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Preparation of multi-allylic dendronized polymers via atom-transfer radical polymerization

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Abstract

Atom-transfer radical polymerization (ATRP) was investigated to polymerize a styrene monomer carrying carbosilane dendrons with 6 terminal allyl branches. Polymers with a monomodal molar mass distribution and low polydispersity have been produced, while by comparison the free-radical polymerization technique led to chain transfer early in the polymerization. Steric effect brought by the dendrons result in a slow polymerization rate, leading to an apparent saturation of the degree of polymerization. By pushing up the polymerization conditions (eg. increase of temperature or concentration), interchain couplings started to take place, most likely from reactions at the allyl branches. These results are very similar to the ones previously reported for the anionic polymerization of this same multi-allylic dendronized monomer.

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Introduction

Polymers carrying functional groups within a precise molecular architecture remain a topical issue of high interest as they often constitute the starting point to the preparation of advanced or “smart” materials for various applications in nanotechnology, bioscience and others...[1] In this respect, dendronized polymers with imbedded side-chain functionalities constitute quite innovative molecular platforms due to their ability to adopt by steric effect a cylindrical-shaped morphology, and to the high number of functional groups that can be introduced at the inner branches or/and at the outer periphery.[2,3] In that context, functional dendronized polymers has drawn a strong attention for applications in various fields, including biomaterials,[4] catalysis,[5] drug delivery,[6] waste treatment,[7] sensors[8] and energy storage.[9]

Nevertheless, the preparation of well-defined functional dendronized polymers represents a quite challenging task due to the considerable steric constraints brought by the bulky dendrons attached to the polymer backbone, and also to the high density of potentially sensitive functional groups.[10,11] So far, two efficient synthetic methods have already been developed for the synthesis of this novel class of polymers: i) the macromonomer approach, for which the preformed dendronized monomer (or a precursor) is directly polymerized, and ii) the grafting method, for which the desired dendron units are attached (at once or via a stepwise procedure) to the polymer backbone either by a convergent (“graft to route”) or divergent (“graft onto route”) manner.[2] The macromonomer approach is usually preferred when a perfect dendron structure is targeted, but the trade-off is generally the difficulty to achieve high DPs.[12-14] Among all polymerization techniques, however, ring-opening metathesis polymerization has proven to be quite efficient in producing dendronized polymers of high DPs and of narrow polydispersity.[15,16]

Regarding functional dendronized polymers, only a few of them have been prepared via a controlled polymerization technique of dendritic macromonomers, so far.[2] For instance, atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain-transfer polymerization (RAFT) and ring-opening metathesis polymerization (ROMP) techniques were used to polymerize dendritic monomers carrying protected hydroxyl[14,16-19] and amine[20] end-branches. Anionic polymerization technique was also reported by us to polymerize dendronized monomers fitted with allyl end-branches.[21]

In the specific case of the allyl-ended dendritic monomers polymerized anionically, a slow polymerization rate was observed, leading to an apparent saturation of DP, the value of which being directly correlated to the bulkiness of the dendritic monomer.[21] Optimization

of the experimental conditions (better solvent, higher temperature...) was shown to provide polymers with significantly higher molar masses, but with slightly increased polydispersity, which was explained by the emergence of intermolecular transfer reactions. The polymerization of multi-allylic dendronized monomers represents in itself a fundamental interest indeed, in order to understand and differentiate the reactivity of the vinyl groups in an overcrowded environment, in particular. Moreover, the resulting multi-allyl branched polymers constitute valuable intermediates towards the preparation of surface-functionalized "nanocylinders", as the peripheral allyl branches enable a post-polymerization functionalization via a number of straightforward reactions (eg. thiol radical addition,[22] epoxidation,[23] olefin metathesis,[24] hydrosilylation[12]...). We indeed demonstrated the preparation of cylindrical-like particles covered by siloxane chains, perfluorinated chains or else by ethyleneglycol chains, leading all to unique properties.[7,25,26] It is clear that a huge variety of functional monomers can be directly polymerized by controlled radical polymerization (CRP), without passing through an intermediate post-polymer functionalization.[27] However, the post-modification of allyl-branched polymer remains of high interest in a number of cases, such as i) for the introduction of highly bulky terminal groups,[25] ii) for rapidly preparing series of homologues,[7,26] iii) when the functional monomers can hardly be synthesized[25] or else, iv) when CRP process is not compatible with the functional groups or atoms present on the monomers (eg. bromide and iodine atoms).

In this study our objective is to investigate whether the aforementioned multiallylic dendronized polymers could be prepared by a (controlled) radical polymerization technique. Since the seminal work of Matyjaszewski who demonstrated the excellent ATRP polymerization control by using allyl-halide type initiator,[28] the radical polymerization of asymmetric multi-vinyl monomers has been intensively investigated and has shown to be quite challenging indeed, as the least reactive vinyl groups can also be involved in competing chain transfer reactions. This issue has been intensively investigated for ω -olefin methacrylate[29-31] and ω -olefin styrene[32-35] monomers by ATRP or RAFT techniques, in particular. At least for low conversions, these monomers could be polymerized in a controlled manner and the olefin branches could be preserved, leading to well-defined alkene-branched polymers with low polydispersities.

In this line, we describe herein the preparation of multi-allylic dendronized polymers by using the ATRP technique. The monomer is a styrene derivative substituted by two carbosilane dendrons (**G1bis**) of first generation and terminated with functional allyl groups as shown in Scheme 1. This report aims at investigating the (ATRP) polymerization of the

dendritic monomer **G1bis** to the corresponding **Poly(G1bis)**, by varying different conditions (type of initiator, temperature, solvent...). Free radical polymerization (FRP) of **G1bis** is also used for comparison. Finally, the characteristics of the multiallylic polymers **Poly(G1bis)** obtained by ATRP are compared to the ones previously prepared by anionic polymerization.[21] To the best of our knowledge, this is the first report of polymers carrying multiple ω -olefin branches prepared via a “controlled” radical polymerization technique.

EXPERIMENTAL SECTION

Materials. The monomer **G1bis** was prepared from the commercially available methyl 3,5-dihydroxybenzoate in a multistep synthesis, as previously reported.[21] 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Aldrich and was freshly recrystallized from methanol prior to use. Copper(I) bromide (CuBr), 2-bromopropionitrile (BrPN), malononitrile (MN), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich. Ethyl α -bromoisobutyrate (EBriB) and *p*-toluenesulfonyl chloride (TsCl) were purchased from Alfa Aesar and Acros, respectively. Toluene was dried over KOH overnight and then distilled over sodium/benzophenone. Dimethoxyethane (DME) was provided by Aldrich (anhydrous and inhibitor-free) and used as received.

Instrumentation. Isolation of the polymers was performed by passing the crude polymerization mixtures through a column filled with a SX1 Bio-Beads SEC gel (Bio-Rad) and eluted with THF by gravity flow. Both ^1H (300 MHz) and ^{13}C (100 MHz) NMR spectra were measured in CDCl_3 solvent (unless specified) using a Bruker AC300 spectrometer. Molecular weight determinations were performed in the analytical department of the Institute Charles Sadron (ICS) by size exclusion chromatography (SEC). The analysis was carried out on a Shimadzu chromatograph fitted with five PLGel 10 μm Mixed B columns (styrene-divinylbenzene polymer gel) and by using three detection modes: a differential refractometer (RI) detector (Shimadzu RID-10A) calibrated with polystyrene standards, a UV detector ($\lambda = 254$ and 280 nm), and a multi-angle laser light scattering (MALLS) detector (Wyatt TREOS, $\lambda = 632.8$ nm).

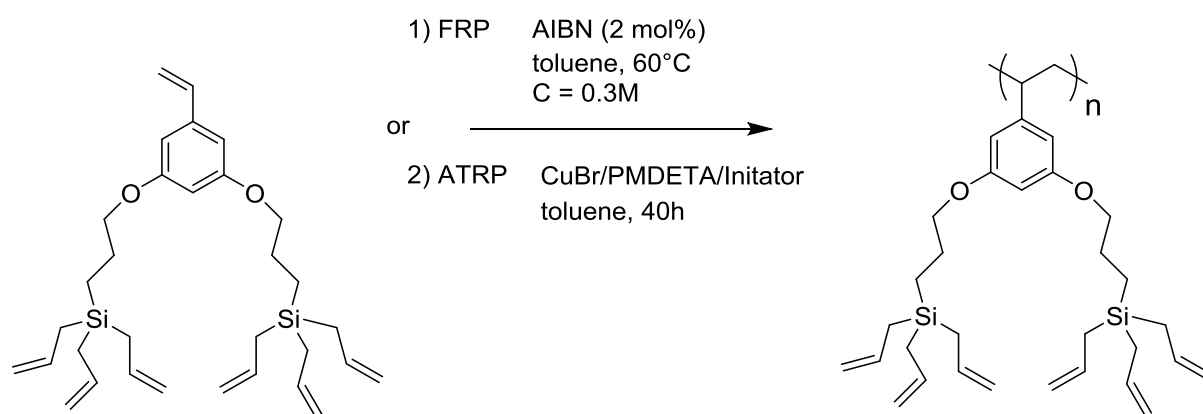
Free radical polymerization (FRP) procedure. The polymerization of monomer **G1bis** was carried out with AIBN as initiator in a degassed sealed tube. Monomer **G1bis** (1 eq), AIBN (0.02 eq), and dry toluene (0.3 M monomer concentration) were placed in a dry glass ampoule equipped with a magnetic stirring bar, and the solution was degassed by five freeze-pump-thaw cycles. Then, the ampoule was flame-sealed under reduced pressure and the mixture was

stirred at 60°C for 4, 8, or 24 hours. At the desired time, the crude polymerization mixture was cooled down and passed through a column filled with SEC gel (eluent THF) to isolate the polymer fraction from the unreacted monomer. Then, the polymer fraction was concentrated, dried under vacuum, and characterized by SEC chromatography. The conversion was calculated from the amount of the recovered polymer and monomer fractions.

Atom-transfer radical polymerization (ATRP) procedure. All polymerization runs of monomer **G1bis** were carried out with EBriB, BPrN, or TsCl as initiator, PMDETA as ligand, and CuBr in a degassed sealed tube. Monomer **G1bis** (25 eq), initiator (1 eq), PMDETA (3 eq), CuBr (1 eq), and dry toluene at different monomer concentrations from 0.75 M to 1.9 M (bulk) were placed in a dry glass ampoule equipped with a magnetic stirring bar, and the solution was degassed by five freeze-pump-thaw cycles. Then, the ampoule was flame-sealed under reduced pressure and the mixture was stirred at 65 or 90°C for 40 hours. The polymerization mixture was cooled down and filtered through a pad of alumina. After concentration, the filtrate was passed through a column filled with SEC gel (eluent THF) to recover the polymer fraction from the unreacted monomer. Finally, the polymer fraction was concentrated, dried under vacuum, and characterized by NMR and SEC chromatography. The conversion was calculated from the amount of the recovered polymer and monomer fractions. The ATRP kinetic investigation was conducted into a Schlenk flask (argon atmosphere) at $[\text{G1bis}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{Initiator}]_0 = 25/1/3/1$, in dry toluene ($C = 1.2$ M monomer concentration) at 65°C. The aliquots taken at different time were filtered through alumina and the filtrate was concentrated and dried, before analysis by SEC. The conversion was determined from the comparison of the (renormalized) areas corresponding to the polymer and monomer fraction signals obtained by SEC-RI detection.

Results and discussion

The styrene dendritic monomer **G1bis** considered in this study is substituted by two carbosilane dendrons and carries a total of six allyl terminal branches. This monomer has been polymerized by FRP and ATRP with the aim to produce the multiallylic dendronized polymer **Poly(G1bis)**, as shown in Scheme 1. The resulting polymers have been characterized by ^1H and ^{13}C -NMR, as well as by SEC in order to analyse the shape of the molar mass distribution and to determine the molar mass, conversion, and polydispersity. In the first part of the report is described the attempts of polymerization by FRP. The results of the investigations by ATRP are extensively described in the second part.



Scheme 1. Polymerization of allyl-branched dendritic monomer **G1bis** under FRP (conditions 1) or ATRP (conditions 2).

Free radical polymerization

G1bis has been polymerized by classical FRP, by using AIBN (2 mol %) as radical promoter (Scheme 1). The polymerizations were performed in sealed tubes at a low monomer concentration (0.3 M) in toluene at 60°C, and at different reaction times (4, 8, and 24 hours). The characterization results and the SEC elution traces of the resulting polymers are given in Table 1 and Figure 1, respectively. As a first observation, all polymers showed a high solubility in toluene. After 4 hours of reaction (entry 1), only a small amount of polymer was produced (14% conversion), which was characterized by a moderate degree of polymerization ($DP_n = 90$) and a clear multimodal mass distribution (Figure 1). The increase of reaction time to 8 hours raised the conversion to 31%, but offered polymers of similar characteristics. Further increase of the reaction time to 24 hours improved both the conversion (72%) and DP_n (420), but led to a significant aggravation of chain-transfer reactions, as deduced by the broad molecular weight distribution ($D = 4.3$) and the multimodal shape signal on the SEC trace (Figure 1). These results clearly show that FRP technique is not suitable to polymerize our multiallylic **G1bis** monomer, as interchain couplings -most likely involving couplings to allyl branches- are already observed at the early stage of the reaction.

Table 1: FRP of monomer **G1bis** using AIBN (2 mol.%) in toluene (0.3 M) at 60°C and at different polymerization times. ^a Mass-average molar mass measured from multi-angle laser light scattering (MALLS) detector.

Entry	Time (h)	Conv. (%)	M_n^a (MALLS)	\bar{D}	DP_n
1	4	14	100000	2.10	90
2	8	31	110000	2.50	85
3	24	72	950000	4.30	420

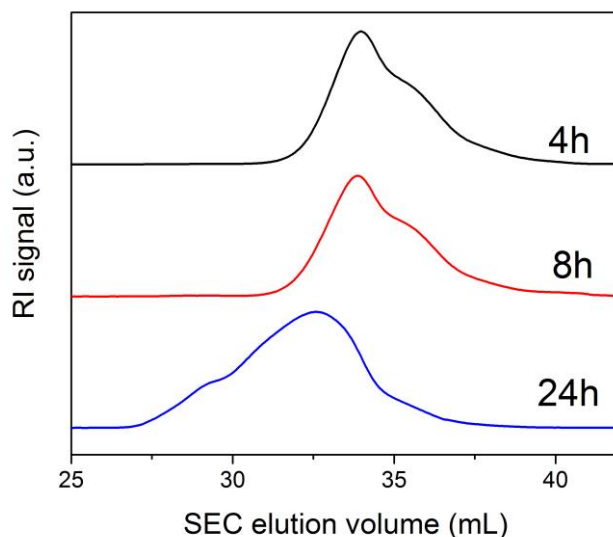


Figure 1: SEC elution traces of **Poly(G1bis)** obtained from FRP (2 mol.% AIBN in toluene, monomer concentration $C = 0.3$ M, at 65°C) at different reaction times.

Atom-Transfer Radical Polymerization

The polymerization of **G1bis** has then been performed by ATRP. In order to optimize the conditions of polymerization, several key parameters have been investigated, namely the type of initiator, the monomer concentration, the polarity of the solvent, the temperature, and the use of a rate-accelerating additive. All conditions and results are summarized in Table 2. Given the bulkiness of **G1bis** and the expected low propagation rate, every polymerization run was performed by using a low $[\mathbf{G1bis}]_0/[\text{Initiator}]_0$ ratio of 25, and for a duration of 40 hours. The polymerization was consistently mediated with the widely used $[\text{CuBr}]/[\text{PMDETA}]$ catalytic system, with a molar ratio $[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{Initiator}]_0 = 1/3/1$ (Scheme 2 and Table 2).

The type of initiator is of high importance indeed, as it determines the number of growing chains. To obtain well-defined polymers with a low polydispersity, it is essential the initiation be fast, and transfer and termination steps be negligible.[36] In this work, three well-known

initiators of styrene polymerization by ATRP were selected: *p*-toluenesulfonyl chloride (TsCl), 2-bromopropionitrile (BrPN), and ethyl α -bromoisobutyrate (EtBriB). TsCl belongs to the sulfonyl halide class of initiators and exhibits a very high rate constant of initiation as compared to propagation.[37] BrPN and EtBriB are common α -halonitrile and α -bromoester types of initiators, respectively, having different activation rate constants ($k_{\text{act}} = 23$ and $2.7 \text{ M}^{-1}\text{s}^{-1}$ for BrPN and EtBriB, respectively).[38] Unless specified, all polymerizations were performed at 65°C in dry toluene at a monomer concentration C of 1.2 M.

Table 2: ATRP of monomer **G1bis** with [PMDETA]:[CuBr]:[Initiator] = 3:1:1 after 40 hours reaction ; ^a Number molar mass determined by THF-SEC with MALLS detector and from \mathcal{D} (RI detector); ^b Calculated as $M_{n(\text{theo})} = \text{Conv.} \times \text{Molar mass of G1bis} \times [\text{M}_0]:[\text{initiator}]$; ^c Indication of gelification (Gel) or SEC trace shape with Mono (monomodal), Bi (bimodal), Multi (multimodal); ^e Bulk polymerization; ^f Utilisation of malononitrile as rate-accelerating additive.

Entry	Initiator	Solvent	Conc. (mol.L ⁻¹)	Temp. (°C)	Conv. (%)	M_n^a (MALLS)	M_n^b (theo)	\mathcal{D}	DP_n	Observation ^c
1	TsCl	Toluene	1.2	65	10	4800	1300	1.24	9	Mono
2	BrPN	Toluene	1.2	65	29	12000	3800	1.25	23	Mono
3	BrPN	Toluene	1.5	65	55	20400	/	2.03	39	Multi
4	EtBriB	Toluene	0.75	65	21	5050	2700	1.09	10	Mono
5	EtBriB	Toluene	1.2	65	52	10800	6800	1.17	21	Mono
6	EtBriB	Toluene	1.5	65	55	10900	/	1.17	21	Bi
7	EtBriB	^d	1.9 ^d	65	/	/	/	/	/	Gel
8	EtBriB	Toluene	1.2	90	61	16300	/	1.63	31	Bi
9	EtBriB	DME	1.2	65	/	/	/	/	/	Gel
10	EtBriB ^e	Toluene	1.2	65	85	39600	/	2.65	76	Multi
11	EtBriB ^e	Toluene	0.75	65	30	15900	3900	1.07	30	Mono

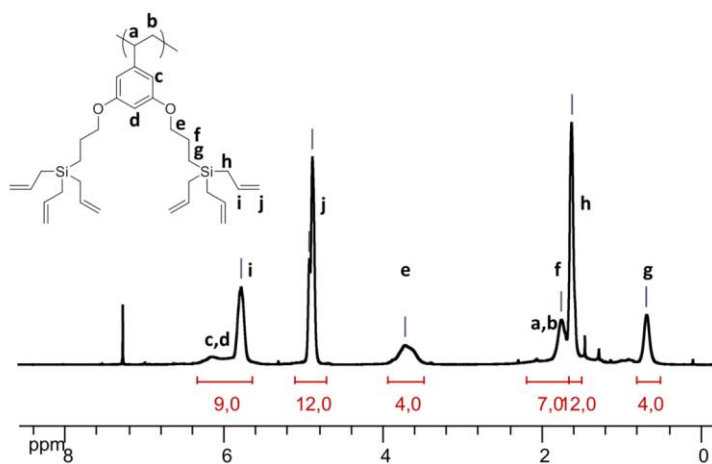
The first examination of the results reported in Table 2 shows that the monomer **G1bis** could be efficiently polymerized by ATRP and that monomodal SEC traces with a low polydispersity (\mathcal{D}) value could be obtained. However, the results drastically depend on the conditions of polymerization. Overall, despite a long reaction time (40 hours) at 65°C, the conversion remained low and the degrees of polymerization obtained ($9 < DP_n < 76$) were found to deviate largely from the expected DP_n ($[M]_0/[I]_0 = 25$). These observations primarily show a very low propagation rate, obviously arising from the high bulkiness of the monomers. Secondly, these results point out a non-quantitative initiation step and the potential presence of transfer reactions, as confirmed by the appearance of multimodal distribution and gel formation in some runs. The initiation step was systematically found to be incomplete, in other words not all molecules of initiator give a polymer chain, as evidenced from the difference $M_{n(\text{MALLS})} > M_{n(\text{theo})}$ (in table 2 are reported the $M_{n(\text{theo})}$ values only for polymers with monomodal shape distribution). A possible explanation is based on an intrinsically low initiation efficiency caused by the poor accessibility of the bulky monomer. Another explanation may arise from the reactional mixture preparation we used. Due to the high viscosity of the monomer and the procedure used (sealed tubes under vacuum), all reagents are mixed together at once, before starting the deoxygenation process. In this case, the active Cu(I) complex mixed with the alkyl halide should probably produce many radicals even at low temperature, leading to a loss of some initiator by radical termination at the early stage of the sample preparation. This phenomenon was further discussed below.

Let us now examine the influence of the conditions of polymerization on the characteristics of the polymers. Among the three initiators investigated, TsCl (entry 1) was the least efficient, as it led to the lowest conversion (9%) and the lowest degree of polymerization ($DP_n = 9$). The use of the α -halonitrile BrPN initiator under the same conditions (entry 2), turned to be more efficient, as it led to a slightly higher conversion (29%) and DP ($DP_n = 23$). With BrPN initiator again, a small increase of the monomer concentration, from 1.2 to 1.5 M in run 3, could further improve the degree of polymerization ($DP_n = 39$), but with a detrimental increase of the polydispersity index ($\mathcal{D} = 1.25$ to 2.03). The SEC analysis of the polymers issued from entries 2 and 3 shows that the increase of concentration was sufficient to promote inter-chains couplings, as deduced from the change from a monomodal (entry 2) to a multimodal (entry 3) mass distribution. Comparison of entries 2 and 5 shows that a higher yield (52% vs 29%) was obtained when substituting initiator BrPN for EtBriB, whilst the resulting polymers were relatively similar in terms of molecular weight characteristics. Logically, the comparison of the ratio $M_{n(\text{MALLS})}/M_{n(\text{theo})}$ should be able to give an insight

about the initiation efficiency of the initiators. A ratio higher than 1 was calculated for all initiators (from 1.5 to 4), but we note that the lowest (and best) values were obtained for EtBriB initiator (< 2). This statement should indicate better initiator efficiency for EtBriB, but it should be considered very carefully, as the number of polymerization runs to be considered was very small. The apparent better initiation efficiency observed for EtBriB might also reflect its low ATRP equilibrium constant (K_{ATRP}). Actually, EtBriB shows the lowest K_{ATRP} value (7.5×10^{-8}) as compared to BrPN (5.9×10^{-7}), [38] and most likely also to TsCl, [38,39]. EtBriB should then be the initiator that reduces the most efficiently the risk of radical termination during the sample preparation, as previously discussed. Comparison of entries 5 to 7 demonstrates that the increase of monomer concentration is directly responsible for the occurrence of inter-chains couplings, as evidenced by the change from a monomodal distribution (for $C \leq 1.2$ M) to a bimodal one (for $C = 1.5$ M), to a fully crosslinked material (for $C = 1.9$ M, corresponding to bulk polymerization). In the literature, the emergence of chain-transfer reactions is classically correlated to the increase of monomer concentration. [40,41] Therefore, the challenge is to find the best compromise between a high concentration leading to a high conversion and DP , and a dilute medium in order to avoid chain-transfers. Here, it seems that the best compromise in terms of molecular weights characteristics is obtained at a concentration of $C = 1.2$ M (i.e. 625 g.L^{-1}). The influence of temperature was also investigated. Whilst an increase of temperature from 60°C to 90°C (entry 8) enabled a slightly higher polymer yield, the major consequence was the emergence of inter-chains couplings, as evidenced by the change of modality of the SEC trace and the increase of the polydispersity value. Changing the polarity of the solvent turned out to be even more catastrophic, as the polymerization medium gelified when toluene was substituted for DME (entry 9). In order to enhance the polymerization rate while preserving a narrow molar mass distribution, the use of malononitrile (MN) as a rate-accelerating additive, was investigated. Previously reported by Yousi and co-workers, [42] the addition of a catalytic amount of MN during ATRP of styrene (optimal molar ratio of MN/initiator 4/1) led to a remarkable rate enhancement while maintaining a low polydispersity value. Thus, **G1bis** was polymerized under the same conditions as for entry 5, but in presence of MN (MN/initiator 4/1, entry 10). The results led to a higher polymerization rate, as demonstrated by the higher yield (85% vs 52%) and DP_n (76 vs 21) achieved (compare entries 11 vs 5). However, significant chain-transfer was obtained for this run, as deduced from the high polydispersity value ($D = 2.65$) and the multimodal mass distribution. Finally, a last attempt with MN was performed at a lower concentration (0.75 M vs 1.2 M, entries 11 vs 10). Despite a moderate

conversion (30%), the resulting polymer **Poly(G1bis)** displayed a relatively high degree of polymerization ($DP_n = 31$) and a narrow mass distribution ($D = 1.07$) of monomodal shape. This last result demonstrates the positive effect of MN additive on the propagation rate, provided that the monomer concentration was sufficiently low.

If one excludes the use of the rate accelerator MN, the best polymerization conditions of **G1bis** were observed for a monomer concentration $C = 1.2$ M, in toluene solvent at a temperature of 65°C and with BrPN or EtBriB as initiator (entries 2 or 5, respectively). Under these conditions, **Poly(G1bis)** was provided in good yield (up to 50% conversion) with $DP_n \sim 20\text{-}25$ and $D < 1.25$. The absence of significant transfer reactions is confirmed by the monomodal shape distribution in the SEC traces and the apparent preservation of the allyl branches in the ^1H and ^{13}C NMR spectra (Figure 2). It is also worth mentioning the remarkable solubility of **PG1bis** polymers in a broad range of solvents, including diethylether and hexane.



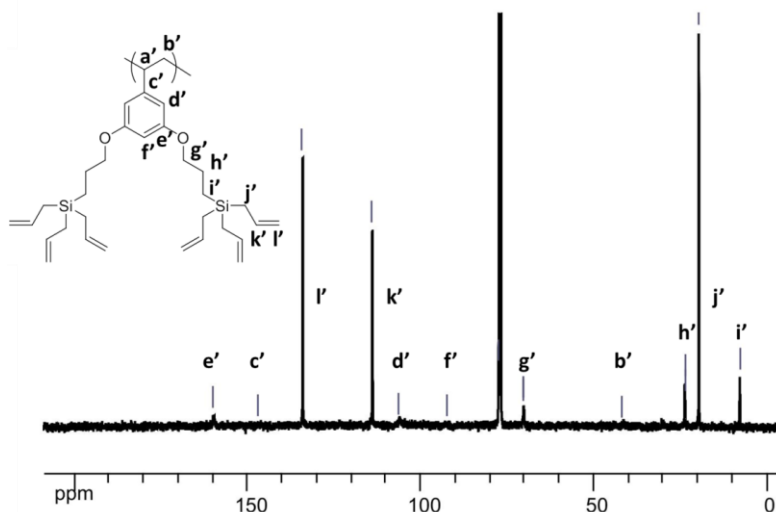


Figure 2. ^1H -NMR (top) and ^{13}C NMR (bottom) spectra of **Poly(G1bis)** obtained from ATRP (entry 5).

Based on these results, a kinetic investigation of the ATRP polymerization of **G1bis** was performed. This study was conducted in similar conditions as for entry 5 (Table 2) and in a time range up to 46 hours ($[\text{G1bis}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{EtBriB}]_0 = 25/1/3/1$; $T = 65^\circ\text{C}$; $C = 1.2\text{ M}$). Figure 3 shows the SEC traces of the polymerization crude recorded at different reaction times. At $t = 0$, only a signal corresponding to monomer **G1bis** is detected (green curve). Then, upon increase of the reaction time ($t = 2$ hours), a new signal appears at a lower elution volume whilst the right-most signal is seen to decrease in intensity. It indicates that **G1bis** is consumed and that the corresponding polymer is formed. By further increasing the reaction time, the left-most signal is seen to increase in intensity and to shift to lower elution volumes. This is in agreement with an increase of the degree of polymerization and of an increase of conversion (see insert in Figure 3). At $t = 36$ and 46 hours, we note the presence of a shoulder in the SEC peaks which reveals the emergence of interchain couplings.

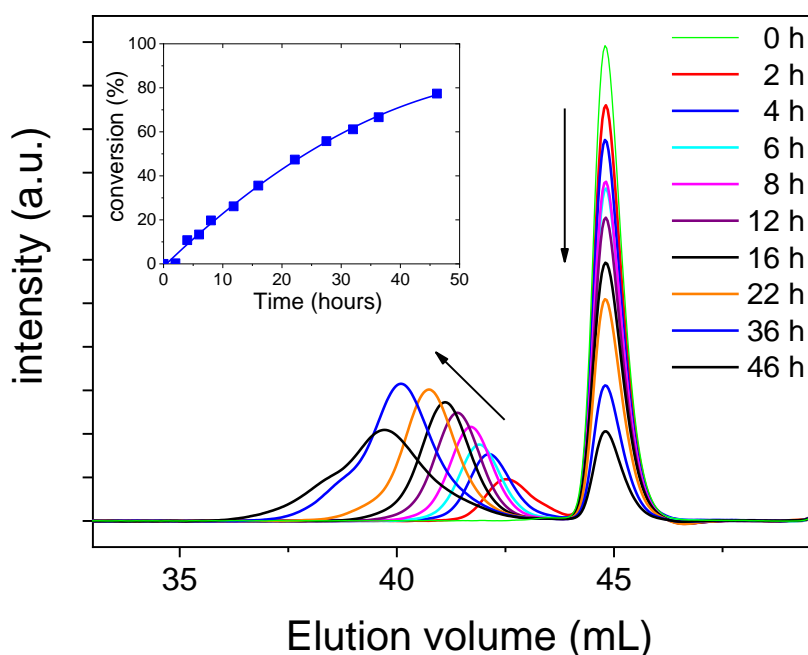


Figure 3. Evolution of the SEC traces as a function of time during ATRP of monomer **G1bis** ($[\mathbf{G1bis}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{EtBriB}]_0 = 25/1/3/1$; solvent: toluene; temperature: 65°C ; monomer concentration: $C = 1.2 \text{ M}$). In insert: polymer conversion with reaction time.

The molecular weight (M_n) dependence with conversion shows three different regimes (Figure 4): M_n is found to rapidly increase at low conversion ($< 30\%$) then, between 30 to 60% its progression is slowed, and eventually seemingly diverges. The two first regimes can be explained by the monomer accessibility to the polymeric radical species. At the early stage of the polymerization, the oligomer growth is not limited by the steric effects, but as the size of the polymer increases (i.e. for $DP_n > 10$), the steric constraints become much stronger and the propagation becomes limited by the monomer diffusion.[43] The last regime is correlated to the onset of interchain couplings (at ca. conversion $> 60\%$ and $DP_n > 25$). The emergence of the competing interchain couplings at longer reactions times can be visualized from the shoulder formation in the polymer SEC peaks (figure 3) and from the slight increase of the polydispersity value (Figure 4) which remains, nevertheless, limited to $\mathcal{D} < 1.5$. The dependency of $\ln([M]_0/[M]_t)$ on polymerization time (Figure 5) shows a first-order kinetics up to about 30 hours ($k_{app} = 5 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$), then a deviation from linearity is observed, in agreement with the interchain coupling formation, as mentioned above.

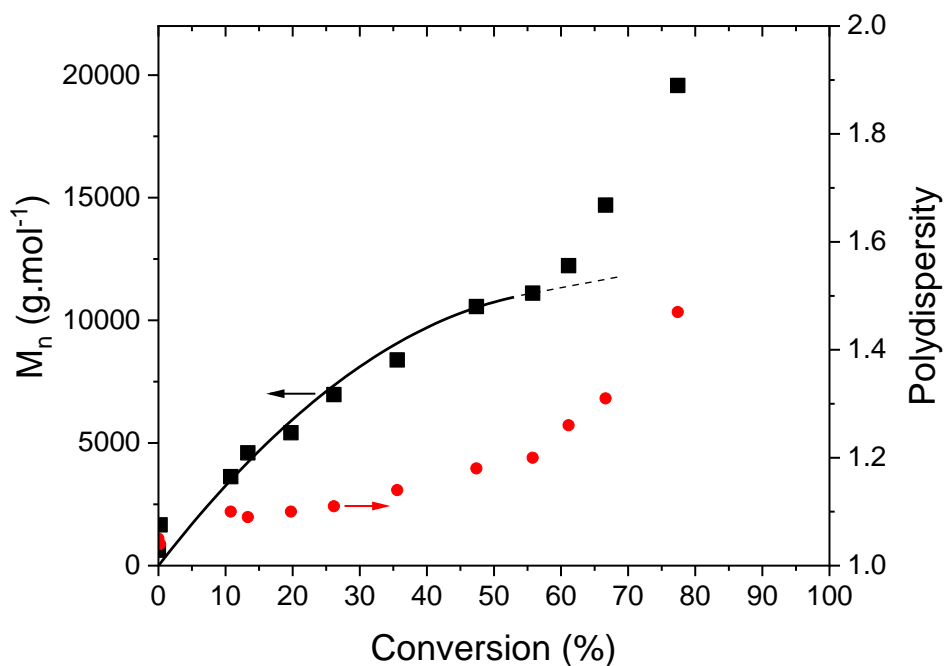


Figure 4. Dependence of molecular weight (M_n) and polydispersity (\mathcal{D}) on the monomer conversion for the polymerization of **G1bis** in toluene ($C = 1.2$ M) at 60°C with $[\mathbf{G1bis}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{EtBriB}]_0 = [25]/[1]/[3]/[1]$.

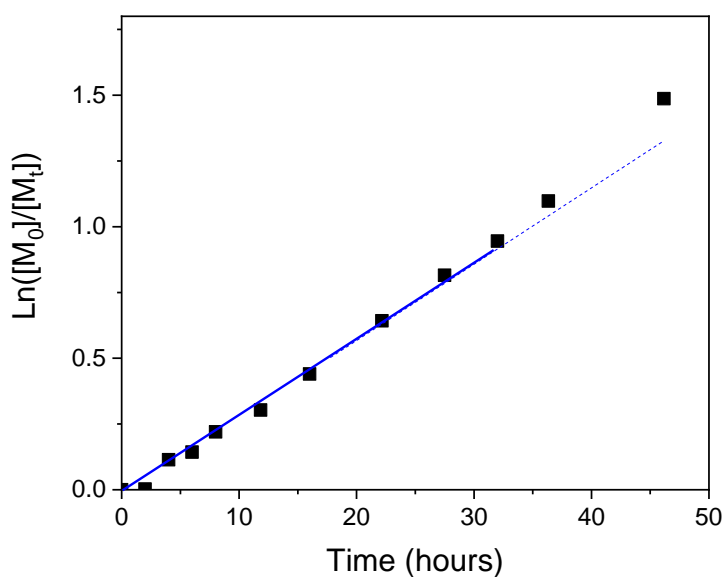


Figure 5. Kinetic plot for the polymerization of **G1bis** in toluene ($C = 1.2$ M) at 60°C with $[\mathbf{G1bis}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{EtBriB}]_0 = [25]/[1]/[3]/[1]$.

Overall, the ATRP polymerization kinetics of **G1bis** described above, strongly resemble the results previously obtained for same monomer by means of anionic polymerization.[20] In both cases, once the early oligomer regime is passed, the huge steric constraints brought by the highly branched **G1bis** monomer lead to a significant slowdown of the propagation. This effect is such that an apparent saturation of DP is observed. It is important to highlight that a similar polymer size limitation (i.e. $DP \approx 25-30$) is observed, whichever ATRP or anionic polymerization conditions are used. This apparent stoppage of the propagation then leaves room to competing chain-transfer reactions (most likely taking place at the allyl branches), leading to an increase of the polymer polydispersity ($\mathcal{D} > 1.2$) when extended reaction times or increased temperature are used.

Conclusion

Dendronized styrene monomer **G1bis** carrying six allyl branches were successfully polymerized under ATRP conditions. Multiallylic dendronized polymer **Poly(G1bis)** of monomodal molar mass distribution and low polydispersity ($\mathcal{D} \leq 1.25$) were thus been prepared. During the polymerization, the increasing steric effects brought by the bulky dendrons attached to the styrene units were found to drastically slow the polymer propagation, ultimately leading to an apparent saturation of DP. Surprisingly, the limitation was found for $DP \approx 25-30$, similarly to what was found when the same **G1bis** monomer was polymerized by anionic polymerization. This observation tends to show that the polymer growth of sterically demanding monomers is first and foremost limited by steric factors (and diffusion), rather than by the polymerization technique.

In order to obtain **Poly(G1bis)** polymers of high DPs with low polydispersities, the ATRP polymerization of **G1bis** required a high monomer concentration and a long reaction time. Best results were obtained by using EtBrIB or BrPN initiator, or alternatively in the presence of malononitrile as a rate-accelerator, provided that a lower monomer concentration was used. All attempts to target very high molecular weights (e.g. by increasing the temperature, the concentration or the reaction time) irremediably resulted in the formation of interchain couplings, as evidenced by the emergence of a multimodal SEC trace and of an increase of polydispersity. These couplings, most likely involving reactions at the allyl branches, were nevertheless substantially fewer than the ones observed when **G1bis** was polymerized by free-radical polymerization. Notably, before the apparent stoppage of the polymer growth, it seems

that most of the allyl branches are preserved during the polymerization, as evidenced by NMR and SEC analyses, in particular.

To the best of our knowledge, these **Poly(G1bis)** polymers reported herein constitute the first example of polymers carrying multiple alkene pendants, prepared by a “controlled” radical polymerization technique. These results then pave the way to the preparation of well-defined polymers with multiple reactive alkene groups, as well as to the controlled-radical polymerization of sterically demanding macromonomers.

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References

- [1] K. Matyjaszewski, N.V. Tsarevsky, Macromolecular engineering by atom transfer radical polymerization, *J. Am. Chem. Soc.* 136 (2014) 6513-6533. <https://doi.org/10.1021/ja408069v>.
- [2] H. Frauenrath, Dendronized polymers – building a new bridge from molecules to nanoscopic objects, *Prog. Polym. Sci.* 30 (2005) 325-384. <https://doi.org/10.1016/j.progpolymsci.2005.01.011>.
- [3] A.D. Schlüter, A. Halperin, M. Kröger, D. Vlassopoulos, G. Wegner, B. Zhang, Dendronized polymers: molecular objects between conventional linear polymer and colloidal particles, *ACS Macro Lett.* 3 (2014) 991-998. <https://doi.org/10.1021/mz500376e>.
- [4] H. Gustafsson, A. Küchler, K. Holmberg, P. Walde, Co-immobilization of enzymes with the help of a dendronised polymer and mesoporous silica particles, *J. Mat. Chem. B* 3 (2015) 6174-6184. <https://doi.org/10.1039/c5tb00543d>.
- [5] C.O. Liang, B. Helms, C.J. Hawker, J.M.J. Fréchet, Dendronized cyclopolymers with a radial gradient of polarity and their use to catalyze a difficult esterification, *Chem. Commun.* (2003) 2524-2525. <https://doi.org/10.1039/B307425K>.
- [6] M.C. García, J.C. Cuggino, C.I. Rosset, P.L. Páez, M.C. Strumia, R.H. Manzo, F.L. Alovero, C.I. Alvarez Izgarzabal, A.F. Jimenez-Kairuz, A novel gel based on an ionic complex from a dendronized polymer and ciprofloxacin: Evaluation of its use for controlled topical drug release, *Mat. Sci. Eng. C* 69 (2016) 236-246. <https://doi.org/10.1016/j.msec.2016.06.071>.

- [7] J. Roeser, B. Heinrich, C. Bourgoigne, M. Rawiso, S. Michel, V. Hubscher-Bruder, F. Arnaud-Neu, S. Méry, Dendronized polymers with silver and mercury cations recognition: complexation studies and polyelectrolyte behavior, *Macromolecules* 46 (2013), 7075-7085. <https://doi.org/10.1021/ma400348v>.
- [8] M. Gao, X. Jia, Y. Li, D. Liang, Y. Wie, Synthesis and thermo-/pH- dual responsive properties of poly(amidoamine) dendronized poly(2-hydroxyethyl)methacrylate, *Macromolecules*, 43 (2010) 4314-4323. <https://doi.org/10.1021/ma1000783>.
- [9] A. Chakrabarti, A. Juilfs, R. Filler, B.K. Mandal, Novel PEO-based dendronized polymers for lithium-ion batteries, *Solid State Ionics* 181 (2010) 982-986. <https://doi.org/10.1016/j.ssi.2010.05.016>.
- [10] D. Messmer, M. Kröger, A.D. Schlüter, Pushing synthesis toward the maximum generation range of dendritic macromolecules, *Macromolecules*, 51 (2018) 5420-5429. <https://doi.org/10.1021/acs.macromol.8b00891>.
- [11] N. Ouali, S. Méry, A. Skoulios, L. Noirez, Backbone stretching of wormlike carbosilane dendrimers, *Macromolecules* 33 (2000) 6185-6193. <https://doi.org/10.1021/ma000327k>.
- [12] A. Zhang, L. Okrasa, T. Pakula, A.D. Schlüter, Homologous series of dendronized polymethacrylates with a methyleneoxycarbonyl spacer between the backbone and dendritic side chain: synthesis, characterization and some bulk properties, *J. Am. Chem. Soc.* 126 (2004) 6658-6666. <https://doi.org/10.1021/ja0494205>.
- [13] V. Percec, C.-H. Hahn, B. Barboiu, Self-encapsulation, acceleration and control in the radical polymerization of monodendritic monomer via self-assembly, *J. Am. Chem. Soc.* 119 (1997) 12978-12979. <https://doi.org/10.1021/ja9727878>.
- [14] A. Carlmark, E.E. Malmström, ATRP of dendronized aliphatic macromonomers of generation one, two and three, *Macromolecules* 37 (2004) 7491-7496. <https://doi.org/10.1021/ma049432a>.
- [15] S. Rajaram, T.-L. Choi, M. Rolandi, J.M.J. Fréchet, Synthesis of dendronized diblock copolymers via ring-opening metathesis polymerization and their visualization using atomic force microscopy, *J. Am. Chem. Soc.* 129 (2007) 9619-9621. <https://doi.org/10.1021/ja0741980>.
- [16] K.O. Kim, T.-L. Choi, Synthesis of rod-like dendronized polymers containing G4 and G5 ester dendrons via macromonomer approach by living ROMP, *ACS Macro Lett.* 1 (2012) 445-448. <https://doi.org/10.1021/mz300032w>
- [17] M. Malkoch, A. Carlmark, A. Woldegiorgis, A. Hult, E.E Malmström, Dendronized aliphatic polymers by a combination of ATRP and divergent growth, *Macromolecules*, 2004, 37, 322-329. <https://doi.org/10.1021/ma0347464>.
- [18] A. Nyström, A. Hult, Dendronized polymers with tailored surface groups, *J. Polym. Sci. Part A: Polym. Chem.* 43 (2005) 3852-3867. <https://doi.org/10.1002/pola.20846>.

- [19] A. Zhang, L. Wei, A.D. Schlüter, Narrowly distributed dendronized polymethacrylates by reversible addition-fragmentation chain transfer (RAFT) polymerization, *Macromol. Rapid Commun.* 25 (2004) 799-803. <https://doi.org/10.1002/marc.200300283>.
- [20] A. Zhang, B. Zhang, E. Wächtersbach, M. Schmidt, A.D. Schlüter, Efficient synthesis of high molar mass, first- to fourth-generation distributed dendronized polymers by the macromonomer approach, *Chem. Eur. J.* 9 (2003) 6083-6092. <https://doi.org/10.1002/chem.200305142>.
- [21] F. Moingeon, P. Masson, S. Méry, Preparation of multiallylic dendronized polymers via anionic polymerization, *Macromolecules* 40 (2007) 55-64. <https://doi.org/10.1021/ma0620666>.
- [22] A.B. Lowe, Thiol-en “click” reactions and recent applications in polymer and materials synthesis, *Polym. Chem.* 1 (2010) 17-36. <https://doi.org/10.1039/C4PY00339J>.
- [23] T.C. Chung, M. Raate, E. Berluche, D.N. Schulz, Synthesis of functional hydrocarbon polymers with well-defined molecular structures, *Macromolecules* 21 (1988) 1903-1907. <https://doi.org/10.1021/ma00185a003>.
- [24] F. Sinclair, M. Alkattan, J. Prunet, M.P. Shaver, Olefin cross metathesis and ring-closing metathesis in polymer chemistry, *Polym. Chem.* 8 (2017) 3385-3398. <https://doi.org/10.1039/c7py00340d>.
- [25] F. Moingeon, J. Roeser, P. Masson, F. Arnaud, S. Méry, Versatile and efficient functionalisation of multiallylic dendronised polymers: can dense packing be reached?, *Chem. Commun.* 11 (2008) 1341-1343. <https://doi.org/10.1039/B718318F>.
- [26] J. Roeser, F. Moingeon, B. Heinrich, P. Masson, F. Arnaud-Neu, M. Rawiso, S. Méry, dendronized polymers with peripheral oligo(ethylene oxide) chains: thermoresponsive behaviour and shape anisotropy, *Macromolecules* 44 (2011) 8925-8935. <https://doi.org/10.1021/ma2016776>.
- [27] V. Coessens, T. Pintauer, K. Matyjaszewski, Functional polymers by atom transfer radical polymerization, *Prog. Polym. Sci.* 26 (2001) 337-377. [https://doi.org/10.1016/S0079-6700\(01\)00003-X](https://doi.org/10.1016/S0079-6700(01)00003-X).
- [28] W. Jakubowski, N.V. Tsarevsky, T. Higashihara, R. Faust, K. Matyjaszewski, Allyl halide (macro)initiators in ATRP: Synthesis of block copolymers with polyisobutylene segments, *Macromolecules* 41 (2008) 2318-2323. <https://doi.org/10.1021/ma7027837>.
- [29] D. Valade, C. Boyer, T.P. Davis, V. Bulmus, Synthesis of SiRNA polyplexes adopting a combination of RAFT polymerization and thiol-ene chemistry, *Aust. J. Chem.* 62 (2009) 1344-1350. <https://doi.org/10.1071/CH09208>.
- [30] X.-Y. Wang, X.-L. Sun, Z.-H. Chen, F. Wang, S.R. Wang, TY. Tang, Highly efficient access to well-defined linear polymers with substantial vinyl pendants via ATRP of divinyl monomers, *Polym. Chem.* 9 (2018) 7309-4315. <https://doi.org/10.1039/C8PY00797G>.
- [31] Z. Jia, J. Liu, T.P. Davis, V. Bulmus, RAFT polymerization and thiol-ene modification of 2-vinyloxyethyl methacrylate: towards functional branched polymers, *Polymer* 50 (2009) 5928-5932. <https://doi.org/10.1016/j.polymer.2009.10.030>.

- [32] A. Nagai, T. Hirabayashi, H. Kudo, T. Nishikubo, Synthesis of star polymer by atom transfer radical polymerization with resorcinol-core multifunctional initiator: the construction of nanocapsule via hydrolysis and olefin metathesis reaction of the obtained star polymer, *J. Polym. Chem. Part A: Polym. Chem.* 46 (2008) 4879-4888. <https://doi.org/10.1002/pola.22824>
- [33] L. Wang, M.A. Hickner, Highly ordered ion-conducting block copolymers by hydrophobic block modification, *J. Mat. Chem. A* 4 (2016)15437-15449. <https://doi.org/10.1039/c6ta05308d>.
- [34] Z.-M. Dong, X.-H. Liu, Y. Lin, Y.-S. Li, Branched polystyrene with abundant pendant vinyl functional groups from asymmetric divinyl monomer, *J. Polym. Sci. Part A: Polym. Chem.* 46 (2008) 6023-6034. <https://doi.org/10.1002/pola.22913>.
- [35] J. Ma, C. Cheng, G. Sun, K.L. Wooley, Well-defined polymers bearing pendent alkene functionalities via selective RAFT polymerization, *Macromolecules* 41 (2008) 9080-9089. <https://doi.org/10.1021/ma802057u>.
- [36] K. Matyjaszewski, J. Xia, Atom transfer radical polymerization, *Chem. Rev.* 101 (2001) 2921-2990. <https://doi.org/10.1021/cr940534g>.
- [37] V. Percec, B. Barboiu, H.-J. Kim, Arenesulfonyl halides: a universal class of functional initiators for metal-catalyzed "living" radical polymerization of styrenes, methacrylates and acrylates, *J. Am. Chem. Soc.* 120 (1998) 305-316. <https://doi.org/10.1021/ja9713845>.
- [38] W. Tang, Y. Kwak, W. Braunecker, N.V. Tasresky, M.L. Coote, K. Matyjaszewski, Understanding atom transfer radical polymerization: effect of ligand and initiator structures on the equilibrium constants, *J. Am. Chem. Soc.* 130 (2008) 10702-10713. <https://doi.org/10.1021/ja802290a>.
- [39] M.B. Gillies, K. Matyjaszewski, P.-O. Norrby, T. Pintauer, R. Poli, P. Richard, A DFT study of R-X bond dissociation enthalpies of relevance to the initiation process of atom transfer radical polymerization, *Macromolecules* 36 (2003) 8551-8559. <https://doi.org/10.1021/ma0351672>.
- [40] A. Goto, T. Fukuda, Kinetics of living radical polymerization, *Prog. Polym. Sci.* 29 (2004) 329-385. <https://doi.org/10.1016/j.progpolymsci.2004.01.002>.
- [41] K. Matyjaszewski, Atom transfer radical polymerization (ATRP): current status and future perspectives, *Macromolecules*, 45 (2012) 4015-4039. <https://doi.org/10.1021/ma3001719>.
- [42] Z. Jiaming, L. Rui, H. Jianying, C. Jiayan, L. Xurong, L. Yutai, Z. Yousi, *J. Polym. Sci. Part A: Polym. Chem.* 45 (2007) 4082-4090. <https://doi.org/10.1002/pola.22217>.
- [43] C. Gstrein, P. Walde, A.D. Schlüter, T. Nauser, *Photochem. Photobiol. Sci.* 15 (2016) 964. <https://doi.org/10.1039/c6pp00191b>.