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ATRP of Dendronized Aliphatic Macromonomers of Generation One, Two, and Three

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ABSTRACT: Atom transfer radical polymerization (ATRP) of dendritic, aliphatic macromonomers has been investigated. The macromonomers were based on acrylate functionalized 2,2-bis(methylol)propionic acid (bis-MPA) dendrons, with a flexible spacer of 10 carbons incorporated in the structure in between the polymerizable group and the dendritic wedge. Dendronized polymers of generation one, two, and three were successfully synthesized by ATRP. The polymerizations proceeded until over 80% conversion was reached, while maintaining control over polydispersity index (PDI). Plots of ln($[M]_0/[M]$) vs time for the polymerization of all three macromonomers showed a linear dependence, indicating that the number of propagating radicals in the reaction solution was constant throughout the reaction, when ethyl 2-bromopropionate (EBrP) was used as an initiator (i.e., radical termination was negligible). All of the resulting polymers had low PDI values and molecular weight close to the theoretical ones. The products were analyzed by ^{1}H and ^{13}C NMR spectroscopies, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and matrix-assisted laser desorption−ionization time-of-flight (MALDI−TOF).

Introduction

When dendritic wedges are attached to a linear polymer backbone instead of a small core molecule, the resulting macromolecule is called a dendronized polymer.[1] Dendronized polymers are a subclass of comb polymers, where the comb's teeth are dendrons instead of linear chains. Depending on the dendron's size, shape, and attachment to the backbone, the dendronized polymer can attain a fully stretched conformation instead of a random coil due to steric repulsion between the dendrons.[1] Interest in these rodlike, cylindrical dendrimers has increased remarkably in the past few years, as they are thought to have new and interesting properties.[1−5] Because of their rigidity, these macromolecules are expected to have very high bending moduli, making them interesting for constructions on the nanometer scale.[2] The surface and backbone are possible to functionalize as well, and potential applications are as catalyst supports, as light harvesting and/or conducting materials, and for variable applications as colloids.[6,7]

This relatively new class of polymers was first suggested by Tomalia in 1987, utilizing a divergent strategy.[8] Because of insufficient analytical techniques, it took a few years before any other work was published. It was not until the early 1990s that Hawker and Fréchet reported the synthesis of styrene and styrenic derivatives containing Fréchet-type dendrons.[9] Later, Percec et al.[3,10,11] and Schlüter et al.[3−5] showed that dendronization of the polymeric backbone indeed could lead to a cylindrical shape.

Dendronized polymers offer synthetic challenges, including (1) incomplete reactions due to steric repulsions, (2) autocatalytic decomposition of the dendrons due to the high density of functional groups, (3) difficulties in meeting the right stoichiometry due to the high molar mass reactants, and (4) difficulties in purification of the high molar mass reactants.[2] The two main routes to dendronized polymers are the "graft-onto" route and the macromonomer route.[1] In the "graft-onto" route, dendrons are coupled to a premade polymer. A drawback of this strategy may be incomplete coupling due to the steric crowding of the dendrons.[12]

The macromonomer route is based on polymerization of dendritic macromonomers, either by step-growth[13−16] or by chain-growth mechanisms.[3,17−19] This route is considered superior since it offers accurate control over the dendritic side groups.[10] However, steric hindrance may become a problem, especially for macromonomers bearing pendant dendrons of generation three or higher. The polymerizable group can be "shielded" and thereby inhibit polymerization, wherefore low molar mass products or no polymers are not unusual.[1] Consequently, incorporation of a spacer between the polymerizable group and the dendron may increase the availability of the polymerizable group.[19] However, difficulties surrounding these polymerizations may depend solely of the monomer concentration in the reaction mixture.[19] For macromonomers of generation three or higher, a monomer concentration of >45 wt % is necessary to reach higher conversions.[2] To obtain a more controlled length of the dendronized polymer controlled radical polymerization methods have been employed, such as atom transfer radical polymerization (ATRP).[20−22] However, as far as the authors know, no publications describe the ATRP of dendronized macromonomers of generation three or higher.[19,23,24] We previously explored ATRP of acrylated dendronized macromonomers based on 2,2-bis(methylol)propionic acid (bis-MPA).[25] Herein we report a continuation of that work. A macromonomer of generation three has been polymerized by ATRP, and the kinetics of the polymerization of generation 1−3 has been investigated.

Experimental Section

Materials. Acetonide protected-[**G-1**]-bis(methylol)propionic acid decane acrylate **(G1)**, acetonide protected-[**G-2**]-bis(meth-

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ylol)propionic acid decane acrylate **(G2)**, and acetonide protected-[**G-3**]-bis(methylol)propionic acid decane acrylate **(G3)** were prepared according to procedures described previously.[25,26] Tris(2-(dimethylamino)ethyl)amine ($\mathrm{Me_6}$-TREN) was prepared according to a procedure described by Ciampolini and Nardi[27] from tris(2-aminoethyl)amine (98%, Aldrich). 2,2-Bis(methylol)propionic acid (bis-MPA) was kindly supplied by Perstorp AB, Sweden. The DOWEX 50W-X2 ion-exchange resin, ethyl 2-bromoisobutyrate (98%, EBiB), and copper(I) bromide (98%) were obtained from Acros Organics. Ethyl 2-bromopropionate (99%, EBrP) was purchased from Sigma-Aldrich. Aluminum oxide, 90 active neutral, and diphenyl ether (98%, DPE) were obtained from Merck. Dichloromethane (DCM), tetrahydrofuran (THF), methanol, and pyridine were HPLC grade and purchased from Lab-Scan. Ethyl acetate and hexane were P.A. grade and obtained from Fischer.

Instrumentation. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.62 MHz) spectra were recorded on a Bruker AM 400 using $\mathrm{CDCl_3}$. The solvent signal was used as internal standard. All purifications were performed by medium-pressure liquid chromatography (MPLC) or by flash chromatography. Size exclusion chromatography (SEC) using THF (1.0 mL min^{-1}) as the mobile phase was performed at 35 °C using a Viscotek TDA model 301 equipped with a $\mathrm{GMH_{HR}}$-M column with TSK-gel (mixed bed, MW resolving range: 300−100 000) from Tosoh Biosep, a Viscotek VE 5200 GPC autosampler, a Viscotek VE 1121 GPC solvent pump, and a Viscotek VE 5710 GPC degasser. A universal calibration method was created using broad and narrow linear polystyrenes standards. Corrections for the flow rate fluctuations were made by using THF as an internal standard. Viscotek Trisec 2000 version 1.0.2 software was used to process data. Molecular weights and polydispersities were also determined by SEC on a Waters 6000A pump, a PL-EMD 960 light scattering evaporative detector (multiwavelength visible, halogen bulb with tungsten filament), two PL gel 10 μm mixed-B columns (mixed bed, MW resolving range: 500−10 000 000) from Polymer Labs, and one Ultrahydrogel linear column (blend of pore sizes) from Waters. DMF was used as solvent at a flow rate of 1.0 mL min^{-1}, preheated to 70 °C. Linear poly(ethylene oxide)s (PEO), ranging from 620 to 78 000 g mol^{-1}, were used for calibration.

Acetonide-[G1]-Dendronized Polymer, P(G1). General Polymerization Procedure. Acetonide-[**G1**]-$\mathrm{CO_2(CH_2)_{10}OCOCH{=}CH_2}$ **(G1)** (1.5 g, 3.9 mmol) was dissolved in DPE (1.5 g). $\mathrm{Me_6}$-TREN (1.8 mg, 7.8 μmol) and EBrP (1.4 mg, 7.8 μmol) were added to the solution, and the flask was sealed with a rubber septum. The vessel was quickly evacuated and back-filled with Ar gas two times. Cu(I)Br (1.1 mg, 7.8 μmol) was added under Ar flow, and one more cycle of vacuum and Ar gas was performed. The polymerization was left to proceed for 7 h at room temperature (RT). Samples were withdrawn at time intervals throughout the reaction. During the reaction the viscosity increased dramatically. The reaction mixture was diluted with THF (10 mL) and passed through a column of $\mathrm{Al_2O_3}$ in order to remove the Cu complex. The crude product was precipitated into cold (−78 °C) hexane to give **P(G1)** as a colorless, sticky polymer (1.1 g, 73%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.18 (s, 3H, $\mathrm{-CH_3}$), 1.27−1.42 (m, 18 H, $\mathrm{-CH_3}$ and $\mathrm{-CH_2CH_2-}$), 1.59−1.65 (m, 4H, $\mathrm{-CH_2CH_2O-}$), 1.87 (br, 2H, $\mathrm{-CH_2CH}$), 2.24 (br, 1H, $\mathrm{-CHCH_2-}$), 3.63 (d, 2H, J = 11.4 Hz, $\mathrm{-CH_2C-}$), 3.98 (br, 2H, $\mathrm{-CH_2OCO-}$), 4.10−4.19 (m, 4H, $\mathrm{-CH_2C-}$ and $\mathrm{-CH_2OCO-}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 18.88 ($\mathrm{-OCOC(-CH_2)_2}\mathit{C}\mathrm{H_3}$), 23.13 and 24.51 ($\mathrm{-O_2C(}\mathit{C}\mathrm{H_3)_2}$ acetonide group), 26.03−29.75 (alkyl chain and polymer chain), 41.88 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$), 65.03−66.14 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2OCO-}$ and $\mathrm{-}\mathit{C}\mathrm{H_2O-}$), 98.13 ($\mathrm{-O_2}\mathit{C}\mathrm{(CH_3)_2}$ acetonide group), 174.35 $\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ and $\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2H}$).

Acetonide-[G2]-Dendronized Polymer P(G2). General Polymerization Procedure. Acetonide-[**G2**]-$\mathrm{CO_2(CH_2)_{10}OCOCH{=}CH_2}$ **(G2)** (1.0 g, 1.5 mmol) was dissolved in DPE (1.0 g). $\mathrm{Me_6}$-TREN (3.5 mg, 15 μmol) and EBrP (5.5 mg, 30 μmol) were added to the solution, and the flask was sealed with a rubber septum. The vessel was quickly evacuated and back-filled with Ar gas two times. Cu(I)Br (2.2 mg, 15 μmol) was added under an Ar flow, and one more cycle of vacuum and Ar gas was performed. The flask was inserted into an oil bath thermostated at 50 °C, and the polymerization was left to proceed for 8 h. Samples were withdrawn at time intervals throughout the reaction. During the reaction the viscosity increased dramatically. The reaction mixture was diluted with THF (10 mL) and passed through a column of $\mathrm{Al_2O_3}$ in order to remove the Cu complex. The crude product was precipitated into hexane (−78 °C) to give **P(G2)** as a colorless, sticky polymer (0.77 g, 77%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.15 (s, 6H, $\mathrm{-CH_3}$), 1.27−1.40 (m, 27H, $\mathrm{-CH_3}$ and $\mathrm{-CH_2CH_2-}$), 1.61−1.63 (m, 4H, $\mathrm{-CH_2CH_2O-}$), 2.05 (br, 2H, $\mathrm{-CH_2CH-}$), 2.24 (br, 1H, $\mathrm{-CH-CH_2}$), 3.61 (d, 4H, J = 12.8 Hz, $\mathrm{-CH_2C}$), 3.98 (br, 2H, $\mathrm{-CH_2CH_2OCO}$), 4.07−4.16 (m, 6H, $\mathrm{-CH_2C-}$ and $\mathrm{-CH_2CH_2OCO}$), 4.28−4.35 (m, 4H, $\mathrm{-CH_2C}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 17.64 ($\mathrm{-OCOC(-CH_2)_2}\mathit{C}\mathrm{H_3}$ of **G1**), 18.39 ($\mathrm{-OCOC(-CH_2)_2}\mathit{C}\mathrm{H_3}$ from **G2**), 22.19 and 24.73 ($\mathrm{-O_2C(}\mathit{C}\mathrm{H_3)_2}$ acetonide group), 25.76−29.48 (alkyl chain and polymer chain), 41.83 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$ from **G2**), 41.88 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$ of G1), 64.51−65.87 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2OCO-}$ and $\mathrm{-}\mathit{C}\mathrm{H_2O-}$), 97.95 ($\mathrm{-O_2}\mathit{C}\mathrm{(CH_3)_2}$ acetonide group), 172.36 ($\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ of **G1**), 173.39 ($\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ of **G2** and $\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2H}$).

Acetonide-[G3]-Dendronized Polymer P(G3). Acetonide-[**G3**]-$\mathrm{CO_2(CH_2)_{10}OCOCH{=}CH_2}$ **(G3)** (1.0 g, 0.8 mmol) was dissolved in DPE (1.0 g). $\mathrm{Me_6}$-TREN (3.8 mg, 17 μmol) and EBrP (3.0 mg, 17 μmol) were added to the solution, and the flask was sealed with a rubber septum. The vessel was quickly evacuated and back-filled with Ar gas two times. Cu(I)Br (2.4 mg, 17 μmol) was added under Ar flow, and one more cycle of vacuum and Ar gas was performed. The flask was inserted into an oil bath thermostated at 50 °C, and the polymerization was left to proceed for 24 h. During the reaction the viscosity increased dramatically. The reaction mixture was diluted with THF (10 mL) and passed through a column of $\mathrm{Al_2O_3}$ in order to remove the Cu complex. The crude product was precipitated into hexane (−78 °C) to give **P(G3)** as a colorless, sticky polymer (0.54 g, 54%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.13 (s, 12H, $\mathrm{-CH_3}$), 1.26−1.40 (m, 45H, $\mathrm{-CH_3}$ and $\mathrm{-CH_2CH_2}$), 1.51−1.63 (br, 4H, $\mathrm{-CH_2CH_2O}$), 3.61 (d, 8H, J = 12.0 Hz, $\mathrm{-CH_2C}$), 4.10−4.16 (br, 12H, $\mathrm{-OCOCH_2CH_2}$ and $\mathrm{-CH_2C}$), 4.20−4.35 (m, 12H, $\mathrm{-CH_2C}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 17.58 ($\mathrm{-OCOC(-CH_2)_2}\mathit{C}\mathrm{H_3}$ of **G1**), 18.25 ($\mathrm{-OCOC(-CH_2)_2}\mathit{C}\mathrm{H_3}$ of **G2** and **G3**), 21.89 and 24.83 ($\mathrm{-O_2C(}\mathit{C}\mathrm{H_3)_2}$ acetonide group), 25.15−28.61 (alkyl chain and polymer chain), 41.88 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$ of **G3**), 46.32 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$ of **G1**), 46.69 ($\mathrm{-OCO}\mathit{C}\mathrm{(-CH_2)_2CH_3}$ of **G2**), 64.70−65.82 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2OCO-}$ and $\mathrm{-}\mathit{C}\mathrm{H_2O-}$), 97.90 ($\mathrm{-O_2}\mathit{C}\mathrm{(CH_3)_2}$ acetonide group), 171.71 ($\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ of **G1**), 171.95 ($\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ of **G1**), 173.31 ($\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2CH_3}$ of **G3** and $\mathrm{-O}\mathit{C}\mathrm{OC(-CH_2)_2H}$).

Results and Discussion

To obtain a well-defined dendronized polymer, a controlled, or “living”, polymerization technique must be utilized. In our earlier work we reported the synthesis of dendritic macromonomers based on acrylate functional acetonide-protected bis-MPA.[25] The acetonide protection group was used since it is easily hydrolyzed. Thus, a highly hydroxyl-functionalized dendronized polymer can be obtained by this approach. A flexible spacer of 10 carbons was incorporated in the molecules between the acrylate function and the dendrons in order to increase the availability of the polymerizable group (the acrylate functionality). This macromonomer was subsequently polymerized by ATRP. However, no optimization of the ATRP was performed, and only macromonomers of generation one and two were successfully polymerized. All attempts at polymerizing macromonomers of higher generations failed. Herein we report the successful ATRP of the macromonomer of generation three. Also, the reaction conditions for the polymerizations have been optimized, and an investigation of the

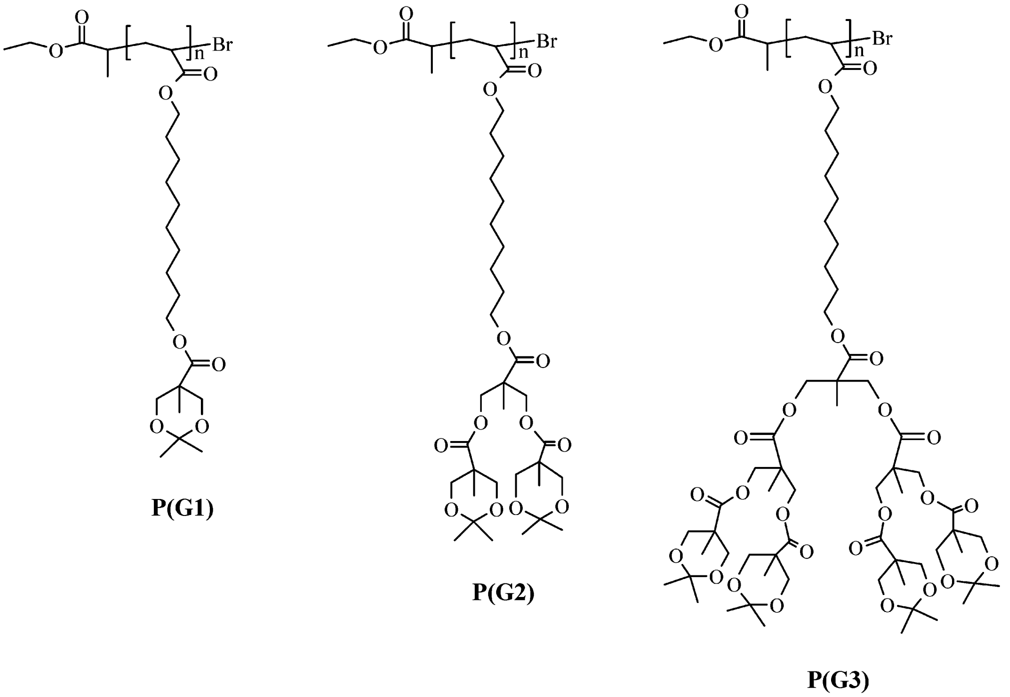

Figure 1. Structures of the resulting polymers of **G1**−**G3**.

reaction kinetics for generation one, two, and three has been performed.

Polymerization of Macromonomers (G1−G3) with ATRP. All of the macromonomers were subjected to MPLC prior to polymerization to remove small amounts of impurities. ATRP was performed in DPE (50% w/w) since the macromonomers themselves are quite viscous. To monitor the polymerizations, samples were withdrawn at time intervals throughout the reaction and analyzed by ^{1}H NMR spectroscopy and SEC (in DMF). The conversion was calculated from ^{1}H NMR spectroscopy by calculations of the shift around 3.6 ppm (originating from the CH_2 group in the acetonide groups in **G1**, **G2**, **G3**, **P(G1)**, **P(G2)**, and **P(G3)**). These protons give rise to the same shift in the NMR spectra, regardless of the dendron being attached to a polymer backbone or not. Hence, from this peak and from the declining peaks originating from the double bonds around 5.7, 6.1, and 6.3 ppm, the conversion of the reaction can be calculated. According to Matyjaszewski, the kinetics of ATRP can be described by eq 1.[28] This expression was used herein to investigate the kinetics of the polymerizations. As can be seen from the equation, there is a linear dependence between $\ln([M]_0/[M])$ and reaction time t. The equation is based on the assumption that radical termination is negligible and that k_p is constant throughout the polymerization.

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p K_{eq} \frac{[RX][Cu(I)]}{[Cu(II)]}\, t = k_p[R^\bullet]t = k_{app}t \tag{1}$$

*Polymerization of **G1** Macromonomer.* **G1** has a molecular weight of 384 g mol^{-1}. It was polymerized at room temperature using conventional ATRP conditions,[29] yielding polymer **P(G1)** (Figure 1). The reaction mixture became viscous after ca. 7 h. The final polymer was analyzed by NMR, DSC, and SEC, in both DMF and THF.

Table 1. SEC Analysis of Polymers P(G1)−P(G3)

sample	M_n[a] [g/mol]	PDI	DP_{aimed}	DP_{calc}[b]	conv [%]
P(G1)[c]	30 240	1.4	50	79	81
P(G1)[c]	66 560	1.2	100	173	50
P(G1)[d]	25 540	1.2	50	67	85
P(G2)[c]	37 360	1.1	50	57	97
P(G2)[d]	46 670	1.1	50	71	83
P(G3)[c]	62 660	1.8	100	52	53
P(G3)[c]	31 690	1.3	50	26	45
P(G3)[d]	53 000	1.6	50	44	80

[a] M_n obtained by SEC using universal calibration in THF. [b] Calculated from M_n obtained by SEC. [c] Initiator: ethyl 2-bromoisobutyrate (EBiB). [d] Initiator: ethyl 2-bromopropionate (EBrP).

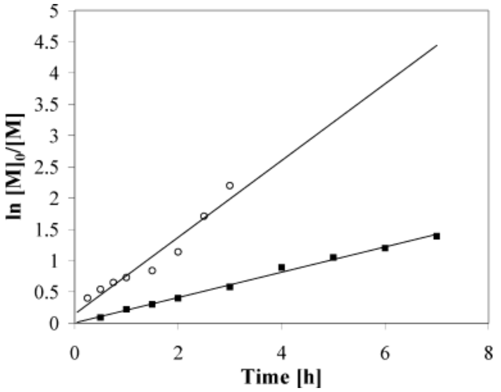

Figure 2. First-order kinetic plots of $\ln([M]_0/[M])$ vs time in the solution polymerization of **G1**, [M]:[I]:[Cu(I)Br]:[tris(2-(dimethylamino)ethyl)amine] = [50]:[1]:[0.1]:[0.1], reaction at RT. (○) I = ethyl 2-bromoisobutyrate (EBiB); (■) I = ethyl 2-bromopropionate (EBrP).

As shown in Figure 2, the polymerization did not follow first-order kinetics when EBiB was employed as initiator, as the curve deviates from linearity. However, as shown in Table 1, the final polymer still had fairly low polydispersity index (PDI) of 1.2−1.4. Upon changing the initiator to EBrP, the reaction became more controlled and followed first-order kinetics (Figure 2). The difference between the two initiators' efficiency in ATRP has earlier been described by Matyjaszewski et al.[30] as well as by Van Der Linde et al.[31] In the case of

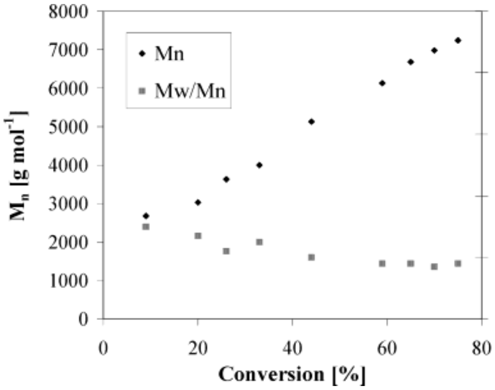

Figure 3. Dependence of molecular weight and molecular weight distribution on the monomer conversion for the polymerization of **G1**, using ethyl 2-bromopropionate (EBrP) as initiator in diphenyl ether at RT.

Van Der Linde et al. similar observations were done when utilizing EBiB as initiator for butyl acrylate.[31] They attributed the higher initial polymerization rate to the fact that the methacrylic, tertiary radical that is formed in the beginning of the reaction from EBiB is much more stable than the acrylic, secondary one formed when one acrylate monomer unit has been added. Thus, the radical concentration will be relatively high in the beginning of the reaction, resulting in high initial k_{app} values and increased rates of irreversible termination.

The polymerization of **G1** proceeded to 81% conversion, and the resulting polymer had a low PDI, indicating a controlled polymerization. The withdrawn samples were analyzed by SEC in DMF using conventional calibration with linear PEO standards. As shown in Figure 3, the molecular weight increased linearly with conversion. However, the curve does not approach zero at zero conversion. This indicates that the initial reaction is fast. The PDI values are low throughout the reaction. The values in Figure 3 are obtained by conventional calibration using linear PEO standards, a method that underestimates the values of the molecular weights of branched polymers or polymers with large side groups.[32] Therefore, the values of the molecular weight in Figure 3 will be different from the values of the final polymer in Table 1. In Table 1 the molecular weights are measured in THF using universal calibration. The resulting molecular weight using this calibration is closer to the real one.[33] Unfortunately, it is very sensitive to the concentration of the samples and could therefore only be employed when analyzing the isolated polymers. The withdrawn samples also contain solvents and monomer, and the real concentration of the polymer is difficult to determine and for that reason only conventional calibration against linear poly(ethylene oxide) standards was possible for these samples.

*Polymerization of **G2** Macromonomer.* ATRP of **G2** was also conducted in PDE (50% w/w). The macromonomer has a molecular weight of 656 g mol^{-1}. Since the macromonomer itself had rather high molecular weight, the concentration of reactive sites in the solution was low. Consequently, the reaction was performed at 50 °C. The best results were obtained when an initiator-to-Cu(I) ratio of 1:0.2 was used. When a ratio of 1:0.1 was used, as in the case of **G1**, the reaction rate was very similar, but the reaction showed slightly less control. This indicates that the polymerization show some type of self-regulation.

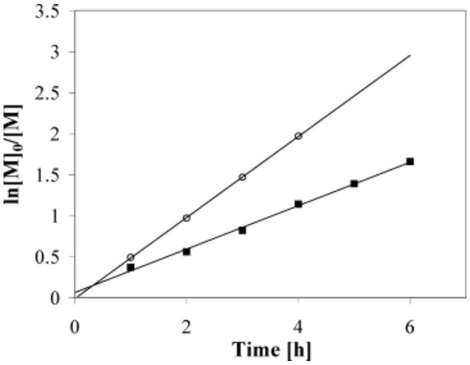

Figure 4. First-order kinetic plots of $\ln([M]_0/[M])$ vs time in the solution polymerization of **G2**, [M]:[I]:[Cu(I)Br]:[tris(2-(dimethylamino)ethyl)amine] = [50]:[1]:[0.2]:[0.2], reaction at 50 °C. (○) I = ethyl 2-bromoisobutyrate (EBiB); (■) I = ethyl 2-bromopropionate (EBrP).

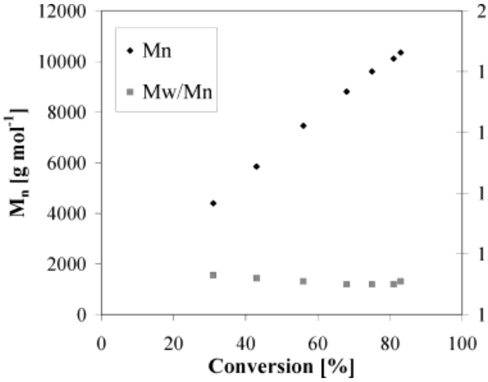

Figure 5. Dependence of molecular weight and molecular weight distribution on the monomer conversion for the polymerization of **G2**, using ethyl 2-bromopropionate (EBrP) as initiator at 50 °C in diphenyl ether.

The resulting polymer **P(G2)** was also analyzed by SEC in the same way as polymer **P(G1)**. As shown in Figure 4, the polymerization of **G2** followed first-order kinetics with both initiators. EBiB gave a faster polymerization. Furthermore, the final polymers from both polymerizations had low PDI values. It seems that EBiB gave a better control with respect to the targeted molecular weight. As shown in Figure 5, the PDI values for the polymerizations remained low throughout the reaction and decreased with increasing monomer conversion. Also, the molecular weight increased linearly with increasing monomer conversion.

*Polymerization of **G3** Macromonomer.* ATRP of **G3** was performed using similar conditions as for **G2**. The monomer concentration was kept at 50% w/w as in the case for **G1** and **G2**. **G3** has a molecular weight of about 1200 g mol^{-1}, and the reaction solution was slightly viscous at RT. Because of the high molecular weight of the macromonomer itself, a very small amount of Cu(I)Br needed to be used in order to keep a 1:0.1 ratio of initiator-to-Cu(I) at a 1 g scale of macromonomer. Since in the polymerizations of **G2** doubling the amount of catalyst did not result in faster polymerization rates, an even higher ratio of initiator-to-Cu(I) was used here. A ratio of 1:0.5 or 1:1 was investigated. A 1:1 ratio resulted in slightly higher conversions, wherefore this ratio was selected for this study. The purification of the final polymer was difficult. The **G1** macromonomer is fairly insoluble in hexane, and a fractionated precipitation was necessary. Nonetheless, all final polymers contained traces of macromonomer as well as of DPE.

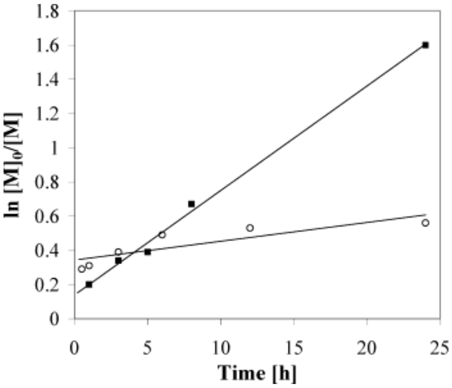

Figure 6. First-order kinetic plots of ln($[M]_0$/[M]) vs time in the solution polymerization of **G3**, [M]:[I]:[Cu(I)Br]:[tris(2-(dimethylamino)ethyl)amine] = [50]:[1]:[1]:[1], reaction at 50 °C. (○) I = ethyl 2-bromoisobutyrate (EBiB); (■) I = ethyl 2-bromopropionate (EBrP).

When EBiB was employed as the initiator, the reaction did not follow first-order kinetics (Figure 6). The polymerization would only proceed to 50% conversion. Higher conversions could not be reached, even at longer reaction times (96 h) or by increasing the reaction temperature (100 °C). Nonetheless, as shown in Table 1, the PDI value of the final polymer was low. We speculate that the slower polymerization rate originates from side reactions, such as irreversible termination, at early stages of the polymerization leading to the persistent radical effect,[34] accumulating $Cu(II)Br_2$ in the system, which functions as deactivator and subsequently slows down the reaction. A slower reaction rate might enable the polymer to adopt a conformation that will inhibit further polymerization, either by shielding the polymerizable group or by micellization.[35] The declining concentration of monomers in the reaction solution together with a lower concentration of Cu(I) and increased concentration of Cu(II) may also make propagation highly unfavorable.

When EBrP was utilized instead, the reaction reached 80% conversion in 24 h. At that time the reaction mixture was very viscous. The polymerization followed first-order kinetics (Figure 6). However, the final polymer had broader molecular weight distribution, as is indicated by a higher PDI value when the polymerizations were conducted to higher conversions (Table 1). The higher PDI originated from tailing on the high molecular weight side in the SEC chromatogram. We hypothesize that side reactions begin to take place at higher conversions, when the reaction medium is highly viscous and the monomer concentration is low. This is somewhat corroborated in Figure 7, where the PDI value increases slightly with increasing conversion. This is unusual for ATRP where typically most of the termination reactions take place in the beginning of the reaction, and the PDI value decreases with increasing conversion.[30] In the polymerization of **G3** the molecular weight increases linearly with increasing monomer conversion (Figure 7). As in the case of **G1**, the molecular weight does not approach zero at zero conversion. However, in this case the molecular weight should approach 1200 g mol^{-1} due to the high molecular weight of the macromonomer. **P(G3)** is a highly branched polymer, wherefore the deviations in SEC using conventional calibration will be very large. For that reason it is difficult to estimate M_n vs conversion using this method.

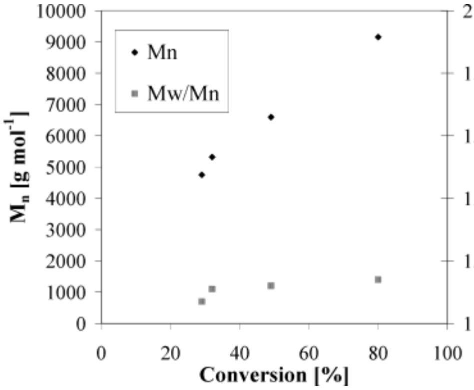

Figure 7. Dependence of molecular weight and molecular weight distribution on the monomer conversion for the polymerization of **G3**, using ethyl 2-bromopropionate (EBrP) as initiator at 50 °C in diphenyl ether.

Conclusions

ATRP of acrylate functional dendritic macromonomers based on bis-MPA has been investigated. Dendronized polymers of generation 1−3 were successfully polymerized when Me_6-TREN was used as a ligand in conjunction with Cu(I)Br in DPE. The initiator-to-Cu(I) ratio was increased from 1:0.1 as in the case for the **G1** polymerization to 1:0.2 and 1:1 for the **G2** and **G3** polymerizations, respectively. Only the **G2** macromonomer followed first-order kinetics when EBiB was used as an initiator, although all the macromonomers yielded polymers with fairly low PDI's with this initiator. However, the **G1** polymerizations did not follow first-order kinetics, and the **G3** polymerization did only proceed to about 50% conversion. When EBrP was used as an initiator instead, all polymerizations followed first-order kinetics and proceeded to high conversions. The **G1** and **G2** polymers exhibited low PDI values, whereas for the **G3** polymers they were slightly increased. Whether or not the incorporation of a spacer between the dendrons and the polymerizable group was important for the polymerization was not investigated here but is currently under investigation in our labs.

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