# Complex of Hyperbranched Polyethylenimine with Cuprous Halide as Recoverable Homogeneous Catalyst for the Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT: A crucial issue in the context of atom transfer radical polymerization (ATRP) is removal of the transition metal catalyst after the polymerization. In this context hyperbranched polyethylenimine (HPEI) was modified by ethyl acrylate or butyl acrylate via the Michael addition reaction. The resulting hyperbranched materials were utilized as macroligands for the copper-mediated ATRP of methyl methacrylate (MMA), representing an efficient catalyst system. Kinetic curves show a linear dependence of $\ln([M]_0/[M]_t)$ on time. Molecular weights of the resulting poly(methyl methacrylate) (PMMA) increase linearly with conversion. Molecular weight distributions are narrow ($M_w/M_n < 1.4$), even at high conversion (96%), confirming that the ATRP of MMA with the hyperbranched macroligand/Cu(I) catalyst system represents a controlled process. However, the initiation efficiency of the polymerization using hyperbranched macroligands was less than 100%, usually in the range of 41−83%. The compact structure for hyperbranched macroligands leads to low viscosity. The catalyst system was easily separated from the PMMA product by convenient precipitation of PMMA in methanol. Copper was removed together with the hyperbranched macroligand. No additional purification steps are required to separate the polymer from Cu contamination. The hyperbranched macroligand/CuCl catalyst system can be reused for the ATRP of MMA, maintaining high activity in subsequent polymerization runs.

## Introduction

During the past couple of years, several procedures for controlled or "living" radical polymerizations have been developed and used to prepare various well-defined polymers and polymers with complex polymer architectures.[1−6] Among these methods, atom transfer radical polymerization (ATRP), a living radical polymerization technique based on a reversible activation/deactivation equilibrium between the active and dormant species mediated by transition metal complexes, is a very versatile tool for the synthesis of well-defined polymers and complex macromolecular architectures[7,8] like block,[9] star,[10,11] and hyperbranched (co)polymers.[12]

Various systems based on Cu, Ru, Fe, Ni, and Rh have been developed for the ATRP of styrenic, acrylic, and methacrylic monomers.[7,8] Among them, the complexes of Cu(I) with nitrogen-based ligands have been widely used because of their good catalytic efficiency for the polymerization of most common monomers and their low cost.[7,8] However, the high amount of catalyst required to realize reasonable rates of polymerization leads to deeply colored polymerization solutions and polymer products contaminated with toxic heavy metals. Additional purification steps are required to remove the catalyst from the product, usually by passing the solution over silica[13,14] or alumina[15,16] gel after the polymerization, which is only possible on lab scale. For industrial application of ATRP more efficient removal of the catalyst from the polymer is a crucial issue. To date, research efforts have been directed at the use of heterogeneous catalysts immobilized onto inorganic or organic polymer supports,[17−21] since these materials can be removed from the final product by simple filtration or sedimentation and reused several times, reducing cost. However, heterogeneous catalysts show reduced efficiency for the control of the polymerization, producing polymers with higher molecular weights than the theoretical values and broad molecular weight distributions due to a reduction of the radical deactivation rate, resulting in radical termination reactions and uncontrolled chain growth. More efficient heterogeneous catalyst systems are also being explored at present.[22−25] Addition of a small amount of soluble catalyst to the heterogeneous system enhances the deactivation rate, affording polymers with controlled molecular weights and low polydispersity;[26−29] however, obviously the soluble catalyst remains in the final polymer, if no additional purification step is applied.

Because of the problems encountered with heterogeneous ATRP catalysts, the interest in recoverable homogeneous catalysts is growing, since catalyst molecules can diffuse freely and take part effectively in the activation−deactivation cycle. To date, recoverable homogeneous catalysts can be classified into three categories: (i) Thermoresponsive catalyst complexes: the formed catalyst complex is soluble under reaction conditions, permitting a homogeneous transformation, but precipitates under workup conditions to render catalyst recycling possible. In this case good control of both polydispersities and molecular weights of the polymers was obtained.[22,30−33] The drawback of this kind of catalyst system is that only specific apolar solvents such as toluene and 1,4-dioxane can be used, which limits the monomers to apolar structures. (ii) Catalyst complexes conjugated with a second component that can be isomerized after the catalyzed transformation and thereby

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precipitated.[34] Stilbene-bound ligands successfully mediate the ATRP of methyl methacrylate (MMA) and allow for facile and fast removal of the copper catalyst by exposure of the solution to a UV light source. However, in this case the recovered catalyst complex loses its catalytic activity.[34] (iii) Catalyst complexes with good solubility in both polar and apolar solvents can be employed.[35] For the ATRP of apolar monomers, separation of the final products from the catalyst complex was achieved by pouring the solution into polar solvents.[35] The catalyst complex in the solution can be recovered by ultrafiltration[36,37] or simple evaporation of the volatiles.

Dendrimers and their less-defined hyperbranched analogues are attracting tremendous interest at present due to their specific shape and multifunctionality, which are powerful motifs in the design of new molecular and supramolecular structures.[38−42] Both dendrimers and hyperbranched polymers covalently or noncovalently functionalized with catalytically active transition-metal complexes are promising scaffolds with respect to catalyst recovery.[35−37,43−48] While the preparation of structurally perfect dendrimers suffers from its tedious multistep nature, hyperbranched polymers made from $AB_m$-type monomer in one step have emerged as excellent alternatives. To date, catalysis using hyperbranched macromolecules functionalized covalently or noncovalently with catalytic sites has received surprisingly limited attention.[35,44−48] Except for hyperbranched polycarbosilanes modified with aryldiamine−palladium(II) complexes,[44] the well-defined hyperbranched polyglycerol represents the only hyperbranched material used as polymeric support for the catalyst complexes.[35,45−48]

Herein we report the use of one-step modified hyperbranched polyethylenimine (HPEI) as support and macromolecular ligands ("macroligands") for the Cu(I)-catalyzed ATRP of MMA. The use of HPEI possesses the following advantages: (i) Simple one-step-modified HPEI can be used directly as macroligand to form a complex with the Cu(I) catalyst for ATRP; however, as for other hyperbranched polymers, low-molecular-weight ligands have to be attached by multistep reactions. (ii) HPEIs possess low toxicity and are used widely in gene transfection,[49−51] while low-molecular-weight ligands for ATRP, such as 2,2-bipyridines and their derivatives as well as multidentate amines, are toxic for humans as described by Aldrich. (iii) In addition, various molecular weight HPEIs are commercially available and considerably cheaper than other hyperbranched polymer supports.

## Experimental Section

**Materials.** CuBr (98%, Acros) was purified as described in the literature.[52] Methyl methacrylate (MMA, Aldrich, 99%) and styrene (St, Aldrich, 99%), were distilled under reduced pressure, stored in a refrigerator, and bubbled with argon for 1 h prior to use. *N*,*N*,*N*′,*N*′,*N*′′-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were distilled under reduced pressure and degassed with argon for 30 min prior to use. Ethyl 2-bromoisobutyrate (EBIB, 98%) was used as received from Aldrich. Butyl acrylate (BA, 99+%), ethyl acrylate (EA, 99%), CuCl (99.99%), $CuCl_2$ (99%), and $CuBr_2$ (99+%) were used as received from Acros.

The hyperbranched polyethylenimines HPEI1.2K (Polysciences, $M_n = 1200$, $M_w/M_n = 1.03$,), HPEI1.8K (Polysciences, $M_n = 1800$, $M_w/M_n = 1.04$), HPEI10K (Aldrich, $M_n = 10^4$, $M_w/M_n = 2.5$), and HPEI25K (Hyperpolymers GmbH, $M_n = 2.5 \times 10^4$, $M_w/M_n = 2.5$) were dried under vacuum prior to use.

**Characterization.** $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker ARX 300 spectrometer, operated at 300 and 75.4 MHz, respectively. The chemical shifts are given in parts per million (ppm). Molecular weights and molecular weight distributions were determined on a size exclusion chromatograph (SEC) consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, and a set of three PSS-SDV 5 $\mu$m columns with $10^2$, $10^3$, and $10^4$ Å porosity. Samples were measured with a Optilab DSP interferometric refractometer (RI detector) in chloroform (30 °C, flow rate of 1.0 mL/min) by injection of 150 $\mu$L of the polymer solution. Polystyrene standards provided by Polymer Standards Service were used for calibration. IR spectra were recorded on a Nicolet 5DXC FTIR spectrometer. Viscosities were measured by Lauda Processor-Viscosity-System 2.52a using $CHCl_3$ as solvent at 25 °C. Atomic absorption spectroscopy (AAS) was used to determine copper traces in the final polymer products. Samples were measured in THF solution with a Perkin-Elmer 5100 ZL AAS.

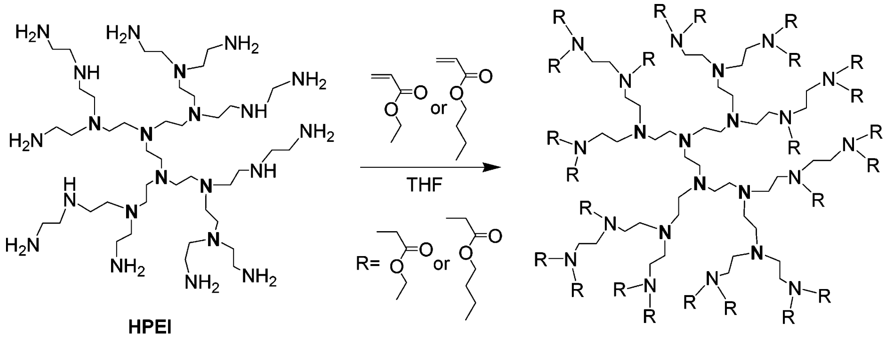
**Synthesis of the Hyperbranched Macroligands via Michael Addition of Butyl or Ethyl Acrylate with HPEI**. The synthetic procedure for partially EA- or BA-modified HPEI is exemplified for HPEI25K-$EA_{0.79}$: 1.00 g of HPEI25K ($M_n = 2.50 \times 10^4$, 23.3 mmol of amine groups) was dissolved in 5.00 mL of THF, and then 2.52 mL (23.3 mmol) of EA was added. The mixture was stirred at room temperature for 24 h and subsequently at 50 °C for another 24 h. The solvents were removed under vacuum, and a yellow honeylike polymer was obtained (2.83 g). $M_n = 7.09 \times 10^4$, yield = 100%. IR: $\nu = 1735$ cm$^{-1}$ (C═O). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ ($CH_3CH_2OOC-$), 2.38−2.73 ($-NCH_2CH_2$-$COO-$, $-NCH_2CH_2COO-$, $-NCH_2CH_2N-$ of PEI), 4.08 ($CH_3CH_2$-$OOC-$). $^{13}C$ NMR (75.4 MHz, $CDCl_3$, 25 °C): $\delta = 14.2$ ($CH_3CH_2OOC-$), 32.7 ($-NCH_2CH_2COO-$), 49.7−52.7 ($-NCH_2$-$CH_2COO-$, $-NCH_2CH_2N-$ of PEI), 60.3 ($CH_3CH_2OOC-$), 172.4 ($-NCH_2CH_2COO-$).

The synthetic procedure for fully EA- or BA-modified HPEIs is exemplified for HPEI25K-$EA_{1.01}$: 2.50 g of HPEI25K ($M_n = 2.50 \times 10^4$, 58.1 mmol of amine groups) was dissolved in 10.00 mL of THF, and then 20.00 mL (184.5 mmol) of EA was added. The mixture was stirred at room temperature for 5 days. Then the solvent was removed, and the residual polymer was redissolved in 20.00 mL of EA. The mixture was stirred for another 5 days at room temperature in order to obtain full conversion. This procedure was repeated until the reaction reached the maximum degree of conversion (followed by $^1H$ NMR). Solvents were evaporated to yield a yellow honeylike polymer (8.00 g). $M_n = 8.38 \times 10^4$, yield = 95.5%. IR: $\nu = 1735$ cm$^{-1}$ (C═O). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ ($CH_3CH_2OOC-$), 2.38−2.73 ($-NCH_2CH_2$-$COO-$, $-NCH_2CH_2COO$-, $-NCH_2CH_2N-$ of PEI), 4.08 ($CH_3CH_2$-$OOC-$). $^{13}C$ NMR (75.4 MHz, $CDCl_3$, 25 °C): $\delta = 14.2$ ($CH_3CH_2OOC-$), 32.7 ($-NCH_2CH_2COO-$), 49.7−52.7 ($-NCH_2$-$CH_2COO-$, $-NCH_2CH_2N-$ of PEI), 60.3 ($CH_3CH_2OOC-$), 172.4 ($-NCH_2CH_2COO-$).

All ligands were additionally purified by dialysis against chloroform for 2 days to completely remove low-molecular-weight impurities, using a benzoylated cellulose membrane (MWCO 1000 g/mol).

**ATRP of MMA Using the Hyperbranched Macroligand.** In a typical experiment, 84.1 mg (0.690 mmol of amine groups) of macroligand HPEI25K-$EA_{0.79}$, 8.1 mg (0.082 mmol) of CuCl, 4.00 mL (37.4 mmol) of MMA, and 2.00 mL of 1,4-dioxane were placed in a flask with a magnetic stir bar. The flask was sealed with a rubber septum and degassed by three freeze−pump−thaw cycles. Then 12 $\mu$L (0.082 mmol) of ethyl 2-bromoisobutyrate (EBIB) was introduced into the flask by an argon-purged syringe. The flask was then immersed in an oil bath thermostated at 80 °C. After 3 h, the flask was immersed into liquid nitrogen to quench the reaction. Samples were taken, diluted with deuterated chloroform, and subsequently analyzed by $^1H$ NMR spectroscopy (operated at 300 MHz). Comparing the integration of the double bonds of MMA monomers (2H, 6.06 and 5.52 ppm) with that of methyl groups of monomers and polymers (3H, 0.97 and 0.80 ppm), the monomer conversion was calculated. The residue was diluted with acetone and precipitated into 10-fold excess of methanol directly. The precipitated polymer was collected via filtration. In some cases, the material was then redissolved in acetone and reprecipitated in methanol. Pure samples were obtained after drying at 40 °C in vacuo for 2 days. Conversion: 79%. $M_{n(SEC)} = 2.63 \times 10^4$, PDI = 1.27.

**Scheme 1. Synthesis of Hyperbranched Macroligands via Michael Addition Reaction of Acrylates with Hyperbranched Polyethylenimine (HPEI)**



**Recovery and Reuse of the Macroligand−Copper Catalyst.** In a typical experiment, 84.1 mg (0.690 mmol of amine groups) of macroligand HPEI25K-$EA_{0.79}$, 8.1 mg (0.082 mmol) of CuCl, 4.00 mL (37.4 mmol) of MMA, and 2.00 mL of 1,4-dioxane were placed in a flask with a magnetic stir bar. The flask was sealed with a rubber septum and degassed by three freeze−pump−thaw cycles. Then 12 $\mu$L (0.082 mmol) of ethyl 2-bromoisobutyrate (EBIB) was introduced into the flask by an argon-purged syringe. The flask was then immersed in an oil bath thermostated at 80 °C. After 6 h, the conversion reached ca. 95%, verified by $^1$H NMR spectroscopy. The flask was then immersed into liquid nitrogen to quench the reaction. The mixture was diluted with acetone and directly precipitated into 10-fold excess of methanol. The precipitate was quickly removed using a Büchner funnel under reduce pressure. After the volatiles of the solution were distilled off under reduced pressure (the catalyst-containing solution and filtrate had to be exposed to air for a short period of time), the residue was redissolved in 2.00 mL of 1,4-dioxane and 4.00 mL of MMA, as in the first polymerization run. After the degassing step, the same amount of initiator, 12 $\mu$L (0.082 mmol) of EBIB, was introduced, and the flask was immersed in an oil bath thermostated at 80 °C under stirring. After 9 h, the polymerization was stopped, and the macroligand−copper catalyst was recovered as described above. The recovered macroligand−copper catalyst was reused for the third polymerization run under the same conditions as in the second polymerization run. First run: conversion = 95% (6 h); $M_{n(SEC)} = 2.83 \times 10^4$; PDI = 1.23; second run: conversion = 96% (9 h); $M_{n(SEC)} = 2.82 \times 10^4$; PDI = 1.29; third run: conversion = 94% (15 h); $M_{n(SEC)} = 2.73 \times 10^4$; PDI = 1.25.

## Results and Discussion

**Synthesis of the Hyperbranched PEI-Based Macroligands.** Efficient ligands for copper-mediated ATRP are usually composed of pyridine, tertiary amines, or Schiff bases.[7,8] Commercially available hyperbranched polyethylenimines consist of primary, secondary, and tertiary amine groups, and their structures are similar to tris(2-aminoethyl)amine (TREN), which is the precursor of the efficient ligands for copper-mediated ATRP, tris(2-dimethylaminoethyl)amine ($Me_6$-TREN),[53,54] and acrylate-TRENs[16] derived from Michael addition of TREN with acrylates. Compared with $Me_6$-TREN, the properties of acrylated TRENs can be tailored conveniently, and a broader range of monomers can be polymerized in a controlled manner with acrylate-based TRENs as the ligand for the copper-mediated ATRP.[16] Thus, we modified HPEI with EA or BA via Michael addition reaction to generate the macroligands for the copper-mediated ATRP (Scheme 1).

The resulting polymers were characterized by $^1$H and $^{13}$C NMR spectroscopy. All signals can be assigned, as shown in Figure 1. The ratio of EA or BA moieties (R groups in Scheme 1) relative to amine groups of HPEI ([R]/[amine]) can also be calculated from their corresponding integration (I) in the $^1$H NMR spectra (Figure 1) according to eq 1.

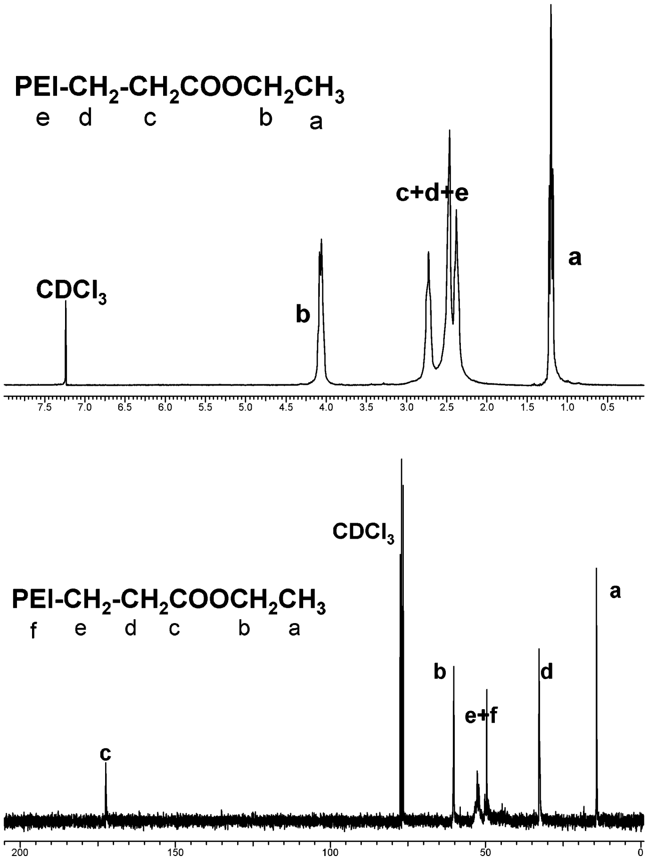


**Figure 1.** Typical $^1$H and $^{13}$C NMR spectra (operated at 300 and 75.4 MHz, respectively) of hyperbranched macroligands obtained from the Michael addition of hyperbranched PEI with ethyl acrylate (HPEI25K-$EA_{1.01}$).

$$[\mathrm{R}]/[\mathrm{amine}] = 2I_{(b)}/[I_{(c+d+e)} - 2I_{(b)}] \qquad (1)$$

$I_{(b)}$ is the integration of protons of methylene units attached to ester groups ($CH_3CH_2OOC-$); $I_{(c+d+e)}$ is the integration of protons of ethylene groups adjacent to carbonyl groups and amine groups and ethylene units from HPEI ($-NCH_2CH_2$-COO−, $-NCH_2CH_2COO$-, $-NCH_2CH_2N-$ of PEI).

Clearly, one primary amine can react with two EA or BA molecules, one secondary amine can only react with one EA or BA molecule, and tertiary amines usually do not react with EA or BA by the Michael addition reaction.[55] Thus, on the basis of the mole ratio of primary, secondary, and tertiary amine groups ($NH_2$:NH:N) of HPEIs, the theoretical maximum ratio of EA or BA moieties relative to amine groups of HPEI can be

**Table 1. Hyperbranched Polyethylenimine (HPEI)-Based Macroligands**

| ligand name[a] | $M_{n-\mathrm{HPEI}} \times 10^{-3}$ | [R]/[amine][b] | $M_n \times 10^{-4}$ [c] |
|---|---|---|---|
| HPEI1.2K-EA$_{0.73}$ | 1.2 | 0.73 | 0.32 |
| HPEI1.8K-EA$_{0.87}$ | 1.8 | 0.87 | 0.55 |
| HPEI10K-EA$_{1.06}$ | 10 | 1.06 | 3.46 |
| HPEI10K-EA$_{0.77}$ | 10 | 0.77 | 2.79 |
| HPEI10K-BA$_{0.76}$ | 10 | 0.76 | 3.27 |
| HPEI25K-EA$_{1.01}$ | 25 | 1.01 | 8.38 |
| HPEI25K-EA$_{0.79}$ | 25 | 0.79 | 7.09 |
| HPEI25K-BA$_{1.01}$ | 25 | 1.01 | 10.0 |
| HPEI25K-BA$_{0.76}$ | 25 | 0.76 | 8.17 |

[a] Nomenclature: HPEI*X*-*Y*$_z$: HPEI, hyperbranched polyethylenimine scaffold; *X*, $M_n$ of HPEI; *Y*, BA or EA; *z*, ratio of EA or BA moieties relative to amine groups of HPEI. [b] Ratio of EA or BA moieties relative to amine groups of HPEI, $[R]/[amine] = 2I_{(b)}/[I_{(c+d+e)} - 2I_{(b)}]$ according to the typical $^1$H NMR in Figure 1. [c] Calculated from $^1$H NMR operated at 300 MHz.

calculated according to eq 2.

$$([R]/[amine])_{max} = (2[NH_2] + [NH])/([NH_2] + [NH] + [N]) \quad (2)$$

The mole ratio of primary, secondary, and tertiary amine groups ($NH_2$:NH:N) for HPEI1.2K, HPEI1.8K, HPEI10K, and HPEI25K has been obtained from their inverted gate $^{13}$C NMR spectra to be 37:35:28, 37:35:28, 33:40:27, and 33:35:32, respectively. Since the amount of primary amines is higher than that of tertiary amines for all the employed HPEIs, the maximum ratio [R]/[amine] should exceed 1, i.e., 1.09, 1.09, 1.06, and 1.01 for HPEI1.2K, HPEI1.8K, HPEI10K, and HPEI25K, respectively.

Syntheses of hyperbranched macroligands with maximum ratio [R]/[amine] were time-consuming (more than 10 days), and a considerable excess of EA or BA was required. For comparison, we also prepared the more easily available hyperbranched macroligands with ratio [R]/[amine] less than maximum, which can be obtained in a one-pot procedure within 2 days. All obtained hyperbranched macroligands are listed in Table 1.

**ATRP of MMA with HPEI-Based Macroligands.** All hyperbranched macroligands can complex with Cu(I), and the complexes are fully soluble in toluene, acetone, 1,4-dioxane, tetrahydrofuran (THF), and methanol. For the copper-mediated ATRP with Me$_6$-TREN or acrylate-TREN as ligand, the ratio of amine groups of the ligands to copper were usually set to be 4:1. The structure of the obtained macroligands is similar to acrylate-TREN; thus, the lowest ratio of amine groups of macroligands to copper should be 4:1. In the first experiments the ratio of amine groups of macroligands to copper was set to 4:1. Detailed polymerization conditions for the ATRP of MMA are described in the experimental part. EBIB was used as initiator. However, after purification by precipitating the polymerization mixture into methanol, the resulting polymer was greenish, indicating that the material was still contaminated with large amounts of copper. Increasing the ratio of amine groups of the macroligands to copper to 5:1, the same phenomenon was observed. From the typical structure of hyperbranched macroligands shown in Scheme 1, it is obvious that the amine groups of the macroligands are also present in the interior. The interior amine groups may not coordinate well with copper due to steric effects, resulting in a fraction of uncomplexed copper ions in the polymerization system, when the ratio of amine groups of macroligands to copper is chosen to be 4:1 or 5:1. The greenish color of the resulting polymer is therefore ascribed to trapped free copper ions during precipitation of PMMA. To reduce the concentration of free copper ions in the polymerization system, the ratio of amine groups of the macroligand to copper was raised to 10:1. After polymerization and purification, a colorless material was obtained, indicating that nearly no free copper ions were present in the polymerization system, when the ratio of amine groups of macroligands to copper was set to be approximately 10:1 or higher. Therefore, in all subsequent polymerization runs, the ratio of amine groups of macroligands to copper was fixed to be 10:1.

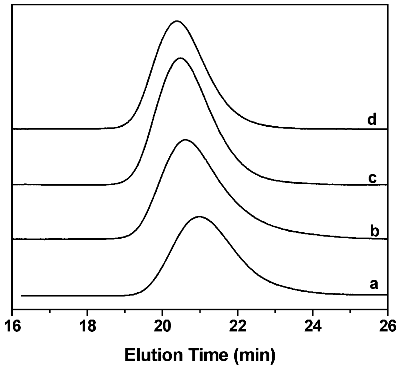


**Figure 2.** Typical SEC traces of poly(methyl methacrylate) prepared with HPEI25K-EA$_{0.79}$ as macroligand; polymerization conditions: [M]:[I]:[CuCl]:[amine groups of ligands] = 254:1:1:10. Ethyl 2-bromoisobutyrate (EBIB) was used as initiator, $V_{MMA}/V_{solvent} = 2$ (volume ratio of MMA to solvent), at 80 °C in 1,4-dioxane. $M_n$ was measured by SEC in $CHCl_3$ at 30 °C. (a) $M_n = 1.50 \times 10^4$, PDI = 1.31; (b) $M_n = 1.95 \times 10^4$, PDI = 1.37; (c) $M_n = 2.54 \times 10^4$, PDI = 1.28; (d) $M_n = 2.72 \times 10^4$, PDI = 1.25.

Molecular weights ($M_{n(SEC)}$) and polydispersities of the resulting poly(methyl methacrylate) samples were measured by SEC equipped with a RI detector. Figure 2 shows typical SEC traces for the obtained polymers. All molecular weight distributions are unimodal, and the polydispersity index (PDI) values are in the range of 1.2−1.4 (Table 2), indicating that EA- or BA-modified HPEIs are suitable macroligands for the copper-mediated ATRP of MMA.

Kinetic studies have been carried out using the following ratios: [M]:[I]:[CuCl]:[amine of ligands] = 254:1:1:10, $V_{MMA}/V_{dioxane} = 2$ (volume ratio of MMA to 1,4-dioxane). Samples were taken from the reaction mixture via syringes at certain time intervals for conversion measurements ($^1$H NMR) and molecular weight determination (SEC). The respective first-order kinetic plot is depicted in Figure 3. Ln($[M]_0/[M]_t$) shows a linear dependence on time, indicating a constant concentration of propagating species throughout the reaction. Molecular weights increase linearly with conversion, and the molecular weight distributions are fairly narrow ($M_w/M_n < 1.4$) (Figure 4), demonstrating that the ATRP of MMA with macroligands derived from HPEI represents a controlled process.

The preparation of hyperbranched PEI macroligands with maximum [R]/[amine] value was time-consuming and laborious. Thus, it is important to clarify whether the maximum [R]/[amine] value is a necessary precondition. It is obvious from Table 2 that the polymerization results using hyperbranched macroligands with maximum and lower [R]/[amine] values are similar (entries 1−6 in Table 2), indicating that the extent of control over the polymerization does not critically depend on full acrylate substitution of the macroligand. The effect of the nature of the alkyl group (EA or BA) at the hyperbranched macroligands on the ATRP of MMA has also been studied, and also this parameter does not lead to obvious differences in the catalytic activities for the polymerization or the quality of the resulting polymers (entries 1−4, 6, and 7 in Table 2). However, variation of the molecular weight of the HPEI scaffold showed

**Table 2. Atom Transfer Radical Polymerization (ATRP) of Methyl Methacrylate (MMA) Using Hyperbranched Polyethylenimine (HPEI)-Based Macroligands**[a]

| entry | ligands | time (h) | conv (%) | $M_{n(calc)} \times 10^{-4}$ | $M_{n(SEC)} \times 10^{-4}$ | initiation efficiency[b] | PDI |
|---|---|---|---|---|---|---|---|
| 1 | HPEI25K-EA$_{1.01}$ | 3 | 76 | 1.95 | 2.70 | 0.72 | 1.26 |
| 2 | HPEI25K-EA$_{0.79}$ | 3 | 79 | 2.03 | 2.63 | 0.77 | 1.27 |
| 3 | HPEI25K-BA$_{1.01}$ | 3 | 79 | 2.03 | 2.61 | 0.78 | 1.32 |
| 4 | HPEI25K-BA$_{0.76}$ | 3 | 82 | 2.10 | 2.63 | 0.80 | 1.29 |
| 5 | HPEI10K-EA$_{1.06}$ | 2.5 | 68 | 1.75 | 2.30 | 0.76 | 1.31 |
| 6 | HPEI10K-EA$_{0.77}$ | 2.5 | 71 | 1.83 | 2.48 | 0.74 | 1.27 |
| 7 | HPEI10K-BA$_{0.76}$ | 2.5 | 73 | 1.88 | 2.59 | 0.73 | 1.29 |
| 8 | HPEI1.8K-EA$_{0.87}$ | 3 | 89 | 2.28 | 3.87 | 0.59 | 1.27 |
| 9 | HPEI1.2K-EA$_{0.73}$ | 3 | 92 | 2.36 | 4.06 | 0.58 | 1.33 |

[a] ATRP conditions: [M]:[I]:[CuCl]:[amine of ligands] = 254:1:1:10, ethyl 2-bromoisobutyrate (EBIB) as initiator, $V_{MMA}/V_{solvent} = 2$ (volume ratio of MMA to 1,4-dioxane), at 80 °C in 1,4-dioxane. The conversion was calculated from $^1$H NMR; $M_{n(calc)}$ was calculated from conversion. [b] Initiation efficiency = $M_{n(calc)}/M_{n(SEC)}$.

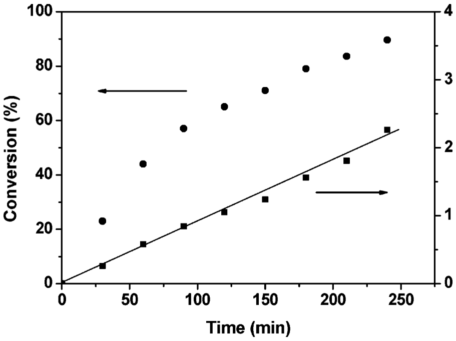


**Figure 3.** Dependence of monomer conversion and ln([M]$_0$/[M]$_t$) on time for the polymerization of methyl methacrylate in 1,4-dioxane, using HPEI25K-EA0.79/CuCl as homogeneous catalyst at 80 °C. Ethyl 2-bromoisobutyrate (EBIB) was used as initiator, [M]:[I]:[CuCl]:[amine groups of HPEI25K-EA0.79] = 254:1:1:10, $V_{MMA}/V_{dioxane} = 2$ (volume ratio of MMA to 1,4-dioxane).

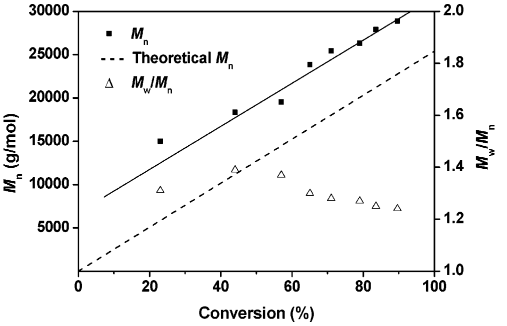


**Figure 4.** Dependence of molecular weight and polydispersity on conversion for poly(methyl methacrylate) obtained from atom transfer radical polymerization of methyl methacrylate, using HPEI25K-EA$_{0.79}$/CuCl as homogeneous catalyst at 80 °C.

obvious effects on the catalytic activity (entries 2, 6, 8, and 9 in Table 2). Upon lowering the molecular weight of HPEI, the polymerization rate increased.

The $M_n$ values of PMMA obtained from SEC using polystyrene calibration standards can be taken as absolute molecular weights, since they have been demonstrated to exhibit very little difference with those from SEC using PMMA standards for calibration.[17,32,33] To confirm this, the viscosity of two PMMA samples has been measured, and their respective absolute molecular weights were calculated on the basis of their respective viscosities. These were found to be very similar to the values obtained from SEC using polystyrene standards for calibration. Thus, in this paper the $M_{n(SEC)}$ of the obtained PMMA samples was also regarded as absolute $M_n$. This is important, since by comparing the molecular weights obtained from the theoretical calculations ($M_{n(cacl)}$) with $M_{n(SEC)}$, the polymerization initiation efficiency ($M_{n(cacl)}/M_{n(SEC)}$) can be calculated. The initiation efficiencies for the polymerization with the hyperbranched macroligands from HPEI1.2K and HPEI1.8K are obviously lower than those from the macroligands with higher molecular weights, indicating that the control of polymerization with the hyperbranched macroligands from low-molecular-weight HPEI is limited. In addition, the separation of the low-molecular-weight macroligand complex with copper from the resulting PMMA by a precipitation procedure is difficult; i.e., the PMMA products still show greenish color after the precipitation purification, confirming that the products are contaminated with copper. From Table 2 it is obvious that all initiation efficiencies of the ATRP of MMA with hyperbranched macroligands are below 100%. Similar phenomena have also been observed by other groups. For example, Brooks et al.[35] observed reduced initiation efficiency when using multiamines supported on hyperbranched polyglycerol as a ligand. The lower initiation efficiency might be attributed to the very high activation ability of the CuX−macroligand catalyst system, leading to a high concentration of primary radical species from the sacrificial initiators at the beginning of the polymerization, which result in a loss of initiator due to termination reactions, just as in the ATRP of MMA using the low-molecular-weight analogue of HPEI, Me$_6$-TREN, as a ligand.[53,54]

For an additional improvement of the initiation efficiencies and the polydispersity of the polymers, the easy available hyperbranched macroligand, HPEI25K-EA$_{0.79}$, showing better control of the ATRP of MMA and purification of the products, was chosen. The results are listed in Table 3. A fast and reversible transition between the activating agent CuX (X = Cl or Br) and the deactivating agent CuX$_2$ is the key parameter in ATRP systems to ensure a controlled radical polymerization process. CuX$_2$ can deactivate most of the active propagating radical species into dormant ones, suppressing radical coupling side reactions.[7,8] Since the lower initiation efficiency for the Cu(I)−HPEI macroligand catalyst system might be attributed to the very high concentration of primary radical species from the sacrificial initiators activated by CuX at the beginning of the polymerization, ATRP experiments of MMA with additional CuX$_2$ preintroduced into the polymerization mixture have been carried out. To our surprise, the introduction of an excess amount CuX$_2$ did not improve the polymerization but contrarily reduced the initiation efficiency (comparing entries 7 with 3 and entries 8 with 2 in Table 3). The cause for this phenomenon is currently being explored.

When CuBr was used as a catalyst, the initiation efficiency was much lower than with CuCl as a catalyst (comparing entries 9 with 6 in Table 3), which may be due to the higher activity of CuBr,[7,8] resulting in a considerably higher concentration of primary radical species at the beginning of the polymerization. Other parameters, such as the ratio of CuCl to macroligand and

**Table 3. Atom Transfer Radical Polymerization of Methyl Methacrylate Using HPEI25K-EA$_{0.79}$ as Macroligand**[a]

| entry | solvent | $T$ (°C) | time (h) | conv (%) | $M_{n(calc)} \times 10^{-4}$ | $M_{n(SEC)} \times 10^{-4}$ | initiation efficiency[g] | PDI |
|---|---|---|---|---|---|---|---|---|
| 1 | 1,4-dioxane | 80 | 0.5 | 23 | 0.61 | 1.50 | 0.41 | 1.31 |
| 2 | 1,4-dioxane | 80 | 1 | 44 | 1.14 | 1.83 | 0.62 | 1.40 |
| 3 | 1,4-dioxane | 80 | 2 | 65 | 1.67 | 2.30 | 0.73 | 1.30 |
| 4 | 1,4-dioxane | 80 | 3 | 79 | 2.03 | 2.63 | 0.77 | 1.27 |
| 5 | 1,4-dioxane | 80 | 3.5 | 84 | 2.16 | 2.72 | 0.80 | 1.25 |
| 6 | 1,4-dioxane | 80 | 4 | 90 | 2.31 | 2.89 | 0.83 | 1.24 |
| 7[b] | 1,4-dioxane | 80 | 4 | 71 | 1.83 | 2.90 | 0.63 | 1.23 |
| 8[c] | 1,4-dioxane | 80 | 7 | 45 | 1.20 | 3.56 | 0.34 | 1.29 |
| 9[d] | 1,4-dioxane | 80 | 3 | 91 | 2.33 | 3.97 | 0.59 | 1.31 |
| 10[e] | 1,4-dioxane | 80 | 2.5 | 68 | 1.75 | 2.48 | 0.71 | 1.23 |
| 11 | toluene | 80 | 2.5 | 62 | 1.60 | 2.49 | 0.64 | 1.25 |
| 12 | acetone | 60 | 20 | 67 | 1.73 | 2.22 | 0.78 | 1.39 |
| 13[f] | acetone | 60 | 48 | 72 | 1.85 | 2.76 | 0.67 | 1.26 |

[a] ATRP conditions: [M]:[I]:[CuCl]:[amine groups of ligands] = 254:1:1:10, ethyl 2-bromoisobutyrate (EBIB) as initiator, $V_{MMA}/V_{solvent} = 2$. The conversion was calculated from $^1$H NMR, operated at 300 MHz; $M_{n(calc)}$ was calculated from conversion. [b] With 5% $CuBr_2$. [c] With 10% $CuCl_2$. [d] Using CuBr as catalyst. [e] $V_{MMA}/V_{Solvent} = 0.5$. [f] [M]:[I]:[CuCl]:[amine groups of ligands] = 254:1:1:20. [g] Initiation efficiency = $M_{n(calc)}/M_{n(SEC)}$.

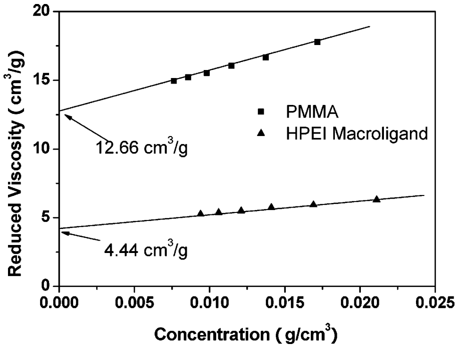


**Figure 5.** Viscosity of (■) poly(methyl methacrylate) (PMMA) ($M_n = 2.49 \times 10^4$, PDI = 1.25) and (▲) HPEI macroligand HPEI25K-EA$_{0.79}$ ($M_n = 7.09 \times 10^4$) in $CHCl_3$ at 25 °C.

the type or amount of solvent, have also been tested in this context; however, the initiation efficiency could not be improved significantly.

**Separation of the Hyperbranched Macroligand/Copper Complex from PMMA.** Usually silica or alumina gels have to be used to separate low-molecular-weight copper complexes from the polymers. However, in this case large amounts of waste are produced, and the catalyst complex can usually not be recovered and reused. In our case, the hyperbranched macroligand−copper complex can be separated from the PMMA product by simple precipitation of the polymerization mixture into methanol, which is due to the large solubility difference between the macroligand and the polymer. As we described before, all the hyperbranched macroligands can complex with Cu(I), and the complexes are fully soluble in solvents with a range of different polarities, such as toluene, acetone, dioxane, THF, and methanol, while PMMA is not soluble in the polar solvent methanol.

After filtration, the precipitated PMMA polymers are obtained as white materials, while the solution is green (Figure S1, Supporting Information), indicating that the copper had been effectively transferred into the methanol phase in a complexation form with the hyperbranched macroligand. The catalyst complex could be recovered by removing the volatiles under vacuum. Moreover, a control experiment with PMDETA as ligand has also been conducted, and the resulting polymer was obtained as an intensely green material (Figure S2, Supporting Information), indicating that the complex of copper with low-molecular-weight ligands cannot be efficiently separated from PMMA by simple precipitation in methanol.

Figure 5 shows the viscosity of HPEI25K-EA$_{0.79}$ and the corresponding PMMA synthesized with this hyperbranched macroligand using the ATRP method. As expected, the hyperbranched macroligand possesses much lower viscosity than the final PMMA due to its compact structure. Therefore, it can be deduced that the presence of a hyperbranched macroligand will not lead to a problematic contribution to the final viscosity of the reaction system. This may represent an additional advantage besides the solubility issue. Modified linear PEI has not been used as a macroligand since it possesses higher viscosity as reported previously,[56,57] which is comparable to that of the obtained linear PMMA product. Moreover, chain entanglement or interaction between linear polymers might prevent efficient transfer of the copper complex into methanol during the precipitation process, resulting in Cu-contaminated PMMA.

**Table 4. Atom Transfer Radical Polymerization of Methyl Methacrylate with Recycled Catalyst System**[a]

| run | time (h) | conv (%) | $M_{n(SEC)}$ $\times 10^{-4}$ | $M_{n(calc)}$ $\times 10^{-4}$ | PDI |
|---|---|---|---|---|---|
| 1st cycle with fresh catalyst | 6 | 95 | 2.83 | 2.44 | 1.23 |
| 2nd cycle with recycled catalyst | 9 | 96 | 2.82 | 2.46 | 1.29 |
| 3rd cycle with recycled catalyst | 15 | 94 | 2.73 | 2.41 | 1.25 |

[a] ATRP conditions: [M]:[I]:[CuCl]:[amine groups of ligands] = 254:1:1:10, ethyl 2-bromoisobutyrate (EBIB) as initiator, $V_{MMA}/V_{solvent} = 2$, at 80 °C, 1,4-dioxane as solvent, HPEI25K-EA$_{0.79}$/CuCl as catalyst system.

**Residual Copper.** Atomic absorption spectroscopy (AAS) was used to determine the residual copper content in the PMMA with THF as solvent. According to AAS, 16.5 ppm of Cu remained in the final PMMA products after the first precipitation from methanol. The copper concentration can be reduced to 12 ppm via a second precipitation step, which is still higher than the value of 5 ppm achieved with a heterogeneous catalyst system,[17] but is comparable to the value of 15 ppm with a heterogeneous catalyst system combined with a small amount of soluble catalyst,[26] and considerably better than the value of 200 ppm reported for thermoresponsive catalyst complexes.[33]

**Recycling of the Hyperbranched Macroligand−Cu Complex.** After recovering the complex of the hyperbranched macroligand with copper, it was reused for the ATRP of MMA. The polymers obtained using recycled catalyst systems during the second cycle and the third cycle still possess similarly narrow molecular weight distributions at high conversion (Table 4) as the product from the first run.

Kinetic studies for the fresh and the reused catalyst system have also been carried out. All the curves of ln([M]$_0$/[M]$_t$) vs time are linear (Figure 6), indicating a constant number of propagating species throughout the reaction. Molecular weights

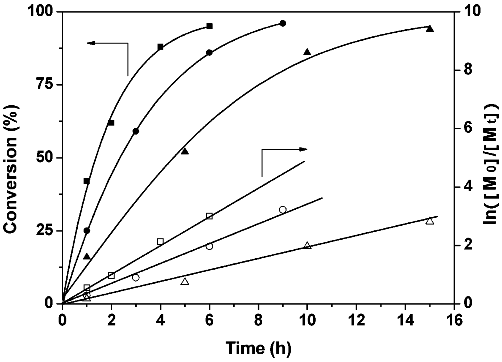


**Figure 6.** Dependence of monomer conversion and $\ln([M]_0/[M]_t)$ on time for the polymerization of methyl methacrylate in 1,4-dioxane, reusing hyperbranched HPEI25K-EA$_{0.79}$/CuCl as recoverable homogeneous catalyst at 80 °C. Reaction conditions as indicated in Table 4. (■, □) first cycle, (●, ○) second cycle, and (▲, △) third cycle.

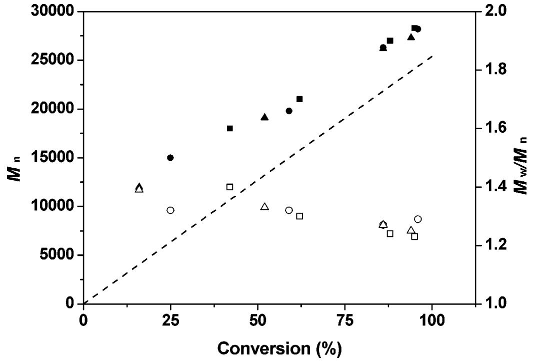


**Figure 7.** Molecular weight vs conversion for poly(methyl methacrylate) obtained from recycled catalyst at 80 °C: (■, □) first cycle, (●, ○) second cycle, and (▲, △) third cycle.

increase in a linear fashion with conversion, and the molecular weight distributions are fairly narrow in all cases ($M_w/M_n$ < 1.4) (Figure 7), demonstrating that the recycled catalysts are still active for the ATRP of MMA. Clearly, the polymerizations can still be controlled until the third cycle.

However, the concentration of propagating species in the polymerization decreased, and consequently the reaction time required for the same conversion had to be raised with increasing the number of cycles (Figure 6). We tentatively explain this by partial oxidation of the active Cu(I) catalyst to the deactivating Cu(II) agent. The deactivating Cu(II) agent can be formed in two ways: (i) during polymerization or (ii) during precipitation of the macroligand−Cu(I) catalyst complex since the catalyst is inevitably exposed to air for some time, resulting in partial oxidation of the active Cu(I) catalyst. In the reported heterogeneous catalytic system,[25,32] because of the generation of the deactivating Cu(II) agent, better control for the polymerization was observed when recycled catalyst was used. However, in our system the generated deactivating Cu(II) agent in the second and third cycles did not aid to improve the polymerization initiation efficiency and the quality of the final products. The products obtained from different cycles at the same conversion possess similar molecular weight and polydispersity.

## Conclusions

Hyperbranched macroligands were successfully prepared by the facile Michael addition reaction of hyperbranched PEI with EA or BA. The resulting hyperbranched macroligand/Cu(I) complexes are efficient catalyst systems for the ATRP of MMA. The ATRP of MMA with hyperbranched macroligands is a controlled process since $\ln([M]_0/[M]_t)$ is a linear function of time. Molecular weights of the resulting PMMA increase linearly with conversion, and the molecular weight distributions are fairly narrow ($M_w/M_n$ < 1.4) even at very high conversion. However, the initiation efficiency of the polymerization using hyperbranched macroligands is less than 100%, usually in the range of 0.41−0.83. The compact structure not only leads to very low viscosity compared with the synthesized linear PMMA but also imparts facile separation from the PMMA product by precipitation of the polymerization mixture in methanol. Copper is separated together with the hyperbranched macroligands, and no extra steps are required to purify the polymer from copper contamination. The hyperbranched macroligand/CuCl system can be recycled for the ATRP of MMA, keeping relatively high activity.

Preliminary tests of these macroligands for the ATRP of acrylate monomers (ethyl acrylate and butyl acrylate) and styrene have also been carried out. The results for acrylate monomers are comparable to those for MMA. However, in the case of styrene monomer, first experiments indicated larger polydispersity for the obtained polystyrene samples (around 1.6−1.9). Additional optimization for the ATRP of styrenic monomers is still in progress.

**Supporting Information Available:** Figures showing separation of HPEI25K-EA$_{0.79}$/CuCl from polymerization mixture (Figure S1) and PMMA products after purification by precipitation, using either hyperbranched macroligands or low-molecular-weight ligands (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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