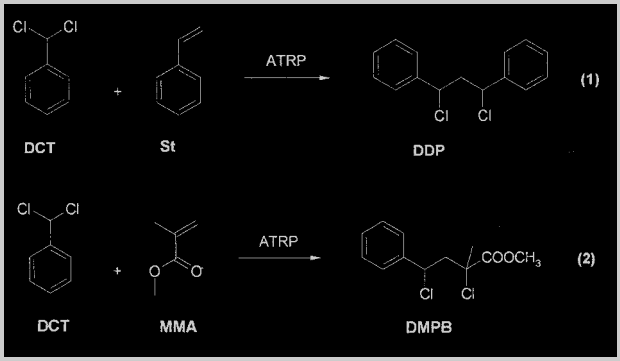
Full Paper: The atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate with α,α-dichlorotoluene (**DCT**) as initiator results in the respective chlorotelechelic polymers. From a kinetic point of view, however, the polymerization of styrene and methyl methacrylate show a different behavior: for the polymerization of styrene **DCT** is a bifunctional, for the polymerization of methyl methacrylate it is a monofunctional initiator.



Atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate with α,α-dichlorotoluene as initiator; a kinetic study

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Introduction

Living polymerization via atom transfer radical polymerization (ATRP) provides a facile yet versatile method to prepare a wide selection of polymers with controlled molecular weights and low polydispersity index. Homo-, co-, and hyperbranched polymers were successfully prepared by several groups[1–7]. To obtain a Poisson distribution of the molecular weight, an initiation reaction as fast, preferably faster than the propagation reaction is required. To generate a rate of initiation at least equal to the rate of propagation, the structure of the alkyl halide initiator should be adjusted for each class of monomers. Considering this, most authors prefer to employ activated alkyl initiating systems with a chemical surrounding as similar to the growing polymer chain end as possible. Matyjaszewski et al.[1] used 1-phenylethyl chloride for the ATRP of styrene and 2-bromoisobutyrate for the ATRP of MMA. Arenesulfonyl chlorides, e.g. substituted benzenesulfonyl chlorides introduced by Percec et al. are universal initiators for metal-catalyzed "living" radical polymerization, since the rate constants of initiation for styrene, methacrylates, and acrylates are by five to three orders of magnitude higher than the rate constants of propagation[8, 9].

For a simplified preparation of ABA block copolymers the use of bifunctional initiators is preferable. α,α′-*p*-Dihaloxylenes (**DHX**) have been employed in the ATRP of styrene and acrylates. As benzylhalide, **DHX** shows a slow initiation for styrene polymerization as evidenced by an induction period[10]. However, after initiation, the first order kinetic plot is linear up to 90% conversion, $\overline{M}_n$ is close to the calculated value, and the polydispersity index $\overline{M}_w/\overline{M}_n < 1.3$. The polymerization of acrylates, e.g. 2-ethylhexyl acrylate and butyl acrylate, is affected by the nature of the solvent used for polymerization[11]. For ethylene carbonate or diphenyl ether, in which both monomer and polymer are soluble, a linear dependence of $\overline{M}_n$ on conversion and a low polydispersity index was observed. However, for poor solvents for monomer and/or polymer, lower molecular weights and higher values of $\overline{M}_w/\overline{M}_n$ than expected were observed. Bifunctional sulfonyl chlorides, e.g. phenoxybenzene-4,4′-disulfonyl chloride (**PDSC**), have been used as a bifunctional initiator for the ATRP of styrene, methacrylates, and acrylates[12]. The drawback of this class of initiators is their relatively complicated structure which differs significantly from that of the repeating unit of vinylic or acrylic polymers and the resulting sulfonyl group in the chain[2, 12, 13].

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In our laboratory a novel bifunctional initiator for the ATRP was developed on the basis of ethylene bis(chlorophenyl acetate) (**ECPA**)[14]. The initiating alkyl chloride species is activated by both an α-phenyl and an α-alkoxycarbonyl group; thus, styrene and acrylate type monomers are initiated with high efficiency. The drawback of this initiator is the existence of a heteroatom in the main chain representing a weak link.

In the present communication we present our results on the ATRP initiated by α,α-dichlorotoluene (**DCT**) as a bifunctional initiator for the controlled radical polymerization of both styrene and methyl methacrylate.

Experimental part

Materials

Styrene (St, from Bayer AG) and methyl methacrylate (MMA, from Bayer AG) used for polymerizations were of high purity. Inhibitors contained in St and MMA were removed by passing the monomers through an aluminium oxide column. α,α-Dichlorotoluene (DCT, Aldrich), CuCl (98%, Aldrich) and 2,2′-bipyridine (bipy) (ABCR) were used as received without purification. Butyl acetate (from Bayer AG) was used as a solvent without purification. Polymerizations were carried out in nitrogen atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz, respectively. Deuterated chloroform ($CDCl_3$) was used as a solvent, and tetramethylsilane (TMS) served as internal standard.

Gel-permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump (Waters), a refractive index detector (ERC), and a UV-detector (ERC, λ = 254 nm). The eluting solvent was tetrahydrofuran (THF) stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.25 g/L), the flow rate was 0.5 mL · min^{-1}. Calibration was achieved with polystyrene and poly(methyl methacrylate) standards. Four columns with PL-gel (from Polymer Laboratories) were applied: length of the column 300 mm, diameter 7.5 mm, diameter of gel particles 5 μm, nominal pore width 100 Å, 500 Å, 10^3 Å, and 10^4 Å.

Polymerization of styrene and methyl methacrylate in butyl acetate as a solvent

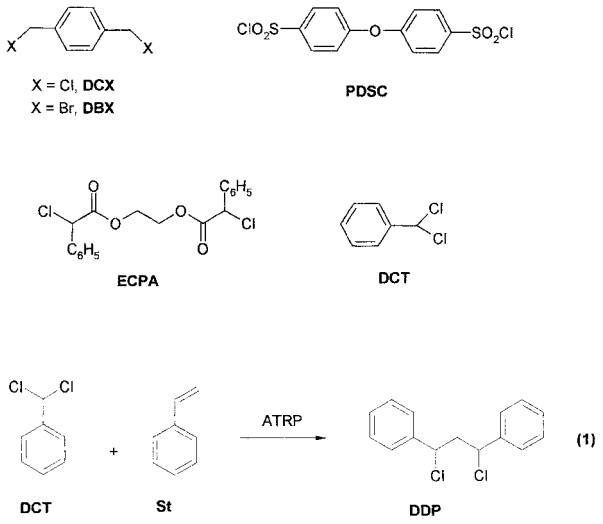
General procedure:

DCT (or MCT), CuCl, and bipy in a molar ratio of 1:1:3 were introduced into a Schlenk-glass-tube. Monomer and butyl acetate (1:1 vol.) were added and the heterogeneous mixture was degassed (3 times), filled with nitrogen and immersed in an oil bath at 130 °C. After a certain time the polymerization was terminated by cooling to room temperature (r.t). The product was dissolved in THF and precipitated into methanol. The polymer was isolated by filtration and dried to constant weight.

The experimental results and the kinetic data for the polymerization of St and MMA are summarized in Tab. 1 and Tab. 2.

Results and discussion

The application of α,α-dichlorotoluene (**DCT**) as an initiator for the living radical polymerization of styrene is the most evident conclusion if a bidirectional chain growth is desired. Upon addition of the first styrene molecule, 1,3-dichloro-1,3-diphenylpropane (**DDP**) is formed, which is a symmetrical molecule (Eq. (1)). The two chlorine atoms are in an identical chemical surrounding which, in addition, is similar to a growing polystyrene chain end. Thus, it is to be expected that ATRP of styrene proceeds bidirectionally with this initiator.



The dependence of conversion and of ln([M]$_0$/[M]) on time for the polymerization of **St** initiated with **DCT**, catalyzed by CuCl/bipy in butyl acetate is shown in Fig. 1a. The linearity of the plot ln([M]$_0$/[M]) vs. time shows that the polymerization follows first order kinetics with respect to the monomer and that the concentration of growing radicals remains constant. To confirm the bidirectional chain growth during the polymerization, several polymerizations initiated with α-chlorotoluene (**MCT**) were performed under the same conditions. From the kinetic data (Fig. 1b, Tab. 1) it is apparent that, while proceeding in a living manner, the ATRP with **MCT** exerts a rate constant of propagation which is lower by a factor of 2 than the rate constant observed with **DCT** ($k^{app}_{p,DCT}$ = 6.49 · 10^{-5} s^{-1}, $k^{app}_{p,MCT}$ = 2.43 · 10^{-5} s^{-1}). The calculation of the stationary concentration of radicals [P$^{\bullet}$]$_{St}$ in the reaction mixture gives a value of 2.78 · 10^{-8} mol · L^{-1} for **DCT** and 1.04 · 10^{-8} mol · L^{-1} for **MCT** as initiator, respectively. These values are in good accordance with

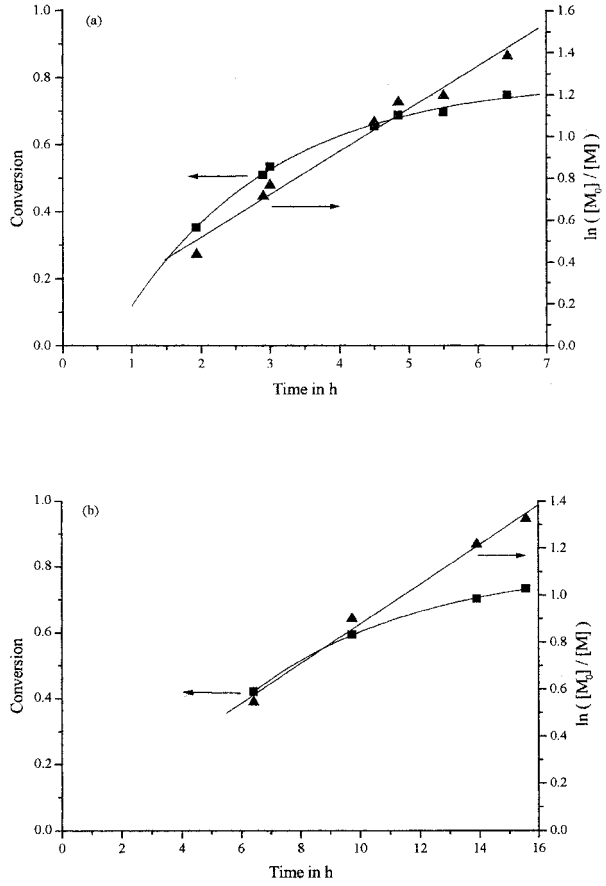


Fig. 1. Plots of conversion and ln([M]$_0$/[M]) vs. time for the polymerization of styrene in butyl acetate at 130 °C with (a) DCT and (b) MCT as initiator (I). (Polymerization conditions: [St]$_0$/[I]$_0$ = 100, [I]/[CuCl]/[bipy] = 1/1/2.5, [St]$_0$ = 4.35 mol/L)

Tab. 1. ATRP of styrene in butyl acetate initiated with α,α-dichlorotoluene (**DCT**) and α-chlorotoluene (**MCT**); kinetic data[a)]

Initiator	Time in h	Conversion in wt.-%	ln([M]$_0$/[M])	$\overline{M}_{n,th}$[b)]	$\overline{M}_{n,exp}$[c)]	$\overline{M}_w/\overline{M}_n$[c)]
DCT	1.93	35.25	0.4346	3580	4430	1.34
DCT	2.90	51.00	0.7134	5600	6730	1.28
DCT	3.00	53.50	0.7657	5590	6410	1.30
DCT	4.50	65.56	1.0660	7150	7980	1.27
DCT	4.85	68.70	1.1616	7360	8020	1.32
DCT	5.50	69.65	1.1924	7340	7970	1.30
DCT	6.43	74.93	1.3835	7500	8250	1.28
MCT	6.42	42.00	0.5447	4500	5740	1.39
MCT	9.72	59.29	0.8987	6230	7150	1.36
MCT	13.90	70.35	1.2157	7560	7530	1.38
MCT	15.57	73.39	1.3239	7770	8350	1.37

a) Polymerization conditions: [St]$_0$ = 4.35 mol/L, [St]/[I]/[CuCl]/[bipy] = 100 : 1 : 1 : 2.5 (molar ratio), reaction temperature T = 130 °C.

b) Calculated according to: $\overline{M}_n$ = [St]/[I] · x_p · 104 + 161 (for DCT) and +127 (for MCT).

c) Determined by means of GPC with polystyrene standards.

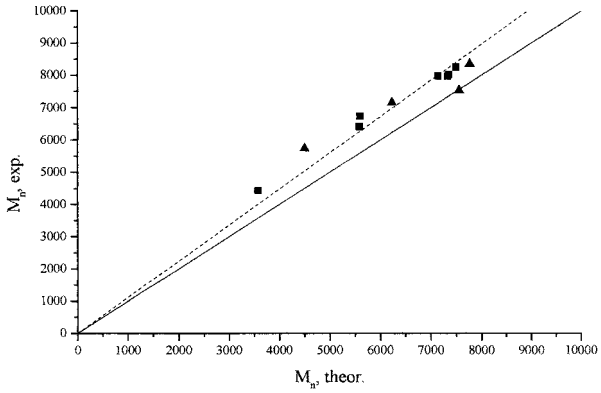
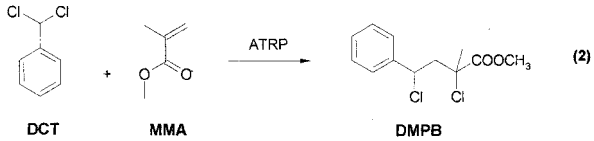


Fig. 2. Plots of $\overline{M}_{n,th}$ vs. $\overline{M}_{n,exp}$ for polystyrene samples prepared with (■) DCT and (▲) MCT as initiators. (Polymerization conditions: [St]$_0$/[I]$_0$ = 100, (I)/[CuCl]/[bipy] = 1/1/2.5, solvent: butyl acetate; [St]$_0$ = 4.35 mol/L, T = 130 °C)

the expectation that **DCT** is a bifunctional initiator. The order of magnitude of the stationary radical concentration is in agreement with that calculated by other groups for the ATRP of styrene[1, 2)]. The stationary radical concentration is low enough to prevent bimolecular side reactions such as recombination or disproportionation which would result in a loss of control over the polymerization. Fig. 2 shows the plot of $\overline{M}_{n,th}$ vs. $\overline{M}_{n,exp}$ for polystyrene samples obtained with **DCT** and **MCT** as initiators. All experimental values are slightly higher than the calculated values but increase linearly with conversion (cf. Tab. 1) demonstrating the living nature of both polymerization systems. Since the polymers were precipitated from THF solution into methanol, the deviation of $\overline{M}_{n,exp}$ from $\overline{M}_{n,th}$ is due to fractionation. The polydispersity index of all polystyrene samples is typical for polystyrene prepared via ATRP in heterogeneous systems.

Since some of the styrene polymerization initiators are known to be active in the ATRP of (meth)acrylates, we investigated the performance of **DCT** and, for comparison reasons, of **MCT** in the ATRP of MMA. Upon addition of the first MMA monomer to **DCT**, methyl 2,4-dichloro-2-methyl-4-phenylbutyrate (DMPB) is formed (Eq. (2)), which represents a bifunctional initiator with two different activated halogen atoms and, hence, with different initiation efficiencies toward MMA.



(2)

Methyl methacrylate was polymerized with **DCT** (or **MCT**) as initiator and CuCl/bipy as catalyst in butyl acetate at 130 °C. A conversion of 88% was reached after 50 min for **DCT**, while with **MCT** as initiator the polymerization proceeds slowlier (Tab. 2). The first order kinetic plots for both initiators are linear indicating that

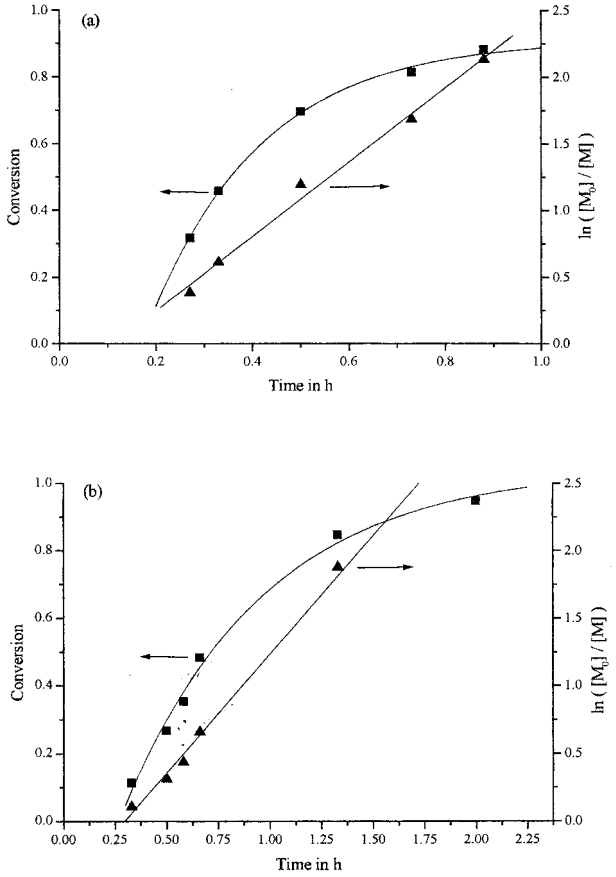


Fig. 3. Plots of conversion and $\ln([M]_0/[M])$ vs. time for the polymerization of methyl methacrylate in butyl acetate at 130 °C with (a) DCT and (b) MCT as initiator (I). (Polymerization conditions: $[MMA]_0/[I]_0 = 100$, $[I]/[CuCl]/[bipy] = 1/1/3$, $[MMA]_0 = 4.67$ mol/L)

the concentration of radicals is constant during the polymerization (Fig. 3). However, for both initiators an induction period is observed indicating slow initiation. The stationary radical concentrations were determined to be higher by approximately one order of magnitude (as compared to styrene polymerization), i.e. $2.33 \cdot 10^{-7}$ mol · L^{-1} for **DCT** and $1.26 \cdot 10^{-7}$ mol · L^{-1} for **MCT** as initiator. These values are again in accordance with the values found by other groups[1].

The ATRP of MMA with **DCT** gives well defined polymers with controlled molecular weight, a linear increase of molecular weight with conversion, and low polydispersities. In contrast to this, the polymerization with **MCT** displays a lack of control with respect to both polydispersity and molecular weight (Tab. 2) while first order kinetics with respect to the monomer are observed. A comparison of the experimental number average molecular weight ($\overline{M}_{n,exp}$) with the calculated value reveals a good agreement for **DCT** and assignment discrepancy for **MCT** as initiator (Fig. 4). These data do not allow a firm conclusion with respect to a mono- or a bidirectional chain growth for **DCT** as initiator for the MMA polymerization. For kinetical reasons, however, we assume a monodirectional chain growth. Slow initiation of MMA polymerization with 1-phenylethyl chloride has been already reported, however, the slow initiation can be improved by exchanging the chlorine with bromine in the dormant species[15, 16].

These data put some doubt on the feasibility of a combined TEMPO/ATRP "living" radical polymerization of *p*-chloromethylstyrene and MMA to receive well-controlled comb-shaped polymers as described in the literature[17].

Tab. 2. ATRP of methyl methacrylate in butyl acetate initiated with α,α-dichlorotoluene (**DCT**) and α-chlorotoluene (**MCT**); kinetic data[a]

Initiator	Time in h	Conversion in wt.-%	$\ln([M]_0/[M])$	$\overline{M}_{n,th}$[b]	$\overline{M}_{n,exp}$[c]	$\overline{M}_w/\overline{M}_n$[c]
DCT	0.27	31.71	0.3814	3310	4720	1.53[d]
DCT	0.33	45.80	0.6125	4650	6110	1.40[d]
DCT	0.50	69.62	1.1914	7260	9330	1.38[d]
DCT	0.73	81.40	1.6820	7870	10100	1.45
DCT	0.88	88.16	2.1337	9610	13300	1.44
MCT	0.33	11.34	0.1072	1180	26400	1.40
MCT	0.50	26.65	0.3099	2780	33500	1.47
MCT	0.58	35.30	0.4354	3800	38000	1.52
MCT	0.66	48.30	0.6597	4960	39000	1.53
MCT	1.33	84.70	1.8773	8510	37000	1.72
MCT	2.00	94.80	2.9565	9760	33500	1.82

a) Polymerization conditions: $[MMA]_0 = 4.67$ mol/L, $[MMA]/[I]/[CuCl]/[bipy] = 100:1:1:3$ (molar ratio), reaction temperature $T = 130$ °C.
b) Calculated according to: $\overline{M}_n = [MMA]/[I] \cdot x_p \cdot 100 + 161$ (for DCT) and +127 (for MCT).
c) Determined by means of GPC measurements with poly(methyl methacrylate) standards.
d) From GPC with column combination: 2 × 100 Å, 2 × 500 Å, and 10^3 Å.

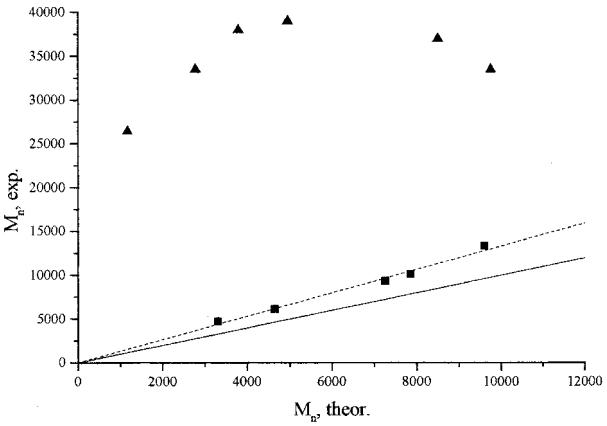


Fig. 4. Plots of $\overline{M}_{n,th}$ vs. $\overline{M}_{n,exp}$ for poly(methyl methacrylate) samples prepared with (■) DCT and (▲) MCT as initiators. (Polymerization conditions: $[MMA]_0/[I]_0 = 100$, $[I]/[CuCl]/[bipy] = 1/1/3$, solvent: butyl acetate, $[MMA]_0 = 4.67$ mol/L, $T = 130$ °C)

Conclusion

α,α-Dichlorotoluene acts as an efficient initiator for the ATRP of both styrene and methyl methacrylate. Furthermore, for styrene polymerization it is the first initiator for which bidirectional chain growth was proven from kinetic data. For the polymerization of methyl methacrylate the bidirectional chain growth is not probable. The feasibility of **DCT** as an initiator for the facile preparation of ABA block copolymers via ATRP is currently under investigation.

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[1] J.-S. Wang, K. Matyjaszewski, *Macromolecules* **28**, 7901 (1995)
[2] V. Percec, B. Barboiu, A. Neumann, J. C. Ronda, M. Zhao, *Macromolecules* **29**, 3665 (1996)
[3] K. Matyjaszewski, T. E. Patten, J. Xia, *J. Am. Chem. Soc.* **119**, 674 (1997)
[4] J.-L. Wang, T. Grimaud, K. Matyjaszewski, *Macromolecules* **30**, 6507 (1997)
[5] (a) S. G. Gaynor, S. Edelman, K. Matyjaszewski, *Macromolecules* **29**, 1079 (1996); (b) K. Matyjaszewski, S. G. Gaynor, A. Kulfan, M. Podwika, *Macromolecules* **30**, 5192 (1997)
[6] S. G. Gaynor, K. Matyjaszewski, *Macromolecules* **30**, 4241 (1997)
[7] D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, A. J. Shooter, *Macromolecules* **30**, 2190 (1997)
[8] V. Percec, B. Barboiu, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **38**, 733 (1997)
[9] V. Percec, H.-J. Kim, B. Barboiu, *Macromolecules* **30**, 6702 (1997)
[10] K. Matyjaszewski, Y. Nakagawa, S. G. Gaynor, *Macromol. Rapid. Commun.* **18**, 1057 (1997)
[11] K. Matyjaszewski, Y. Nakagawa, C. B. Jasieczek, *Macromolecules* **31**, 1535 (1998)
[12] V. Percec, H.-J. Kim, B. Barboiu, *Macromolecules* **30**, 6702 (1997)
[13] V. Percec, B. Barboiu, *Macromolecules* **28**, 7970 (1995)
[14] B. Reining, H. Keul, H. Höcker, *Polymer* **40**, 3555 (1999)
[15] K. Matyjaszewski, J.-L. Wang, T. Grimaud, D. A. Shipp, *Macromolecules* **31**, 1527 (1998)
[16] K. Matyjaszewski, D. A. Shipp, J.-L. Wang, T. Grimaud, T. E. Patten, *Macromolecules* **31**, 6836 (1998)
[17] C. J. Hawker, G. G. Barclay, R. B. Grubbs, J. M. J. Frechet, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **37(2)**, 515 (1996)