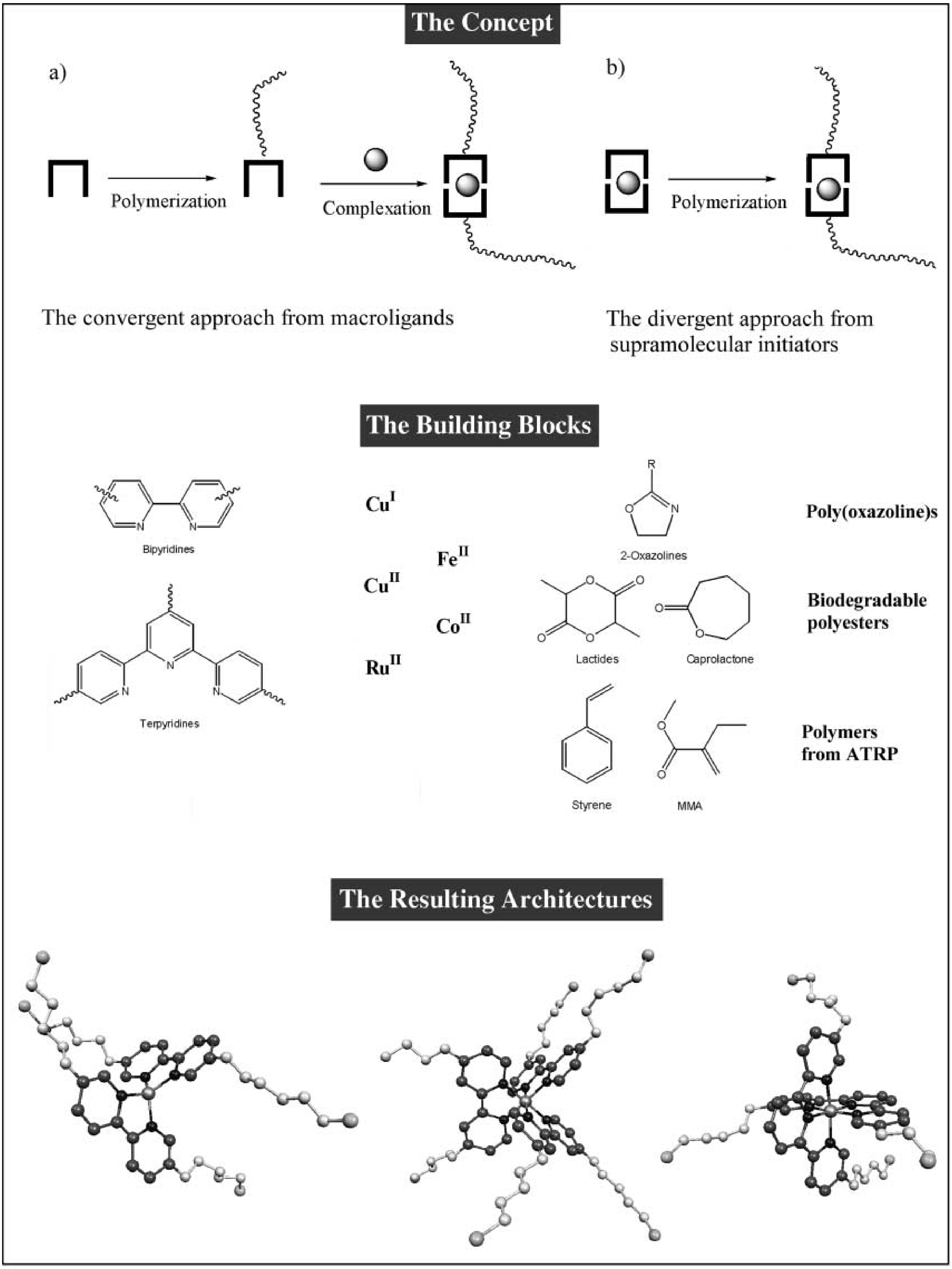
The Concept
a)
Polymerization
Complexation
b)
Polymerization
The convergent approach from macroligands
The divergent approach from supramolecular initiators
The Building Blocks
Bipyridines
Terpyridines
N
Cu^{I}
Fe^{II}
Cu^{II}
Co^{II}
Ru^{II}
R
O
2-Oxazolines
Lactides
Caprolactone
Styrene
MMA
Poly(oxazoline)s
Biodegradable polyesters
Polymers from ATRP
The Resulting Architectures

Metallo-Supramolecular Initiators for the Preparation of Novel Functional Architectures

Ulrich S. Schubert*[a] and Marcel Heller[b]

Dedicated to Prof. Dr. Max Herberhold on the occasion of his 65th birthday

Abstract: Polymeric materials containing coordinative units have become a field of increasing interest. The combination of inorganic metal-containing units and macromolecules leads to supramolecular structures with new properties. One promising approach to such systems is the application of metallo-supramolecular initiators for living and controlled polymerization methods. The utilization of bi- and terpyridine units and complexes for this purpose will be discussed in this article.

Keywords: bipyridine · initiators · polymerization · supramolecular chemistry · terpyridine

Introduction

In order to obtain materials for novel fields of application, the incorporation of metal complexing units into macromolecular structures is of central interest. Ordered architectures are formed and held together by coordinative interactions. Polymer chemistry provides the opportunity for specifically designing material properties by the use of selected monomers, different functionalities, and combinations. The coordinative binding sites contribute to the typical properties of inorganic metal complexes. One of the aims pursued is the "switching" of material properties (e.g. absorption/emission, viscosity, adhesion) by changing electrochemical, thermal, or pH conditions. There are several ways to integrate metal complex units into polymers (Scheme 1).[1] In this context, bi- and terpyridine transition metal complexes are of special interest as a result of their multifaceted properties in the fields of catalysis,[2–6] photo-[7, 8] and electrochemistry.[5, 6, 9] Resulting applications for such supramolecular compounds can be imagined in opto-electronics and in medicine for targeted drug delivery or imaging. Surface functionalization could lead to "smart" sensing or adhesive materials.

Bi- and terpyridine units have been introduced into the side chain of polymers by either grafting procedures[10, 11] or from utilizing bi-[12, 13] or terpyridine[14] -functionalized monomers for block copolymerizations. Another way to produce macromolecules containing bi- and terpyridines is to make the ligands part of the backbone. For this purpose, *bis*functionalized bipyridine monomers can be polymerized by means of coupling procedures—for example, Heck-[15] and Stille-type coupling techniques[16]—or polycondensation reactions.[17–19] A possibility for synthesizing well-defined polymers with terminal ligand functionalities is to introduce bi-[20] or terpyridine[21, 22] units into functionalized polymers like poly(ethylene oxide)s. Coordinative units can be utilized as initiators for different kinds of living polymerization methods. This approach offers a controlled and stoichiometric functionalization of the polymer chain ends with the discussed ligands. In addition, molecular weight and architectural control as well as narrow polydispersities can be obtained. In this initiator concept, two alternative ways are possible to create metal-complexed supramolecular polymers. The "convergent" approach utilizes the uncomplexed ligands as initiators to yield polymers with metal complexing units. The other option is a "divergent" route starting from "metallo-supramolecular" initiator complexes and leading to already complexed polymer architectures (Scheme 2).

This article will provide an overview of supramolecular initiator systems based on bi- and terpyridines. Different living polymerization techniques and the resulting macroligands and polymer complexes are presented. In historical order, poly(oxazoline)s will be discussed first, followed by polyesters and the application of atom-transfer radical polymerization (ATRP). Finally, possible future trends are discussed.

For the sake of completeness concerning the utilization of metal-complex initiator systems, we shall mention the polymerization of isocyanides by nickel(II) salts, performed by

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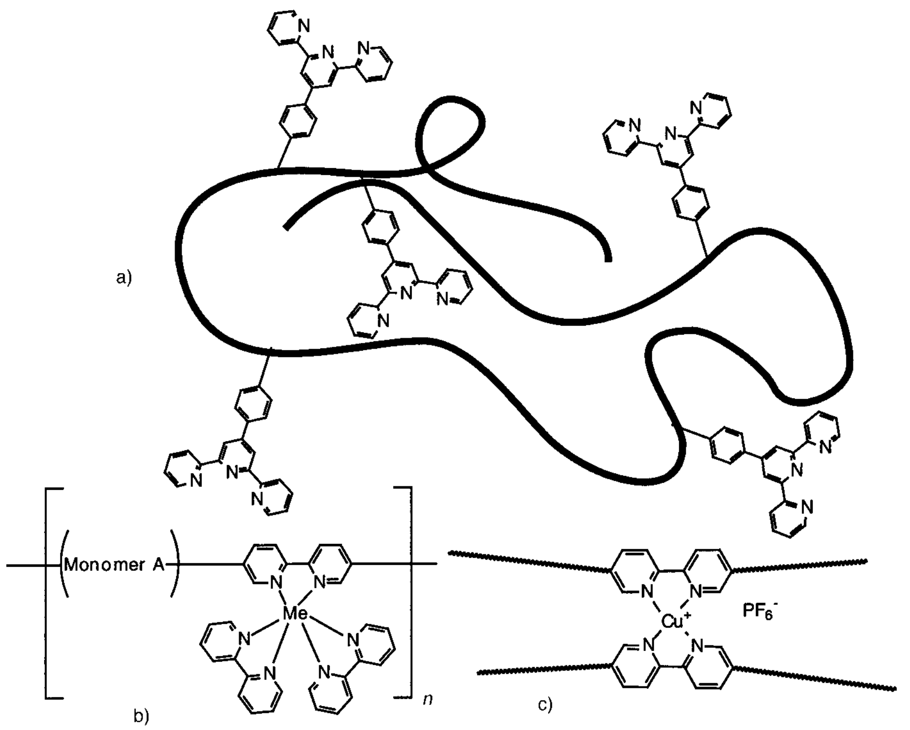
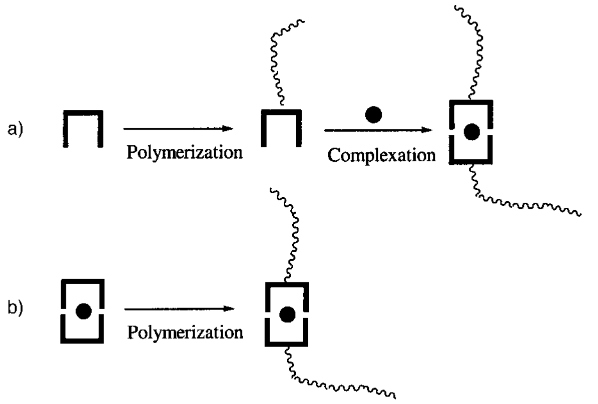
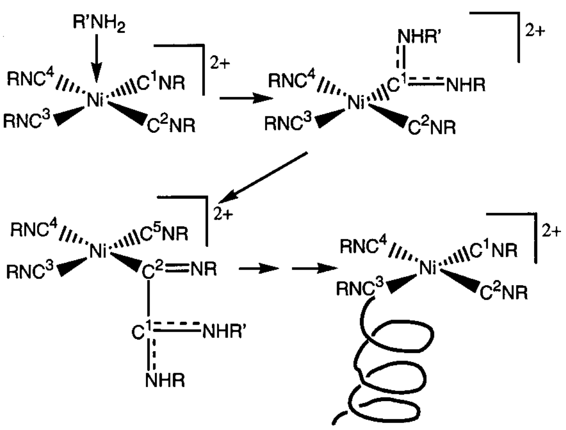


Scheme 1. Different ways of introducing ligands into polymers: a) terpyridine units in the side chain; b) repeating bipyridine units in the backbone; c) single bipyridine units in the backbone (Me = metal ion, n = number of repeating units).



Scheme 2. Two ways to supramolecular polymers: a) "convergent" route; b) "divergent" route.

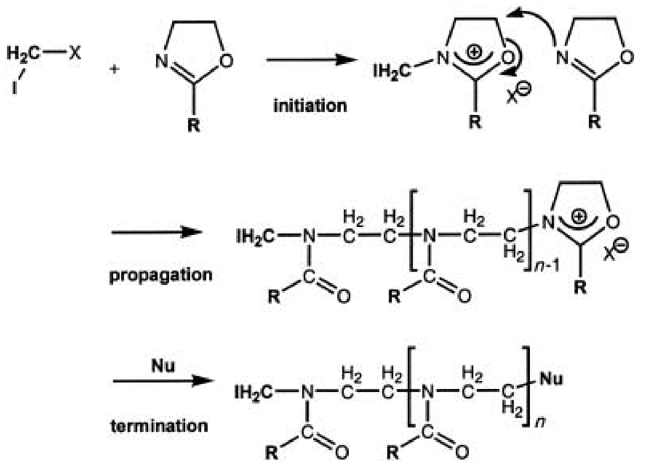


Scheme 3. Polymerization of chiral isocyanides with $NiCl_2$ and "co-initiator"-amine $R'NH_2$ (see ref. [25], R, R' = different chiral or achiral groups).

Nolte et al.[23, 24] The reaction starts from a nickel–isocyanide complex (Scheme 3). The first added "co-initiating" nucleophile becomes the chain-end functionality of the polymer formed. By the use of a chiral initiator or chiral isocyanide monomers, left- or right-handed helices can be obtained. Such helical polymers have well-defined structures and can be prepared from a great variety of amines and amino acids (see also ref. [25, 26]).

Metallo-supramolecular initiators for 2-oxazoline polymerization: Poly(oxazoline)s are accessible by living cationic ring-opening polymerization. Variation of the substituents in the 2-position of oxazolines leads to polymers with strongly differing properties (Scheme 4). Short alkyl chains (Me, Et) ensure outstanding solubility in polar solvents such as water and alcohols. Such polymers can be also interpreted as DMF/DMAc (dimethylformamide/dimethylacetamide) polymer analogues; they are easily dissolved in chloroform or acetonitrile. In addition, they can be used as powerful hydrophilic segments of nonionic surfactants. Poly(oxazoline)s with longer alkyl chains in the 2-position (nonyl, undecyl) possess hydrophobic properties. Block copolymers, for example, with polar and perfluorinated functionalities, are used as water soluble, surface active agents.[27] Possible applications include hydrogels, adhesives, surfactants, and drug-delivery systems.[28] In the following two sections, the use of different metallo-supramolecular initiators for the living cationic polymerization of oxazolines will be described based on bipyridine and terpyridine units.

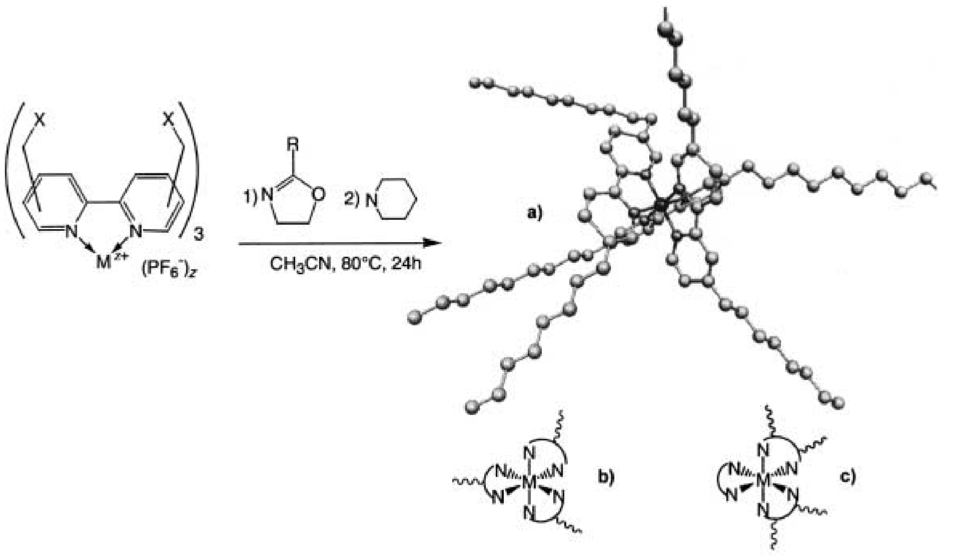
Bipyridine initiating systems: Bipyridine based systems are the most investigated metallo-supramolecular initiators for the polymerization of oxazolines. For this purpose, different substituted bipyridines (4,4'-, 5-, and 6,6'-, synthesized by efficient Negishi-[29] and Stille-type[30] cross-coupling procedures), different functional groups (chloro, bromo, and iodomethyl), and metal ions (iron(II), copper(I), cobalt(II), and ruthenium(II)) were used. The metallo-supramolecular initiators were utilized to polymerize different 2-oxazolines (2-methyl, 2-ethyl, 2-nonyl, 2-undecyl, and 2-phenyl) in acetonitrile at 80–110 °C within 1–2 days. After termination, washing, and re-precipitation, starlike metal-centered poly(oxazoline)s were obtained (Scheme 5).



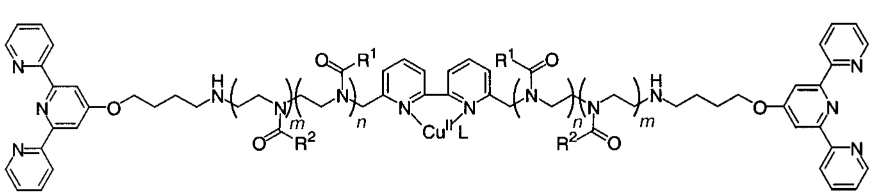
Scheme 4. Cationic ring-opening polymerization mechanism of 2-oxazolines. I = initiator rest; X = Cl, Br, I; R = for example, alkyl chain; Nu = nucleophilic group; n = number of repeating units.

A living polymerization mechanism could be verified for all combinations (except phenyloxazoline, see also ref. [31]). The molecular weight of the polymers correlated directly with the expected stoichiometric values, the molecular mass distributions were monomodal and narrow (polydispersities of 1.04 to 1.35), and the plots of the molecular weight versus [monomer]/[initiator] ratios showed a linear correlation.[21, 32, 33] More detailed kinetic investigations on polymer iron(II) complexes[33] indicated linear progression of the first-order kinetics plots (monomer conversion versus time, determined by ^{1}H NMR spectroscopy). This living character of the oxazoline polymerizations offers the possibility of a well-defined termination with different nucleophilic groups (typically piperidine and dipropylamine) and therefore of an additional functionalization of the polymer chain ends. For example, a poly(ethyloxazoline) polymerization could be terminated by using a 4′-piperidine-functionalized 2,2′:6′,2″-terpyridine unit; the termination results in a system which contains two different types of metal binding sites (Scheme 6).[34] Since bipyridines (contrary to terpyridines) are able to chelate copper(I) to form tetrahedral complexes, these molecules are able to act as specific *bis*functional ligands. In addition, the living polymerization features can be utilized for the preparation of block copolymers. After the complete polymerization of monomer I, another oxazoline monomer (II) can be added. The living cationic chain end will continue propagation with the new monomer. Fraser et al. showed on the basis of 4,4′-*bis*(chloro)-functionalized 2,2′-bipyridine iron(II) complexes with NaI (iodide conversion according to Kobayashi[35]) that 2-ethyloxazoline is the most useful monomer to act as the first polymer block because the blocks stay active, and the reaction proceeds smoothly to completion.[36] As a second block poly(phenyloxazoline) or poly(undecyloxazoline) are suitable revealing defined systems with molar masses up to 40 000 dalton (after decomplexation, see below). Other AB blocks like (poly(ethyloxazoline)-*block*-poly(nonyloxazoline) have been prepared with 6-*mono*(bromo)- and 6,6′-*bis*(bromo)-functionalized 2,2′-bipyridine copper(I) complexes as initiators.[37]

Besides the utilization of complexed bipyridines as initiators, it would also seem logical to use the pure ligands for this purpose as well. By this approach, poly(oxazoline)s with narrow polydispersities could be obtained as well, but a higher molecular weight shoulder was always detected in the GPC (gel permeation chromatography).[31, 38] One possible explanation is that nucleophilic bipyridine nitrogens are capable of end-capping reactions (by the formation of pyridinium salts[39]). Another reason for the described phenomenon, discussed by Fraser, is chain transfer and subsequent repolymerization effects, which would also lead to higher polymer masses. Finally, poor initiator efficiency of the ligands compared with the complexes can be discussed. In the complexed supramolecular initiators, the complexing



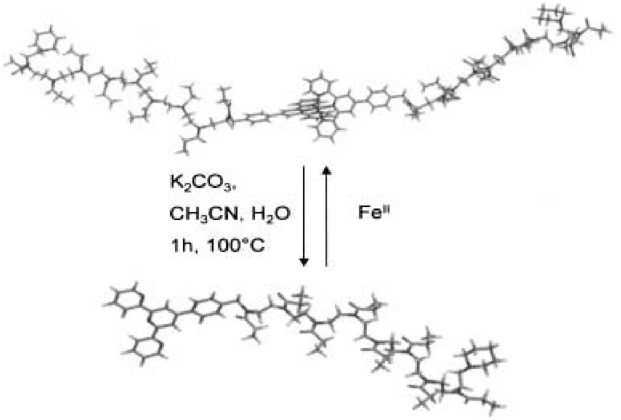
Scheme 5. Polymerization of oxazolines by using supramolecular bipyridine initiators (X = Br, Cl; M = $\mathrm{Cu^I}$, $\mathrm{Ru^{II}}$, $\mathrm{Fe^{II}}$; substituents can be in the 4-, 5-, and 6-positions).



Scheme 6. Amphiphilic poly(oxazoline) block copolymer with two different metal binding sites (R^1, R^2 = different side chains, L = ligand, n = number of repeating units).

metal ion acts as a protecting group for the nitrogen atoms of the bipyridines and in parts as an activator for both initiation and propagation (in particular iron(II)[32]).

In addition to growing polymers from metallo-supramolecular initiators, a second goal is to disassemble the starlike structures (e.g. Scheme 7). This can be easily done by treatment with K_2CO_3 solution. It was shown by UV/Vis spectroscopy and atomic absorption spectroscopy that iron(II)[38] and cobalt(II)[34] central ions could be removed almost quantitatively, whereas only 90% of copper(II)[31] was removable. Ruthenium(II) complexes turned out to be inert.[40] It could be demonstrated that the process of decomplexation is reversible. That means re-complexation can take place by addition of new metal salts.[34, 38] The quantification of polymer complexation depends on the kind of metal ion and has not yet been investigated in detail. In addition, it could be observed that films of iron(II) polymers undergo thermal bleaching at about 210 °C, and the color returns after cooling.[38]



Scheme 7. Example of a decomplexation–re-complexation process. Model of the “switching” of a terpyridine based supramolecular poly(oxazoline).

For characterization of the star-shaped metal-containing polymers, UV/Vis spectroscopy is a very suitable technique regarding the polymer metal complex formation as well as the investigation of decomplexation or re-complexation processes. Furthermore, the molar masses as well as the stability of the polymer metal systems could be studied by utilizing GPC. The labile iron(II) and cobalt(II) polymer complexes fragment on the GPC column in most cases quantitatively, and the detected masses correspond with the uncomplexed macroligands. In-line diode array UV/Vis detection showed that the eluting polymer fractions contained little or no evidence of the red-violet iron(II) chromophores. The inert ruthenium(II) polymers maintain their structural integrity during GPC characterization.[40] Since the stability of copper(I) poly(oxazoline)s lies in between those of iron(II) and ruthenium(II), it depends on the length of the polymer chain whether the starlike polymer fragments on the column or if the whole expected polymer masses are detected.[37] However, inaccuracies of GPC data are related to the utilized polystyrene standards, which are not always suitable for poly(oxazoline)s and even less for starlike polymer structures. Therefore, MALDI-TOF mass spectrometry was applied to determine the absolute molar masses.[34] Investigation of the thermal properties of such complexed polymers revealed a higher stability of the obtained polymers compared with the utilized initiator systems. With increasing chain length, the thermal behavior becomes more similar to the uncomplexed poly(oxazoline)s.[41]

Terpyridine initiating systems: Besides bipyridine, the terpyridine molecule is known as an excellent ligand for a large number of transition metal ions, which form octahedral complexes with interesting physical properties as well as high stabilities.[42, 43] As the first metallo-supramolecular initiator system based on this ligand class, an iron(II) complex of 5,5″-*bis*(bromo)methyl-2,2′:6′,2″-terpyridine was utilized.[44, 45] The living character of the polymerization was proven by the linear relationship between M_n and [monomer]/[initiator] ratios; the molecular masses could be controlled, and the polymers revealed low polydispersities. In addition, block copolymers have also been prepared successfully.

Since terpyridines can also be functionalized at the central pyridine ring, a second approach was the utilization of 4′-(4-(bromomethyl)phenyl)-2,2′:6′,2″-terpyridine metal complexes as initiating systems.[46–48] Again the living character of the oxazoline polymerization could be demonstrated. It was shown that it is possible to decomplex the supramolecular terpyridine-functionalized poly(oxazoline)s with diluted K_2CO_3 solution to yield colorless “macroligands” (Scheme 7). Supplementary re-complexation experiments were carried out by performing a titration experiment. The stepwise increase of the iron(II) ion concentration in the solution of the decomplexed polymers resulted the typical iron(II)–terpyridine charge-transfer band (Figure 1). This decomplexation–re-complexation process (“supramolecular switching”) revealed a reversibility of 94%.

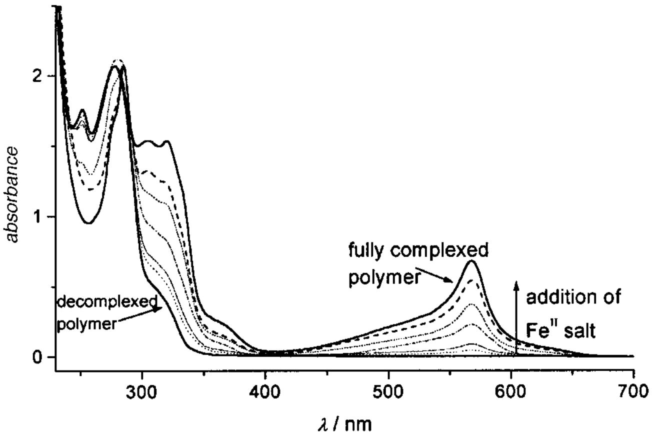
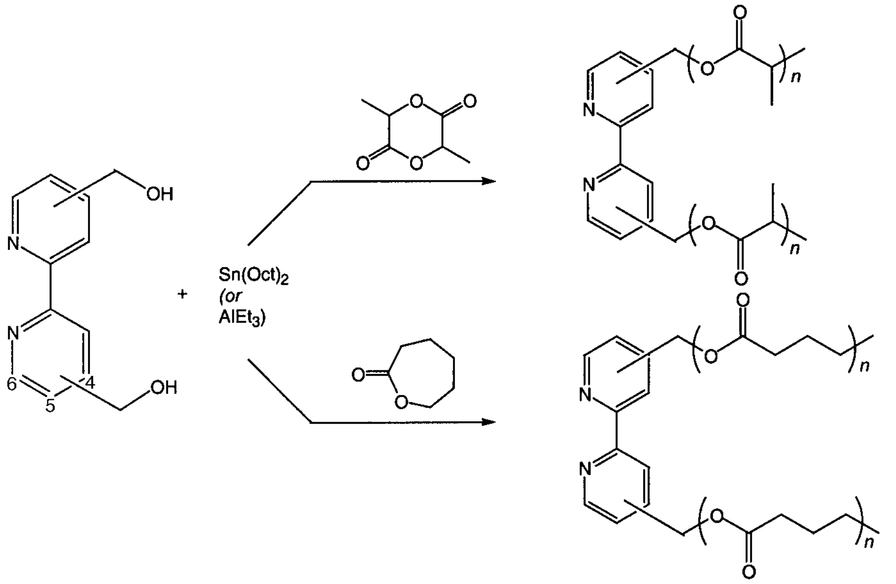


Figure 1. UV/Vis titration of a decomplexed terpyridine–macroligand solution (CH_3CN) with Fe^{II} salt.

Bi- and terpyridine end-capped biodegradable polyesters: The concept of supramolecular initiators presented for 2-oxazoline polymerizations can also be transferred to other polymerization methods and monomers. An interesting example is the controlled coordinative ring-opening polymerization of lactides and caprolactones by an insertion mechanism catalyzed by $Al(OR)_3$ that was described by Kricheldorf et al.[49, 50] A large number of metal alkoxides, for example, $Sn(Oct)_2$, titanium, zinc, and zirconium alkoxides are also known as catalysts for this technique.[51–53] The resulting poly(lactide)s and poly(caprolactone)s are biocompatible and biodegradable polyesters which have already been found promising applications in medicine and tissue engineering.[54–56] Utilizing different alcohols as so-called "co-initiators", chain-end functionalization of the considered polymers can be realized (Scheme 8). The well-defined incorporation of chelating ligands and thereby metals into such compounds provides the opportunity to obtain biocompatible materials with a wide range of properties, suitable for example, for catalysis or novel diagnostic procedures. In addition, high molar mass polyesters with improved mechanical properties could be accessed by this method.



Scheme 8. "Macroligands" through coordinative ring-opening polymerization (in bulk or toluene) of lactide and ε-caprolactone by utilizing hydroxymethyl-bipyridines as "co-initiators". Substituents can be in the 4-, 5-, and 6-positions (n = number of repeating units).

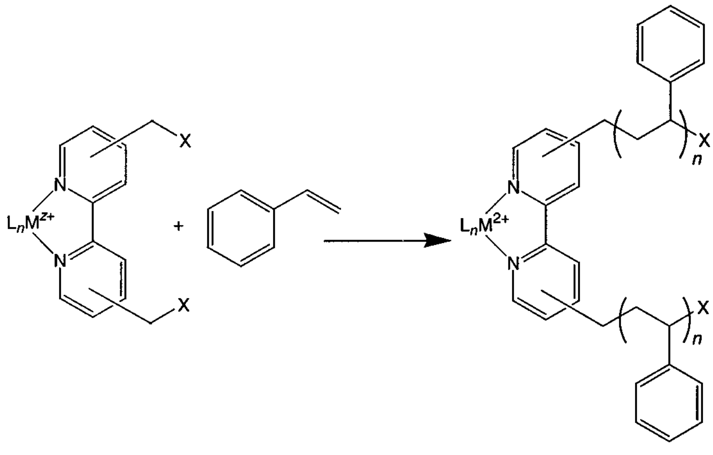
The compounds 6-methyl-6′-monohydroxymethyl-2,2′-bipyridine and 6,6′-*bis*hydroxymethyl-2,2′-bipyridine and their copper(I) complexes were applied as co-initiators for the polymerization of lactide and ε-caprolactone monomers by utilizing $AlEt_3$ as a catalyst in dry toluene.[57, 58] The GPC data of the obtained polymers revealed rather narrow monomodal weight distributions (connected with slightly higher molar masses than expected with respect to the monomer to initiator ratio, as also obtained from ^1H NMR data). In contrast to the initiation of 2-oxazoline polymerizations with uncomplexed ligands (see above), no perturbation compared with the use of metallo-initiators could be observed.

Fraser et al. synthesized polyester macroligands by using $Sn(Oct)_2$ as a catalyst and 4,4′-*bis*hydroxymethyl-2,2′-bipyridine as a co-initiator.[59, 60] The reactions were carried out in bulk. The presence of the bipyridyl unit in the polymers was verified by ^1H NMR spectroscopy and GPC with in-line UV/Vis diode array detection. In addition to the homopolymers, copolymers consisting of poly(lactide) and poly(caprolactone) blocks were prepared. The homopolymeric macroligands were subsequently chelated to iron(II) as well as ruthenium(II) (with both two and six polymer arms); the chelation generated metal-centered star polymers. As was expected, the iron(II) containing polymers turned out to be unstable on the GPC column, whereas the inert ruthenium(II) star polymers could be accurately determined by GPC analysis. In the case of the iron(II) centered polymers, microscopic studies revealed reversible thermochromic bleaching. Treatment with concentrated acids or bases also caused bleaching of the polymers. Degradation of the polymers has not yet been investigated.

The transfer of the concept shown above to terpyridine systems seems very promising. Results on this topic are being gathered.[61]

Supramolecular bipyridine initiators for ATRP of styrene and methyl methacrylate: Atom-transfer radical polymerization (ATRP) has become a well-established controlled polymerization method for styrene and methyl methacrylate.[62, 63] Bipyridine (and terpyridine) complexes are not only applicable as ATRP catalysts[64–66] but they can also initiate the formation of star-shaped polymers (Scheme 9).

Fraser et al. used, for example, 4,4′-*bis*chloromethyl-2,2′-bipyridine and the corresponding ruthenium(II) complexes with one, two, and three chloromethyl-functionalized bipyridine ligands as initiators in the ATRP of styrene.[67] The



Scheme 9. ATRP polymerization procedure with supramolecular bipyridine initiators (X = Cl, Br; M = Ru^{II}, Cu^I, L = ligand, n = number of repeating units). Reaction conditions: catalyst a) CuCl, $bpy(C_{13}H_{27})_2$, or b) $[Cu^{II}(4,4'\text{-}CH_3)bpy_3](PF_6)_2/Al[OCH(CH_3)_2]_3/C_6H_{12}N_2O$.

authors applied either CuBr/HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetraamine)[68, 69] or CuCl/bpy-$(C_{13}H_{27})_2$ (2,2′-bipyridine) as catalyst systems according to the method of Matyjaszewski et al.[70] All initiators generated polymers with narrow polydispersities, however, the obtained molar masses were higher than expected (this is probably caused by a slow and inefficient initiation by the not completely soluble ruthenium(II) complexes). The formation of the star-shaped polymers was proven by GPC coupled with light scattering and in-line diode array UV/Vis spectroscopy. An alternative approach was the "convergent" synthesis of star-shaped ruthenium(II) centered polymers by macroligand chelation (1 to 6 arms).[71] The polystyrene macroligands were first prepared in bulk by ATRP polymerization methods (Scheme 9) and later complexed with ruthenium(II). However, this convergent polymer synthesis was inefficient for high molar mass systems (limit approx. 65000 dalton for a 6-arm star). The limitation depended on steric crowding around the metal center ("protection" of the metal center) and on the solvent polarity, which controls the degree of aggregation of the polystyrene chains and therefore the access to the metal centers.[72] In addition, the synthesis of poly(methyl methacrylate) macroligands[73] and "block" copolymers by self-assembly of polystyrene–poly(methyl methacrylate) hetero-arm stars (using ruthenium(II)) prepared by ATRP was reported.[74] However, kinetic experiments with bipyridine initiating systems revealed[75] that a controlled ATRP of styrene with ligand and ruthenium(II) metallo-initiators could only be achieved for well-selected reaction parameters and moderate monomer conversion (≈60%). Otherwise molecular weights will deviate strongly from targeted values due to radical recombination. This suggests the destruction of some initiating species in the early stages of the polymerization.

Further experiments showed that it is possible to apply [copper(II)(4,4′-dimethyl-2,2′-bipyridine)$_3$]$(PF_6)_2$ as an ATRP catalyst in order to prepare copper(I) centered star-shaped polystyrenes.[76] [Copper(I){6,6′-*bis*(bromomethyl)-2,2′-bipyridine}$_2$](PF_6) was used as a supramolecular initiator in this case.

Conclusion and Future Directions

In this article we showed that a considerable number of "living" polymers starting from metallo-supramolecular initiators are available. Obviously, the use of metallo-supramolecular initiators for controlled polymerization methods is an elegant approach to the well-controlled introduction of coordinative segments into polymers. In the case of poly(oxazoline)s, the well-known advantages such as molecular weight and polarity control as well as the possibility of chain-end functionalization and block copolymerization can be fully transferred to the metallo-supramolecular initiator concept. The central metal ion acts as a "protective group" of the nitrogen valences and prevents self-terminating effects.

Biodegradable poly(lactide)s and poly(caprolactone)s bearing bipyridine ligands at the chain ends from coordinative ring-opening methods can also be prepared by the use of the concept described. Block copolymers are also available. As the protection of the nitrogen valences is not necessary in this case, the synthesis can be carried out in both ways by utilizing metallo-supramolecular initiators or even uncomplexed ligands. Furthermore, high-molecular-weight polyesters can be prepared in this way; the method drastically improves their mechanical properties.

Atom-transfer radical polymerization (ATRP) is the third method at present, in which the metallo-supramolecular initiator concept can be applied and it yields polystyrene and poly(methyl methacrylate) macroligands as well as metal-centered star compounds.

The combination of the "switching concept" and the supramolecular polymers or macroligands connected to surfaces could lead to entirely new materials in the future (Figure 2), for example, in the area of sensors. In our opinion, this universal concept will be extended to a wide range of other monomers and polymers as well as supramolecular moieties.

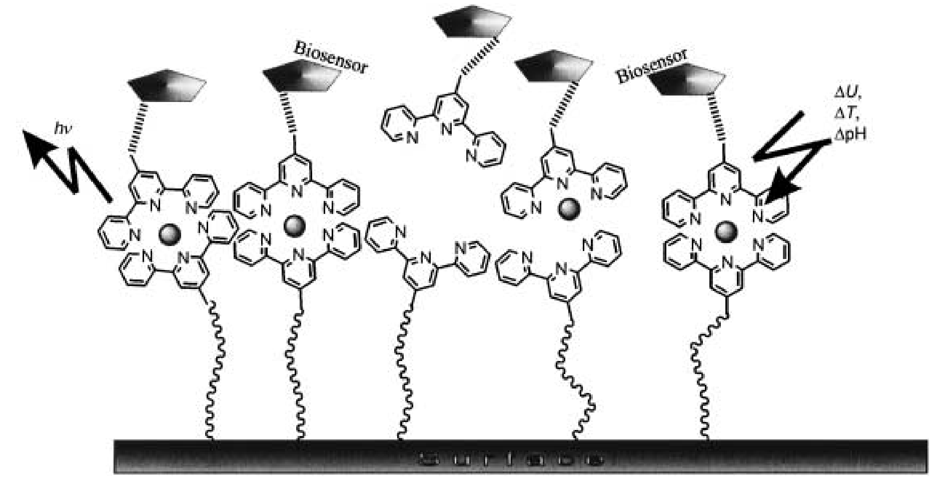


Figure 2. Multifunctional supramolecular compounds.

Acknowledgements

The research was supported by the Bayerisches Staatsministerium für Unterricht, Kultus, Wissenschaft und Kunst, the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (DFG), BAYER AG, and the Dutch Polymer Institute (DPI). We thank O. Nuyken for his support.

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[1] U. S. Schubert, C. Eschbaumer, *Angew. Chem.* **2002**; *Angew. Chem. Int. Ed.* **2002**, in press.
[2] E. B. Easton, P. G. Pickup, *Electrochem. Solid-State Lett.* **2000**, *3*, 359.
[3] J. Suh, S. H. Hong, *J. Am. Chem. Soc.* **1998**, *120*, 12545.

[4] H. Nishiyama, T. Shimada, H. Itoh, H. Sugiyama, Y. Motoyama, *Chem. Commun.* **1997**, 1863.
[5] C. Arana, M. Keshavarz, K. T. Potts, H. D. Abruna, *Inorg. Chim. Acta* **1994**, *225*, 285.
[6] H. Nagao, T. Mizukawa, K. Tanaka, *Inorg. Chem.* **1994**, *33*, 3415.
[7] H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* **2000**, 229.
[8] G. Cross, *Nature* **1995**, *374*, 307.
[9] J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993.
[10] M. Kaneko, A. Yamada, Y. Kurimura, *Inorg. Chim. Acta* **1980**, *45*, L73.
[11] L. M. Dupray, M. Devenney, D. R. Striplin, T. J. Meyer, *J. Am. Chem. Soc.* **1997**, *119*, 10243.
[12] M. Antonietti, S. Lohmann, C. D. Eisenbach, U. S. Schubert, *Macromol. Rapid Commun.* **1995**, *16*, 283.
[13] Z. Q. Lei, X. G. Han, Y. L. Hu, R. M. Wang, Y. P. Wang, *J. Appl. Polym. Sci.* **2000**, *75*, 1068.
[14] K. Hanabusa, A. Nakamura, T. Koyama, H. Shirai, *Makromol. Chem.* **1992**, *193*, 1309.
[15] Z. Peng, A. R. Gharavi, L. Yu, *J. Am. Chem. Soc.* **1997**, *119*, 4622.
[16] L. Troillet, A. D. Nicola, S. Guillerez, *Chem. Mater.* **2000**, *12*, 1611.
[17] C.-T. Chen, T.-S. Hsu, R.-J. Jeng, H.-C. Yeh, *J. Polym. Sci. Part A.* **2000**, *38*, 498.
[18] L. S. Tan, J. L. Burkett, S. R. Simko, M. D. Alexander, *Macromol. Rapid Commun.* **1999**, *20*, 16.
[19] S. C. Yu, S. Hou, W. K. Chan, *Macromolecules* **2000**, *33*, 3259.
[20] G. I. Konishi, Y. Chujo, *J. Polym. Sci.* **1999**, *43*, 9.
[21] U. S. Schubert, O. Hien, C. Eschbaumer, *Macromol. Rapid Commun.* **2000**, *21*, 1156.
[22] U. S. Schubert, C. Eschbaumer, *Macromol. Symp.* **2001**, *163*, 177.
[23] P. C. J. Kamer, R. J. M. Nolte, W. Drenth, *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 175.
[24] P. C. J. Kamer, R. J. M. Nolte, D. Wiendelt, *J. Am. Chem. Soc.* **1988**, *110*, 6818.
[25] R. J. M. Nolte, *Chem. Soc. Rev.* **1994**, 11.
[26] J. J. L. M. Cornelissen, M. Fischer, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **1998**, *280*, 1427.
[27] K. Aoi, M. Okada, *Prog. Polym. Sci.* **1996**, *21*, 151.
[28] Y. Chujo, T. Saegusa, *Ring Opening Polymerization* (Ed.: D. J. Brunelle), Carl Hanser Verlag, Munich, **1993**, 239.
[29] S. A. Savage, A. P. Smith, C. L. Fraser, *J. Org. Chem.* **1998**, *63*, 10048.
[30] U. S. Schubert, C. Eschbaumer, M. Heller, *Org. Lett.* **2000**, *2*, 3373.
[31] Q. Liu, M. Konas, J. S. Riffle, *Macromolecules* **1993**, *26*, 5572.
[32] G. Hochwimmer, O. Nuyken, U. S. Schubert, *Macromol. Rapid Commun.* **1998**, *19*, 309.
[33] J. E. McAlvin, S. B. Scott, C. L. Fraser, *Macromolecules* **2000**, *33*, 6953.
[34] U. S. Schubert, O. Nuyken, G. Hochwimmer, *J. Macromol. Sci.* **2000**, *A37*, 645.
[35] S. Kobayashi, H. Uyama, Y. Narita, J.-I. Ishiyama, *Macromolecules* **1992**, *25*, 3232.
[36] J. E. McAlvin, C. L. Fraser, *Macromolecules* **1999**, *32*, 1341.
[37] U. S. Schubert, O. Nuyken, G. Hochwimmer, *Des. Monomers Polym.* **2000**, *3*, 245.
[38] J. J. S. Lamba, C. L. Fraser, *J. Am. Chem. Soc.* **1997**, *119*, 1801.
[39] O. Nuyken, G. Maier, A. Groß, H. Fischer, *Macromol. Chem. Phys.* **1996**, *197*, 83.
[40] J. E. McAlvin, C. L. Fraser, *Macromolecules* **1999**, *32*, 6925.
[41] G. Hochwimmer, U. S. Schubert, unpublished results.
[42] E. C. Constable, *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69.
[43] R. Bhula, D. C. Weatherburn, *Aust. J. Chem.* **1991**, *44*, 303.
[44] U. S. Schubert, C. Eschbaumer, O. Nuyken, G. Hochwimmer, *J. Inclusion Phenom.* **1999**, *32*, 23.
[45] U. S. Schubert, C. Eschbaumer, G. Hochwimmer, *Synthesis* **1999**, 779.
[46] U. S. Schubert, M. Heller, G. Hochwimmer, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2000**, *41*, 932.
[47] U. S. Schubert, G. Hochwimmer, M. Heller in "*Synthetic Macromolecules with Higher Structural Order*" (Ed.: I. Khan), *ACS Symp. Ser.* **2001**, in press.
[48] M. Heller, U. S. Schubert, *Macromol. Symp.* **2001**, in press.
[49] H. R. Kricheldorf, I. Kreiser-Saunders, *Macromol. Symp.* **1996**, *103*, 85.
[50] H. R. Kricheldorf, D.-O. Damrau, *J. Macromol. Sci.* **1998**, *35*, 1875.
[51] H. R. Kricheldorf, M. Berl, N. Scharnagl, *Macromolecules* **1988**, *21*, 286.
[52] T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 4072.
[53] D. Mecerreyes, R. Jerome, P. Dubois, *Adv. Polym. Sci.* **1999**, *147*, 1.
[54] T. H. Barrows, *High Perform. Biomater.* **1991**, 243.
[55] R. Jain, N. H. Shah, A. W. Malick, C. T. Rhodes, *Drug Dev. Ind. Pharm.* **1998**, *24*, 703.
[56] R. Langer, *Acc. Chem. Res.* **2000**, *33*, 94.
[57] U. S. Schubert, G. Hochwimmer, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2000**, *41*, 433.
[58] U. S. Schubert, G. Hochwimmer, *Macromol. Rapid Commun.* **2001**, *22*, 274.
[59] P. S. Corbin, J. E. McAlvin, M. P. Webb, S. Shenoy, C. L. Fraser, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2000**, *41*, 1199.
[60] P. S. Corbin, M. P. Webb, J. E. McAlvin, C. L. Fraser, *Biomacromolecules* **2001**, *2*, 223.
[61] U. S. Schubert, M. Heller, unpublished results.
[62] T. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **1996**, *272*, 866.
[63] K. Matyjaszewski in "*Controlled Radical Polymerization*" (Ed.: K. Matyjaszewski), *ACS Symp. Ser.* **1998**, *685*, 483.
[64] U. S. Schubert, G. Hochwimmer, C. E. Spindler, O. Nuyken, *Macromol. Rapid Commun.* **1999**, *20*, 351.
[65] U. S. Schubert, G. Hochwimmer, C. E. Spindler, O. Nuyken, *J. Polym. Sci.* **1999**, *43*, 319.
[66] U. S. Schubert, G. Hochwimmer, C. E. Spindler, O. Nuyken in "*Controlled Radical Polymerization*" (Ed.: K. Matyjaszewski), *ACS Symp. Ser.* **2000**, *768*, 248.
[67] J. E. Collins, C. L. Fraser, *Macromolecules* **1998**, *31*, 6715.
[68] V. Percec, B. Barboiu, A. Neumann, J. C. Rhonda, M. Zhao, *Macromolecules* **1996**, *29*, 3665.
[69] V. Coessens, K. Matyjaszewski, *Macromol. Rapid Commun.* **1999**, *20*, 66.
[70] K. Matyjaszewski, T. Patten, J. Xia, *J. Am. Chem. Soc.* **1997**, *119*, 674.
[71] X. Wu, C. L. Fraser, *Macromolecules* **2000**, *33*, 4053.
[72] X. Wu, C. L. Fraser, *Macromolecules* **2000**, *33*, 7776.
[73] C. L. Fraser, A. P. Smith, *J. Polym. Sci. Part A.* **2000**, *38*, 4704.
[74] C. L. Fraser, A. P. Smith, X. Wu, *J. Am. Chem. Soc.* **2000**, *122*, 9026.
[75] X. Wu, J. E. Collins, J. E. McAlvin, R. W. Cutts, C. L. Fraser, *Macromolecules* **2001**, *34*, 2812.
[76] U. S. Schubert, G. Hochwimmer, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1999**, *40*, 340.