. The researchers cited studied in detail the effects of solvent and the concentrations of copper and the initiator on the polymerization kinetics and the molecular-weight characteristics including polydispersity. The influence of the solvent on the polymerization behaviour was estimated. In particular, it was shown that ethylene carbonate solvent is preferred over DMSO or DMF as regards the polymerization rate and the control of the MW and MWD. The increase in the copper concentration from 2.5 to 50 ppm results in a higher polymerization rate and better control over the polymerization process. Furthermore, post-polymerization of AN in the presence of these systems was carried out, which also unambiguously confirms the living polymerization mechanism.

The activity of copper compounds in the polymerization can be increased by using ionic liquids.[78] Ionic liquids with the $[BF_4]^-$ anion were used for the first time as the reaction medium for atom transfer polymerization of acrylonitrile. The reaction was catalyzed by various copper halides in the presence of PMDTA, which served as both a ligand and a reducing agent. From the practical standpoint, it is important that polymerization smoothly proceeded in air. Actually, the authors implemented the ARGET ATRP protocol. Copper bromide proved to be a more efficient catalyst than copper chloride. The use of TMEDA as a ligand was less successful: the polymerization was substantially retarded and the polydispersity index increased. The $CuBr_2$–PMDTA system is suitable for the synthesis of block copolymers based on polyacrylonitrile. The resulting PAN-b-PMMA block copolymer samples had high molecular weights (>100 kDa) and relatively narrow MWD ($M_w/M_n < 1.35$). The obtained polyacrylonitrile was used to fabricate fibres that meet the demands of the modern industry.

Chen *et al.*[79] reported the first example of successful use of chiral ionic liquids as both the ligands and the medium for atom transfer radical polymerization of acrylonitrile. The authors used the AGET ATRP protocol with ascorbic acid as the reducing agent in the presence of air. A slight, but clear-cut increase in the degree of isotacticity of polyacrylonitrile in the case of AGET ATRP synthesis in ionic liquid was detected. The molecular weights varied from 70 to 80 kDa and the polydispersity index was $\sim$1.27, which confirms the controlled/living polymerization mechanism.

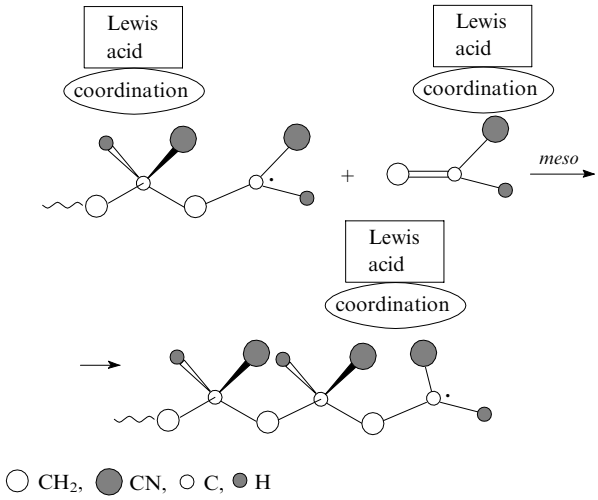
An interesting AGET ATRP procedure was first used for the one-pot two-step emulsion synthesis of PAN with polyethylene glycol ether as the surfactant, $CuCl_2$ as the catalyst and HMTA as the ligand.[80] Carbon tetrachloride served as the initiator and ascorbic acid was the reducing agent. Polymerization proceeded in the controlled/living manner as a first-order reaction with respect to the monomer and was characterized by a linear growth of the MW of polyacrylonitrile with increase in the monomer conversion and by low polydispersity of the product. The dependence of the monomer conversion on the ligand concentration was non-monotonic: first, the conversion increased with increase in the amount of the nitrogen-containing ligand and then decreased. The polymerization rate substantially increased with increase in the CCl_4 initiator concentration. The apparent activation energy

of the polymerization was 46.6 kJ mol^{-1}. Ma *et al.*[80] developed an efficient procedure for the synthesis of polyacrylonitrile with MW ~ 20 kDa and the polydispersity index of 1.3–1.4.

It is known [13,18] that the conditions of synthesis have a crucial influence on the most important parameters and characteristics of polymer materials, including microstructure and MWD. As noted above,[1–5] the mechanical and chemical properties of PAN and the PAN-based carbon fibre are largely determined by the structure of the polymer backbone, the stereoregularity and the MWD. A control of the stereochemistry of radical polymerization of acrylonitrile can be achieved in a number of ways, including addition of special solvents — fluorinated alcohols or Lewis acids, which interact with the monomer (or the growing radical) *via* hydrogen bonding or coordination bonding,[81] thus enhancing the stereospecificity of the polymer formed. It was found that isotactic polyacrylonitrile can be prepared upon low-temperature γ-initiation of the polymerization.[82,83]

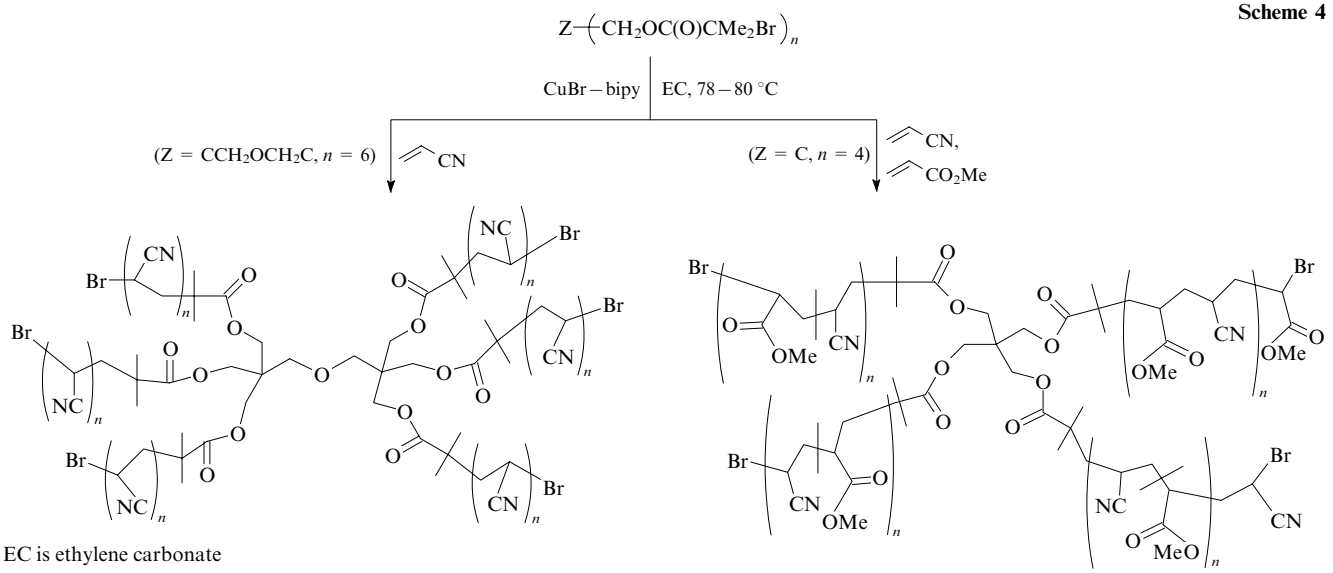
Simultaneous control over both MWD and stereoregularity of PAN was achieved[71] by using the $BrCH_2CH_2CN-Cu_2O-TMEDA$ system with addition of a Lewis acid. Polymerization was performed at the AN : initiator : Cu_2O : TMEDA ratio of 190 : 1 : 0.5 : 1.5 in ethylene carbonate at 60 °C for 48 h. The polydispersity indices of the resulting samples were at the level of 1.13 and the molecular weight corresponded to 13–14 kDa. A study of the polymerization kinetics was indicative of the living mode of the process without the gel effect and a linear growth of the MW with increase in the conversion. The tacticity of the obtained polymer was controlled using two Lewis acids — aluminium chloride and yttrium triflate. It was shown that introduction of a Lewis acid (0.01 equiv. with respect to AN) into the polymerization system enables the preparation of PAN with increased isotacticity index (the fraction of *meso*-triads is 0.321) and very low polydispersity (M_w/M_n < 1.1). The researchers[71] explained the increase in the polymer isotacticity as being due to coordination of the growing macroradical and the monomer to the Lewis acid (Scheme 3).

Scheme 3



Living polymerization is known[8–10] to open up exceptionally wide opportunities for macromolecular design. The atom transfer controlled/living radical polymerization was used[84] to synthesize a number of novel PAN-based macromolecular structures. For initiating the polymerization in DMF, dimethyl acetate and DMSO, a CuBr- and 2-bromoisobutyronitrile-based system was used. The authors found the optimal conditions for the synthesis of linear samples of polyacrylonitrile and its copolymers with methyl acrylate (containing ⩽ 5 mol.% of the latter) having controlled MW and MWD characteristics. In addition, by using a polyfunctional initiator containing several halogen atoms, star-branched polymers with 3, 4 and 6 arms were prepared apart from the linear structures (Scheme 4).[84] The effect of the conditions of synthesis on the molecular weight characteristics of the polymers was elucidated. Viscosity measurements of polymer solutions demonstrated that the star-branched polymers have a rigid structure. The inclusion of a moderate amount of methyl acrylate as the comonomer was found to have a

Scheme 4



EC is ethylene carbonate

greater influence on the chain flexibility than the inclusion of star-branched fragments into the macromolecules.

Copper(II) bromide was also successfully used for copolymerization of acrylonitrile with ethyl methacrylate.[85] The reaction was shown to follow atom transfer mechanism at room temperature in the presence of various halogen-containing initiators, which provided a high degree of control over the molecular-weight characteristics of the product. The effects of concentrations of the initiator, the ligand and metal-containing catalyst and the temperature on the molecular-weight distribution of PAN and the kinetics of synthesis were studied. It was found that at room temperature, controlled/living radical polymerization of acrylonitrile does not take place in the presence of CuBr and PMDTA as the ligand. The order of polymerization rate with respect to the initiator (2-bromopropionitrile) calculated from experimental data was 0.86. Meanwhile, first-order kinetics was observed when ethyl 2-bromoisobutyrate or methyl 2-bromopropionate was used as the initiator. Successful polymerization was accomplished using a copper-based catalyst in a concentration from 25% to 10% with respect to the initiator without the loss of control over the polymerization. The optimal bipy : CuBr molar ratio for copolymerization of acrylonitrile and ethyl methacrylate was 3 : 1. The resulting acrylonitrile–ethyl methacrylate copolymers were used as macroinitiators for the synthesis of block copolymers and further elongation of the polymer chain by methyl methacrylate and styrene units.

Acrylonitrile polymerization using the CuCl–bipy catalyst system in ethylene carbonate at 70 °C was reported;[86] also PAN–poly(2-methoxyethyl acrylate) block-copolymers were synthesized, which unambiguously confirmed the living polymerization mechanism with participation of the copper complex. The same study presents the only published example of controlled/living ATRP for a functional monomer such as 2-methoxyethyl acrylate (MEA). The CuBr–PMDTA complex served as the catalyst system and methyl 2-bromopropionate (MBP) was the initiator. Polymerization proceeded in the controlled/living fashion and was rather effective at 60 °C. Under the same conditions, post-polymerization involving the synthesized PAN can be carried out. The process kinetics and MWD data confirm the controlled mechanism of the polymerization. The effects of initiator concentration and the ratio of the system components on the reaction rate were investigated. The controlled/living nature of the polymerization was retained even at low catalyst concentration (< 10% relative to the initiator). The effect of solvents, in particular, ethylene carbonate, toluene, *etc.*, on the polymerization was studied. Ethylene carbonate proved to be the solvent of choice for the synthesis of homo- and copolymers of acrylonitrile under the given conditions. The polymer terminal groups were examined by ^{1}H and ^{13}C NMR spectroscopy and the high degree of their functionality was demonstrated.

Thus, the large body of published data considered above indicates that catalyst systems based on copper in various oxidation states can be successfully used to perform controlled/living synthesis of homo- and copolymers of acrylonitrile. Of particular interest for the prospects of practical application to prepare narrow-MWD polyacrylonitrile samples are catalytic compositions based on zerovalent copper.

III.2. Application of iron compounds for the controlled/living radical polymerization of acrylonitrile

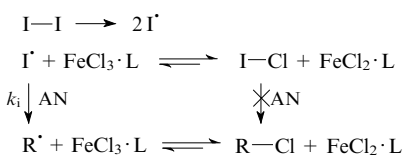
Like copper and ruthenium compounds, iron compounds[9,10,13] are often used for controlled/living atom transfer polymerization. This is due, first, to the fact that iron can easily and, what is more important, reversibly change the oxidation state and, second, to rather low cost of iron compounds. Furthermore, unlike copper and ruthenium complexes, iron compounds are as a rule nontoxic, which makes them suitable for a broad range of applications including controlled synthesis of biopolymers and physiologically active compounds.

It is not surprising that iron compounds, in particular, di- and trihalides have been widely used in recent years for the synthesis of PAN in the living chain fashion. Wang and co-workers[87] demonstrated that $FeCl_3$ in combination with succinic acid can be used as a catalyst of reverse ATRP of acrylonitrile. The traditional AIBN initiator served as the primary source of free radicals. Polymerization was carried out in DMF, as the rate of PAN synthesis was higher in DMF than in toluene or propylene carbonate. The ratio of the catalyst components $FeCl_3$: succinic acid = 1 : 2 was found to be the optimal as regards the polymerization kinetics and control of the MWD. The molecular weight of PAN determined experimentally was in fairly good agreement with the theoretical value. The polymerization rate increased with temperature rise, and the apparent activation energy of PAN synthesis catalyzed by the system in question was 64.8 kJ mol^{-1}.The polydispersity indices of the samples did not exceed 1.3.

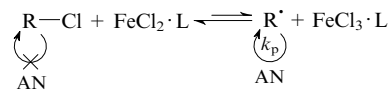
The same research group obtained similar results by using isophthalic acid instead of succinic acid.[88] Polymerization successfully proceeded in various media including DMF, toluene and propylene carbonate. The process was most efficient in DMF: in this case, the highest polymerization rate was achieved, the degree of control over the process being rather high. Experimentally, it was found that the $FeCl_3$: isophthalic acid ratio of 1 : 2 is optimal for polymerization efficiency, providing not only the best control over the MW and MWD but also a rather high rate of the process. The theoretically calculated and experimentally determined molecular weights of PAN were in good agreement. The polymerization rate increased with temperature rise, and the apparent activation energy was < 60 kJ mol^{-1}. Using this procedure, polyacrylonitrile with MW > 80 kDa and rather narrow

Scheme 5

Initiation:



Chain propagation:



L = $C_6H_4(CO_2H)_2$-1,3; k_i is the rate constant for initiation

MWD (M_w/M_n = 1.22) was synthesized for the first time by reverse ATRP. The researchers cited noted that the PAN they synthesized was an excellent raw material for the manufacture of carbon fibres. Scheme 5 shows AN polymerization with these systems.

Of no less interest are the results obtained using a system comprising $FeCl_3$, iminodiacetic acid (IDA) and AIBN as the radical initiator.[89] Polymerization occurred in the controlled/living fashion. The optimal composition of the catalyst system determined experimentally was $FeCl_3$: IDA = 1 : 2; this provided not only fairly high polymerization rate but also low polydispersity of the products. Study of the solvent effect on the polymerization of acrylonitrile showed that DMF is preferred over propylene carbonate or toluene; the MW of the polymer determined experimentally for the reaction in DMF was in good agreement with theoretical values. The polymerization rate increased with temperature; the apparent activation energy was 54.8 kJ mol^{-1}. If $CuCl_2$ was used as the catalyst instead of $FeCl_3$ under analogous conditions, polymerization of acrylonitrile occured in the uncontrolled manner.

The replacement of AIBN as the initiator of the reverse ATRP synthesis of PAN by DCDPS does not change fundamentally the pattern of AN polymerization catalyzed by $FeCl_3$.[90] The polymerization was performed in DMF; this not only provided good control over MWD but also a fairly high reaction rate. Iminodiacetic acid was also used as the activator and the complexing reagent for $FeCl_3$. The optimal reactant ratio was as follows: AN : DCDPS : $FeCl_3$: IDA = 500 : 1 : 2 : 4. The polymerization rate increased with temperature. The calculated apparent activation energy was 49.9 kJ mol^{-1}. In order to prepare high-molecular-weight PAN samples, the researchers carried out post-polymerization experiments in the presence of $FeCl_2$–IDA by conventional ATRP mechanism using the obtained PAN samples as macroinitiators. They noted that the synthesized polyacrylonitrile was successfully employed for the manufacture of high-strength carbon fibre with 1.16 dtex thick thread having the strength of 6.01 cN dtex^{-1}.

The proposed DCDPS initiator can also be used to perform reverse ATRP in the presence of the $FeCl_3$–isophthalic acid (IPA) system in DMF.[91] According to experimental data, the optimal reactant ratio was AN : DCDPS : $FeCl_3$: IPA = 500 : 1 : 2 : 4. By IR and NMR spectroscopy, the resulting polyacrylonitrile was found to contain chlorine atoms at the polymer chain ends and, therefore, it was used as the macroinitiator for the post-polymerization in the presence of the $FeCl_2$–IPA catalyst system in the conventional ATRP process. The resulting polyacrylonitrile had the following parameters: M_n = 39 260, M_w/M_n = 1.25 and was successfully used to manufacture high-strength carbon fibre.

Triphenylphosphine is suitable as the ligand for controlled/living polymerization of acrylonitrile. Chen *et al.*[92] reported living reverse atom transfer polymerization of acrylonitrile. The authors used the $FeCl_3$–PPh_3 catalyst system. The polymerization carried out at 70 °C was initiated by DCDPS. The most efficient control of the process was achieved at $FeCl_3$: PPh_3 of 1 : 3. The highest reaction rate was also observed at this ratio. The polymerization rate increased with temperature, and the apparent activation energy was found to be 54.9 kJ mol^{-1}. Since the resulting polymers had halogen atoms at the end of the chain, they were used as macroinitiators for the post-polymerization of acrylonitrile by conventional ATRP in the presence of the $FeCl_2$–PPh_3 catalyst system.

As the triphenylphosphine complex, $FeCl_3$ can serve as the catalyst for reverse atom transfer radical polymerization of acrylonitrile[93] also with a different initiator — 1,1,2,2-tetraphenylethane-1,2-diol. However, unlike the above study, in this case, the optimal $FeCl_3$: PPh_3 ratio is 1 : 2. The components taken in this ratio provided the most efficient control of molecular weight and polydispersity and the optimal high polymerization rate. As was to be expected, the polymerization rate increased with temperature. The apparent activation energy for polymerization was 62.4 kJ mol^{-1}. It is noteworthy that the use of $CuCl_2$ instead of $FeCl_3$ under the same conditions precludes the controlled/living polymerization mode. The facts that acrylonitrile polymerization in the presence of the $FeCl_3$–PPh_3 system follows a living mechanism and that the macromolecules bear halogen atoms at the ends were proved by block copolymerization and post-polymerization in which the synthesized PAN served as the macroinitiator. The synthesis of block copolymers and post-polymerization were carried out using the CuCl–bipy system, which had been repeatedly successfully used by Di Lena and Matyjaszewski[14] as the catalyst for controlled/living ATRP.

Acetic acid has also been used as a component of the catalyst system for reverse ATRP in the presence of $FeCl_3$.[94] The process was carried out in DMF at 65 °C and initiated by AIBN. According to experimental results, the $FeCl_3$: AcOH ratio of 1 : 2 is the best as regards the polymerization kinetics and the molecular-weight characteristics of the polymer. The polymerization rate increased with increasing temperature. The calculated apparent activation energy for the polymerization was 80.6 kJ mol^{-1}. Comparative analysis of the efficiency of solvents used for the synthesis of PAN unambiguously indicated that DMF is the best medium for acrylonitrile polymerization. In the authors' opinion, this is due first of all to high polarity of DMF. The authors concluded that polymerization follows a living mechanism relying on the analysis of the end groups of macromolecules by physicochemical methods including NMR and IR spectroscopy. Note high molecular weights of the resulting polymer, which do not correspond to the calculated values for the same ratio between the initiator, the monomer and iron chloride.[88]

The possibility of using lactic acid for the synthesis of PAN by the reverse ATRP mechanism in the presence of anhydrous $FeCl_3$, $CuBr_2$ or $CuBr_2$ in combination with Cu^0 was analyzed.[95] For a system based on anhydrous $FeCl_3$ and lactic acid, the highest degree of control of the polydispersity was achieved at the $FeCl_3$: lactic acid ratio of 1 : 2. The use of DMF as the solvent resulted in the preparation of the polymer with the narrowest MWD. The molecular weight increased linearly with conversion; however, the corresponding plot did not pass through the origin of coordinates. The replacement of $FeCl_3$ by $CuBr_2$ deteriorated the control over the process. The addition of Cu^0 powder to $CuBr_2$ substantially shortened the induction period and increased the polymerization rate. The structure of end groups for the resulting PAN samples was studied by NMR spectroscopy; the polymers were shown

to be suitable for further initiation of polymerization and chain propagation upon the addition of a fresh monomer portion into the system.

Iron chloride-based systems can also be used for conventional ATRP.[96] The system of $FeCl_2$ and succinic acid can be successfully used in the radical polymerization of acrylonitrile in DMF in the presence of 2-chloropropionitrile as the initiator. As in the case of reverse ATRP, the $FeCl_2$: succinic acid ratio of 1 : 2 provided the best control of the MW and MWD values and a fairly high reaction rate. It was shown that DMF is the solvent of choice for the synthesis of PAN with the $FeCl_2$- and succinic acid-based system. The induction period is substantially shorter in this solvent than in propylene carbonate or toluene, while the polymerization rate is much higher. The experimental values of the molecular weight of PAN were in good agreement with the theoretical value. As was to be expected, the polymerization rate considerably increased and the induction period shortened with temperature rise. The apparent activation energy for the polymerization of acrylonitrile with the proposed systems was 56.5 kJ mol^{-1}.

As noted above, development of new methods (AGET, ARGET and ICAR) for radical polymerization in the presence of transition metal complexes has currently made it possible to markedly decrease the required amount of catalyst by additional introduction of initiators or activators.[36–41, 55] These methods are also actively used for AN polymerization in the presence of iron compounds.

Characteristic features of the radical polymerization of acrylonitrile with a catalyst based on anhydrous $FeCl_3$ and iminodiacetic acid have been considered.[97] The authors employed CCl_4 as the initiator and DMF as the solvent. The polymer was formed by the ARGET ATRP mechanism with ascorbic acid functioning as the reducing agent. The kinetic data for the polymerization unambiguously pointed to the controlled/living mode of the process; the conversion markedly increased with increase in the concentrations of CCl_4 and the $FeCl_3$ complex with IDA or ascorbic acid. Conversely, the polymer molecular weight simultaneously decreased and the polydispersity index increased. Analysis of the NMR spectra of the synthesized PAN, in particular, the signals for the end groups of macromolecules confirmed the controlled/living radical mode of polymerization under the indicated conditions and pointed to the ATRP mechanism.

The radical copolymerization of acrylonitrile with styrene according to the AGET ATRP mechanism using activators regenerated by electron transfer was carried out in DMF at 90 °C in the presence of air and the $FeCl_3 \cdot 6H_2O$–succinic acid catalyst system in combination with 2-bromoisobutyrate as the halogen initiator and ascorbic acid as the reducing agent.[98] The controlled/living ARGET ATRP mechanism of the polymerization of styrene and acrylonitrile was indicated unambiguously by the linear increase in the molecular weight of the polymers following increase in the monomer conversion and relatively low polydispersity indices (< 1.25) even at high conversions. The obtained polyacrylonitrile was used for post-polymerization, which is also indicative of the presence of living chains in the polymer. The structure of the resulting copolymer was supported by NMR and gel permeation chromatography (GPC).

In order to enhance the efficiency of CLRP in the presence of metal complexes including iron compounds, some researchers used microwave radiation. In particular, a procedure for PAN synthesis by atom transfer mechanism under the action of microwave radiation has been developed.[99] The synthesis proceeded in the living chain fashion in the presence of $FeCl_2$- and succinic acid-based composition as the catalyst system. The reaction was initiated by 2-chloropropionitrile. It was found that the reaction involving the proposed catalyst system proceeds more efficiently under microwave treatment than in the case of conventional thermal initiation. From the standpoint of MWD width, the optimal ratio of the catalyst components $FeCl_2$: succinic acid is 1 : 2; this also ensures rather high polymerization rate. To prove that polymerization follows a living mechanism, the authors carried out post-polymerization of acrylonitrile using the obtained polymer as the macroinitiator and also synthesized block copolymers. It was shown in the same study that $CuCl_2$ in the presence of succinic acid and 2-chloropropionitrile is less efficient for the control of the AN polymerization process than $FeCl_2$. This can probably be attributed to the irreversible reaction of copper halide with succinic acid, resulting in the loss of the activity of the metal-containing catalyst.

Similar results have been obtained[100] by using microwave radiation in the AN polymerization involving $FeBr_2$, isophthalic acid and 2-bromopropionitrile as the initiator. Comparative analysis of the polymerization kinetics in the case of usual thermal initiation and in the case of microwave treatment shows that the rate constant for the polymerization was much higher in the latter case. It was found experimentally that $FeBr_2$ should be deficient with respect to isophthalic acid. The excess of isophthalic acid ensures good control of the MWD and high conversions of the monomer. The authors were able to reach a conversion of $> 90\%$ upon polymerization conducted for 30 h. The optimal component ratio was as follows: AN : $FeBr_2$: isophthalic acid = 800 : 1 : 2. The resulting polymers were found to contain bromine atoms at the ends of the backbone and, hence, they can serve for reinitiation of polymerization and chain elongation and for the synthesis of block copolymers. The polydispersity index of the obtained samples was fairly low ($M_w/M_n < 1.3$).

Microwave radiation is used not only to perform ATRP processes but also for the controlled/living synthesis of PAN by reverse ATRP. An early study[101] along this line was published in 2008. The reaction was catalyzed by the above-noted $FeCl_3$–isophthalic acid composition, while AIBN served as the source of free radicals that initiate polymerization. To improve the solubility of the catalyst and the ligand as well as of the resulting polymer, the reaction was carried out in DMF. Under similar experimental conditions, the rate constant for polymerization under microwave treatment was higher than with usual heating. The polymerization was subject to efficient control over the molecular-weight parameters and had a fairly high rate. The polymers thus obtained were used as macroinitiators for elongating the polymer chain and successful synthesis of acrylonitrile-based polymers with the molecular weight of > 50 kDa and relatively low polydispersity ($M_w/M_n < 1.30$).

Microwave radiation has been used not only to increase the efficiency of radical homopolymerization of acrylonitrile but also for controlled/living copolymerization. For example, an acrylonitrile–styrene copolymer

was successfully synthesized by controlled/living reverse ATRP in the presence of the $FeCl_3$–isophthalic acid catalyst system.[102] AIBN served as the source of free radicals initiating polymerization. Both thermally initiated synthesis and synthesis under microwave irradiation were carried out; in the latter case, the reaction was faster: the monomer conversion was 30% over a period of 38 min (in the case of thermal initiation, it was not more than 8%). The kinetic measurements indicated the living character of radical polymerization, which was manifested as a linear growth of the molecular weight with increase in the monomer conversion and relatively narrow MWD (polydispersity index < 1.25) even at high conversions. The resulting copolymer of acrylonitrile with styrene was comprehensively characterized by IR and NMR spectroscopy and GPC.

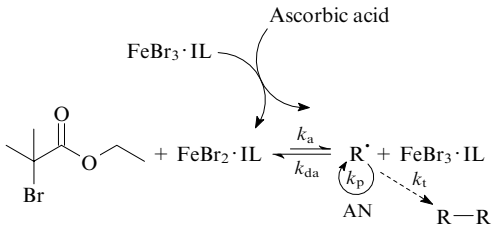
Thus, microwave radiation increases the efficiency of controlled/living synthesis of PAN in the presence of iron compounds. Another method for increasing the efficiency of the PAN preparation by controlled/living polymerization is the use of ionic liquids.[103–107] The ionic liquid 1-n-butyl-3-methylimidazolium tetrafluoroborate was first used as the solvent for the reverse atom transfer radical polymerization of AN.[104] The reaction was catalyzed by the $FeCl_3$ complex with succinic acid and initiated by AIBN. Conducting the acrylonitrile polymerization in the ionic liquid compares favourably with bulk polymerization as regards the rate and the control over the process. The AN : $FeCl_3$: succinic acid : AIBN ratio of 200 : 1 : 2 : 4 was found to be optimal from the standpoint of polymerization kinetics and the synthesis of narrow-MWD PAN (M_w/M_n < 1.3). Using the experimental data, the apparent activation energies for acrylonitrile polymerization with the catalyst system used were found to be 48.2 and 55.7 kJ mol^{-1} in the ionic liquid and in block, respectively. The synthesized PAN was subsequently used as the macroinitiator for post-polymerization and in the synthesis of block copolymers by conventional ATRP. The catalyst system based on iron halide and 1-n-butyl-3-methylimidazolium tetrafluoroborate was successfully regenerated after polymerization and reused for the controlled/living synthesis of macromolecules.

Other ionic liquids are also suitable for polymerization of acrylonitrile. For example, Chen *et al.*[104] carried out atom transfer polymerization of AN in 1-methylimidazolium acetate, valerate and caproate with $FeBr_2$ as the component of the catalyst system. It is of interest that the process was efficient without addition of any ligand. Apparently, in this case, the ionic liquid, which is able to be complexed with the metal atom, functioned as the ligand. Ethyl 2-bromoisobutyrate (EBiB) was used as the initiator. In all of these ionic liquids, polymerization proceeded in the controlled/living fashion. The highest process rate was observed in 1-methylimidazolium acetate. The optimal AN : $FeBr_2$: EBiB ratio from the standpoint of the polymerization rate and polydispersity of the produced samples was found to be 200 : 2 : 1. Polyacrylonitrile formed under these conditions was successfully used as the macronitiator in the post-polymerization and the synthesis of block copolymers. For practical reasons, it is important that after the synthesis, ionic liquids and iron bromide can be regenerated and reused for living polymerization.

Reverse atom transfer radical polymerization of methacrylonitrile initiated by AIBN and involving $FeCl_3$ has also been accomplished in ionic liquid.[105] As in the above example of AN polymerization, methacrylonitrile polymerization involving the iron salt was carried out in four different ionic liquids (1-methylimidazolium acetate, butyrate, caproate and heptanoate) without addition of any ligand. The reaction in 1-methylimidazolium acetate was the best regarding the control of the MWD and, moreover, had the highest rate; the optimal monomer : $FeCl_3$: AIBN component ratio was 300 : 2 : 1. The proposed catalyst system was suitable for the synthesis of polymethacrylonitrile-block-polystyrene block copolymers with the prepared polymethacrylonitrile as the macroinitiator. This fact unambiguously confirms the living character of methacrylonitrile polymerization in ionic liquids with the participation of $FeCl_3$. As in the cases described above, the ionic liquids and iron halide can be regenerated after the polymerization and used once again for the controlled/living synthesis of polymethacrylonitrile or for block copolymerization. In particular, Chen *et al.*[105] prepared PAN-block-polystyrene block copolymers with the molecular weight of ~50 kDa and polydispersity index of 1.34.

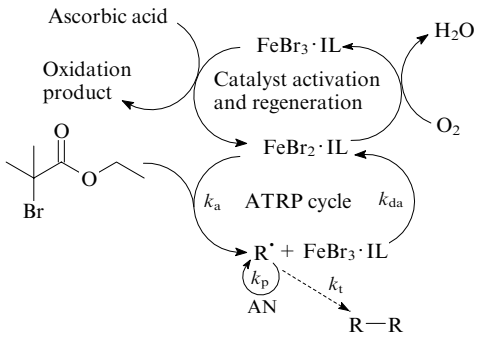
In ionic liquids (1-methylimidazolium acetate, propionate and butyrate), atom transfer radical polymerization of AN with the participation of reducing agents (AGET ATRP) was carried out.[106] Ascorbic acid was used as the reducing agent involved in the ATRP process activation, while ethyl 2-bromoisobutyrate, which is traditionally employed in controlled/living ATRP processes, served as the initiator. The role of the metal-containing catalyst belonged to $FeBr_3$, which was introduced without additional ligands. The authors evaluated for the first time the contribution of atmospheric oxygen to the ATRP of AN in ionic liquids. According to kinetic measurements, rad-

Scheme 6



IL is 1-methylimidazolium acetate

Scheme 7



ical polymerization of acrylonitrile involving the above-indicated system has a controlled/living nature both without oxygen and in air. The putative mechanisms of acrylonitrile polymerization according to the AGET ATRP pattern catalyzed by the indicated catalyst system in the absence and in the presence of air oxygen is shown in Schemes 6 and 7.[106]

Of interest is the fact that polymerization in the presence of atmospheric oxygen has a rather low rate; however, the control over the molecular-weight parameters is better than without oxygen. The apparent rate constants for AN polymerization by the AGET ATRP mechanism in the three ionic liquids tested decreases in the series 1-methylimidazolium acetate > 1-methylimidazolium propionate > 1-methylimidazolium butyrate. The living nature of the process was supported by examining the end groups of PAN and by conducting block copolymerization of MMA using PAN synthesized as described above as the macroinitiator. For practical purposes, it is important that all the three ionic liquids as well as $FeBr_3$ can be isolated, regenerated and reused for the synthesis of polyacrylonitrile, their reactivity remaining unchanged after regeneration.

A number of examples of using ionic liquids for controlled/living radical copolymerization of acrylonitrile have been published. Wang *et al.*[107] investigated the radical copolymerization (reverse ATRP) of styrene and AN in ionic liquid using AIBN as a source of free radicals, $FeCl_3 \cdot 6H_2O$ as the catalyst and hexadecyltrimethylammonium bromide as the surfactant (the synthesis was performed in a microemulsion). Copolymers of styrene and acrylonitrile with specified molecular weights and narrow MWD were obtained. The results indicate that polymerization continued in the controlled/living fashion up to high conversions and was characterized by linear growth of molecular weight with increase in the monomer conversion. The particle size of the copolymer was studied and was found to be in the nano-sized range (from 10 to 20 nm), and the effect of the monomer ratio in the initial mixture on the polymerization rate was estimated. The structure of the copolymers was characterized by NMR and IR spectroscopy.

Quite interesting and promising are the results of the controlled/living synthesis of PAN involving zerovalent iron. In particular, Fe^0 was first used as the catalyst for living atom transfer radical polymerization of AN.[108] The polymerization was initiated by CCl_4. Hexamethylenetetramine served as the ligand stabilizing the iron complex. Polymerization was carried out in DMF at 65 °C. The synthesis of PAN proceeded in the controlled/living fashion and was described by first-order kinetics with respect to the monomer. The living mechanism of polymerization was unambiguously supported by the synthesis of block copolymers with MMA using the prepared polymer as the macroinitiator. In addition, the authors modified polyacrylonitrile in order to introduce amidoxime groups into the polymer chain for the subsequent application of the polymer for the extraction of heavy metal ions, including Hg^{2+}, from aqueous solutions. The chemical composition and structure of polymers were described by FTIR spectroscopy, which unambiguously confirmed their structure.

An environmentally friendly and ingenious method for the synthesis of PAN in the presence of a Fe^0-based catalyst was proposed by Ma *et al.*[109] In this case, iron was used without any ligands and the process was performed in ionic liquids: 1-methylimidazolium acetate, propionate and valerate. As the initiator, 2-bromopropionitrile was used. All three ionic liquids were readily regenerated after polymerization and were used many more times for the synthesis of polymers. The polymerization occurred in the controlled/living fashion, which was proven by a study of polymerization kinetics (first order with respect to the monomer), linear growth of the molecular weight with increase in the conversion, and low polydispersity of the resulting polymer. Furthermore, to prove the living polymerization mechanism, the authors synthesized the block copolymer of PAN with MMA. The copolymer thus obtained was characterized by GPC and NMR spectroscopy.

Fairly efficient regulating initiators based on iron complexes with various ligand environments have been proposed.[110–112] In particular, it was found[110] that iron carbonyl complexes $CpFe(CO)_2Cl$ and $Cp_2Fe_2(CO)_4$ ($Cp = \eta^5$-C_5H_5) in combination with CCl_4 are active towards the initiation of radical polymerization of AN. In the presence of these systems, the solution polymerization of acrylonitrile is not accompanied by significant gelation up to high conversion of the monomer. The polymerization time up to the limiting conversion is much longer in the presence of the mononuclear $CpFe(CO)_2Cl$ complex in combination with CCl_4 than in the case of the binuclear metal complex. An increase in the content of the metal complex component of the initiating system [$CpFe(CO)_2Cl$] results in the considerable increase in the reaction rate and polymer yield. Polyacrylonitrile synthesized in the presence of iron complexes in DMSO has an unimodal MWD and is readily soluble in organic solvents, unlike the PAN prepared with classical radical initiators.

The introduction of excess ascorbic acid into the $Cp_2Fe_2(CO)_4 - CCl_4$ system results in a considerable decrease in the MW of polyacrylonitrile samples (up to 22–25 kDa) and narrowing down of the MWD of the polymer prepared in DMSO ($M_w/M_n = 1.6$). The observed effect of the ascorbic acid on the molecular-weight characteristics of the polymer are apparently related to the high chain transfer activity of the compound.

The nature of the solvent was shown[111] to have a substantial effect on the molecular-weight characteristics of the polymer. Acrylonitrile polymerization with metal complexes in DMF was found to proceed at considerably lower rate and to a lower limiting degree of conversion of the monomer than polymerization of AN in a DMSO solution under similar conditions considered above. Comparative analysis of the molecular-weight characteristics of the resulting polymers showed that PAN samples synthesized in DMF have lower molecular weights and broader MWD than the polymers obtained in DMSO.

Thus, systems based on iron carbonyl complexes are highly active in the initiation of radical polymerization of AN, providing the synthesis of PAN at fairly high rates up to high degrees of monomer conversion under conditions as close as possible to conditions of industrial processes.

An original approach to the synthesis of polyacrylonitrile has been proposed.[112] It is based on using Fe^0 in the presence of halohydrocarbons. As indicated above, this approach, defined as single electron transfer living radical polymerization (SET-LRP), is a relatively new trend in the

controlled synthesis of polymers.[9] Currently, the SET-LRP protocol is successfully used in the polymer synthesis, providing products with specified molecular weights and relatively narrow MWD. This type of processes can be catalyzed by various metal compounds, including zerovalent metals. It was shown[112] that CCl_4 is the most efficient organic halogen initiator in the Fe^0 + RHal system. An additional increase in the CCl_4 concentration relative to Fe^0 increases the number of active sites of polymerization, thus enabling PAN synthesis at a higher rate to give a soluble polymer having lower molecular weight. The presence of triphenylphosphine and triphenylamine as electron-donating additives does not provide the formation of narrow-MWD samples when PAN synthesis occurs in DMSO. However, with the participation of the phosphine ligands, the reaction rate markedly increases and a high conversion of the monomer is achieved (> 80% in 6 h); meanwhile, triphenylamine has no significant influence on the synthesis of PAN, including polymerization kinetics and molecular-weight characteristics of the polymer.

The data presented in this Section demonstrate that iron-based compositions and catalyst systems, including iron complexes with various ligands, are fairly promising in the controlled/living synthesis of polyacrylonitrile and are barely inferior in activity to copper-based systems.

III.3. Trends of controlled/living synthesis of copolymers based on acrylonitrile

Currently, copolymerization is a highly efficient tool for macromolecular design and synthesis of polymers with specified properties,[53] because combination of chemically different monomer units in the same polymer molecule may endow macromolecules with unique sets of properties and characteristics. Particularly acrylonitrile copolymers, including those with methyl acrylate and some other monomers are used most often for the manufacture of high-quality carbon fibres.[2, 113, 114] Therefore, in recent years, the issues related to the synthesis of AN-based copolymers, including the living chain synthesis, has received quite a lot of attention.

Note that recent publications on effective methods for the synthesis of acrylonitrile copolymers by conventional radical polymerization are very few. For example, the spontaneous thermal copolymerization of acrylonitrile with styrene (St) has been experimentally studied at 100 and 125 °C.[115] It was shown in special experiments that acrylonitrile does not polymerize spontaneously at these temperatures. However, on mixing acrylonitrile with styrene under the same conditions, initiating radicals are formed in the system starting from the 4 : 1 ratio, which is in good agreement with the data on self-initiation upon thermal polymerization of styrene.[116] When the monomer ratio in the mixture was 1 : 1, copolymerization at 100 °C was much faster than homopolymerization of styrene under similar conditions. As the AN concentration in the system was increased, the rate of copolymerization increased, which is in good agreement with the known reactivity of vinyl monomers in radical homo- and copolymerization processes.[117] When copolymerization was carried out in propionitrile as the hydrogenated analogue of acrylonitrile, the characteristic viscosity of the system is virtually invariable during the synthesis. The copolymerization rate is maximum for the monomer ratio St : AN = 40 : 60 both for the bulk process and for the solution process in propionitrile. During copolymerization, high-molecular-weight products were mainly formed, the yield of oligomers being not higher than 3% (the oligomers were mainly styrene trimers).

The kinetics and mechanism of free radical polymerization of acrylonitrile and methyl acrylate in DMSO in the presence of AIBN have been studied.[118] The initiation efficiency was found to be unity. Polymerization occurs up to high conversions for both monomers; however, the MW and the polydispersity of the synthesized samples are rather high ($M_w/M_n > 3$), which is typical of uncontrolled free-radical polymerization processes.

An original method for the synthesis of acrylonitrile–styrene copolymers in the presence of β-cyclodextrin (β-CD) and its derivatives has been described.[119] The composition of the obtained copolymers, including the sequence of units and the molecular-weight characteristics was studied in detail by GPC and ^{13}C NMR spectroscopy. It was found that upon increase in the St : β-CD ratio, the average length of the acrylonitrile sequence and the number of acrylonitrile units in the polymer increase. The glass transition temperature and the melting point of copolymers also increase at higher St : β-CD ratios. The molecular weights of the resulting polymers increase with a decrease in the β-cyclodextrin concentration.

The interaction of acrylonitrile with diene monomers of various structure, namely, 2,3-dimethylbuta-1,3-diene, 4-methylpenta-1,3-diene and isoprene, has been studied in 1,2-dichloroethane in the presence of various amounts of zinc chloride at various temperatures.[120] It was shown that along with alternating copolymerization, [4 + 2]-cycloaddition to give the corresponding adducts takes place under these conditions. The structure and the electron-donating behaviour of the diene have a pronounced influence on the product ratio. In the reaction of acrylonitrile with 2,3-dimethylbuta-1,3-diene, the temperature rise and an increase in the $ZnCl_2$ concentration induce an increase in the yield of cycloaddition products, while the highest conversion is observed when the reaction is carried out at 45 °C. At higher temperatures, no cycloaddition products are formed. In the case of 4-methylpenta-1,3-diene, only the copolymer is formed as the presence of two terminal methyl groups rules out the concerted [4 + 2]-cycloaddition. Isoprene is less reactive than 2,3-dimethylbuta-1,3-diene; therefore, the reaction with acrylonitrile under analogous conditions occurs at a lower rate, and, as a consequence, the total yield of the final product is much lower.

Li *et al.*[121] reported the first attempt to perform the radical copolymerization of acrylonitrile with β-pinene. The relative reactivities of the monomers calculated from the experimental data by the Fineman–Ross method were $r_{\beta\text{-pinene}} = 0$ and $r_{AN} = 0.66$. Copolymerization was carried out in dichloroethane at 60 °C using AIBN as the initiator. The introduction of a Lewis acid, Et_2AlCl, into the system increased the copolymerization rate and considerably increased the content of the β-pinene units in the copolymer, thus promoting the formation of an alternating copolymer. Actually, this is the first example of the synthesis of an alternating copolymer of acrylonitrile with β-pinene under radical initiation conditions.

It was also shown that controlled/living copolymerization of β-pinene and AN by reversible addition–fragmentation chain transfer mechanism is possible.[121] When the β-pinene : AN ratio is low (such as 10 : 90 or 25 : 75), copolymerization in the presence of 2-cyanoprop-2-yl dithiobenzoate as a chain transfer agent bears typical features of living polymerization, this influence being most pronounced for low conversions of the monomers. At higher conversion, copolymerization deviates from the controlled/living process due to the competing destructive chain transfer to β-pinene. The β-pinene and AN copolymers with high degree of alternation and the controlled molecular weight were obtained by combined use of cumyl dithiobenzoate as the reversible chain transfer agent and Et_2AlCl as the Lewis acid.

The free radical homopolymerization of acrylonitrile and its copolymerization with itaconic acid were carried out in DMSO with AIBN as the initiator.[122] The reaction proceeds up to a high conversion in the temperature range from 50 to 80 °C. The copolymerization constants of these monomers were estimated and it was found that the copolymerization constant for itaconic acid is less than 1 and is always greater than the corresponding constant for acrylonitrile. Thus, in this case, copolymerization corresponds to the type in which the constants for both monomers are < 1. The polymerization of AN in the presence of the indicated systems follows first-order kinetics. The initiation, chain propagation and chain termination constants were determined; they are in good agreement with analogous parameters of traditional radical copolymerization processes of acrylic monomers.[117]

For controlled/living radical (co)polymerization of acrylic and methacrylic monomers, including acrylonitrile, chromium(II) acetate-based systems have been proposed.[123] The polymerization follows an atom transfer mechanism and makes it possible to synthesize homo- and copolymers with high molecular weight and relatively low polydispersity index (< 1.3). The disadvantages of the proposed method for the synthesis include the necessity of using high concentrations of the metal complex and the colour of the obtained polymer caused by traces of the transition metal.

Chinese researchers investigated characteristic features of acrylonitrile homo- and copolymerization in the presence of samarium compounds. It was shown[124] that DCDPS is able to perform effective reverse atom transfer radical polymerization of methacrylonitrile in DMF catalyzed by $SmCl_3$ with lactic acid as the ligand. The polymerization proceeded in the controlled/living fashion, as was unambiguously indicated by the results of kinetic studies. As compared with the AIBN-initiated reverse atom transfer radical polymerization in the presence of Sm^{III}, polymerization in the presence of DCDPS was subject to more efficient control of the molecular-weight parameters. The use of cyclohexanone and toluene instead of DMF as the reaction medium resulted in a noticeable decrease in the polymerization rate and in broader MWD of the synthesized samples. The polymerization rate and the polydispersity index were virtually independent of the initial concentration of the monomer. Using the obtained polymethacrylonitrile as the macroinitiator, the authors successfully synthesized the polymethacrylonitrile and polystyrene block copolymer by the ATRP process.

Using the CLRP strategy, block copolymers of acrylonitrile with butyl acrylate (BA) were prepared by the atom transfer mechanism.[125] It was shown that block copolymers of BA and AN can be synthesized both based on the PBA macroinitiator and using the PAN macroinitiator. The latter approach is more efficient. The main difficulty arising in the synthesis of block copolymers is the poor solubility of polyacrylonitrile in the monomer and in the solvents and the loss of functionality of terminal groups during the synthesis.

Random acrylonitrile – styrene copolymers were prepared using a $CuBr_2$- and 2,2′-bipyridine-based system.[126] Azeotropic copolymerization of St and AN occurring by the atom transfer mechanism under these conditions is characterized by simultaneous consumption of both comonomers and affords narrow-MWD copolymers of a constant composition. It is noteworthy that the use of functionalized polyethylene oxide samples as macroinitiators allowed the researchers to prepare mixed multi-block-copolymers comprising polyethylene oxide and azeotropic copolymer blocks.

Generally, analysis of recent publications attests to the increase in the number of papers on the controlled/living synthesis of copolymers based on acrylonitrile under radical initiation conditions.

III.4. Catalyst systems and compositions based on lanthanides and other elements in acrylonitrile polymerization

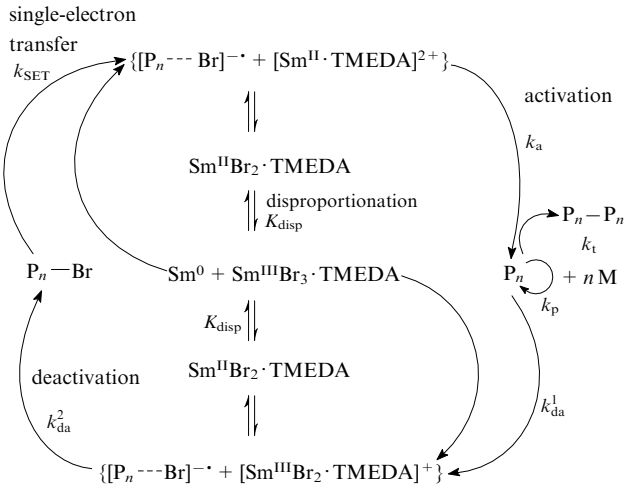
It is known[127] that lanthanides, like transition metals, can exist in several oxidation states and, in some cases, the lanthanide conversion from one oxidation state to another can be reversible, as in the case of copper, iron or ruthenium derivatives, which were considered above in detail. Therefore, lanthanide complexes, salts and even the metals have found use as catalysis for controlled/living atom transfer radical polymerization, in particular, involving acrylonitrile.

Chen *et al.*[128] performed for the first time the radical polymerization of acrylonitrile by the AGET ATRP mechanism using samarium compounds in the presence of ethyl 2-bromoisobutyrate as the initiator; they also synthesized block copolymers of acrylonitrile with styrene using these catalyst systems. The (co)polymerization was carried out both in the absence and in the presence of atmospheric oxygen using a new catalyst based on the complex of $SmBr_3 \cdot 6H_2O$ and isophthalic acid as well as ascorbic acid as the reducing agent. The polymerization of AN both in the absence of oxygen and in the presence of air proceeded in the controlled/living fashion. As compared with the polymerization in the absence of oxygen, the process in the presence of air had a lower rate and provided better control of the molecular weight and MWD under the same conditions. The calculated values for the apparent activation energy for polymerization in the absence and in the presence of oxygen are 47.1 and 51.3 kJ mol^{-1}, respectively. When anisole or toluene was used as the solvent instead of more polar DMF, the polymerization rate decreased. The resulting polymer had a greater polydispersity index. The synthesized PAN was successfully employed as the macroinitiator in the synthesis of the block copolymers of acrylonitrile with styrene catalyzed by the proposed catalyst system. The preparation of the narrow-MWD polyacrylonitrile–po-

lystyrene block copolymer unambiguously confirms the living mechanism of polymerization with the proposed catalyst system.

Of interest is the application of Sm^0 powder as the catalyst of the single-electron transfer living radical polymerization of acrylonitrile in the medium of 1,1,1,3,3,3-hexafluoropropan-2-ol with 2-bromopropionitrile as the initiator and TMEDA as the ligand.[129] The pattern of the polymerization process proposed by the authors is shown in Scheme 8.

Scheme 8

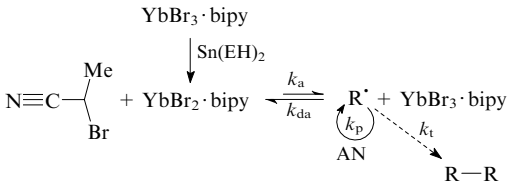


K_{disp} is the disproportionation constant

The process is described by first-order kinetics with respect to the monomer and characterized by a linear increase in the polymer molecular weight with the monomer conversion. From the practical standpoint, it is important that the polymer has an enhanced degree of syndiotacticity. Thus, the proposed system makes it possible to affect both the molecular-weight characteristics and syndiotacticity of the samples. The degree of syndiotacticity of PAN obtained in the 1,1,1,3,3,3-hexafluoropropan-2-ol medium was markedly increased as compared with that synthesized in DMF under analogous conditions; also, the degree of syndiotacticity substantially increased with increase in the content of the fluorinated alcohol in the system. A comparison with PAN prepared under similar conditions using copper powder instead of samarium demonstrated that the syndiotacticity of PAN synthesized with samarium as the catalyst is higher than that with copper. The catalyst system based on samarium is also suitable for controlled synthesis of the polyacrylonitrile-block-poly(methyl methacrylate) block copolymer with a molecular weight of ~50 kDa and polydispersity index of 1.34.

One more example of using lanthanides in the synthesis of PAN is the use of ytterbium complexes. In particular, an original method for conducting polymerization of acrylonitrile has been proposed.[130] The researchers used the catalyst system based on ytterbium complexes with bipy for the atom transfer radical polymerization (Scheme 9).

Scheme 9



In this case, moreover, one of the most effective protocols of atom transfer polymerization was used, namely, AGET ATRP. Tin(II) bis(2-ethylhexanoate) [$Sn(EH)_2$] served as the activator and the reducing agent and 2-bromopropionitrile was the initiator. It was found that polymerization may occur both in the absence and in the presence of air oxygen. Comparative analysis of a similar AGET ATRP process with a $CuBr_2$-based catalyst indicates that by using ytterbium complexes, it is possible to prepare polyacrylonitrile with enhanced content of syndiotactic units. An increase in the degree of syndiotacticity became more pronounced as the concentration of $YbBr_3$ was increased. A system based on the ytterbium complexes also provided successful synthesis of the PAN-b-PMMA block copolymer with a molecular weight of ~60 kDa and a polydispersity index of ~1.36. The data presented in the paper unambiguously indicate that polymerization of acrylonitrile occurred in the controlled/living fashion.

An original catalyst system based on lanthanum(0) and hexamethylenetetramine was proposed[131] for single-electron transfer living polymerization of acrylonitrile (SET-LRP). The polymerization efficiently proceeded in the presence of ascorbic acid, which functioned as the activator, and CCl_4 as the initiator in DMF. The process had a rather high rate and the conversion was 77% over a period of 12 h. The optimal AN : CCl_4 : La : ascorbic acid ratio of the components was 200 : 1 : 0.5 : 2.5 : 0.23. Ascorbic acid had a noticeable influence on the monomer conversion, which was substantially higher in the presence of the acid. From the practical standpoint, it is important that polymerization is efficient also in the presence of atmospheric oxygen. The kinetic studies demonstrated that polymerization of acrylonitrile both in the absence and in the presence of oxygen proceeded in the controlled/living fashion. However, the synthesis of PAN in the presence of air was noticeably slower than polymerization without oxygen and gave a polymer with broader MWD. The authors studied in detail the effect of the ratio and concentrations of the metal, ascorbic acid and CCl_4 on the polymerization kinetics and sample polydispersity.

Apart from lanthanides, complexes of cobalt, which can have oxidation states +2 and +3, also exhibit fairly high catalytic activity in the controlled/living macromolecule synthesis.[16] Cobalt derivatives are quite efficient toward polymerization of AN, MMA and some other monomers.[132–134] Indeed, Debuigne *et al.*[135] reported for the first time successful cobalt-mediated radical polymerization (CMRP). The polymerization was initiated by the azo initiator R—N=N—R [R = $CMe(CN)CH_2CMe_2OMe$, commercial name V-70], cobalt(II) bis(acetylacetonate) [$Co(acac)_2$] and cobalt(III) complexes. The reactant molar ratios and concentrations as well as the reaction temperature and the solvent were varied over broad ranges in order to optimize the con-

ditions of synthesis. The best control of the molecular-weight characteristics was found to be attained if polymerization was initiated by the Co^{III} adduct at 0 °C in DMSO. Under these conditions, it was possible to synthesize polyacrylonitrile with a specified molecular weight and very narrow MWD ($M_w/M_n < 1.1$). The solvent was found to be highly important in the synthesis of narrow-MWD polyacrylonitrile. Using cobalt complexes proposed in the cited publication,[135] a method for the synthesis of the PVA-b-PAN block copolymers was developed.

Radical polymerization of acrylonitrile in DMSO using $Co(acac)_2$ as a mediator has been described.[136] The change in the molecular weight following increase in the conversion under experimental conditions was estimated. The polymer molecular weight was found to sharply increase in the early process stage and then to increase linearly with the conversion. According to ^{13}C NMR data, the polymer was linear. The polymer molecular weight at 90% conversion exceeded 120 kDa. The polydispersity index, however, was too high for a controlled/living process (~2.4). Copolymerization of AN with MMA in the same system and in the same solvent at 30 °C was studied; the relative monomer reactivities determined by the Kelen–Tüdös method were 0.33 and 0.71 for AN and MMA, respectively. These values differ somewhat from analogous parameters for copolymerization of the same monomers in the presence of classical radical initiators (0.15 and 1.2 for AN and MMA, respectively).[118] Apparently, these differences can be attributed to the direct participation of the metal complex in chain propagation, in particular, to metal atom coordination to the growing macroradical or monomer (radical-coordination polymerization). This coordination is known[137] to change the reactivity of monomers and the corresponding growing macroradicals, which, in turn, results in a change in the monomer reactivity ratio.

Polyacrylonitrile, which serves as the base for the manufacture of carbon fibres, can be prepared by free-radical polymerization initiated by redox systems containing transition metals.[138] It was shown by calculations that polymerization of acrylonitrile follows a more complex kinetics than polymerization of other vinyl monomers, which is associated to a large extent with the heterogeneous nature of AN polymerization and with the formation of cyclic structures during polymer synthesis. Therefore, targeted control of polymerization of this monomer is often complicated. It was also shown by calculations[138] that for the manufacture of high-quality carbon fibre, polyacrylonitrile should preferably be linear because the presence of ring structures complicates polymer processing into the fibre.

Almost completely isotactic polyacrylonitrile (> 99% of *meso*-triads) was successfully synthesized by Zou *et al.*[139] by radiation-induced polymerization of AN in the presence of urea. The process exhibited the key features of controlled/living polymerization, including the linear dependence of the polymer molecular weight on the conversion and relatively narrow MWD (polydispersity index of < 1.5). Thus, both the molecular weight and tacticity were controlled, which, in the authors' opinion,[139] was due to participation of urea. Variation of the polymerization conditions demonstrated that the synthesis of fully isotactic polyacrylonitrile requires that the following conditions be met simultaneously: (i) mixing of acrylonitrile and urea before the onset of γ-irradiation, (ii) temperature of the synthesis at the chain propagation step of < −90 °C, (iii) active withdrawal of the heat formed during polymerization. From the standpoint of synthesis of stereoregular PAN, the result obtained by the researchers cited are certainly impressive. However, implementation of the process below −90 °C appears impracticable and, hence, of low utility.

IV. Characteristic features of reversible addition – fragmentation chain transfer radical homo- and copolymerization of acrylonitrile

As noted above, reversible addition – fragmentation chain transfer is one of the three principal methods for conducting living polymerization of vinyl monomers and, most often, it involves the use of sulfur compounds capable of reversible interaction with the growing macroradicals.[17] This procedure has been used rather actively in recent years for the synthesis of homo- and copolymers based on styrene and methyl methacrylate and used much more rarely for polymerization of acrylonitrile.

An early mention of the use of this method to prepare polyacrylonitrile was made by Liu *et al.*[140] In particular, reversible addition – fragmentation chain transfer radical polymerization of AN has been successfully performed with dibenzyl trithiocarbonate as the chain transfer agent. They studied the influence of several experimental parameters, including the molar ratio and concentrations of the initiator (AIBN) and trithiocarbonate, on the polymerization kinetics, molecular weight and sample polydispersity. Time-of-flight mass spectrometry and ^1H NMR spectroscopy measurements confirmed the presence of a thiocarbonate moiety at the end of the polymer chain, indicating the possibility of using the polymer for post-polymerization, which was demonstrated experimentally.

Reversible addition–fragmentation chain transfer (RAFT) polymerization in the presence of 2-cyanoprop-2-yl dithiobenzoate was first applied for the synthesis of polyacrylonitrile with a high molecular weight (> 30 kDa) and low polydispersity index (< 1.3).[141] The key to success was optimizing the experimental conditions in order to increase the living time of the chain. Ethylene carbonate was found to be the solvent of choice for the CLRP of acrylonitrile, providing a better control over the process than DMF or DMSO. The authors studied in detail the effect of various conditions on the polymerization, including the temperature, the ratio of 2- cyanoprop-2-yl dithiobenzoate, the initiator and the monomer and introduction of a comonomer with the goal to enhance the control over the molecular weight and MWD.

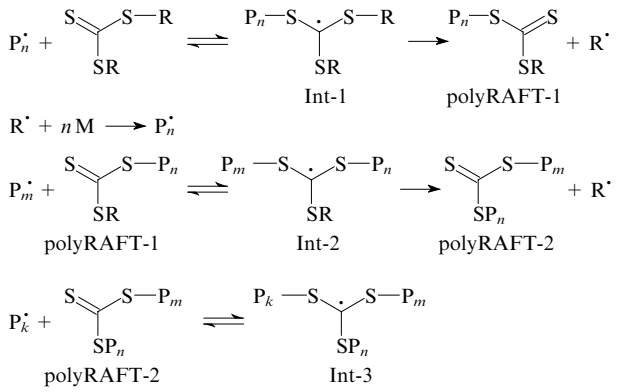
Of considerable interest are studies of E V Chernikova and co-workers, who also used thiocarbonates of various structure for homo- and copolymerization of acrylonitrile.[142] Previously, they used same chain transfer agents for the synthesis of narrow-MWD polymers based on styrene and methacrylates.[143] For example, the publication[142] presents a detailed study of pseudo-living radical polymerization of AN in DMSO in the presence of trithiocarbonates, in particular, bis(2-methoxycarbonylprop-2-yl)trithiocarbonate and bis(1-methoxycarbonyl-

ethyl)trithiocarbonate as reversible chain transfer agents: $S{=}C(SR)_2$ (R = CMe_2CO_2Me, CO_2Me, $CHMeCO_2Me$).

Furthermore, Chernikova *et al.*[142, 143] investigated the key trends of copolymerization of acrylonitrile with vinyl monomers of various structure over a broad range of monomer ratios using unsymmetrical thiocarbonates. From the practical standpoint, it is important that the investigations ascertained the relationship between the conditions of synthesis of acrylonitrile homo- and copolymers and the thermal behaviour of the obtained samples, which can be utilized to predict the type and structure of the polyconjugated chain preceding the formation of the graphite-like carbon matrix upon high-temperature pyrolysis.

Chernikova *et al.*[144] were the first to report pseudo-living reversible chain transfer radical polymerization of acrylonitrile in CO_2 at elevated pressure. Acrylonitrile and other vinyl monomers were polymerized in the presence of various trithiocarbonates $S{=}C(SR)_2$ (R = Bn, CMe_2CO_2Me and $CHMeCO_2Me$) as reversible chain transfer agents. Study of the polymerization mechanism, in particular, by EPR using spin traps showed that the radical polymerization of vinyl monomers in the presence of trithiocarbonates is a fairly complex process due to the presence of two leaving groups (Scheme 10).

Scheme 10



The propagation radical $P_n^{\bullet}$ formed upon initiation of the polymerization *via* decomposition of the initiator reversibly adds to the RAFT agent to give intermediate Int-1. This intermediate can be irreversibly converted to the polymeric RAFT agent (polyRAFT-1) by eliminating one leaving group as the $R^{\bullet}$ radical, which re-initiates polymerization. The polymer polyRAFT-1 reacts in a similar way with another macroradical $P_m^{\bullet}$ to give intermediate Int-2, which can release one of the polymeric substituents as a radical able to initiate polymerization. If this intermediate decomposes with elimination of the second leaving group $R^{\bullet}$, a new polymeric RAFT agent (polyRAFT-2) is formed in the system and can also be involved in the addition–fragmentation reaction sequence. Irrespective of the decomposition pattern of intermediate Int-3, a macroradical able to be involved in chain propagation is always regenerated in the system.

Conducting polymerization in DMSO provided narrow-MWD PAN with controlled molecular weight. The structure of the resulting polymers was studied by NMR and IR spectroscopy. The thermal behaviour of the synthesized PAN was examined by DSC and IR pyrolysis and was found to be dictated by both the polymer molecular weight and MWD width and conditions of synthesis. The introduction of functional groups of the reversible chain transfer agent into the macromolecule changes the structure of the polyconjugated system and allows one to control the conditions of its formation.

Exceptionally interesting data on the synthesis of acrylonitrile-based polymers were reported by Niu *et al.*[145] In particular, they prepared polyacrylonitrile with high viscosity-average molecular weight (>400 kDa) using reversible addition — fragmentation chain transfer polymerization. As the RAFT agent, a heterocyclic sulfur-containing compound — 1,4-[2-(carbazole-9-carbodithioate)-2-methyl propionic acid] phenyl ester — was used for the first time. The polymerization was accompanied by a linear increase in the molecular weight with conversion and the product had a narrow MWD. The introduction of $AlCl_3$ (0.01 equiv. with respect to AN) as a Lewis acid into the polymerization system increased the degree of isotacticity of PAN by more than 8%. Also, the effect of the molecular weight and MWD of the samples on the morphology of the resulting carbon fibre was investigated. According to the results, the average fibre diameter increases with increase in the molecular weight and fibres of the same diameter are manufactured much more easily when a narrow-MWD polymer is used as the precursor.

Bulk radical polymerization of acrylonitrile was carried out at room temperature using a binary system based on 1,1,3-trimethyl-5-methylene-2,6-dioxa-l-silacyclohexene and tetra-n-butylammonium bibenzoate.[146] Experimental results indicate that 1,1,3-trimethyl-5-methylene-2,6-dioxa-1-silacyclohexene acts as a chain transfer agent in acrylonitrile polymerization and provides a polymer in a rather high yield and with efficiently controlled molecular weight and polydispersity ($M_w/M_n < 1.4$). Actually, the authors proposed a new high performance agent for reversible addition–fragmentation chain transfer polymerization of acrylic monomers.

The reversible addition–fragmentation chain transfer polymerization protocol was successfully used to perform controlled/living radical copolymerization of acrylonitrile not only with vinyl but also with other monomers. For instance, Kaiser *et al.*[147] reported the results of a study of controlled/living RAFT radical copolymerization of acrylonitrile and buta-1,3-diene. The copolymerization of acrylonitrile with butadiene in solution using dithioacetate and trithiocarbonate as chain transfer agents for the synthesis of butadiene–nitrile rubber was described for the first time. The number-average molecular weight of the rubber varied from several thousand to 60 000 Da with polydispersity indices from 1.2 to 2.0 (depending on the monomer conversion to the polymer). A very good correlation was observed between the experimental and theoretical molecular weights of the copolymer. Detailed information on the structure of the resulting polymers was obtained by modern physicochemical methods, including IR and NMR spectroscopy, DSC and matrix-assisted laser desorption ionization mass spectrometry.

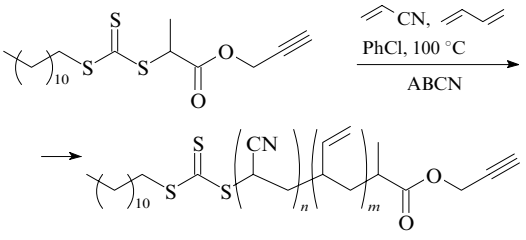
Acrylonitrile–butadiene rubbers were synthesized in the presence of trithiocarbonate as a chain transfer agent by copolymerization of AN and buta-1,3-diene under azeotropic conditions (38 : 62 monomer ratio) in a broad

range of solvents — *N*,*N*-dimethylacetamide, chlorobenzene, 1,4-dioxane, *tert*-butyl alcohol, isobutyronitrile, toluene, trimethylacetonitrile, dimethyl carbonate, acetonitrile, methyl acetate, acetone and *tert*-butyl methyl ether.[148] The synthesis was carried out at 100 °C, the conversion over a period of 22 h being 15% to 35% depending on the solvent. The highest conversion was achieved in the copolymerization conducted in DMF. As the radical initiator, 2,2′-azobis(*N*-butyl-2-methylpropioamide) was used.

Reversible chain transfer polymerization was used to prepare an acrylonitrile–maleic anhydride copolymer.[149] The control of the copolymerization was achieved by specially synthesized high-molecular-weight trithiocarbonate containing an oligomer moiety and a nitrile group in the molecule. The authors comprehensively studied the process kinetics and thermodynamics and ascertained that polymerization occurs in a controlled/living fashion. Using precision calorimetry, thermodynamic properties and characteristics of the resulting copolymers were studied. It was found that the introduction of maleic anhydride as a comonomer smooths down the exothermic effect of the cyclization of PAN during manufacture of carbon fibre. The copolymer can serve as a precursor for the manufacture of cross-linked carbon fibre.

A method for the synthesis of acrylonitrile–buta-1,3-diene-propargyl methacrylate terpolymer by RAFT polymerization using 1,4-bis(azidomethyl)benzene has been developed.[150] This was the first example of successful application of RAFT polymerization for the synthesis of demanded and practically valuable synthetic rubbers based on terpolymers. The reaction occurs at 100 °C and is initiated by 1,1′-azobis(cyclohexanecarbonitrile) (ABCN); chlorobenzene or acetone was used as the solvent. Butadiene–styrene rubber was synthesized by a similar procedure using the compounds indicated above (Scheme 11). The resulting copolymer had MW from 2500 to 97 000 Da, a linear structure and the polydispersity index in the range of 1.1–1.6.

Scheme 11



RAFT copolymerization of styrene with acrylonitrile was performed in the presence of cumyl dithiobenzoate as the chain transfer agent and AIBN as the initiator.[151] The process proceeded in the controlled/living fashion, the composition of the copolymer depended on the monomer ratio in the initial mixture. Apart from random copolymers of styrene with acrylonitrile, block copolymers containing polystyrene and PAN blocks were synthesized. These block copolymers had a rather narrow MWD (polydispersity index of 1.29–1.46). The composition and structure of functional copolymers were confirmed by GPC and ^{1}H NMR and FT IR spectroscopy.

Analysis of published data dealing with the application of sulfur compounds as chain transfer agents in homopolymerization and, mainly, copolymerization of acrylonitrile unambiguously indicates that the synthesis in the presence of these compounds follows the controlled/living mechanism. However, it is noteworthy that the practical application of sulfur compounds for the control of AN polymerization has substantial limitations, because the polymerization rates are in this case moderate and the range of controlled molecular-weight characteristics is quite limited.

V. Homo- and copolymerization of acrylonitrile by reversible inhibition mechanism

Generally, it should be noted that 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and other nitroxides are less efficient for the synthesis of narrow-MWD samples in the case of AN homopolymerization [152] than in the case of polymerization of styrene and styrene derivatives (in the latter case, polymers with the polydispersity index of $< 1.2-1.3$ can be formed in the presence of nitroxides).[8,15] Meanwhile, TEMPO and its analogues can be quite useful for controlling copolymerization of AN with other vinyl monomers, first of all, styrene, which effectively undergoes living reversible inhibition polymerization in the presence of stable radicals.

A typical example of using reversible inhibition for the radical homo- and copolymerization of acrylonitrile was reported by Zaremski *et al.*[153] The authors demonstrated that azeotropic radical copolymerization of acrylic monomers, including AN and St, in the presence of TEMPO is subject to the effect of self-targeting to the steady state and obeys the rule of zero-order kinetics with respect to the initiator. Also, copolymerization obeys the living chain law. The process rate can be increased by introducing accelerating additives (trichloroacetic acid, acetic anhydride, *etc.*). Actually, the authors developed an original concept of controlled/living synthesis of copolymers by TEMPO-mediated copolymerization of styrene with unreactive monomers. A drawback of the proposed synthesis of acrylonitrile or methacrylonitrile copolymers with styrene is some increase in the polydispersity index following increase in the monomer conversion.

The same Russian research group [154] theoretically predicted and experimentally confirmed the copolymerization mechanisms in the presence of TEMPO in relation to two chemically similar systems, styrene–acrylonitrile and styrene–methacrylonitrile. In the former system, living copolymer–TEMPO adducts are mainly formed, being capable of thermal decomposition and reinitiation of pseudo-living polymerization. The reaction occurs in the steady-state mode and is accompanied by an increase in the number-average molecular weight of the copolymer as the conversion increases. In the latter system, according to researchers' opinion,[154] the probabilities of formation of 'living' and 'non-living' macromolecules are close. As a result, the living growth of M_n of the copolymer ceases and the reaction soon transforms into conventional copolymerization mode.

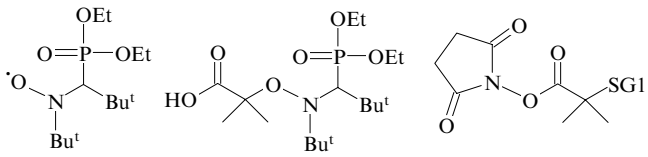
As noted above, CLRP of acrylic monomers, including acrylonitrile, can be activated by using various additives. In particular, Baumann and Schmidt-Naake [155] studied

the effect of acetic anhydride on the controlled radical copolymerization of styrene and acrylonitrile initiated by benzoyl peroxide and mediated by TEMPO. The addition of Ac_2O in 2 : 1 molar ratio with respect to TEMPO at 125 °C induces a 12-fold increase in the polymerization rate. The copolymer MW markedly increases but simultaneously MWD is broadened. Further increase in the concentration of the additive does not increase the polymerization rate but has adverse effect on MWD parameters. According to spectral data, the decrease in the control over the molecular-weight characteristics may be due, among other factors, to irreversible reaction of TEMPO with Ac_2O, which reduces the concentration of the nitroxide mediator in the polymerization system.

A TEMPO analogue, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (HTEMPO), was also successfully used to prepare copolymers of acrylonitrile with styrene.[156] Benzoyl peroxide, AIBN and dicyclohexyl peroxide carbonate, which have different half-lives, were used to initiate radical polymerization. The synthesis was carried out at relatively high temperature (140 °C). It was shown that copolymerization of styrene with acrylonitrile proceeded in a living fashion. The relatively low polydispersity of the samples was retained up to 40% conversion of the monomers. According to EPR and FT IR spectroscopy data, during polymerization, a hydrogen atom is detached from monomer units by the growing macroradical or radical of the initiator, resulting in a decrease in the degree of control of the process.

Pseudo-living radical copolymerization of AN with MMA was successfully carried out in the temperature range of 80–99 °C in the reversible inhibition mode involving the known nitroxide SG1 (**1**) obtained from the alkoxyamine BlocBuilder (**2**).[157] The concentration of acrylonitrile in the monomer mixture did not exceed 9 mol.%. The molecular weight of the resulting copolymer mainly composed of MMA units was in the range from 6 to 32 kDa and the polydispersity index was not more than 1.24. The presence of AN units in the copolymer was proven by ^1H and ^{13}C NMR spectroscopy and DSC and thermogravimetric analysis (TGA). The fact that a nitroxide fragment containing a phosphorus atom was present in the copolymer was established by ^{31}P NMR spectroscopy.

Structures 1–3

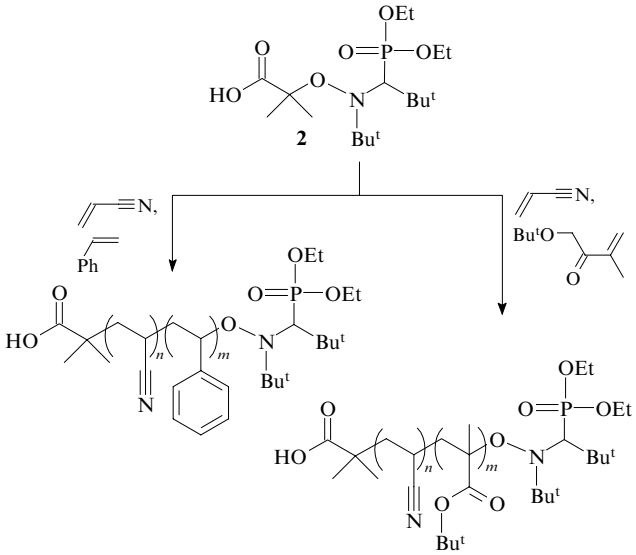


1 (SG1) **2** (BlocBuilder) **3** (NHS-BlocBuilder)

The syntheses of polystyrene and random and block copolymers of styrene and AN in the presence of some alicyclic amines[158] able to generate *in situ* nitroxides, which mediate polymerization, were studied. It was found that both the parent amines and the nitroxides they form upon oxidation with benzoyl peroxide, which acts as both a radical initiator and oxidant, directly influence the polymerization kinetics and molecular-weight characteristics of the copolymers. It was shown that binary compositions based on secondary amines and peroxides provided the most efficient control of polymerization kinetics and molecular-weight characteristics of the product. Copolymerization was not accompanied by gel effect and demonstrated a linear increase in the molecular weight with conversion up to exhaustion of the monomers.

The random copolymers styrene–acrylonitrile and *tert*-butyl methacrylate–acrylonitrile were synthesized by controlled/living reversible inhibition polymerization using the nitroxide SG1 and the alkoxyamines BlocBuilder (MAMA-SG1, **2**) and NHS-BlocBuilder (**3**) in dioxane as the solvent (Scheme 12).[159]

Scheme 12



These compounds, which were first proposed by Tordo and co-workers[160] for reversible inhibition polymerization of vinyl monomers, pertain to most efficient mediators of radical polymerization of MMA and other acrylic monomers. It was shown that the use of SG1 provides a linear increase in the MW with conversion, which is an indication of living polymerization. The polydispersity index of AN–St copolymers formed at 115 °C was 1.14–1.26, while that of AN–*tert*-butyl methacrylate copolymers obtained at 90 °C was 1.23–1.50.

An alkoxyamine containing the SG1 moiety was used as the initiator and the mediator to perform copolymerization of acrylonitrile with 4-vinylpyridine (VP) at 125 °C.[161] Comparison with the results of usual (non-living) radical copolymerization of the same monomers demonstrated that the copolymer obtained *via* reversible inhibition had a narrower MWD and was able to reinitiate polymerization. Using this copolymer containing a nitroxyl group at the end, Poláková *et al.*[161] prepared the AN-b-VP-b-St block terpolymer, which also confirms the living mechanism of polymerization. The structure of the synthesized block copolymers was comprehensively characterized and unambiguously proved by physicochemical methods including IR and NMR spectroscopy.

Yet another example of using alkoxyamines for the synthesis of acrylonitrile copolymers in the living mode has been reported.[162] The authors studied AN copolymerization with styrene and *tert*-butyl methacrylate at 90 °C in dioxane in the presence of alkoxyamine BlocBuilder.

For copolymerization of *tert*-butyl methacrylate with AN, the nitroxide SG1 was additionally introduced into the system. Acrylonitrile–styrene copolymers had a narrow unimodal MWD and low polydispersity indices (1.14–1.26). Also, the polymer MW was found to increase linearly with conversion, indicating living polymerization. The copolymers of acrylonitrile with *tert*-butyl methacrylate also had unimodal and relatively narrow MWD (M_w/M_n = 1.17–1.50). The experimental data were used to calculate the relative reactivities of the monomers: 0.07(±0.01) for AN and 0.27(±0.02) for styrene (Fineman–Ross method) or r_{AN} = 0.10(±0.01) and r_{St} = 0.28(±0.02), respectively (Kelen–Tüdös method). The obtained values were almost equal to the copolymerization constants of these monomers in conventional (non-living) radical copolymerization.[117] Similar trends were found in a study of copolymerization of acrylonitrile with *tert*-butyl methacrylate in the presence of above-indicated nitroxides. In particular, the copolymerization constants of AN and *tert*-butyl methacrylate under experimental conditions are 0.07(±0.01) and 1.24(±0.20) (Fineman–Ross method) or 0.14(±0.01) and 0.89(±0.19) (Kelen–Tüdös method), respectively, which is in good agreement with analogous polymerization parameters of the same monomers in the conventional radical polymerization.

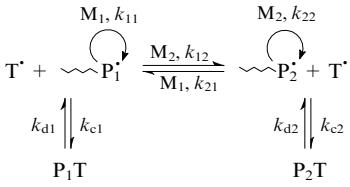
The effect of the penultimate unit on the copolymerization of acrylonitrile with styrene was determined by quantum chemical simulation.[163] In particular, the carbon–oxygen bond dissociation energies for several *N*-alkoxyamines derived from TEMPO were calculated by B3-LYP6-31G(d), B3-LYP/6-311++G(2df,p), UB3-LYP/6-311+G(3df,2p) and IMOMO [G3:ROMP2/6-31G(d)] methods. These *N*-alkoxyamines were studied as models for dormant forms of the propagating chain in the copolymerization of AN with styrene. The terminal and penultimate models were considered and analyzed. The effect of substituents on the bond dissociation energy was estimated and the role of the polar, steric and stabilization factors during oxygen–carbon bond dissociation in alkoxyamines was studied. It was shown that the C–O bond in alkoxyamines containing two successive styrene units in the propagating chain was substantially weakened, which was ascribed to several geometric parameters characterizing the energetically unfavourable conformation of substituents. These findings can be interpreted as the penultimate effect in the controlled/living radical copolymerization of styrene with acrylonitrile.

Comparative analysis of the synthesis of block copolymers of acrylonitrile with n-butyl acrylate by two CLRP procedures was performed, namely, by the ATRP mechanism and nitroxide-mediated polymerization (NMP).[126,164] The authors cited[126] established that the ATRP process was more preferable for controlled/living synthesis of block copolymers. The efficiency of the control was higher when polybutyl acrylate was used as the precursor for block copolymerization than in the synthesis of a similar copolymer using PAN as the macroinitiator. In the researchers' opinion, these features are due to different energies of the carbon–halogen bond being cleaved in this polymers. In the synthesis of the block copolymer of AN with butyl acrylate by reversible inhibition polymerization, effective transition from the poly(butyl acrylate) prepolymer to the block copolymer with acrylonitrile required the use of an excess of nitroxide. However, the synthesis of a similar block copolymer based on PAN as the initial macroinitiator was still less efficient even with excess nitroxide. GPC analysis of the product unambiguously attested to a bimodal MWD and a rather high polydispersity index (~2).

Procedures for the synthesis of AN–styrene, AN–butyl methacrylate and AN–5-vinyl tetrazole block copolymers have been considered in detail.[165–169] Polymerization of these monomers with TEMPO as the reversible inhibitor can be implemented both in bulk and in suspension.[167] The use of nitroxides opens up broad opportunities for macromolecular design. The procedures described in the cited publications[166–169] are suitable for the synthesis of not only diblock copolymers but also triblock copolymers or tetrablock copolymers.[168]

A known[8,12,15] trend in the controlled/living nitroxide-mediated polymerization is the use of nitroxides generated *in situ* from available precursors. This approach was successfully used to prepare acrylonitrile copolymers.[170] In particular, radical homo- and copolymerization of styrene with acrylonitrile at 70 °C in the presence of AIBN as the radical initiator and *N*-*tert*-butyl-*C*-phenylnitrone as the precursor of stable nitroxide radicals was found to exhibit no gel effect with some decrease in the reaction rate, uniform increase in the MW of the polymer and the shift of the unimodal MWD curves toward higher molecular weights following increase in the conversion, and relatively low polydispersity indices (~1.5). The polymer chain propagation is controlled in this case under relatively mild conditions (50–70 °C). For practical purposes, it is especially important that the time it takes to reach a high conversion increases not more than twofold as compared with the process without additives. Considering the obtained experimental data, including kinetic measurements, quantum chemical modelling and EPR spectra, a possible copolymerization scheme was proposed (Scheme 13).

Scheme 13



M_1, M_2 are the copolymerizing monomers;
P_1, P_2 are the propagating radicals of the monomers;
T is the nitroxide; k_{d1} and k_{d2} are rate constants for the dissociation of the adducts P_1T and P_2T; k_{c1} and k_{c2} are the rate constants for the reaction of the propagating macroradicals P_1 and P_2 with the nitroxide T

One more example of using nitroxides generated *in situ* to mediate copolymerization of acrylonitrile was reported by Detrembluer *et al.*[171] They proposed using *N*-*tert*-butyl-α-isopropylnitrone, which can be easily prepared from accessible chemicals, as a source of nitroxides for controlled/living radical homo- and copolymerization of AN and styrene. This method based on the use of nitroxides formed directly in the polymerization system is a good alternative to classical controlled/living nitroxide-mediated radical polymerization in the presence of

TEMPO or SG, which requires a multistage and expensive synthesis of nitroxides or alkoxyamines. Copolymerization of AN with styrene in the presence of this nitrone occurs in the controlled/living fashion and gives a relatively narrow-MWD polymer.

As sources of nitroxides generated *in situ* and mediating (co)polymerization of acrylonitrile, not only nitrones [158, 170, 171] but also nitroso compounds can be used. In particular, we found [172] that styrene and acrylonitrile copolymerization in the presence of nitrosodurene proceeds in the controlled/living fashion. The gel effect is degenerated in this case and the intrinsic viscosity and the molecular weight of the samples linearly increase with increase in the conversion. Meanwhile, copolymers prepared without addition of nitrosodurene are subject to spontaneous uncontrolled increase in the molecular weight with conversion. The MWD curves of the copolymers showed a shift towards higher molecular weights typical of the controlled/living polymerization. However, polydispersity of the copolymers somewhat increases with conversion, although it is still considerably lower than the polydispersity of copolymers synthesized using a radical initiator without addition of the nitroso compound.

As follows from analysis of the above data, controlled/living synthesis by the nitroxide-mediated reversible inhibition mechanism is efficient only for AN-based copolymers and is not virtually used for AN homopolymerization.

* * *

Detailed analysis of the published data surveyed in the review on the deliberate control of polymerization kinetics and molecular-weight characteristics of homo- and copolymers based on acrylonitrile unambiguously demonstrates that controlled/living radical polymerization is a powerful tool for targeted synthesis of polyacrylonitrile as a precursor of high-quality high-strength carbon fibre. Living atom transfer radical polymerization is the most efficient method for the preparation of acrylonitrile-based polymers with desired molecular-weight characteristics including narrow MWD. Of special interest is the use of lanthanide compounds, in which, as in copper, iron and ruthenium complexes, the metal oxidation state can reversibly change and this can serve for the controlled synthesis of polymers with low polydispersity ($M_w/M_n < 1.2$). Furthermore, derivatives of these metals including lanthanides can affect not only the molecular-weight parameters of homo- and copolymers of acrylonitrile but also the stereoregularity of macromolecules, thus promoting the synthesis of high-molecular-weight samples with enhanced syndiotacticity. According to published data,[3, 114, 173–175] acrylonitrile-based homo- and copolymers with particularly such characteristics are most promising and demanded as precursors of high-strength carbon fibres and carbon fibre reinforced plastics.

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