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Environmental aspects of controlled radical polymerization

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SUMMARY: Controlled radical polymerization is an important recent development in polymer synthesis with a potential strong impact on various environmental aspects. This technique enables facile preparation of novel environmentally friendly materials such as polar thermoplastic elastomers, coatings with the reduced amount of VOCs or even solventless coatings and several other specialty materials such as efficient non-ionic surfactants, dispersants, lubricants, adhesives, etc. The controlled radical polymerizations have been successfully performed in bulk or in water and require only a modest deoxygenation of the reaction mixtures. These polymerizations have been applied to homogeneous systems and also to emulsions, dispersions and suspensions. Atom transfer radical polymerization is one of the most efficient methods to control radical polymerization in the presence of various transition metal complexes. Development of new more efficient catalytic systems enables reduction of the amount of catalysts and their recycling. Use of ligands which better stabilize higher oxidation state metal compounds, such as linear and branched aliphatic polyamines, allowed a significant reduction of the catalyst concentration in comparison with the originally used bipyridine complexes. Immobilization of catalysts enables their efficient reclamation but is accompanied by the formation of polymers with higher polydispersities than in the homogeneous systems.

Introduction

Controlled radical polymerization (CRP) has recently become one of the most rapidly developing areas of polymer science1) . This can be ascribed to the possibility of controlling architectures, compositions and functionalities for various polymers and copolymers under undemanding reaction conditions. Polymers with degrees of polymerization predetermined by the ratio of concentrations of the reacted monomer to the introduced initiator and with low polydispersities have been prepared from a variety of different monomers which include styrenes, acrylates, methacrylates, dienes and other alkenes. Radicals are tolerant to

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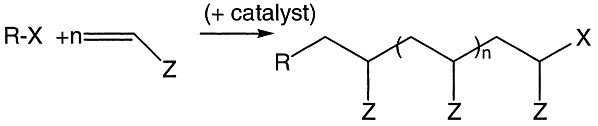
the presence of many functionalities and CRP may be carried out with monomers containing unprotected alcohol, acid or amino groups. In addition, facile cross-propagation enables synthesis of many copolymers not only with random but also with gradient and blocky structures. The controlled polymerizations have been performed in solution, in bulk or in water and require only a modest deoxygenation of the reaction mixtures. CRPs have been applied to homogeneous systems and also to emulsions, dispersions and suspensions. This paper discusses three general environmental aspects of CRPs and will focus primarily on the atom transfer radical polymerization (ATRP). The first area is related to a synthesis of new environmentally friendly materials such as thermoplastic elastomers, solventless coatings and non-ionic surfactants. The second topic covers reduction of the VOCs and polymerizations carried out in aqueous media, in bulk and in liquid carbon dioxide. The third topic is more specific for ATRP and describes recent progress in development of more efficient catalysts and their potential recycling.

Results and discussion

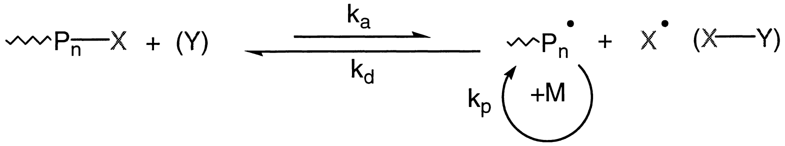
Controlled radical polymerization

Controlled radical polymerization resembles in many aspects living polymerizations in which molecular weights grow linearly with conversion and molecular weight distributions (MWD) are close to Poisson distribution[2]. End groups in the obtained polymers are defined by the structure of the initiator used and can incorporate many functionalities:



(1)

Formally, chain growth can be described by the monomer insertion between R-X bond but in reality it proceeds via radical intermediates and more than one monomer unit can be added at the radical stage.

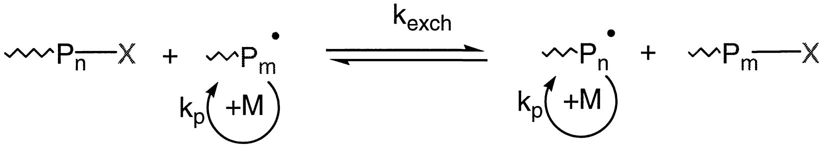


(2)

Currently there are three CRP systems, which seem to be most successful. They include CRP mediated by nitroxides (e.g. X=TEMPO and no catalyst, Y, is required)[3, 4], by the transition metal catalyzed ATRP process (X=halogen and Y=transition metal compound complexed by the corresponding ligand)[5, 6], and by the degenerative transfer [7, 8] which requires continuous flux of radicals provided by conventional initiators.

The equilibrium constant for the TEMPO mediated styrene polymerization is $K=k_a/k_d=10^{-11}$ mol/dm^3 at 120 °C,[9, 10] whereas it is $K=10^{-7}$ at 120 °C for styrene ATRP with X=Br and catalyzed by CuBr complexed by two 2,2'-bipyridine molecules (Y)[11]. Obviously, polymerization rate depends on K and the catalyst concentration. More powerful catalysts (larger K) can be used in smaller concentrations but can still provide sufficient polymerization rates.

The equilibrium constant for the degenerative transfer is by default equal K=1[12]. From the point of view of control, a very important parameter is the number of monomer units added during one activation stage which is defined by the ratio of the propagation rate to that of deactivation (k_d in eq. 2) or exchange (k_{exch} in eq. 3) [13].



(3)

Styrene polymerizes relatively slowly (propagation rate constant is $k_p=2040$ mol^{-1}dm^{3}s^{-1} at 120 °C) [14]. Under typical conditions, during one activation step, only a few monomer units are added for TEMPO mediated systems, less than one for ATRP and degenerative transfer mediated by dithioesters (so called RAFT process, reversible addition fragmentation chain transfer) [8] but more than ten units for the degenerative transfer mediated by alkyl iodides [12, 15].

In polymerization of acrylates usually more units are added because propagation rate constants are nearly two orders of magnitude larger than for styrene[16]. Thus, currently ATRP and RAFT can, but TEMPO can not, be used for preparation of well-defined polyacrylates [8, 17].

New materials by controlled radical polymerization

The Figure 1 shows examples of some polymeric structures prepared by ATRP and some other CRP methods[18].

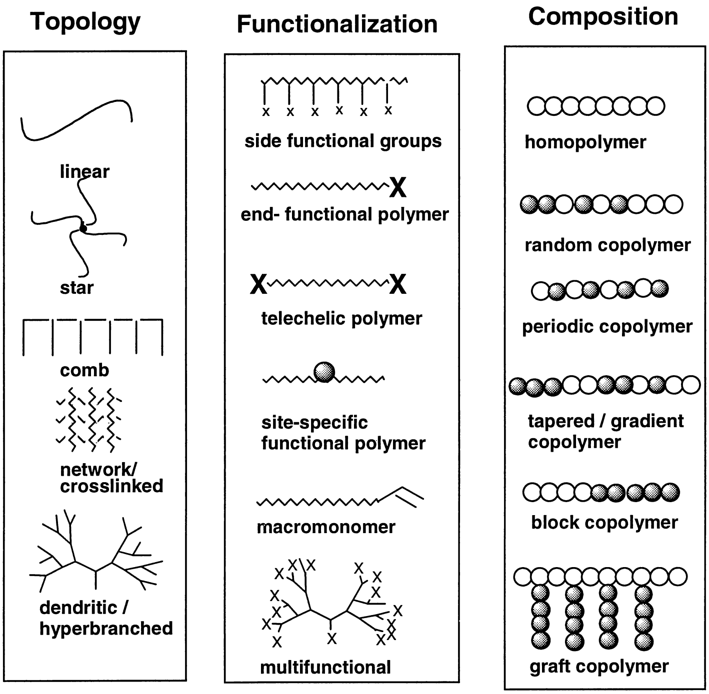


Fig. 1: Materials prepared by controlled radical polymerization

The majority of these structures have been already prepared by anionic and cationic methods but have required very stringent reaction conditions (very low level of moisture, use of large amounts of organic solvents and subambient temperatures; T<-70 °C) and were limited to non-polar alkenes[19, 20]. CRP enables much larger range of monomers and can be easily carried out in bulk and at convenient range of temperatures.

The control of the macromolecular structures can be grouped into three categories: chain topology (architecture), functionality and composition. CRP has been used successfully to prepare linear chains, which can grow in one or in two directions, as well as to synthesize nonlinear chains with either regular multiarmed and comb-like structures or with irregular branched/hyperbranched structures. The non-linear chains have much smaller hydrodynamic volumes than the linear analogs with the same molecular weights. Therefore, they have lower melt viscosities and can be more easily processed. It is expected that some hyperbranched polymers with controlled chain end functionalities can be used directly as coatings without organic solvents[21)]. Such solventless acrylate-based coatings can revolutionize the coatings industry, especially in the automotive areas.

Control of end functionalities is very important for low molar mass oligomers, which are used not only as components of coatings but also as adhesives, surfactants, dispersants and lubricants. CRP allows for incorporating functionality into each macromolecule by using inexpensive functional initiators. Potentially, the other chain end can be also functionalized. This enables preparation of various telechelics with identical and/or different structure of end groups which may be hydrophilic, hydrophobic or carry some additional special features and can be well suited for non-ionic surfactants and lubricants[22)]. It has been possible to incorporate functionality in the center of a macromolecule by using multifunctional initiators as well as the outer part and "decorate" in this way hyperbranched polyacrylates with azide, hydroxide and epoxy groups. Finally, macromonomers have been prepared using functional initiators and subsequently copolymerized to form graft copolymers.

The relatively low values of reactivity ratios in radical systems contrast the large values found for ionic systems. Therefore, it has been possible to prepare a multitude of controlled copolymers by CRP. It has to be stressed that all of the copolymers made by simultaneous CRP are different from those prepared by conventional RP, unless under azeotropic conditions. In conventional free radical polymerizations, the faster consumption of one monomer results in a distribution of comonomer compositions among the polymer chains. That is, the polymer chains have varying amounts of comonomers; some contain more monomer A, while some others more monomer B. The distribution of compositions arises from the continuously changing monomer feed in the polymerization system as one monomer is consumed faster than another is. In CRP all of the polymer chains grow at nearly the same rate and do not terminate. Therefore, the change in monomer feed composition is recorded in each individual polymer chains resulting in variation of monomer concentration along the polymer chain. Examples of these polymers are the Sty/BA, Sty/AN, Sty/MMA, MA/MMA, and Sty/MA 23-26). If one comonomer can not homopolymerize radically but is used in sufficient excess, alternating structures has been formed, for example in the copolymerization of acrylates with isobutene 27).

Block copolymers are polymers, which consist of two or more monomers that are segregated into regions of the polymer chain, but are covalently bound to each other. The simplest method to prepare block copolymers is by sequential addition of monomer B to a "living" polymer comprised of monomer A. ATRP has been used in such a manner to prepare block copolymers of radically polymerizable monomers 28). It is, however, important to add monomers in the order corresponding to their decreasing overall ATRP reactivity: MMA>S≈MA. It is possible to utilize the concept of halogen exchange if the order of addition of monomers should be reversed 29).

Block copolymers have novel physical/mechanical properties when the polymer segments have different characteristics, i.e., hard/soft, polar/non-polar, hydrophilic/hydrophobic, i.e. amphiphilic copolymers. There are several water-soluble polymers, which have been polymerized by ATRP and other CRPs: 2-hydroxyethyl acrylate 30) and methacrylate 31), 2- and 4-vinylpyridines 32), and 2-dimethylaminoethyl methacrylate (DMAEMA)33). The hydrophilic blocks were combined with a variety of hydrophobic blocks 34). For example, poly(methyl acrylate) was prepared (M_n=24 100; M_w/M_n=1.15) as a macroinitiator for the polymerization of DMAEMA. The second block was polymerized using the copper(I) bromide/linear tetraamine catalyst in a 1:1 molar ratio with the poly(methyl acrylate) at 90 °C to form the block copolymer with M_n=39 200 and M_w/M_n=1.15, cf. Fig.2 below.

Triblock copolymers have also been prepared by ATRP by using the described above diblock copolymers as macroinitiators followed by the addition of the third segment (A->AB->ABA), or using a difunctional initiator. In the latter case, the polymer chain grows in two directions, thus allowing for the central B block to be prepared first. This macroinitiator is then used to polymerize the outer A blocks (B->ABA). This strategy assures that the resulting polymer is symmetrical and saves a step in the polymerization process.

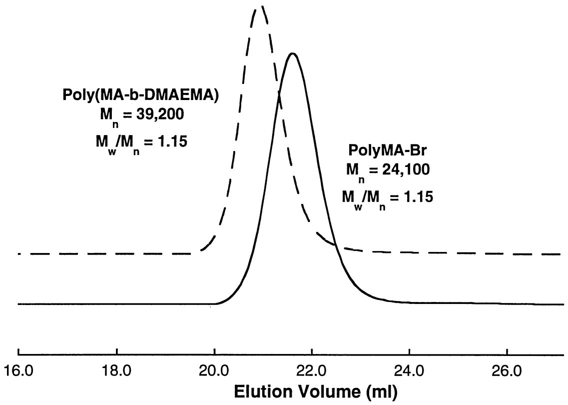


Fig.2: SEC traces of poly(methyl acrylate) macroinitiator and poly(methyl acrylate-*b*-DMAEMA)

The synthesis of a triblock copolymer was accomplished with bis(2-bromopropionyloxy)-ethane as an initiator to prepare a difunctional polyMMA macroinitiator and then using it to initiate the polymerization of DMAEMA. The SEC traces of the polyMMA macroinitiator (M_n=33 000; M_w/M_n=1.17) and the poly(DMAEMA-*b*-MMA-*b*- DMAEMA) (M_n=69 300; M_w/M_n=1.24) are illustrated in Fig. 3.

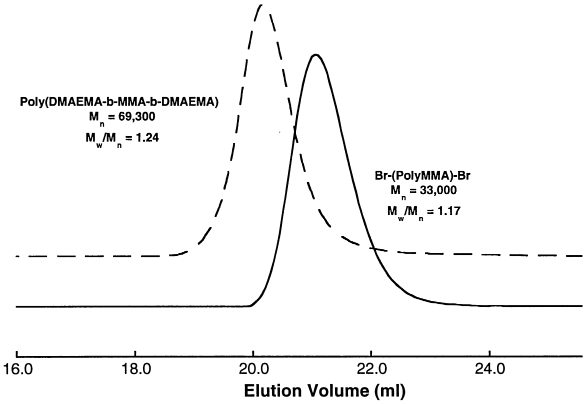


Fig. 3: SEC traces of the difunctional poly(MMA) macroinitiator and resulting triblock copolymer, poly(DMAEMA-*b*-MMA-*b*-DMAEMA)

Special features of bulk controlled radical polymerizations

Bulk controlled radical polymerization behaves differently from bulk conventional process. The most important difference is perhaps a much smaller contribution of the Trommsdorf (gel) effect 35). In conventional radical polymerization, the first order kinetics in monomer observed at low monomer conversion indicates a constant concentration of growing radicals. This stationary concentration is achieved by balancing slow initiation with termination by coupling/disproportionation between either two growing chains or a growing chain and a newly formed radical. As polymerization continues, monomer is consumed, and the viscosity increases due to progressively higher polymer concentrations. In some cases when the polymerization temperature is below the glass transition temperature of the formed polymer, vitrification can be observed resulting in incomplete monomer conversion due to a glass formation. Under such conditions propagation rate constants decrease but termination rate constants decrease even more. A significant reduction of the termination rate, in comparison with initiation may result in an increase in the concentration of radicals, acceleration of the polymerization and the Trommsdorf or gel effect. This effect may lead to an uncontrolled polymerization when the heat transfer becomes inefficient. The imbalance between termination and initiation rates originates in the increase of viscosity, but it is progressively enhanced with temperature (energy of activation of initiation is much higher than that of termination).

In controlled radical polymerizations, the stationary concentration of radicals is established not due to the balance between rates of termination and initiation but due to a balance between rates of activation and deactivation. In ATRP, both bimolecular reactions include the polymer chain end and low molar mass species [activator Cu(I) and deactivator Cu(II), respectively]. Both reactions should be affected by viscosity in the same way and similar to propagation, which also involves low molar mass monomer. It may happen that at the very end of the reaction, the diffusion control limit is significantly reduced and deactivation will become slower but this effect should be much smaller than in the case of termination between two growing polymer radicals. It has been reported that the rate constant of termination is strongly chain length dependent 36). At high conversion, the value of the termination rate coefficient between two macroradicals may be as low as $k_t \approx 10^2$ $mol^{-1} \cdot dm^3 \cdot s^{-1}$ though a small radical/deactivator may react much faster, with $k_d \approx 10^7$ $mol^{-1}.dm^3 \cdot s^{-1}$. Thus, the main reason for the absence of the

Trommsdorf effect in both ATRP and nitroxide [37)] mediated bulk polymerization is that rates of both propagation and deactivation are affected in a similar way by changes of viscosity.

Additional peculiarities of bulk CRP include a progressive change of viscosity of the reaction mixture due to the continuous removal of the solvent (monomer) and its conversion to polymer as well as an increase of molecular weights with conversion. Termination occurs between chains of nearly the same length, which scales linearly with conversion. Thus, initially termination is much more important than at higher conversion.

Controlled radical polymerization in water

CRP can be carried out in water either under homogeneous or heterogeneous conditions. Both reactions are sometimes simple and straightforward, other times difficult. The reason for this is that the polar nature of the medium used to conduct the polymerization may shift the equilibrium in uncontrolled directions, resulting in higher (or lower) radical concentrations and/or selective extraction of the catalyst to the aqueous phase.

Homogeneous aqueous polymerization

2-Hydroxyethyl acrylate (HEA) was polymerized both in bulk and in aqueous solution with methyl 2-bromopropionate (MBrP) as the initiator and with Cu(I)Br complexed with two equivalents of 2,2'-bipyridine (bpy) as the catalyst [30)]. The bulk polymerization obeyed first order kinetics with respect to monomer to 90 % conversion and the molecular weights of the growing polymer increased with conversion, although they were higher than predicted by $DP_n=\Delta[M]/[I]_o$ and the polydispersity of the growing polymer decreased with conversion to a final value of $M_w/M_n=1.2$.

The polymerization has also been carried out in water. Using a 50/50 mixture of water and monomer, by volume, the polymerization was conducted at 90 °C, with a ratio of monomer to initiator of 100:1; the catalyst was in a 1:1 ratio with initiator. After 12 hours, the polymerization had reached 87% conversion and the molecular weight, as determined by SEC in DMF, was $M_n=14\,700$; $M_w/M_n=1.3$. In all of the polymerizations, the hydroxyl groups appeared to be unaffected during the polymerization (as observed by NMR).

Controlled radical polymerization in emulsion

Recently ATRP has been carried out successfully in emulsion [38)]. The stability of emulsion and control of molecular weights and polydispersities require careful selection of reagents and reaction conditions. The best results are obtained with non-ionic surfactants such as Brij, Tween or even poly(ethylene oxide) and with ligands which assure sufficient solubility of the catalyst/deactivator in the organic phase. Thus, bipyridyls and oligoamines with long alkyl substituents are necessary. Initiator of appropriate solubility in the aqueous phase should be used and added as the last component. If all of the conditions are carefully controlled, polymerization of styrene, butyl acrylate and butyl methacrylate is well controlled resulting in polymers with low polydispersities ($1.05<M_w/M_n<1.3$) and molecular weights slightly higher than theoretically predicted for the quantitative initiation38). Stable emulsions have been prepared with particles size in the range 0.2 nm to 2 nm and relatively low size distribution (<1.5).

Controlled radical polymerization in CO_2

Successful CRP in CO_2 requires sufficient solubility of the catalytic mixture in the reaction mixture. Thus, 2,2'-bipyridyls with fluorinated 4,4' substituents (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) were used to dissolve complexes of both CuBr and $CuBr_2$ species. Using this catalytic system, homopolymers of pentadecafluorooctyl acrylate (FOA) and methacrylate (FOMA) as well as diblock and triblock copolymers with MMA were successfully prepared, polyFOA: M_n=12 000; poly(MMA-b-FOA-b-MMA): M_n=16 900 and polyFOMA M_n=19 000; poly(FOMA-b-MMA) M_n=25 400 39).

In addition, a successful dispersion polymerization of MMA was carried out using the same catalytic system and poly(heptadecafluorodecyl acrylate) as a dispersion stabilizer. PMMA with M_n=21 000 and M_w/M_n=1.15 was formed as a colorless free flowing powder.

Towards more efficient ATRP catalysts

There are several approaches to improve a catalytic system for ATRP. The basic requirements for the good catalyst include high chemoselectivity, meaning that the catalyst should be involved in the fast, reversible inner sphere electron transfer process but should not participate in the formation of organometallic species, in the outer sphere electron transfer (OSET) processes and in the β-hydrogen abstraction. Better catalysts should form more radicals, meaning that they can be used at lower concentrations to provide the same rate of polymerization. The increase of the equilibrium constant can be accomplished either by the reduction of the rate constant of deactivation or the increase of the rate constant of activation. The first pathway will also enhance polydispersities and therefore the second pathway is preferred.

The improvements in the catalytic system can be approached by changing the transition metal compound, ligand, additive and/or the reaction medium. Additionally, immobilization of the catalyst may facilitate its removal and recycling.

It seems that copper-based catalysts are among most efficient from the point of view of rates, selectivities and cost. The replacement of originally used bipyridyls 5) and substituted bipyridyls40) with linear polyamines such as N,N,N',N",N"-pentamethyldiethylenetriamine 41) and the corresponding heptamethyltriethylenetetramine allowed to reduce nearly ten fold the amount of the catalyst under similar conditions and also reduced the cost of the ligand and color of the reaction mixtures. Most recently, the application of hexamethylated TREN as a ligand for methyl acrylate allowed for preparing well-defined polyacrylates at room temperature with less than 0.1 mol % catalyst 42).

The small addition of metal in the zero valency enables a greater tolerance towards oxygen and radical inhibitors. The Cu(0) reduces the corresponding Cu(II) species via OSET and accelerates polymerization as well as enables using smaller amounts of ligands in the polymerization 43).

The catalyst have been immobilized on solid inorganic (silica) and organic supports (various types of crosslinked functionalized resins). Although in some cases molecular weights can be relatively well controlled, polydispersities are higher than in the homogeneous systems ($M_w/M_n > 1.5$). For example, using aerosil with the immobilized diethylenetriamine as a complexing agent for CuBr in the bulk polymerization of styrene initiated by 1-phenylethyl bromide (molar ratios 4:4:480:1) 40 % monomer conversion was obtained after 20 hours at 90°C, molecular weights were close to predicted for quantitative initiation (M_n=18 900, $M_{n,th}$=18 800) but the polydispersity was high (M_w/M_n=4.76). Better results were obtained using crosslinked polystyrene as a support for CuBr complexed by immobilized bis(2-pyridylmethyl)-2-hydroxyethylamine. Using additional amount of $CuBr_2$ as a deactivator and methyl 2-bromopropionate as initiator in the bulk polymerization of MA at 90°C (molar ratios 0.25:1:0.75:1:230), a polymer with M_n=26 700 ($M_{n,th}$=13 400) and polydispersity M_w/M_n=1.62 was obtained in 67 % yield after 15 hours 44). In all systems, a clear polymer solution was observed after decantation or filtering through 0.45 μm filter. The potential improvements in the immobilization technique include resins with higher swellability, spacers which decouple catalytic sites from the solid support, better design of ligands and better mixing processes.

Polymers prepared by ATRP carry halogen atoms at the chain end. These halogens have been replaced by nucleophiles via the corresponding substitution with azides, phosphines and amines, as well as via electrophilic and radical addition reactions 22, 45). In such a way polymers with terminal hydroxy, amino, allyl, epoxy and other useful functionalities were prepared.

Conclusions

Controlled radical polymerization is an important recent development in polymer synthesis with a potential strong impact on various environmental aspects. This technique enables the facile preparation of novel, environmentally friendly materials such as polar thermoplastic elastomers, coatings with reduced amounts of VOCs or even their entire elimination and several other specialty materials such as efficient non-ionic surfactants, dispersants, lubricants, adhesives, etc. Controlled radical polymerizations have been successfully performed in bulk or in water and require only a modest deoxygenation of the reaction mixtures. These polymerizations have been applied to homogeneous systems and also to emulsions, dispersions and suspensions. Atom transfer radical polymerization is one of the most efficient methods to control radical polymerization in the presence of various transition metal complexes. Development of new more efficient catalytic systems enables reduction of the amount of catalysts use and their recycling. Use of ligands which better stabilize higher oxidation state metal compounds, such as linear and branched aliphatic polyamines, allowed for a significant reduction of the catalyst concentration with the originally used bipyridine complexes. Immobilization of catalysts enables their efficient reclamation but is accompanied by the formation of polymers with higher polydispersities than in the homogeneous systems.

Acknowledgments

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