# Macromolecules

### Kinetics of Free Radical Polymerization of Spacerless Dendronized Macromonomers in Supercritical Carbon Dioxide

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Supporting Information

**ABSTRACT:** The kinetics of the free radical polymerization in supercritical carbon dioxide of third (G3) and fourth (G4) generation spacerless dendronized macromonomers, bearing a methacrylate group at the focal point, is experimentally investigated. Conversions up to 90% could be achieved in few hours for both monomers, with degrees of polymerization on the order of thousands of monomer units for G3 and 100–200 for



G4. Experimental data are interpreted using a conventional free radical kinetic scheme. Within this frame, chain termination is dominated by chain transfer to monomer and the extremely high reactivity of the macromonomers when polymerized in supercritical carbon dioxide is reflecting reduced termination rate at increasing dendron generation.

#### **1. INTRODUCTION**

Dendronized polymers (denpols) are comb polymers in which regularly branched dendrons are the chain substitutents.<sup>1–3</sup> The high steric demand of the peripheral branched units stretches and stiffens the polymer backbone, forcing the resulting denpol to uncoil and adopt a cylindrical shape characterized by a tunable thickness, with a well-defined external surface dense of sites available for functionalization.<sup>4,5</sup> Backbone stiffening is more and more pronounced as the generation of the attached dendrons, and therefore the crowding effect on the conformation of the resulting denpol, increases.<sup>4–8</sup>

Properly functionalized denpols allow unprecedented control over self-assembly and hierarchical structure formation.<sup>8–10</sup> Single chains may behave as glassy systems,<sup>11</sup> can be visualized and manipulated at the molecular level by atomic force microscopes (AFM),<sup>12–14</sup> and self-fold when negatively charged on the peripheral groups, thus mimicking biomacromolecules.<sup>15</sup> For all these features, such molecules are promising materials for nanotechnology applications. Nevertheless, the efficient synthesis of high generation (i.e., from the third generation on) dendronized polymers with high degree of polymerization still constitutes an issue.

Three synthetic strategies are most commonly applied to produce dendronized polymers: the "graft-from", the "graft-to", and the "macromonomer" route.<sup>1–3</sup> Each of them presents specific advantages and disadvantages. In the graft-from approach, first generation dendrons are stepwise divergently coupled onto a linear polymer backbone up to the desired generation. This way a large number of synthetic and purification steps are required, and the resulting polymers inevitably bear

structural defects, even though high generation denpols with large degree of polymerization can be produced. In the graft-to approach, preformed dendrons of the final desired generation are coupled to a linear polymer backbone. This way, all the pendant dendrons are structurally perfect, an aspect that can be critical in the graft-from approach, but high dendron coverage on the backbone is difficult to achieve, especially for high generations.<sup>12</sup> For example, according to the last previous citation, Fréchet-type dendrons functionalized with an azide group in the focal point were reacted with poly(vinyl acetylene) bearing pendant alkynes on the repeating units, by an efficient Cu(I)-catalyzed azidealkyne 1,3-dipolar cycloaddition. The authors could synthesize denpols with coverage >98% up to the third generation, while the fourth generation dendron, G4, was not reacting at all. A reasonable explanation is that, at high dendron generation, the branches fold back hiding the focal point and hindering its coupling with the acetylene units. The third route is the macromonomer one, which involves the direct polymerization of dendrons of the desired generation functionalized with a polymerizable unit at the focal point (e.g., a vinyl group). This way, fully covered denpols can be produced with structurally perfect dendrons. On the other hand, a long reaction time is required to achieve decent conversions (typically larger than 20 h), and the degree of polymerization dramatically decreases at increasing generation.<sup>16,17</sup> The crowding effect is presumably the main reason for this general trend: for higher generations, dendrons

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#### Scheme 1. Reagents and Conditions for the Synthesis of G4 Monomer (3b) from 1a and 2a<sup>a</sup>



<sup>*a*</sup>:Key: (a) HCl/dioxane, rt, 3 h (96%); (b) EDC · HCl, DCM/DMF, -15 °C, 24 h (80%); (c) TEA, DMF/methanol, -20 °C, 24h (72%); (d) MAC, TEA, DMAP, THF/DMF, 24 h (71%).

are compressed and forced away from the backbone,<sup>4</sup> so the steric repulsion thus generated may cause the dendrons close to the chain end to bend outward, limiting the reacting site's accessibility.

Recently, we found that the free radical polymerization of dendronized macromonomers carried out in supercritical carbon dioxide ( $scCO_2$ ) is superior to the conventional polymerization in solution. Indeed, although neither the monomers nor the forming polymers were soluble in  $scCO_2$ , higher degrees of polymerization were obtained compared to solution polymerization.<sup>18</sup> In the same work, it has been demonstrated that

even a fifth generation macromonomer (G5) could be oligomerized by the macromonomer approach. Driven by such promising preliminary results, the polymerization kinetics of third (G3) and fourth (G4) generation macromonomers in  $scCO_2$  is further investigated in this work.

The selected dendrons are spacerless macromonomers bearing a methacrylate group on the focal point. The chemical structure of G3 (molecular weight = 2625 g/mol) and its homologous G4 monomer (molecular weight = 5428 g/mol) are shown in our previous contribution<sup>18</sup> and in Scheme 1 (compound **3b**), respectively. Monomers, as well as their polymers were found to be insoluble in the reaction medium.<sup>18</sup> Therefore, the reactions occur in a two-phase system, the  $scCO_2$  supercritical phase and the  $CO_2$ -swollen phase composed of monomer and forming polymer. SEM images of the samples collected after the reaction end suggest that the reaction temperature was above the glass transition temperature of the monomer/polymer mixture,<sup>19</sup> thus supporting the assumption that polymerization occurred in a highly viscous rubbery phase.

#### 2. EXPERIMENTAL SECTION

2.1. Synthesis of the Macromonomers. All reagents were purchased from Aldrich, Acros, or Fluka. Methacryloyl chloride (MAC) was freshly distilled before use. Tetrahydrofuran (THF) and triethylamine (TEA) were refluxed over Na with benzophenone as indicator, dichloromethane (DCM) was dried by distillation over CaH<sub>2</sub>. All other reagents and solvents were used as received. All reactions were performed under nitrogen atmosphere. Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm/230-400 mesh) was used as stationary phase for column chromatography. Whenever possible, reactions were monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminum plates 60F254 (Merck). Compounds were detected by UV light (254 or 366 nm) and/or by treatment with a solution of ninhydrin in ethanol followed by heating. If not otherwise noted, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AM 300 (<sup>1</sup>H, 300 MHz; <sup>13</sup>C, 75 MHz) and AV 500 (<sup>1</sup>H, 500 MHz; <sup>13</sup>C, 125 MHz) spectrometers at room temperature. High-resolution mass spectral (HRMS) and ESI-MS analyses were performed by the MS-service of the Laboratorium für Organische Chemie at ETH Zürich. ESIMS and MALDI-MS were run on an IonSpec Ultra instrument. In the case of MALDI-MS, 2,5dihydroxybenzoic acid (DHB), 2-[(2E)-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB) or 3-hydroxypyridine 2-carboxylic acid (3-HPA) served as the matrix. The FAB experiments were carried out with 3-nitrobenzyl alcohol (MNBA)/CH<sub>2</sub>Cl<sub>2</sub>. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. The samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules.

The third generation monomer G3 and compounds 1a, and 2a (Scheme 1) were synthesized according to literature methods.<sup>16,20,21</sup> In the following, the synthesis of the fourth generation monomer G4 (3b in Scheme 1) from 1a and 2a is described.

3,5-[Bis(3-{3,5-bis[3-aminopropylox-

y]benzoyl}amino)propyloxy]benzyl alcohol·4HCl (1b). A solution of HCl in dioxane (12 mL, 4 mol/L) was added to 1a (2.6 g, 2.25 mmol) in 10 mL dioxane at room temperature. The reaction mixture was stirred at rt for 3 h, until the product precipitated. The solvent was removed in vacuo and the residue was washed 3 times with dioxane and dried over high vacuum to yield **1b** as a white solid (1.95 g, 96%). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta = 2.03 - 2.19$  (m, 12 H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.18 - 3.23 (m, 8 H; CH<sub>2</sub>NH), 3.50–3.54 (m, 4 H; CH<sub>2</sub>NH), 4.06–4.13 (m, 12 H; PhOCH<sub>2</sub>), 4.48 (s, 2 H; PhCH<sub>2</sub>O), 6.34 (s, 1 H; Ph), 6.52 (d, 2 H; Ph), 6.74 (d, 2 H; Ph), 6.86 (d, 4 H; Ph) ppm; <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O):  $\delta = 26.40, 27.74$  (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 37.34, 37.44 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 63.68 (OCH<sub>2</sub>), 65.85, 65.53 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 100.67, 104.96, 105.63, 105.96, 106.11, 135.95, 143.16, 143.24, 159.28, 159.31 (Ar), 169.47 (NHCO) ppm; HRMS MALDI: *m/z*: calcd: 755.4344 [*M* +  $H^{+}$ ; found: 755.4348  $[M + H^{+}]$ . Anal. calcd for  $C_{39}H_{62}N_6O_9Cl_4$ : C 52.00, H 6.94, N 9.33; found: C 49.62, H 7.33, N 8.83.

2,5-Dioxopyrrolidin-1-yl 3,5-Bis(3-{3,5-bis[3-(tert-butyloxycarbonylamino)propyloxy]benzoylamino}propyloxy)benzoate (**2b**). EDC-HCl (4.12 g, 20.0 mmol) was added to the solution of **2a** (19.6 g, 16.7 mmol) and N-hydroxysuccinimide (2.10 g, 18.4 mmol) in dry DCM/DMF (400 mL/10 mL) at -15 °C. The reaction mixture was allowed to warm up to room temperature and then was stirred for 24 h. After washing by saturated NaHCO<sub>3</sub> solution and then brine, the organic phase was dried by MgSO4 and purified by column chromatography (ethyl acetate/hexane 2:1) affording the product as a white solid (16.9 g, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.42$  (s, 36 H; <sup>t</sup>Bu), 1.90–2.12 (m, 12 H;  $OCH_2CH_2CH_2N$ ), 2.88 (d, 4 H;  $COCH_2CH_2CO$ ), 3.25-3.27 (m, 8 H; CH<sub>2</sub>NH), 3.60-3.62 (m, 4 H; CH<sub>2</sub>NH), 3.87-4.08 (m, 12 H; PhOCH<sub>2</sub>), 4.89 (br, 4 H; NH), 6.50 (s, 2 H; Ph), 6.69 (d, 1 H; Ph), 6.88 (d, 4 H; Ph), 7.04 (br, 2 H; NH), 7.18 (d, 2 H; Ph) ppm. <sup>13</sup>C NMR:  $\delta$  = 25.68 (COCH<sub>2</sub>CH<sub>2</sub>CO), 28.42 (C(CH<sub>3</sub>)<sub>3</sub>), 28.86, 29.48 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 37.54, 37.77 (OCH<sub>2</sub>C-H<sub>2</sub>CH<sub>2</sub>N), 65.85, 66.62 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 104.50, 105.66, 108.64, 108.76, 126.66, 136.68, 156.08 (Ar), 159.96 (NHCOO), 161.60, 167.41 (NHCO), 169.23 (NCOCH<sub>2</sub>) ppm. HRMS MALDI, m/z: calcd, 1288.6219 [M + Na]<sup>+</sup>; found, 1288.6211  $[M + Na]^+$ . Anal. Calcd for C<sub>63</sub>H<sub>91</sub>N<sub>7</sub>O<sub>20</sub>: C, 59.75; H, 7.24; N, 7.74. Found: C, 59.80; H, 7.27; N, 7.54.

3,5-Bis{3-[3,5-bis(3-{3,5-bis(3-[3,5-bis(3-tert-butoxycarbonylamino propyl)benzoylamino]propyloxy)benzoylamino{propyloxy)benzoylamino]propyloxy}benzyl Alcohol (3a). A solution of 1b (1.90 g, 2.12 mmol) and TEA (3.43 g, 34.0 mmol) in DMF/methanol (15 mL/ 3 mL) was added dropwise to a solution of 2b (13.41 g, 10.06 mmol) in DMF (120 mL) at -20 °C. The reaction mixture was allowed to warm up to room temperature and then was stirred for 24 h. After washing with KHSO<sub>4</sub> solution (10%) and brine successively, the organic phase was dried over MgSO4 and purified by column chromatography (ethyl acetate/hexane 3:1) affording 3a as a white solid (8.17 g, 72%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta = 1.35$  (s, 144 H; <sup>t</sup>Bu), 1.79–1.84 (m, 32 H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.96 (m, 28 H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.04–3.10 (m, 32 H; CH<sub>2</sub>NH), 3.38-3.40 (m, 28 H; CH<sub>2</sub>NH), 3.96-3.99 (m, 32 H; PhOCH<sub>2</sub>), 4.04 (m, 28 H; PhOCH<sub>2</sub>), 4.40 (d, 2 H; PhCH<sub>2</sub>O), 5.13 (t, 1 H; OH), 6.34 (s, 1 H; Ph), 6.47 (s, 2 H; Ph), 6.59 (s, 8 H; Ph), 6.62 (s, 6 H; Ph), 6.88 (br, 16 H, NH), 6.99 (m, 16 H; Ph), 7.03 (s, 8 H; Ph), 8.49 (m, 14 H; NH) ppm. <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 28.19 (C(CH<sub>3</sub>)<sub>3</sub>), 28.84, 29.16 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 36.36, 36.89 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 62.84 (OCH<sub>2</sub>), 65.51, 65.67 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 77.47 (C(CH<sub>3</sub>)<sub>3</sub>), 103.66, 104.51, 105.73, 136.49, 145.06, 159.57, 159.59 (Ar), 155.60 (NHCOO), 165.73, 165.76 (NHCO) ppm; HRMS MALDI-TOF, m/z: calcd, 5379.8363  $[M + Na]^+$ ; found, 5380.87  $[M + Na]^+$ . Anal. (%) Calcd for C<sub>275</sub>H<sub>402</sub>N<sub>30</sub>O<sub>77</sub>: C, 61.62; H, 7.56; N, 7.84. Found: C, 60.66; H, 7.53; N, 7.67.

3,5-Bis{3-[3,5-bis(3-{3,5-bis(3-[3,5-bis(3-tert-butoxycarbonylamino propyl)benzoylamino]propyloxy)benzoylamino}propyloxy)benzoylamino]propyloxy}benzyl Methacrylate (3b). A solution of methacryloyl chloride (MAC) (43 mg, 0.41 mmol) in dry THF (5 mL) was added dropwise to a mixture of 3a (1.03 g, 0.193 mmol), TEA (115 mg, 1.14 mmol), and DMAP (8 mg) in dry THF/DMF (70 mL/15 mL) at 0 °C. After the reaction mixture had been stirred for 24 h at room temperature, it was successively washed with saturated NaHCO3 solution and brine. The organic phase was dried over MgSO<sub>4</sub>. Evaporation of the solvents *in vacuo* at room temperature followed by chromatographic separation (DCM/methanol 15:1) yielded 3b as a white solid (0.74 g, 71%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta = 1.35$  (s, 144 H; <sup>t</sup>Bu), 1.78-1.85 (m, 32 H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.87 (s, 3 H; C=CCH<sub>3</sub>), 1.95 (m, 28 H;  $OCH_2CH_2CH_2N$ ), 3.03-3.09 (m, 32 H;  $CH_2NH$ ), 3.38–3.40 (m, 28 H; CH<sub>2</sub>NH), 3.95–3.99 (m, 32 H; PhOCH<sub>2</sub>), 4.03 (m, 28 H; PhOCH<sub>2</sub>), 5.06 (s, 2 H; PhCH<sub>2</sub>O), 5.66 (m, 1 H; C=CH<sub>2</sub>), 6.04 (s, 1 H; C=CH<sub>2</sub>), 6.44 (s, 1 H; Ph), 6.51 (s, 2 H; Ph), 6.58 (s, 8 H; Ph), 6.62 (s, 6 H; Ph), 6.85 (br, 16 H, NH), 6.98 (m, 16 H; Ph), 7.01 (s, 8 H; Ph), 8.48 (m, 14 H; NH) ppm. <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  =  $18.44 (C=CCH_3), 28.93 (C(CH_3)_3), 29.34, 29.65 (OCH_2CH_2CH_2N),$ 36.90, 37.34 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 66.01, 66.86 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 66.17 (OCH<sub>2</sub>), 77.96 (C(CH<sub>3</sub>)<sub>3</sub>), 101.12, 104.15, 106.22, 106.49, 136.98, 138.85, 160.07, 160.29 (Ar), 126.56 (CH<sub>2</sub>=C), 136.20 (CH<sub>2</sub>=C),



**Figure 1.** Peak area vs sample concentration for solutions of G4 monomer  $(\bigcirc)$  and PG4 polymer  $(\diamondsuit)$ . Lines: linear fittings.

156.10 (NHCOO), 166.23, 166.75 (NHCO) ppm. HRMS, m/z: calcd, 5449.86  $[M + Na]^+$ ; found, 5449.94  $[M + Na]^+$ . Anal. Calcd for C<sub>279</sub>H<sub>406</sub>N<sub>30</sub>O<sub>78</sub>: C, 61.73; H, 7.54; N, 7.74. Found: C, 60.70; H, 7.31; N, 7.62.

**2.2. Polymerization Procedure.** Batch reactions were carried out in a mechanically stirred stainless steel autoclave (Premex Reactor AG) equipped with inlet and outlet valves, pressure transducer and dip tube with temperature sensor Pt-100. Defined amounts of AIBN initiator (2,2'-Azobis(2-methylproprionitrile), purity >98%, from Fluka, used as received) and monomer (30–50 mg) were separately loaded into two glass vials, which were then put into the high-pressure reactor. The reactor was sealed and loaded/unloaded 8 times by carbon dioxide up to a pressure of 20 bar at room temperature in order to fully remove oxygen. The desired amount of  $CO_2$  (99.95% pure, from PanGas) was injected by a high-pressure piston pump (NWA GmbH, Germany) into the reactor, which was then heated to the reaction temperature by immersion in a thermostatic oil bath. At the final reaction time, the reactor was slowly vented, and the product was sampled from the vial where the monomer was initially loaded.

The selected mass ratio between monomer and  $CO_2$  was always very small (on the order of  $10^{-3}$ ). For this reason, whatever the partition coefficient of the initiator between the two phases, the concentration of AIBN in the supercritical phase, [I<sub>2</sub>], was estimated as the ratio between the charged moles of AIBN and the total reactor volume.

**2.3. Polymer Characterization.** The collected samples were dissolved in DMF (1–2 mg/mL), filtered by porous stainless steel frit (porosity 0.2 $\mu$ m), and characterized by GPC, using a PL-GPC 220 apparatus (Polymer Laboratories) equipped 2x PL-Gel Mix-B LS columns, refractive index detector (RI), and viscosity detector. DMF + 1gr/L LiBr, at 1 mL/min flow rate, was used as eluent at T = 45 °C. GPC columns were calibrated using PMMA standards,  $M_{\rm p} = 2680$  to 3 900 000 g/mol; Polymer Laboratories Ltd., U.K. Sample molecular weights were calculated by universal calibration.

To estimate the monomer conversion, the response factors of monomers (G) and polymers (PG) to the RI detector were first determined. For each pure species, GPC elution profiles were collected using solutions at different concentrations. The peak areas, *A*, were plotted against the corresponding solution concentrations, *c*, and the response factors,  $m_{\rm G}$  and  $m_{\rm PG}$ , were evaluated by linear regression. An example of *A* vs *c* data for solutions of pure G4 and pure PG4 is shown in Figure 1 along with the corresponding linear fittings.

When analyzing by GPC solutions of collected samples, the areas of produced polymer  $(A_{PG})$  and residual unreacted monomer  $(A_G)$  were both measured. From such values, the corresponding conversion is readily calculated in two different ways:

$$X_1\% = 100 \left( 1 - \frac{A_G}{m_G c} \right)$$
 (1)

$$X_2\% = 100 \left( \frac{A_{PG}/m_{PG}}{A_{PG}/m_{PG} + A_G/m_G} \right)$$
 (2)

The differences between the conversion values calculated by the two equations were always less than 10% and average values were considered.

AFM measurements were performed on a Nanoscope IIIa Multi Mode Scanning probe microscope (Digital Instruments, San Diego, CA) with an "E" scanner ( $10 \,\mu m \times 10 \,\mu m$ ) in the tapping mode at ambient condition. Olympus silicon OMCL-AC160TS cantilevers (Atomic Force F&E GmbH, Mannheim, Germany) were applied with a resonance frequency in the range 200–400 kHz and a spring constant of about 42 N/m. The samples were prepared by spin-coating (2000 rpm, 40 s) the polymer solution of PG3 or PG4 (~10 mg/L in chloroform) onto freshly cleaved mica (from PLANO W. Plannet GmbH, Wetzlar, Germany).

## 3. POLYMERIZATION KINETICS OF G3 AND G4 IN SCCO<sub>2</sub>

3.1. Conversion. Recipe conditions and representative results for the reactions carried out at T = 65 °C and P = 130 bar at different initiator concentrations are reported in Table 1. The conversion profiles measured at three different initiator concentrations are shown in Figure 2 and Figure 3 for the polymerization of G3 and G4, respectively. At intermediate and low AIBN content, significant induction times,  $\tau$ , were observed for the polymerization of G3, where shorter reaction times were used. The observed inhibition might be attributed to traces of impurities present in the monomer and acting as radical scavengers. Such explanation is quite possible due to the very large number of synthetic steps required to produce the monomers; moreover, it will be assessed in more quantitative way in section 5. The presence of some kind of inhibitors in the original monomer could also explain why no polymer was obtained when decreasing the initiator concentration to  $[I_2] =$ 0.35 mM (Table 1, run 15); even though monomers of similar chemical structure are known to give thermally induced polymerization.<sup>22</sup>

Monomer conversion increased in all cases with time and initiator concentration, reaching values as high as 90% for both monomers. It is worth noting the extremely fast reaction rate measured for the polymerization of G3, the conversion of which was almost complete within few hours (cf. Table 1 runs 1 and 2). A limiting conversion of about 90% was observed for the polymerization of G3 monomer (Figure 2), presumably due to depressed monomer mobility at the high concentration of denpols reached in the reacting phase mixture.

The high value of monomer conversion to polymer was also proved by <sup>1</sup>H NMR. A representative <sup>1</sup>H NMR spectrum of a sample collected after the reaction of G4 monomer is shown in Figure 4. A <sup>1</sup>H NMR spectrum of the pure G4 monomer is shown in Figure 5a for comparison. Arrows in Figure 4 indicate the characteristic peaks of the monomer. The broadening of such peaks after the reaction is a confirmation of the polymerization occurrence. The peaks associated with the double bond, located at  $\delta$  = 5.6 ppm and  $\delta$  = 6.1 ppm, almost disappeared after the reaction, thus proving the almost complete conversion of the monomer double bonds. Note the peak associated with dioxane in the <sup>1</sup>H NMR spectrum of the monomer (Figure 5a). Such solvent, residue from the G4 synthesis, could not be removed despite monomer being subjected to several freeze-drying cycles before polymerization. It was instead completely extracted by scCO<sub>2</sub>. Indeed, it was visible in the spectrum of neither the polymerized sample spectrum (Figure 4), nor the

Table 1. Recipes and Results for the Polymerization of G3 and G4 in  $scCO_2^a$ 

run	monomer	time [h]	X %	$P_{n}$	$P_{\rm w}$	PDI	
$[AIBN]_0 = 8.6 \text{ mM}$							
1	G3	2.0	63	487	2354	4.8	
2	G3	6.0	93	493	3588	7.3	
3	G3	12.5	93	456	4653	10.2	
4	G3	20.0	94	428	4437	10.4	
		[AIBN] <sub>0</sub>	= 2.7 mN	1			
5	G3	1.5	-				
6	G3	4.0	19	540	1718	3.2	
7	G3	7.5	71	630	2766	4.4	
8	G3	12.3	90	512	3464	6.8	
9	G3	21.0	90	352	4356	12.4	
$[AIBN]_0 = 0.84 \text{ mM}$							
10	G3	2.0	-				
11	G3	6.0	-				
12	G3	11.5	41	451	2147	4.8	
13	G3	16.0	43	406	2094	5.2	
14	G3	20.0	79	448	5136	11.5	
		[AIBN] <sub>0</sub>	= 0.35 mN	N			
15	G3	20.0	-				
		[AIBN] <sub>0</sub>	= 16.3 mN	N			
16	G4	12.0	61	56	106	1.9	
17	G4	20.0	85	58	99	1.7	
18	G4	30.0	89	56	109	2.0	
$[AIBN]_0 = 8.0 \text{ mM}$							
19	G4	12.7	24	78	120	1.5	
20	G4	20.0	53	65	98	1.5	
21	G4	30.3	73	70	116	1.7	
$[AIBN]_0 = 2.6 \text{ mM}$							
$22^b$	G4	19.8	14				
$23^b$	G4	20.3	10				
24	G4	30.5	14	73	109	1.5	
All reactions performed at $T = 65 ^{\circ}C$ and $D = 120$ 140 her Perperted							

<sup>*a*</sup> All reactions performed at T = 65 °C and P = 130-140 bar. Reported initiator concentrations are average values over all corresponding batches. <sup>*b*</sup> At such low conversion, polymer and monomer peak superposition prevented reliable calculation of  $P_n$  and  $P_w$ .

monomer subjected to  $CO_2$  pressure (without adding any initiator; Figure 5b). Comparison of the two spectra in Figure 5 confirms the well-known ability of scCO<sub>2</sub> of extracting solvents and confirms the monomer structure is not affected by high pressure  $CO_2$ .

About the degrees of polymerization, PG3 samples exhibit longer chains and larger values of the polydispersity index (PDI) compared to PG4 samples (cf. Table 1). The number,  $P_{n}$ , and weight-average,  $P_{w}$ , degrees of polymerization for PG3 samples are plotted as a function of conversion in Figure 6 and the corresponding PDI in Figure 7. Weight-average degrees of polymerization,  $P_{w}$ , of the orders of thousands monomer units for the third generation monomer were systematically obtained, corresponding to molecular weights of several million g/mol. Such extremely large  $P_w$  can be produced through conventional



**Figure 2.** Conversion as a function of time for G3 polymerization at  $[AIBN]_0 = 8.6 \text{ mmol/L} (\blacktriangle)$ , 2.7 mmol/L ( $\textcircled{\bullet}$ ), and 0.84 mmol/L ( $\textcircled{\bullet}$ ). Curves: calculated solving eqs 7–10 using  $\alpha = 370$  and inhibition time,  $\tau$ , as reported in Table 4.



**Figure 3.** Conversion as a function of time for G4 polymerization at  $[AIBN]_0 = 16.3 \text{ mmol/L} (\blacklozenge), 8.0 \text{ mmol/L} (\blacktriangle), and 2.6 \text{ mmol/L} (\spadesuit).$  Curves: calculated solving eqs 7–10 using  $\alpha = 60$  and inhibition time,  $\tau$ , as reported in Table 4.

solution polymerization only when using lower generation monomers.<sup>16</sup> To the best of our knowledge, there are no publications reporting almost complete conversion and  $P_w$  on the order of thousands monomer units obtained at the same time using the macromonomer approach with high generation dendronized monomers. These results address the potential of using CO<sub>2</sub> as reacting medium to synthesize denpols by the macromonomer route.

**3.2.** Number-Average Degree of Polymerization,  $P_n$ . In addition to the very large values of final conversion and  $P_w$  obtained, an even more surprising finding is the independence of the number-average degrees of polymerization,  $P_n$ , upon amount of initiator and conversion. This is clearly shown by the  $P_n$  values for PG3 in Figure 6, as well as by the results provided in Table 1 for PG4.  $P_n$  values are always in the range of 450–630 monomer units for PG3, while  $P_n = 56-73$  for PG4. Even though the experimental values exhibit some scatter, the independence of the molecular weight upon the initiator concentration was proved in a fully convincing way when comparing the GPC elution profiles at similar conversions: they were almost superimposed for all samples whatever the amount of initiator.<sup>19</sup>

On average, constant values of  $P_n = 500$  monomer units for PG3 and 65 for PG4 were obtained. If the polymerization kinetics in scCO<sub>2</sub> is somehow similar to that of the conventional free radical polymerization in solution (see section 5), constant  $P_n$  at different initiator concentrations and polymerization rates, would be considered a clear proof that chain transfer to monomer is the dominant chain termination mechanism. This is clear when considering the Mayo equation, for which the number-average degree of polymerization



**Figure 4.** <sup>1</sup>H NMR spectrum of crude reaction mixture for the polymerization of G4 (Table 1 run 17, X % = 85%) in DMSO-*d*<sub>6</sub> at 80 °C. Arrows indicate the peaks characteristics of the monomer G4 (cf. Figure 5). Note that that the peaks of the PG4 are broad, and the peaks at  $\delta = 5.6$  and 6.1 ppm, corresponding to G4 double bond signal, are almost invisible (see the zoomed inset). \* and \*\* denote the signals of DMSO and water, respectively.



**Figure 5.** <sup>1</sup>H NMR spectrum of G4 (a) before and (b) after treatment with  $scCO_2$  at  $T = 60 \circ C$ , P = 140 bar, for 8 h. The signal for residual dioxane (Dox,  $\delta = 3.57$  ppm) in spectrum (a) disappeared after the treatment (b). \* and \*\* denote the signals of DMSO and water, respectively.

in the absence of chain transfer to solvent, initiator, or chain transfer agents, is given by  $^{23,24}$ 

$$\frac{1}{P_n} = \left(\frac{1+\gamma}{2}\right) \frac{k_t R_p}{k_p^2 [G]^2} + C_G \tag{3}$$

where  $R_{p}$ , [G], and  $C_{G}$  are the rate of polymerization, the monomer concentration and the transfer to monomer constant, ratio between the rate constants of transfer to monomer and propagation. In eq 3,  $k_{p}$  and  $k_{t}$  are propagation and radical termination rate constants and the parameter  $\gamma$  is the ratio between the rate constant of radical termination by disproportionation and  $k_{t}$ . From the experimental data in Table 1 average values of  $C_{\rm G} = 1/500$  and  $C_{\rm G} = 1/65$  are estimated for G3 and G4, respectively. We can exclude the chain transfer to occur on the methacrylate group (which is also the reactive site in our dendronized macromonomers) because methyl methacrylate (MMA) exhibits negligible transfer to monomer constant.<sup>25</sup> Alternative sites for chain transfer to monomer to occur by H abstraction could be (i) the CH bonds  $\alpha$  to the ether oxygen atoms and (ii) the benzylic hydrogen at the core of the monomers. Let us consider case (i) first. The CH bonds alpha to the ether oxygen atoms are also present at the dendritic shell. Therefore, they are accessible as potential sites for chain transfer to polymer reactions too, and the value of the chain transfer to polymer constant should be close to the measured  $C_{\rm G}$ ,



**Figure 6.** Number-average,  $P_n$  (open symbols) and weight-average  $P_w$  (filled symbols) degrees of polymerization vs conversion, *X* %, for PG3 samples polymerized in scCO<sub>2</sub> at [AIBN]<sub>0</sub> = 8.6 mmol/L ( $\blacktriangle$ ), 2.7 mmol/L ( $\blacklozenge$ ), and 0.84 mmol/L ( $\blacksquare$ ). Lines are guides for the eye.



**Figure 7.** Polydispersity index, PDI, vs conversion, *X%*, of PG3 samples polymerized in scCO<sub>2</sub> at [AIBN]<sub>0</sub> = 8.6 mmol/L ( $\blacktriangle$ ), 2.7 mmol/L ( $\blacklozenge$ ), and 0.84 mmol/L ( $\blacksquare$ ). The line is a guide for the eye.

because the same reaction is involved. Such extremely large values of chain transfer to polymer constants would have caused branching reactions to occur at severe extent, and more for the polymerization of G4 compared to the polymerization of G3 monomer. This was not the case (cf. section 3.3) and therefore H abstraction by propagating radicals at sites (i) can be tentatively excluded.

Differently, the benzylic C–H bond (case (ii)) is susceptible of hydrogen abstraction but the same hydrogen would unlikely be accessible for chain transfer to polymer reactions. In fact, the benzylic C-H bond is weaker than the aliphatic C-H bond<sup>23</sup> due to the stabilization imparted to the radical resulting from the abstraction by the benzene ring. On the other hand the same C-H group is very close to the backbone of the polymer chain after a monomer is polymerized, and therefore not easily accessible to propagating radicals for the chain transfer to polymer reaction. It is thus interesting to compare the chain transfer constants per number of benzylic hydrogens, n, of the macromonomers used in this work, with that of a quite similar but undendronized system.  $C_G/n$  for the chain transfer reaction of MMA to dibenzyl ether (DBE) is  $2.5 \times 10^{-4}$  (at T = 60 °C),<sup>26</sup> while for G3 and G4 we estimated  $1 \times 10^{-3}$  and  $7.7 \times 10^{-3}$ , respectively. The agreement between the values of  $C_G/n$  for G3 and MMA/DBE supports a chain termination dominated by chain transfer to monomer. On the other hand, the increasing value of  $C_G/n$  from a conventional system (MMA/DBE), to G3 and to G4, suggests that the focal point conformation of the monomers, or of the propagating radicals, favors hydrogen abstraction rather than propagation to the double bond at increasing dendronization.

**3.3.** Polydispersity Index and Branching. With respect to the time evolution of polydispersity, a broadening of the GPC



**Figure 8.** GPC elution profiles of crude PG3 samples at 2 h (continuous line, Table 1 run 1), 6 h (dashed line, Table 1 run 2) and 12.5 h of reaction time (dotted line, Table 1 run 3). Monomer peaks, visible at largest retention time, are also shown.



**Figure 9.** GPC elution profiles of crude PG4 samples at 13 h (continuous line, Table 1 run 19), 20 h (dashed line, Table 1 run 20), and 30 h of reaction time (dotted line, Table 1 run 21). Monomer peaks, visible at largest retention time, are also shown.

elution profiles in the high molecular weight region at increasing conversion and reaction time was observed in all cases for both monomers. Such broadening is evident in Figures 8 and 9, where three elution profiles at different reaction time and constant initial AIBN concentration are shown for PG3 and PG4 samples, respectively.

Such broadening is especially evident for PG3 samples, where much broader distributions were measured: PDI values up to 12 for PG3 samples while maximum PDI values around 2 were found for PG4 samples. The evolution of  $P_w$  and PDI for PG3 samples shown in Figures 6 and 7, indicate that  $P_w$  and PDI increased slightly with conversion for X% smaller than 80%, with PDI ranging from 3 to 5, and then sharply at larger conversions.

Let us consider first the lower conversion range. PDI values ranging from 3 to 5 are not unusual for the free radical polymerization of the herein considered monomers even when chain transfer to polymer is not occurring at severe extent.<sup>16,27</sup> Indeed, chain transfer to polymer is more likely to occur at the dendritic shell rather than at the sterically hindered backbone. In this case, larger PDI values would have been observed for the PG4 samples due to the large number of potential sites available for hydrogen abstraction compared to the PG3 homologue. Instead, this was not the case and polydispersity values for PG4 were always smaller. On the other hand, the very sharp PDI increase at high conversion (higher than 80%) suggests that chain transfer to polymer may become important at least at such conditions (large values of the polymer to monomer ratio in the reacting mixture). Notably, even when the limiting monomer conversion was reached, PDI went on increasing with time (cf. in



Figure 10. Representative AFM phase images of (a) PG3 and (b) PG4 after spin-coating the polymer solutions on mica.

Table 1 run 2 with run 3 and run 8 with run 9). A possible explanation is that when only few percents of unreacted monomer are left, their propagation is hindered by diffusion limitations in the highly viscous denpol-crowded environment. At such condition, the primary radicals produced by the initiator decomposition (half-life time for AIBN at T = 65 °C in scCO<sub>2</sub> is 25 h)<sup>28</sup> start reacting with the polymer chains via transfer to polymer reaction, thus creating branched denpols of very high molecular weight and increasing the broadness of the molecular weight distribution.

Such mechanistic picture could be validated looking for branched macromolecules in the final product. The quantitative assessment of branching for dendronized polymers is difficult, but a rough estimation can be derived by AFM image analysis.<sup>2</sup> Two representative images of PG3 and PG4 samples are shown in Figure 10, parts a and b, respectively. Note that, more than to confirm larger P<sub>w</sub> and PDI for PG3 compared to PG4, Figure 10a is shown here to evidence that polymer aggregates are formed by spin-coating on mica (such as in the right-upper part of the figure). In similar cases, it is difficult to clearly discriminate if the polymer chains were actually branched or just entangled: therefore, all the detected branched-entangled chains were counted as branched points, thus overestimating the extent of branching. Nevertheless, the extent of branching was found to be quite limited: for samples with PDI larger than 10, a maximum of 0.32 to 0.57 average number of branches per chain was estimated by phase and height image analysis of several chains per sample. Therefore, even though chain branching occurred, only at minor extent at conversion exceeding 80%, such limited interchain connections is enough to produce a major PDI increase, most probably because of the large size of the involved macromolecules.

#### 4. ROLE OF PRESSURE AND TEMPERATURE

Finally, a few more reactions were performed to assess the effect of pressure and temperature on kinetics and degree of polymerization. Recipes and characterization results for reactions carried out at T = 65 °C and 20 h of reaction time are provided in Table 2. The polymerization of the third generation monomer (G3) was still almost complete producing samples at extremely high molecular weight and large values of the polydispersity index. Quite interestingly, while samples polymerized at a pressure of about 130 bar were completely soluble in DMF, denpols obtained at higher pressures were not. Clearly, the

Table 2. Effect of Pressure for the Polymerization of G3 and G4 in  $scCO_2^a$ 

run	monomer	AIBN [mM]	P [bar]	time [h]	<i>X</i> %	$P_{n}$	$P_{\rm w}$	PDI
1	G3	8.3	135	20	94	428	4437	10.4
2	G3	8.6	185	20	93	660	8328 + gel	12.6
3	G3	8.5	267	20	94	736	3630 + gel	4.9
4	G3	0.83	138	20	79	448	5136	11.5
5	G3	0.89	190	20	77	516	7222 + gel	14.0
6	G4	8.2	130	20	53	65	98	1.5
7	G4	8.3	280	20	31	115	200	1.7
<sup><i>a</i></sup> All reactions performed at $T = 65$ °C and 20 h reaction time.								

average polymerization degrees reported in Table 2 runs 2, 3, and 5, characterize only the soluble fraction of the polymer, being the small amount of insoluble polymer (defined "gel" in Table 2; about 10 to 40% of the produced polymer) removed by filtration prior to injection into the GPC instrument. Unfortunately, the exact nature of the insoluble fraction could not be assessed, but it is reasonably due to cross-linked high molecular weight denpol chains: such finding supports the role of chain-connecting reactions mentioned above.

About the polymerization of the fourth generation G4 monomer, larger pressures slowed down the reaction and favorably affected the degree of polymerization:  $P_w$  almost doubled when increasing the pressure from 130 to 280 bar (Table 2, run 7).

In general, a pressure increase favors the dissolution of low molecular weight species in the  $scCO_2$  phase.<sup>29</sup> This effect can explain the reduced conversion at larger pressures due to AIBN preferential partitioning into the supercritical phase, thus reducing its amount in the polymer-rich phase. The same reason cannot explain the increased degree of polymerization, which, as shown above, is independent upon the initiator concentration.

Finally, G4 polymerizations were carried out at increasing temperature to check whether or not the G4 polymerization rate could be enhanced while producing denpols of decent degree of polymerization. Recipes and results are listed in Table 3 to be compared with reference reactions carried out at T = 65 °C. A strong effect of temperature on the reaction rate was observed: increasing the temperature, the reaction time could be decreased of almost 20–30 times, with final conversion increasing of a factor from 1.7 (Table 3, run 1 and 3) to almost 4 (Table 3, run 4 and 5). Therefore, also the fourth generation monomer was

Table 3. Effect of Temperature on the Polymerization of G4 in  $scCO_2^a$ 

run	AIBN [mM]	$T [^{\circ}C]$	time [h]	X %	$P_{\rm n}$	$P_{\rm w}$	PDI
1	8.2	65	20	53	65	98	1.5
2	8.3	75	5.1	92	51	94	1.9
3	8.1	83	1.3	88	46	80	1.7
4	2.6	65	30.5	14	73	109	1.5
5	2.7	85	1.3	41	58	110	1.9
<sup><i>a</i></sup> All reactions performed at $P = 130 \pm 10$ bar.							

polymerized up to almost complete conversion within few hours (Table 3 run 3) and, most important, no appreciable effects on the degree of polymerization were observed.

#### 5. DISCUSSION

In general, the polymerization of dendronized monomers may exhibit features which are not involved in the conventional free radical schemes. Two mechanistic pictures are frequently discussed, as shortly illustrated by the following examples.

It has been observed that both conversion and degree of polymerization are depressed by high monomer to solvent ratios (i.e., monomer concentration larger than about 53%) in solution polymerization.<sup>30</sup> Similar results have been reported for non-dendronized macromonomers.<sup>31</sup> Such experimental evidence can be attributed to hindered polymerization reaction either because of limited monomer mobility at high viscosity of the reaction medium, or because of encapsulation and consequent inaccessibility of the active center of the propagating denpol.

Other authors have shown that dendrons may self-assemble and form supramolecular reactors with larger concentration of polymerizable groups (the focal point double bonds).<sup>32–34</sup> In such a case, Percec et al.<sup>34</sup> found enhanced reaction rate and larger degrees of polymerization in the presence of self-assembly compared to conventional solution polymerization, and referred to this case as "self-encapsulated self-accelerated polymerization".

The better conditions established in  $scCO_2$  (fast reaction rate and large degrees of polymerization) demonstrate that the active radical as well as the monomer double bond are always more "accessible" in such reaction medium than in solution.<sup>18</sup> On the other hand, no study has been reported focused on conformation and/or self-assembly behavior of dendrons similar to those under examination in supercritical carbon dioxide. Therefore, as first step of a critical evaluation of the different mechanistic pictures, it makes sense to verify whether or not the kinetics follows a conventional free radical polymerization scheme, and an explanation alternative to self-assembly can be found to justify the enhanced kinetics in  $scCO_2$  compared to solution polymerization. This is done in the following.

As anticipated, the examined monomers are insoluble in  $scCO_2$  and the reaction volume is composed by the  $scCO_2$  phase and by the amorphous monomer/polymer-rich phase swollen by CO<sub>2</sub>. At monomer concentrations equal to zero (i.e., in the supercritical phase), the efficiency of the initiator becomes negligible.<sup>35</sup> It can thus be assumed that all the active radicals are actually produced by dissociation of the initiator present in the monomer/polymer phase. Moreover, it is assumed that AIBN partitioning between the two phases is at thermodynamic equilibrium, and that any inhibiting impurity is completely consumed at reaction time  $\tau$ , after which monomer

Table 4.	Calculated	Inhibition	Times	and	Inhibitor/N	lono-
mer Rati	os <sup>a</sup>					

[AIBN] <sub>0</sub> [mM]	Polymerization of G3 $\tau$ [h]	[Z] <sub>0</sub> /[G] <sub>0</sub>
8.6 2.7 0.84	0.33 2.5 7.0	$1.7 \times 10^{-4}$ $4.0 \times 10^{-4}$ $3.3 \times 10^{-4}$
[AIBN] <sub>0</sub> [mM]	Polymerization of G4 $\tau$ [h]	[Z] <sub>0</sub> /[G] <sub>0</sub>
16.3 8.0	2.0 7.0	$4.0 \times 10^{-3}$ $6.4 \times 10^{-3}$ $4.2 \times 10^{-3}$
2.0	10.0	4.2 × 10

<sup>*a*</sup> Inhibition time,  $\tau$ , for reactions in Table 1, with  $k_d = 7.76 \times 10^{-6}$ /s. The moles of inhibitor per moles of monomer, [Z]<sub>0</sub>/[G]<sub>0</sub>, are estimated through eq 11 using  $2fK_{12} = 1$ , [G3]<sub>0</sub> = 0.457 M, and [G4]<sub>0</sub> = 0.221 M.

consumption starts. At such conditions, the monomer and initiator consumption rates (up to the limiting conversion) can be expressed as:

$$\frac{d[G]}{dt} = 0 \quad \text{at } t < \tau \tag{4}$$

$$\frac{\mathrm{d}[G]}{\mathrm{d}t} = -k_p[G] \sqrt{\frac{2fk_d K_{I2}[I_2]}{k_t}} \quad \text{at } t \ge \tau \tag{5}$$

$$\frac{\mathrm{d}[I_2]}{\mathrm{d}t} = -k_d[I_2] \tag{6}$$

where *f* is the initiator efficiency in the monomer/polymer phase,  $k_{\rm d}$  is the dissociation rate constant (the same value is assumed in both phases) and  $K_{\rm I2}$  is the initiator partition coefficient. By integrating eqs 4-6, the following relation between fractional conversion, *X*, and reaction time is obtained at  $t > \tau$ :

$$F(X) = \alpha F(t) \tag{7}$$

where:

$$F(X) = \ln \frac{1}{(1-X)} \sqrt{\frac{1}{[I_2]_0 \exp(-k_d\tau)}}$$
(8)

$$F(t) = [1 - e^{-(k_d/2)(t - \tau)}]$$
(9)

and the dimensionless constant  $\alpha$  is given by

$$\alpha = \frac{k_p}{\sqrt{k_t}} \sqrt{\frac{8fK_{I2}}{k_d}} \tag{10}$$

According to eq 7, F(X) is a linear function of F(t) whatever the initial initiator concentration,  $[I_2]_0$ , provided that constant value of  $\alpha$  applies (and therefore not after the limiting conversion has been reached). The values of both the functions are readily estimated using the experimental data in Table 1, a value of decomposition rate constant,  $k_d$ , of 7.76 × 10<sup>-6</sup> s<sup>-1</sup>,<sup>28</sup> and the different values of inhibition time as given in Table 4. The values of  $\tau$  were first estimated from an analysis of each kinetic profile and then optimized to improve the linear fit of eq 7. The resulting F(X) values are plotted against F(t) in Figure 11 for both



**Figure 11.** F(X) (eq 8) vs F(t) (eq 9) evaluated through the experimental data in Table 1. Symbols: polymerization of G3 at [AIBN]<sub>0</sub> = 8.6 mmol/L ( $\blacktriangle$ ), 2.7 mmol/L ( $\blacklozenge$ ), and 0.84 mmol/L ( $\blacksquare$ ); polymerization of G4 at [AIBN]<sub>0</sub> = 16.3 mmol/L ( $\diamondsuit$ ), 8.0 mmol/L ( $\bigtriangleup$ ), and 2.6 mmol/L ( $\bigcirc$ ).

monomers: a remarkably nice linearity is found in all cases, thus providing constant values of the slope  $\alpha$  equal to 370  $M^{-0.5}$  for G3 and 60  $M^{-0.5}$  for G4.

To check the compatibility of the estimated  $\tau$  values with the presence of some inhibitor, here indicated by *Z*, the ratio between the moles of inhibitor and the initial moles of monomer is expressed as:

$$\frac{[Z]_0}{[G]_0} = \frac{2fK_{I2}[I_2]_0(1 - \exp(-k_d\tau))}{[G]_0}$$
(11)

Assuming equipartition of the initiator between the two phases  $(K_{I2} = 1)$  and a value of 2*f* equal to one, the  $[Z]_0/[G]_0$  values reported in Table 4 are estimated. The absolute values are quite small and compatible with the very large number of synthetic steps required to synthesize the monomers. Moreover, comparable values are found for each set of data at constant generation: therefore, the assumption of inhibiting impurities entering the system with the monomers seems reasonable.

A reliable absolute value of  $k_p/k_t^{0.5}$  could not be determined from the estimated values of  $\alpha$  because of the unknown initiator efficiency (in the monomer/polymer-rich phase) and partition coefficient (cf. eq 10). On the other hand, a reasonable lower bound of the same ratio can be determined as follows.

With chain termination occurring predominantly by chain transfer to monomer, the first term on the right-hand side of eq 3 must be much smaller than  $C_{G}$ :

$$\left(\frac{1+\gamma}{2}\right)\frac{k_t R_p}{k_p^2 [G]^2} \ll C_G \tag{12}$$

Making explicit  $k_p/k_t^{0.5}$  from eq 10 and plugging it into eq 12, the inequality is rearranged and the upper bound value for the product  $fK_{I2}$  is found:

$$fK_{I2} \ll \frac{\alpha[G]C_G}{4\sqrt{[I_2]}} \left(\frac{2}{1+\gamma}\right) \tag{13}$$

Using the initial values for [G] ([G3]<sub>0</sub> = 0.457 M and [G4]<sub>0</sub> = 0.221 M), and [I<sub>2</sub>], eq 13 provides  $fK_{12} \ll 1.82/(1 + \gamma)$  for G3 and  $fK_{12} \ll 0.8/(1 + \gamma)$  for G4. Using these values, the lower bounds of the ratio  $k_p/k_t^{0.5}$  are finally estimated from eq 10 as

$$G3: \frac{k_p}{\sqrt{k_t}} \gg 0.27\sqrt{1+\gamma} \tag{14}$$

$$G4: \frac{k_p}{\sqrt{k_t}} \gg 0.066\sqrt{1+\gamma} \tag{15}$$

Note that parameter  $\gamma$  is ranging between 0 and 1: therefore, the square root term does not affect our estimation at a significant extent.

As expected, the ratio  $k_p/k_t^{0.5}$  decreases upon increasing dendron generation, but, quite surprisingly, its order of magnitude is in any case larger, or in the worse case (G4) comparable, to that typically observed for the solution polymerization of MMA, that is on the order of 0.1.<sup>23,36</sup> Because of the crowding nature and large molecular size of the used monomers, the absolute values of both propagation and termination rate constants are expected to be smaller than those typical of MMA. This means that the reduction of  $k_t$  due to dendronization is larger than that of  $k_p$  and, as a result, G3 exhibits larger value of  $k_p/k_t^{0.5}$  compared to MMA. On the other hand, moving from the third to the fourth generation, the value of the ratio  $k_p/k_t^{0.5}$  decreases, thus indicating that the decrease of  $k_p$  becomes more important at higher crowding of the monomer.

#### 6. CONCLUSIONS

Third (G3) and fourth (G4) generation spacerless dendronized macromonomers, bearing a methacrylate group at the focal point, were polymerized in supercritical carbon dioxide using AIBN as initiator. Conversion values as high as 90% could be achieved for both monomers within a few hours. A limiting conversion of about 90% was observed for the reaction of G3, attributed to hindered monomer mobility when most of the reacting phase is made of polymerized denpol chains. Weightaverage degrees of polymerizations were on the order of thousands monomer units for PG3 samples, and in the range 100-200 for PG4 samples.

Data collected at constant temperature and different initiator contents were analyzed in the frame of a conventional free radical kinetic scheme. This analysis suggests that chain termination is dominated by transfer to monomer, presumably occurring on the weak benzylic hydrogens. Such finding is especially promising because it implies that even larger degrees of polymerization could be achieved when using monomers not containing weakly bonded hydrogen atoms. Reaction kinetics up to limiting conversion are consistent with a simple kinetic scheme accounting for inhibition due to traces of impurities in the initial monomers. Within this frame,  $k_p/k_t^{0.5}$  ratios larger than that typical of MMA are needed to explain the observed high reactivity of the monomers. Since the propagation rate constants of these macromonomers are expected to be depressed by the crowding effect, this result implies an even stronger reduction of the termination rate when running the polymerization in supercritical carbon dioxide.

#### ASSOCIATED CONTENT

**Supporting Information.** Discussion of the physical state of the monomer/polymer mixture, including SEM images of G3 monomer before polymerization and of G3/PG3 crude mixture after polymerization, and representative GPC elution profiles of PG3 and PG4 samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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