Kinetic Study of the "Living" Cationic Polymerization of a Galactose Carrying Vinyl Ether. MALDI-TOF MS Analysis of the Resulting Glycopolymers

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ABSTRACT: The "living" cationic polymerization of a new saccharidic monomer, namely 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2-vinyloxyethyl)-D-galactopyranose (GVE) has been investigated using acetaldehyde diethyl acetal/trimethylsilyl iodide as the initiating system in the presence of $ZnCl_2$ as co-initiator. To determine if the process is living, the conversion was followed by dilatometry or by regularly withdrawing samples and analyzing them by ^{1}H NMR. Fast polymerization occurred together with a nonlinear $\ln([M]_0/[M]_t) = f(t)$ plot indicating an apparent loss of active centers. Nevertheless, the ^{1}H NMR- and SEC-determined molecular weights proved the absence of termination and transfer reactions during the polymerization process. MALDI−TOF mass spectrometry confirmed the absence of such side reactions and indicated a parallel initiation consecutive to the presence of water traces in the trimethylsilyl iodide solution. The nonlinear $\ln([M]_0/[M]_t) = f(t)$ plot was attributed to specific interactions between the saccharidic rings and $ZnCl_2$ and/or the growing carbocations.

Introduction

Synthetic polymers bearing saccharidic residues as side chains have a variety of potential applications in the pharmacological and biological fields,[1−5] due to their well-known and pronounced hydrophilic character as well as their compatibility with biomolecules.

Recently, various living/controlled polymerization techniques were applied to the synthesis of well-defined glycopolymers.[6] In the particular field of "living" cationic polymerization, Minoda et al.[7−9] and Labeau et al.[10] reported the synthesis and polymerization of vinyl ether type saccharidic monomers. Using a technique initially developed for vinyl ethers by Sawamoto and Higashimura,[11−13] saccharidic polymers of controlled molecular weights (MW) were obtained with a narrow molecular weight distribution (MWD).

However, very few detailed kinetic studies were reported to prove the living character of the cationic polymerization of such saccharidic monomers.[7,14,15] In particular, no article provided a linear semilogarithmic $[M]_0/[M]$ vs time plot together with a linear $\overline{M_n}$ vs conversion plot, both conditions being simultaneously required to demonstrate the absence of detectable transfer and termination reactions, i.e., a polymerization proceeding via a truly "living" mechanism. Indeed, this is particularly challenging with saccharidic derivatives of vinyl ether monomers, since the presence of polar side groups on vinyl ethers (here, the protected OH groups of the sugar ring) favors transfer and termination. In fact, the authors generally report a linear $\overline{M_n}$ vs conversion plot, a sufficient proof that the polymerization proceeds without transfer. However, this criterion is not able to demonstrate termination reactions especially when $\overline{M_n}$ is determined by SEC (although the successful synthesis of block copolymers[7,15] indicates that most of the chains are "living").

As part of a program to produce multifunctional polymers with well-defined architecture for the immobilization of single-stranded DNA fragments, we synthesized a new saccharidic vinyl ether monomer, the 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2-vinyloxyethyl)-D-galactopyranose (GVE), and investigated its ability to homopolymerize via a "living" cationic mechanism.[16] Acetaldehyde diethylacetal/trimethylsilyl iodide (TMSiI) was used as the initiating system in the presence of $ZnCl_2$ as co-initiator, since this system tolerates polar functions.[17,18]

Macromolecules with molecular weights ranging from 2500 to 7500 were obtained,[16] close to the theoretical MW values, with a narrow MWD (polydispersity indexes, PDI = $\overline{M_w}/\overline{M_n}$, 1.10−1.25), suggesting that the polymerization is controlled. However, to show that the process is not only controlled but indeed "living" (absence of termination and transfer reactions), we have investigated in detail the polymerization kinetics of GVE, using several independent techniques, ^{1}H NMR, and dilatometry to follow monomer conversion, as well as SEC and ^{1}H NMR to determine the MW of the polymer chains.

In addition, MALDI−TOF mass spectrometry was used to determine the chain structure and hence the polymerization mechanism.[19] In fact, contrary to ^{1}H NMR and SEC, MALDI−TOF mass spectrometry gives the absolute molecular weight of individual polymer chain[20] and allows accurate end group identification.

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Table 1. Experimental Conditions, Molecular Weight, and Conversion Data for GVE Polymerization in Toluene Solution

run	[diethyl acetal] ($mol \cdot L^{-1}$)	[TMSiI] ($mol \cdot L^{-1}$)	[GVE] ($mol \cdot L^{-1}$)	[$ZnCl_2$] ($mol \cdot L^{-1}$)	T (°C)	reaction time (min)	$\overline{M_n}$ calcd	$\overline{M_n}$ NMR	conversion (%)	PDI (SEC)
A	0.007	0.009	0.075	0.002	−20	120	3551	4100	97.3	1.38
B	0.030	0.036	0.350	0.006	−20	47	3800	3900	94.3	1.17
C	0.030	0.034	0.350	0.006	−30	75	3800	nd	75.1	nd

[a] nd: not determined.

This technique was recently applied successfully to characterize poly(isobutyl vinyl ether),[21,22] a polymer bearing nonpolar and hydrophobic side groups, obtained via "living" cationic polymerization using HCl/$SnCl_4$/*n*-Bu_4NCl as the initiating system. However, to our knowledge, MALDI−TOF mass spectrometry has not been applied to saccharidic polymers synthesized via a "living" polymerization (whether cationic, anionic, ring-opening or radical), or to poly(vinyl ether) with polar side groups.

This paper presents MALDI−TOF analyses of the saccharidic poly(GVE). Some preliminary results have evidenced the end-functionalization reaction from aldehyde end-terminated polymer chains to amine end-terminated polymer chains.[16] Here, the MALDI−TOF analyses elucidate into the polymerization mechanism and corroborate the results obtained from the kinetic study.

Experimental Section

Chemicals and Solvents. The solvent used for polymerization reaction (toluene, 99.5% SDS) was purified and dried by distillation over sodium/benzophenone. Acetaldehyde diethyl acetal (99% Aldrich) was freshly distilled under reduced pressure over calcium hydride before use. Trimethylsilyl iodide (TMSiI, 99% Aldrich) was used without further purification and diluted in dry toluene. Zinc chloride ($ZnCl_2$, 99.999% Aldrich) was dissolved in dry diethyl ether.

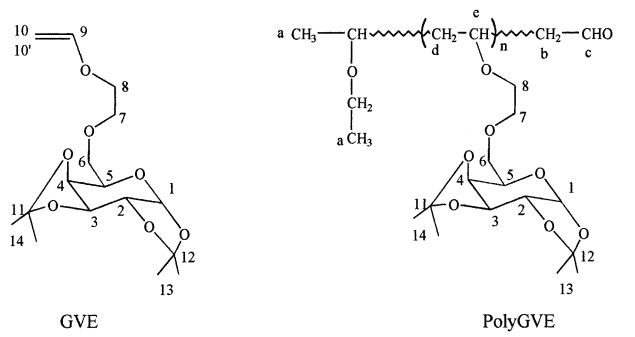
The 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2-vinyloxyethyl)-D-galactopyranose (GVE) monomer was synthesized according to a previously described procedure.[16]

"Living" Cationic Polymerization Procedure. Polymerization experiments (Table 1) were performed in either a Schlenk apparatus or a dilatometer. In both cases, the GVE monomer was dried twice over CaH_2 before use. Each reagent was transferred through a cannula under dry nitrogen. A solution of acetaldehyde diethyl acetal in toluene was cooled to −20 °C (or −30 °C). Then, 1.1 equiv of TMSiI (in toluene solution) relative to the acetal was added. The solution was stirred for 30 min. Then, GVE monomer (in toluene solution) and 0.2 equiv of $ZnCl_2$ (in diethyl ether/toluene mixture) were added. The polymerization mixture was left at −20 °C (or −30 °C) under N_2 and stirred for several hours. The concentrations used in the various experiments are reported in Table 1.

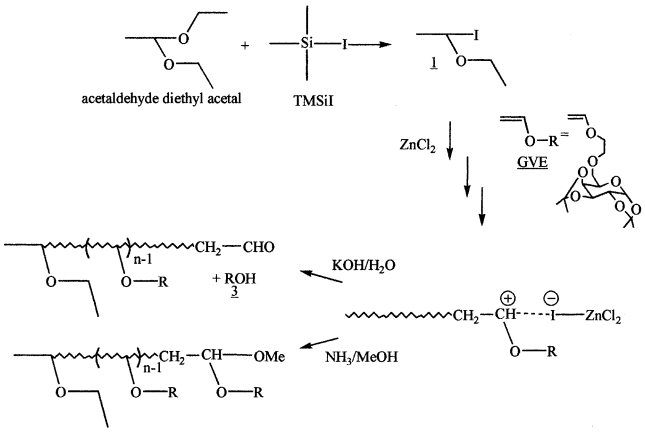
At the end of the polymerization and in order to recover aldehyde end-capped polymers, the reaction mixture was transferred into an aqueous KOH solution (pH = 10−12) under vigorous stirring, and the pH was rapidly neutralized with acetic acid. The heterogeneous mixture was left stirred for 1 h and the organic phase was extracted with dichloromethane, washed several times with an aqueous sodium thiosulfate solution and then with water. After drying over $MgSO_4$, the organic phase was concentrated and the polymer was dried under vacuum to constant weight.

Polymerization Kinetics. For the NMR kinetic study, samples were withdrawn from the polymerization mixture (in a Schlenk flask) at different reaction times and transferred through a cannula into vials containing dried NH_3/MeOH under vigorous stirring and then evaporated to dryness under reduced pressure. Both monomer conversion, C, and number-average polymerization degree, X_n, of the formed polymer at time t were determined by ^{1}H NMR.

Scheme 1



Scheme 2



Peak assignments of the monomer and the polymer were made according to the numbering given in Scheme 1.

GVE: 9, 6.5 ppm; 1, 5.6 ppm; 2, 4.6 ppm; 3,4,10′, 4.1−4.5 ppm; 5,10, 3.9−4.1 ppm; 6,7,8, 3.5−3.9 ppm; 13,14, 1.2−1.6 ppm.

Poly(GVE): ^{1}H NMR: a, 1.2 ppm; b, 2.6 ppm; c, 9.8 ppm; d, 1.5−2 ppm; e, 3.5−3.8 ppm; 6,7,8, 3.6 ppm; 5, 4 ppm; 3,4, 4.3 ppm; 2, 4.6 ppm; 1, 5.6 ppm; 13,14, 1.2−1.6 ppm.

Monomer conversion was calculated by comparing the residual GVE vinylic proton at 6.5 ppm with residual GVE and polyGVE anomeric protons at 5.6 ppm, according to eq 1,

$$C = 1 - \frac{I_M}{I_{M+P}} \qquad (1)$$

where I_M is the integral for the monomer vinylic proton and I_{M+P} the integral for the anomeric protons (one per saccharidic unit either in the monomer or in the polymer).

Characterization of Polymers. Molecular weights and molecular weight distributions of the polymer samples were determined both by (i) SEC and (ii) ^{1}H NMR.

(i) The number- and weight-average molecular weight $\overline{M_n}$ and $\overline{M_w}$ respectively, and the polydispersity index, $\overline{M_w}/\overline{M_n}$, were calculated on the basis of a polystyrene standard calibration.

(ii) Concerning the ^{1}H NMR determination, two cases must be differentiated according to the end group (Scheme 2).

•In the case of polymers with methoxy end groups, the number-average polymerization degree, X_n, was determined

by comparison of the integrals of the three methoxy protons at 3.3 ppm, I_{OMe}, and the anomeric protons along the polymer chain at 5.6 ppm, according to eq 2.

$$X_n = \frac{I_{M+P} - I_M}{I_{OMe}/3} \quad (2)$$

In some samples, the unavoidable water traces present in the NH_3/MeOH solution were responsible for a low proportion of aldehyde end-capped chains (at 9.8 ppm). In these cases, the integral of the corresponding population, I_{CHO}, was taken into account in the X_n determination by applying eq 3.

$$X_n = \frac{I_{M+P} - I_M}{(I_{OMe}/3 + I_{CHO})} \quad (3)$$

•In the case of polymers with aldehyde end groups, X_n was determined by comparing the aldehyde peak at 9.8 ppm, I_{CHO} (one proton per chain-end), with the anomeric protons of the polymer at 5.6 ppm, I_{anomer} (one proton per saccharidic unit). An alternative is to consider the peak relative to the methylene adjacent to the aldehyde ($-CH_2-$CHO) at 2.6 ppm. Then, $(I_{CH2CHO} + I_{CHO})/3$ provides a more accurate estimation of the integral corresponding to one chain-end proton. In addition, X_n must be corrected for the contribution of the anomeric proton of the sugar moiety released during the deactivation process (ROH (**3**), Scheme 2). Then, X_n can be determined using eq 4.

$$X_n = \frac{I_{anomer}}{\frac{I_{CH_2CHO} + I_{CHO}}{3}} - 1 \quad (4)$$

Characterization Techniques. ^{1}H NMR analyses were performed on a Bruker AC 200 spectrometer working at 200 MHz, with $CDCl_3$ as deuterated solvent.

SEC analyses were carried out with a Polymer Laboratories Gel Mixed-E column (bead size 3 μm, upper separation limit: 30 000 g·mol^{-1}) using a Waters 410 refractometric detector. THF was used as eluent (room temperature, flow rate 1.0 mL·min^{-1}), and calibration was done using polystyrene standards.

MALDI−TOF mass spectrometry spectra were recorded on a PE Biosystems Voyager DE-STR equipment. All experiments were done using an accelerating potential of 20 kV and a 337 nm nitrogen laser. The samples were prepared by mixing a solution of polymer in THF (10 mg·mL^{-1}), a solution of dithranol matrix in THF (10 mg·mL^{-1}) and a solution of NaI (cationization agent Na^+) in acetone (10 mg·mL^{-1}) with a volumetric ratio of 5/50/2. Then 1 μL of the resulting mixture was deposed onto the sample slide, and the solvent was evaporated at room temperature. Spectra were recorded either in the linear mode or in the reflectron mode. This last mode, modifying the ion trajectory, provides more accurate structural information.

Results and Discussion

Polymerization Kinetics. We previously reported[16] the ability of the saccharidic GVE monomer to polymerize via a "living" cationic process with TMSiI/$ZnCl_2$ as the initiating system. However, the presence of several polar groups on GVE which might induce undesirable side reactions led us to further investigate the "living" character of this polymerization. We first followed the monomer conversion by ^{1}H NMR (run **A**, Table 1). The polymerization was extremely fast with 55% conversion reached in 5 min. Then, the rate seemed to decrease and polymerization reached complete conversion at 120 min. Considering a polymerization that is first order in monomer which is common for vinyl ethers, the following equation, eq 5, describes the kinetics

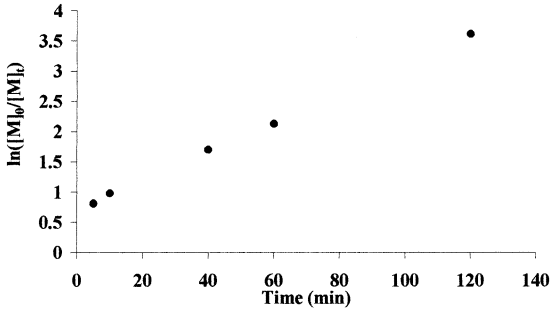


Figure 1. ln([M]$_0$/[M]$_t$) vs time plot for run **A**: [diethyl acetal] = 0.010 mol·L^{-1}, [TMSiI] = 0.012 mol·L^{-1}, [GVE] = 0.078 mol·L^{-1}, [$ZnCl_2$] = 0.002 mol·L^{-1}, polymerization time = 120 min, and T = −20 °C.

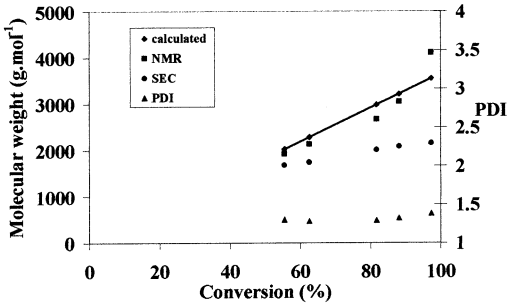


Figure 2. Molecular weight and PDI values for run **A**: [diethyl acetal] = 0.010 mol·L^{-1}, [TMSiI] = 0.012 mol·L^{-1}, [GVE] = 0.078 mol·L^{-1}, [$ZnCl_2$] = 0.002 mol·L^{-1}, polymerization time = 120 min, and T = −20 °C.

$$\ln\frac{[M]_0}{[M]_t} = k_p[C^*]t \quad (5)$$

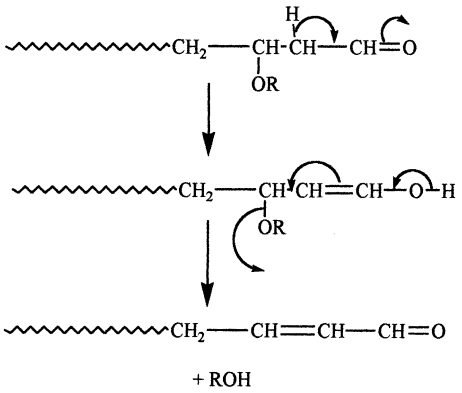
where [M] is the concentration of GVE monomer, k_p is the propagation rate constant, and [C*] is the concentration of $ZnCl_2$-activated chains at time t.

The ln([M]$_0$/[M]$_t$) = $f(t)$ plot should be linear if the concentration of active chains remains constant throughout the polymerization, i.e., if no termination reactions occur. Although the increase with time is linear (Figure 1), this straight line did not pass through the origin but intersected the Y-axis at a value corresponding to around 50% conversion.

The molecular weights of the samples were analyzed using both ^{1}H NMR and SEC. The number-average molecular weights, $\overline{M}_n$, are reported vs conversion in Figure 2, together with the theoretical values (calculated from the molar ratio of introduced monomer to diethyl acetal) and the PDI. The SEC values correspond to the molecular weight at the peak maximum (M_{peak}) rather than the $\overline{M}_n$, due to some overlap of the polymer and the residual monomer peaks.

The M_{peak} values increase linearly between 55% and 100% conversion, which indicates that no transfer reactions occur in this range. These values are considerably lower than the theoretical ones due to the inadequacy of the polystyrene calibration standards for analysis of protected saccharidic polymers, as already reported for similar polymers.[7,14,16] The SEC peaks reflect the whole chains present in the sample. In contrast, the NMR values derived from eq 2 take into account the whole chains for I_{M+P}, whereas only the

Scheme 3



chains bearing a methoxy end group are considered for I_{OMe}, i.e., chains which were still "living" when arriving into the deactivation media. In the case of some termination reactions occurring before the deactivation step, NMR values would be overestimated. Such reactions could explain the high $\overline{M}_n$ of the polymer corresponding to 98% conversion, where the amount of residual monomer might be insufficient to stabilize the "living" chain ends.[23,24] Figure 2 shows that the $\overline{M}_n$ values determined from NMR agree with the theoretical ones, which supports the absence of termination reactions. These results were reproducible over several experiments. In addition, ^{1}H NMR as well as MALDI−TOF mass spectrometry spectra of the polymer chains did not show the presence of any double bond chain ends corresponding to β-proton elimination reactions. The whole results confirm that GVE polymerization proceeds via a "living" pathway.

We also investigated the polymerization at very low conversion using a dilatometer—which does not require the withdrawal of samples—to get information within the first 5 min of polymerization. The first dilatometry experiment (run **B**, Table 1) was performed using the same experimental conditions as with run **A** except for the concentrations which were all increased such that a visible volume contraction occurred during the polymerization. GVE concentration was then of 0.35 M. Four points were obtained during the first 5 min of polymerization (Figure 3), confirming the very high polymerization rate at low conversion and the absence of an induction period. Above 50−60% conversion, polymerization rate decreased as already evidenced from the ^{1}H NMR kinetic study. The whole polymerization was completed in 1 h compared to 2 h for run **A** due to the higher monomer concentration. However, the curve is superimposable on that of run **A** after time normalization. From the data corresponding to less than 10 min of polymerization, a linear $\ln([M]_0/[M]_t) = f(t)$ plot is obtained, with the straight line passing through the origin (Figure 3). This indicates that no loss of active chains and hence no termination reactions occurred below 50% conversion.

However, Figure 4 shows that above 0.67 (50% conversion), the points deviated further from the initial line. Considering eq 5, the experimental data show that the concentration of activated chains does not remain constant throughout the polymerization, which could indicate the presence of some termination reactions. In fact, the strong decrease of the slope of the $\ln([M]_0/[M]_t) = f(t)$ plot would indicate that almost half of the activated chains be lost during the polymerization.

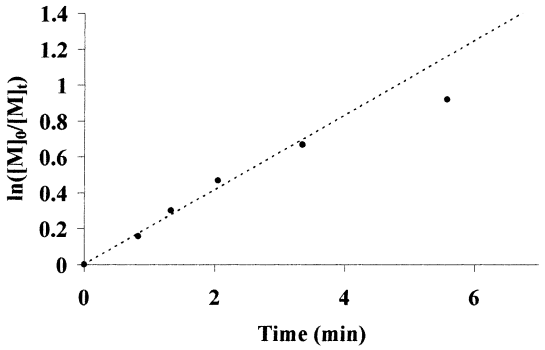


Figure 3. $\ln([M]_0/[M]_t)$ vs time plot for run **B**: first 7 min of polymerization, [diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.036 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, [$ZnCl_2$] = 0.006 mol·L^{-1}, and $T = -20$ °C.

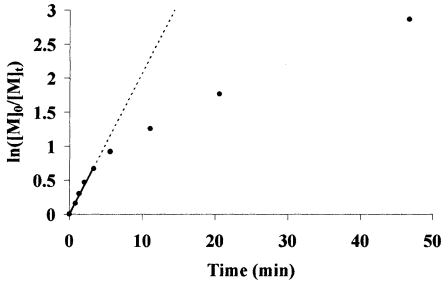
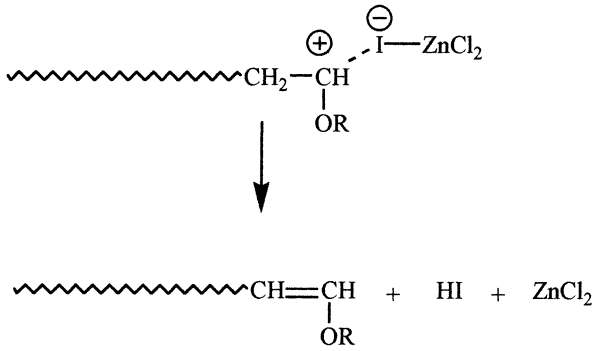


Figure 4. $\ln([M]_0/[M]_t)$ vs time plot for run **B**: [diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.036 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, [$ZnCl_2$] = 0.006 mol·L^{-1} polymerization time 47 min, and $T = -20$ °C.

Scheme 4



Considering the dormant/active chain equilibrium constant, $K_e = [C^*]/([C_{dorm}][ZnCl_2])$, the above observation would imply that $[C_{dorm}]$ be also divided by 2, corresponding to the termination of half of the polymer chain total number. Then, as termination usually occurs through β-proton elimination[12] (Scheme 4), the number of chains terminated with a double bond should be significant. However, analysis of the final poly(GVE) by ^{1}H NMR and by MALDI−TOF mass spectrometry (see characterization part below) did not reveal the presence of any double bonds on the chain ends. Considering that these polymers are of low molecular weight (<3800), the chain ends should be visible and a limitation of the techniques can be overruled. Consequently, no detectable termination reactions could be demonstrated from analysis of the poly(GVE) chains. This apparent contradiction made us to express two assumptions: (*i*) the decrease of the number of activated chains and the occurrence of termination reactions were independent phenomena, (*ii*) the polymerization was not first order in monomer, as suggested by a referee.

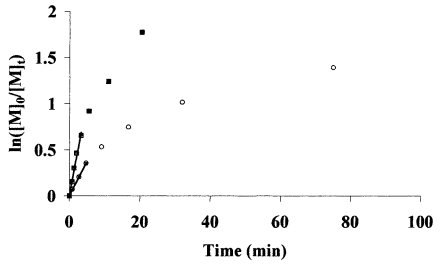


Figure 5. $\ln([M]_0/[M]_t)$ vs time plots for the polymerizations B (■, [diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.036 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, $[ZnCl_2]$ = 0.006 mol·L^{-1}, reaction time = 47 min, T = −20 °C) and C (○, [diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.034 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, $[ZnCl_2]$ = 0.006 mol·L^{-1} reaction time = 75 min, T = −30 °C).

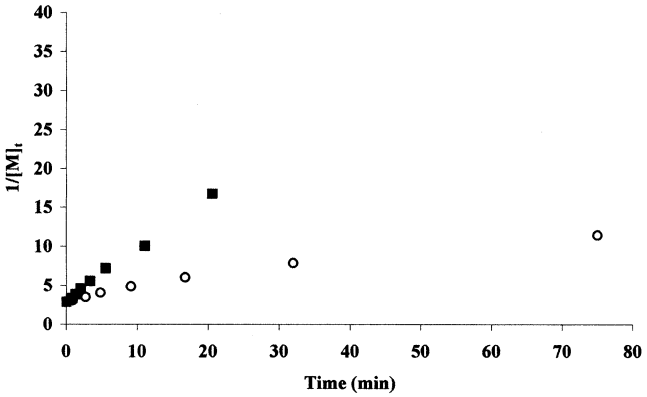


Figure 6. $1/[M]_t$ vs time plots for the polymerizations B: ■ ([diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.036 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, $[ZnCl_2]$ = 0.006 mol·L^{-1} reaction time 47 mins, T = −20 °C), C: ○ ([diethyl acetal] = 0.030 mol·L^{-1}, [TMSiI] = 0.034 mol·L^{-1}, [GVE] = 0.350 mol·L^{-1}, $[ZnCl_2]$ = 0.006 mol·L^{-1} reaction time 75 mins, T = −30 °C).

(*i*) It would be possible to lose some activated chains without any termination reaction, if, for instance, there would be a lack of available activator, $ZnCl_2$. In this case, the equilibrium would shift toward the dormant chains. An explanation might be a gradual complexation of $ZnCl_2$ by sugar rings during the polymerization, preferably onto the polymer since the phenomenon is enhanced with conversion. Complexation or coordination has often been observed for "living" cationic polymerization of functionalized monomers.[14,15,25,26] In addition, complexation of $ZnCl_2$ with ether functions has already been described.[27,28]

The effect of temperature on the loss of activated chains was tested by comparing runs **B** and **C**, similar experiments except for the temperature, −20 °C and −30 °C for runs **B** and **C**, respectively. The $\ln([M]_0/[M]_t) = f(t)$ plot is reported in Figure 5. The polymerization rate is higher at higher temperature. In addition, a decrease of the temperature corresponds to a stronger decrease of the slope of the $\ln([M]_0/[M]_t) = f(t)$ plot than at −20 °C, in agreement with the assumption of a complexation of $ZnCl_2$.

(*ii*) Assumption of an order in monomer different from one is quite unusual for vinyl ethers. However, Heroguez et al[29] reported an order of 0.3 for chloroethyl vinyl ether polymerization in the presence of HI/I_2 as initiating system. For runs B and C, a linear increase of the $1/[M]_t = f(t)$ plot was obtained (Figure 6), characteristic of a second order in monomer, although it is often difficult to differentiate a first order from a second one below 60% conversion. A second order in monomer would indicate that two monomer molecules are involved for insertion of one monomer in the chain. It was reported[30,31] that in living cationic polymerization, weak nucleophiles such as ethers may interact with the growing carbocations through formation of oxonium ions, favoring the controlled growth of the chains. Considering the numerous ether bonds of the saccharidic ring, the GVE monomer could act similarly, such mechanism leading to a second order in monomer. Finally, these two assumptions are based on a possible specific role of the saccharidic rings in the monomer and/or in the chain, and take into account their ability to coordinate—through their numerous ether functions—with the $ZnCl_2$ co-initiator and/or the growing carbocations, thus yielding a modification of the overall reactivity with conversion.

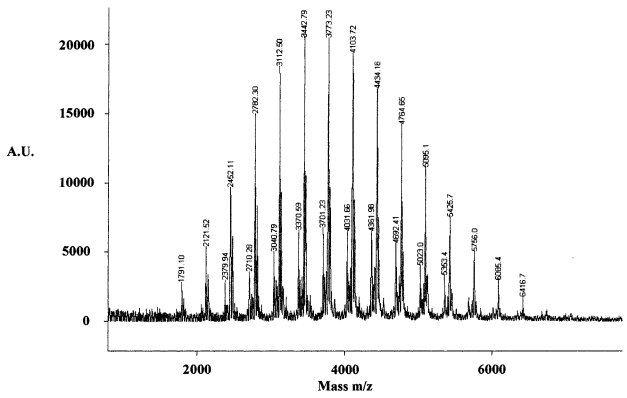


Figure 7. MALDI−TOF mass spectrometry spectrum (linear mode) of poly(GVE).

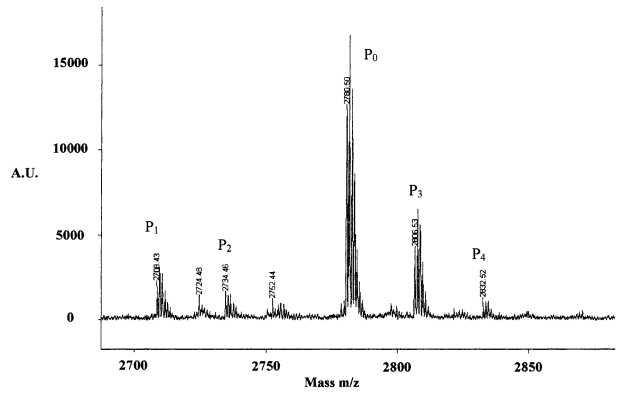


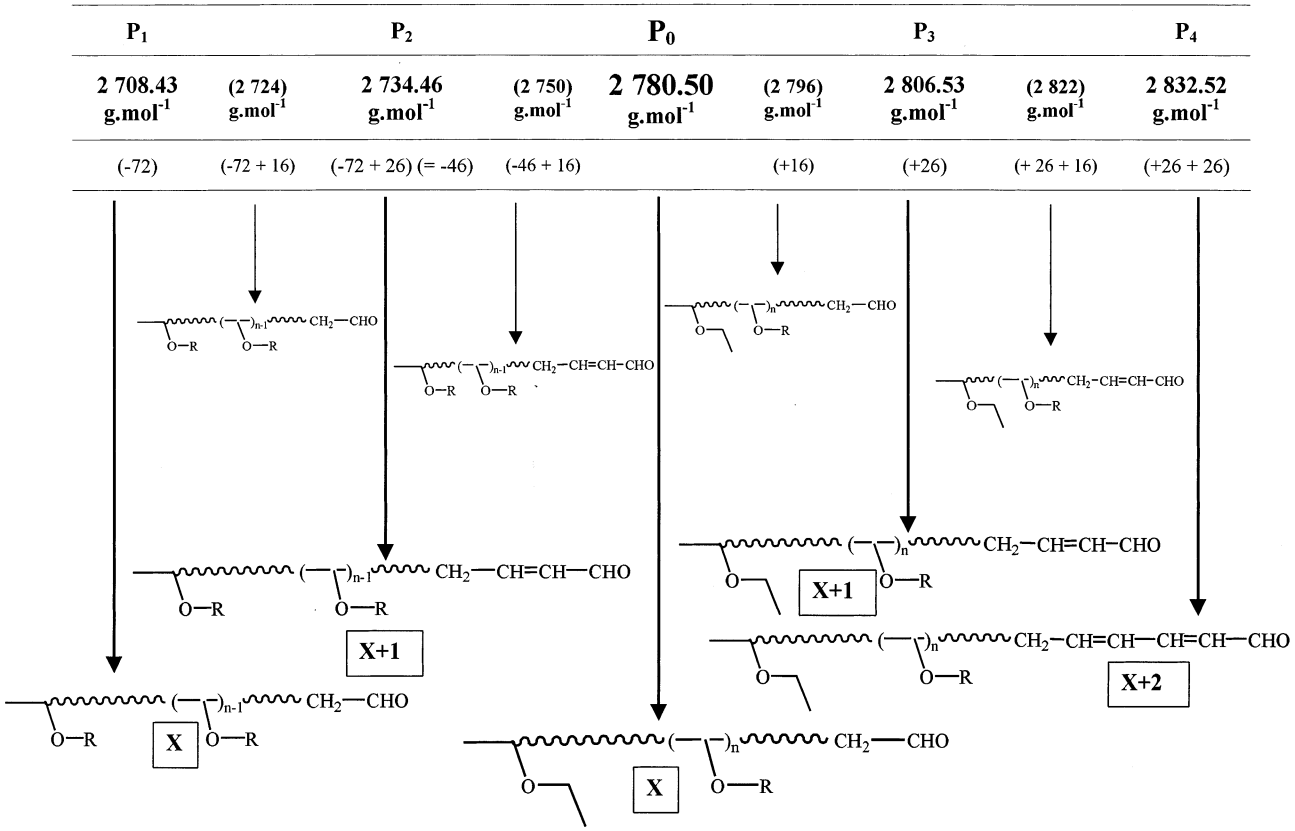
Figure 8. Enlarged part of the MALDI−TOF mass spectrometry spectrum (reflectron mode) of poly(GVE).

Table 2. Molecular Weight Characteristics of Poly(GVE) of Run B

method	$\overline{M_n}$	$\overline{M_w}$	M_{peak}	$\overline{M_w}/\overline{M_n}$
calculated	3800			
^{1}H NMR	3900			
MALDI−TOF	3960	4213	3800	1.06
SEC	2070	2430	2400	1.17

Characterization of the Polymer Chains by MALDI—TOF MS. The MALDI−TOF mass spectrometry spectrum (linear mode) of the aldehyde end-capped polymer **B** is shown in Figure 7 and the molecular weight characteristics obtained by different methods are compared in Table 2. The calculated and the experimental molecular weights obtained from ^{1}H NMR and MALDI−TOF mass spectrometry analyses agree quite well.

Scheme 5

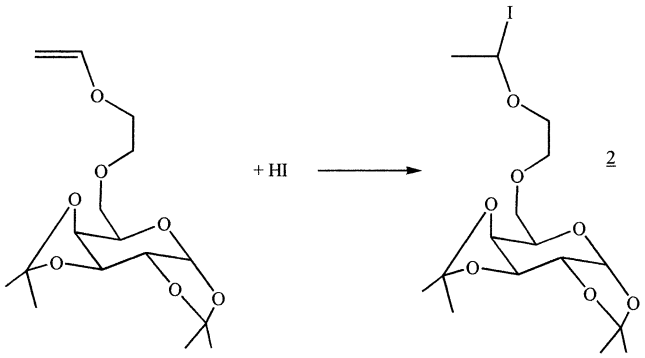


Considering the MALDI−TOF mass spectrum, the molecular weight difference between two consecutive peaks is 330.30, which corresponds to the mass of one GVE monomer unit. Thus, each peak on the spectrum corresponds to a polymer chain of a given polymerization degree, X. For example, the peak of molecular weight, $M_{chain} = 3773.23$, corresponds to $X = 11$. In this calculation, it is necessary to account for the mass of $CH_3CH(OC_2H_5)-$ originating from the initiator (73.0 g·mol^{-1}), for the mass of $-CH_2-CHO$ chain end (43.0 g·mol^{-1}), and for the mass of the attached sodium ion Na^+ (22.9 g·mol^{-1}), according to eq 6.

$$X = \frac{M_{chain} - M_{Na^+} - M_{-CH_2CHO} - M_{CH_3CH(OC_2H_5)}}{M_{repeat\ unit}} \quad (6)$$

The isotopic distribution of each peak can be seen in the reflectron mode. For instance, Figure 8 shows an enlarged part of the spectrum obtained in the reflectron mode, corresponding to the chain population centered on 2780.50 g·mol^{-1}, called P_0. This population has a polymerization degree equal to 8 according to eq 6. Four populations (P_1, P_2, P_3, P_4) of very similar isotopic distribution, are present on either side of the main population P_0, centered respectively at 2708.43, 2734.46, 2806.53, and 2832.52 g·mol^{-1} (Figure 8 and Scheme 5). The main population, P_0, corresponds to polymer chains formed according to the expected "living" cationic polymerization mechanism described in Scheme 2; i.e., they bear at the α-end a fragment coming from the adduct **1**, and they are terminated by an aldehyde function derived from the deactivation process. Similarly to Katayama et al.[22] we did not observe the presence of chains bearing a double bond end group resulting from β-proton elimination next to the active center, a possible side reaction well-known in cationic polymerization. These whole observations corroborate that polymerization of GVE using acetaldehyde diethylacetal/TMSiI/$ZnCl_2$ initiating system at −20 °C in toluene proceeds without termination reactions.

Scheme 6



However, the occurrence of other kinds of side reactions explains the structure of the different chain populations. Some unavoidable water traces present in the TMSiI solution can generate HI which is able to react directly with the monomer, leading to a new iodide adduct, **2** (Scheme 6). Once activated by $ZnCl_2$, **2** is able to add monomer as adduct **1** does. The resulting chains, P_1, bear at the α-end a GVE unit instead of a $CH_3-CH(OC_2H_5)-$ group (hence, P_1 is at −72 g·mol^{-1} from P_0), and an aldehyde function at the ω-end. A rather similar mechanism, leading to the formation of a new chloride adduct and to new polymer chains, has also been described by Katayama et al.[22] However, in our case, the presence of water traces was only effective at the very beginning of the polymerization (initiation step) and not during the propagation step. If so, it would

induce the termination of some chains with an aldehyde group, with simultaneous release of ROH **3**, which in turn would induce termination of active chains with an acetal group.[22] Such chains, bearing two saccharidic moieties at the ω-end, have not been observed here.

After deactivation of the polymer, the aldehyde end-capped chains may encounter a β-elimination of a proton located next to the aldehyde group (Scheme 3), leading to the elimination of the last saccharidic side-group of the chain (loss of 304 g·mol^{-1} or gain of 26 g·mol^{-1} in comparison with the chain having one repetitive unit less). For instance, P_3 is at + 26 g·mol^{-1} from P_0 indicating the loss of one saccharidic side-group on a chain of initial $X = 9$. Similarly, P_2 is at +26 g·mol^{-1} from P_1. Eventually, chains for which two successive β-proton elimination reactions occurred were also observed, corresponding to the population P_4 (at + 52 g·mol^{-1} from P_0) arising from chains of initial $X = 10$.

The chains resulting from this β-elimination were also observed by ^{1}H NMR analysis of the corresponding polymer. A doublet was present at 9.6 ppm close to the aldehyde singlet peak at 9.8 ppm, corresponding to a conjugated aldehyde group (spectrum not shown). Another polymer sample, for which such doublet did not appear on the ^{1}H NMR spectrum, was analyzed by MALDI−TOF MS. Some "P_2" and "P_3" chains were visible, indicating a higher sensitivity of MALDI−TOF MS than ^{1}H NMR technique in this case, but their proportion was significantly smaller than in the previous sample. The presence of chains terminated by an aldehyde end group was also reported by Katayama et al.,[22] but conjugated aldehyde end groups were not observed by MALDI−TOF MS although present on the ^{1}H NMR spectrum in a similar proportion as the nonconjugated aldehydes.

Finally, chain populations P_0, P_1, P_2, P_3 and P_4, cationized by Na^+, can also be cationized by K^+. The corresponding molar mass difference is 16 g·mol^{-1} ($M_{K^+} - M_{Na^+}$) (Scheme 5). Corresponding small peaks are visible in Figure 8.

In conclusion, the main population, P_0, is the one expected according to the mechanistic scheme of the "living" cationic polymerization of GVE monomer initiated by the acetaldehyde diethylacetal/TMSiI/$ZnCl_2$ initiating system. MALDI−TOF mass spectrometry technique also detected some aldehyde-capped chains that underwent a β-proton elimination, and a minor population corresponding to some chains initiated by the iodide adduct **2**.

Conclusion

A new saccharidic vinyl ether type monomer, 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2-vinyloxyethyl)-D-galactopyranose, has been synthesized and its ability to homopolymerize via a "living" cationic process has been tested using acetaldehyde diethylacetal/TMSiI/$ZnCl_2$ as the initiating system. Polymerization kinetics were carefully studied by both ^{1}H NMR and dilatometry. These two complementary methods demonstrate a fast polymerization (completed in less than 2 h) and an unexpected evolution of $\ln([M]_0/[M]_t)$ vs time graph: the linear evolution below 40−50% conversion is followed by a diminution of the slope, apparently suggesting the presence of termination reactions. However, the absence of transfer and termination reactions (not detectable) during the polymerization was evidenced by ^{1}H NMR and MALDI−TOF MS analyses of the polymers, confirming a "living" mechanism. Then, the evolution of $\ln([M]_0/[M]_t)$ vs time was explained by assuming (*i*) a possible decrease of the available $ZnCl_2$ concentration, shifting the equilibrium between dormant and active species toward the dormant ones, and/or (*ii*) a second order in monomer. Both assumptions are related to the saccharidic nature of the monomer, inducing a possible coordination of $ZnCl_2$ and/or of the growing carbocations.

Characterization by MALDI−TOF mass spectrometry of the final polymer appeared to be a powerful tool to confirm the expected polymerization mechanism, and to show the presence of side reactions: a secondary initiation due to water traces present in the TMSiI solution and the occurrence of degradation reactions undergone by some aldehyde chain ends.

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Supporting Information Available: Figures showing NMR spectra and time−conversion curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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