ATOM TRANSFER POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY CARBOSILANE DENDRITIC SPECIES

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Introduction

Dendrimers are a relatively new class of materials which have recently received attention for, e.g., catalysis and supported synthesis[1] The accurate control of these macromolecules in for example the dendritic initiated atom transfer polymerization is an important theme in modern polymer science.[2]

Herein we report a range of carbosilane dendrimers (zeroth and first generation) which have been functionalized with a tertiary bromide species (see Scheme 1 and Figure 1) and, subsequently, polymerized via atom transfer polymerization using methyl methacrylate (MMA) as monomer. Schiff's base ligands were used for Cu(I)Br complexation. The use of these ligands have proven to be extremely effective for atom transfer polymerization of methacrylates and other vinyl monomers.[3] The influence of the dendritic initiators on the molecular weight distributions of the polymer material produced throughout the 'living' radical polymerization process was investigated (see Scheme 2),
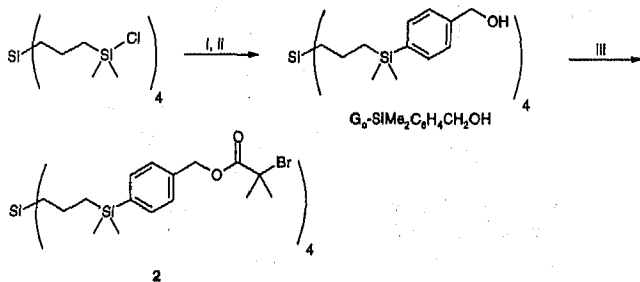
Scheme 1. Synthesis of the functionalized carbosilane dendrimers. Reagents and conditions: (i) $LiC_6H_4CH_2OSiMe_2(tBu)$, Et_2O, -20 °C; (ii) $Et_3N\cdot3HF$, 17 h; (iii) $BrC(O)CMe_2Br$, pyridine, THF, rt.

Experimental

Derivatized G_1 carbosilane dendrimer, 3. To a solution of G_1-$SiMe_2C_6H_4CH_2OH$ (0.21 g, 0.075 mmol) and pyridine (0.11, 1.35 mmol) in THF was added dropwise a solution of 2-bromoisobutyryl bromide (0.23 g, 1.0 mmol) in THF (5 ml). After stirring overnight at room temperature the reaction mixture was poured into aqueous HCl (50 ml, 4 M). The waterlayer was extracted with CH_2Cl_2 (3x100 ml). The combined organic layers were extracted with aqueous solution of NaOH (3x 50 ml, 3 M). The organic layer was dried with Na_2SO_4 and the solvent was removed *in vacuo*. The product was purified by column chromatography on basic alumina and isolated as a viscous slightly yellow oil in 68% yield (0.23 g, 0.051 mmol). ^1H NMR (CDCl₃): δ 7.48 (d, 24 H, Ar(*H*)); 7.34 (d, 24 H, Ar(*H*)); 5.18 (s, 24 H, ArC*H₂*O); 1.95 (s, 72 H, C*Me₂*); 1.23 (m, 32 H); 0.81 (t, 24 H); 0.58 (m, 40 H); 0.22 (s, 72 H). ^{13}C NMR (CDCl₃): δ 171.6 (*C*(O)); 140.1, 136.1, 134.0, 127.2 (Ar(*C*)); 67.7 (*C*H₂); 55.9 (*C*Me2); 31.0 (C*Me₂*); 20.8, 18.9 (two signals overlapping), 18.5, 18.1, 17.7 (inner and outer core CH₂ groups); -2.5 (Si*Me₂*). Calcd. for $C_{204}H_{312}Br_{12}O_{24}Si_{17}$ (4585.0): C, 53.44; H, 6.86; Si, 1041. Found: C, 53.60; H, 6.94; Si, 10.33. MALDI-TOF-MS: 4592.5 (M+ Na)⁺ (Calcd. 4591.9 (M+Na)⁺).

Derivatized model compound ($PhCH_2OC(O)CMe_2Br$) and G_0 carbosilane dendrimer, 1 and 2.

The model compound and the zeroth generation carbosilane dendrimer were synthesized from benzyl alcohol and of G_0-$SiMe_2C_6H_4CH_2OH$, respectively, under similar conditions to the derivatized G_1 carbosilane dendrimer.
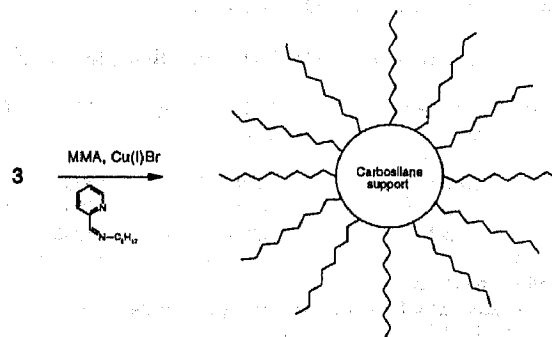
Atom tranfer polymerization of methyl methacrylate with 3 as initiator, $MMA/Cu(I)Br/n$-octyl ligand/actual initiator = 100/1/2/1 in 20 % xylene solution. Initiator, 3, (148.5 mg, $3.2\ 10^{-5}$ mol), Cu(I)Br (55.7 mg, $3.88\ 10^{-4}$ mol), n-octyl-2-pyridylmethanimine (169.7 mg, $7.78\ 10^{-4}$ mol), deoxygenated inhibitor-free MMA (4.15 ml) and deoxygenated xylene (16.6 ml). The solution was freeze-pump-thawed three times and subsequently heated to 90 °C. Samples were removed periodically for 3 h for both gravimetrical and GPC analysis, via syringe. All molecular weight distribution data were recorded using non-precipitated polymer. Polymerization of MMA with 1 and 2 as initiator were carried out under similar conditions.
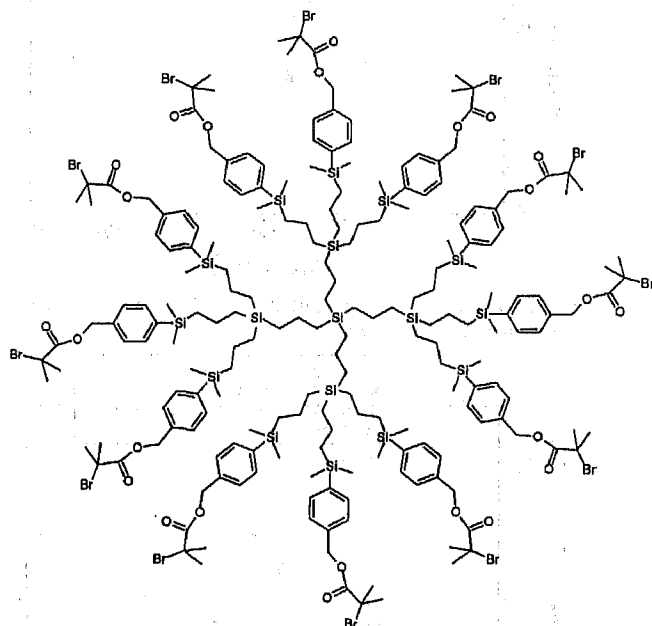
Figure 1. Schematical representation of the dendritic initiator 3.

Results and Discussion

Esterification of the appropriate alcohols with 2-bromo-isobutyryl bromide proceeds at ambient temperature in the presence of base (see Scheme 1 and Figure 1). This is a versatile route that proceeds in quantitative yield to initiators for atom transfer polymerization.

Scheme 2. Synthesis of MMA star from derivatized G1 Carbosilane dendrimer.

Atom transfer polymerization reactions of MMA in xylene (20 %v/v) using n-octyl-2pyridyl-methanimine as bidentate ligand for copper complexation, in conjunction with Cu(I)Br and with 1, 2 or 3 as initiator (see Scheme 2), were carried out at 90 °C. Samples were taken in time for analysis of the monomer conversion and of the cumulative MWD of the polymer material. The results are given in Figures 2 and 3. The concentration of 1, 2 and 3, the actual concentration of initiating sites, and the $<M_n>$ and PDI values of the final polymer product after 3 h of reaction time, are given in Table 1.
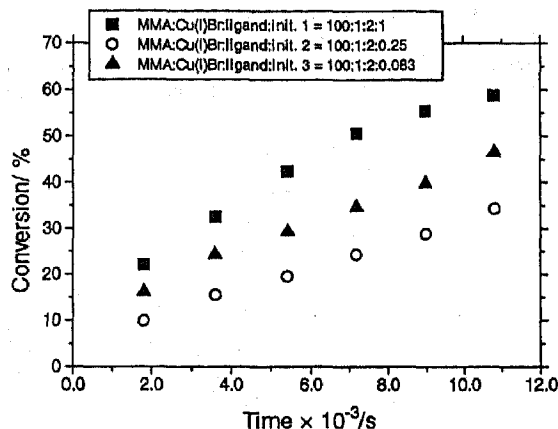

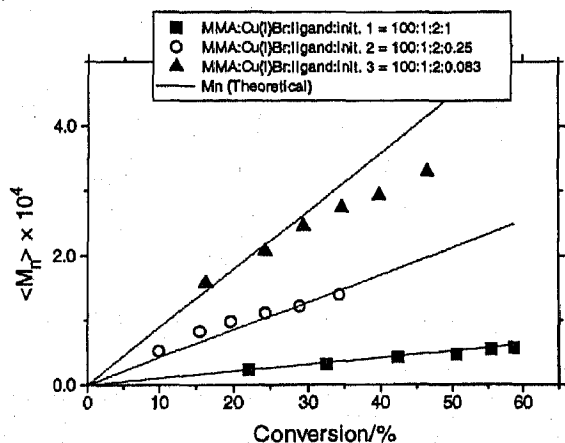**Figure 2.** The conversion of initiators **1, 2** or **3** in the atom transfer polymerization of MMA vs. time.

Figure 3. Evolution of $<M_n>$ vs. conversion for the atom transfer polymerisation of MMA initiated by **1, 2** or **3**.

Table 1. Polymerization of MMA with functional initiators[a]

Initiator	No. of mol	Actual initiating site/mol	$<M_n>$	PDI[b]
1	$3.89\ 10^{-4}$	$3.89\ 10^{-4}$	5673	1.17
2	$9.72\ 10^{-5}$	$3.89\ 10^{-4}$	13858	1.18
3	$3.23\ 10^{-5}$	$3.89\ 10^{-4}$	32982	1.29

[a] Reaction time 3 hours.
[b] Determined using GPC with lineair poly(MMA) standards.

The preliminary results of conversion vs. time (see Figure 2) show no marked difference in the overall rate of polymerization for the three initiators. From Table 1 it can be concluded that the atom transfer polymerization reactions were successful and that reasonable narrow MWDs were obtained. The model compound, i.e., 1 produced a linear polymer and thus GPC analysis will give correct values for the molecular weights of the PMMA produced. As can be

seen in Figure 3 the theoretical values of $<M_n>$ correspond with the experimental ones. The same holds approximately for the dendritic initiator of generation zero, i.e. 2, which will produce a four-armed star polymer. This polymer will be restricted in its hydrodynamic volume. However, the number of branching points is only one, so no marked difference in hydrodynamic volume compared to a free random linear polymer coil will exist. Hence, the apparent molecular weights determined with GPC are a good indication for the actual experimental ones. This can indeed be observed from Figure 3, in which the $<M_n>$ values coincide with the calculated theoretical values.

Conventional GPC analysis of the dendritic initiator of generation one, i.e. 3, however, will not yield correct values for the molecular weight. The presence of five branching points in the dendritic structure (see Figure 1) will restrict its conformational freedom and, thus, lower its hydrodynamic volume, which will result in lower observed values of molecular weights in the GPC analysis. This is clearly seen in Figure 3.

When we take a closer look at the entire MWD development throughout the atom transfer polymerization reaction for initiator 3, higher molecular weight species are formed continuously during reaction (see Figure 4). This is the result of termination via combination of two growing polymer chains from different dendritic molecules (a conventional free radical polymerization of MMA shows ca. 30% termination via combination).
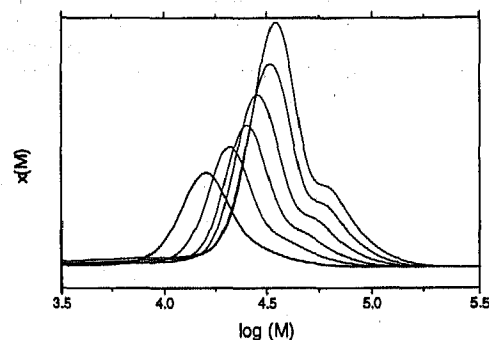

Figure 4. MWD development of MMA polymerized on derivatized G_1 carbosilane dendrimer, **3**

Conclusions

This work demonstrates that atom transfer polymerization using carbosilane dendritic molecules is possible. Care, however, should be taken in analysis of the molecular weight distributions of the produced star polymers as well as in the choice of experimental conditions to minimize the coupling of the starpolymers via bimolecular termination throughout the polymerization process.

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