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Reactivity of Electrophilic Reagents towards Silyl Enol Ether Groups Incorporated into Vinyl Polymers[1]

Jacques Penelle [†,*] and Véronique Mayné

Laboratoire Cinétique et Macromolécules, Département de Chimie,
Université catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

[†] New address : Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003-4530, USA.

Abstract: Vinyl polymers containing about 20 mol-% of trimethylsilyl or tertbutyldimethylsilyl enol ether functionalities were synthesized by copolymerizing styrene or methyl methacrylate with either 2-trimethylsiloxybutadiene or 2-(tertbutyldimethysiloxy)butadiene under classical free-radical polymerization conditions. The reactivity of the resulting polymers toward a set of classical electrophilic reagents was investigated. Selected electrophiles included water, p-toluenesulfonyl isocyanate ([2+2]-cycloaddition), aromatic and aliphatic aldehydes (aldol reaction), benzaldehyde dimethyl acetal (Noyori condensation), and bromine. Detailed analysis of the polymer final structure - including quantitative ^{1}H- and ^{13}C-NMR analysis - demonstrated that in most cases the silyl enol ether group displays the same reactivity pattern as low-molecular weight analogs.

Introduction

Polymers including specific reactive groups on their backbone have found numerous applications in organic synthesis. Polystyrene beads containing benzyl chloride moieties are routinely used for example in the solid-phase synthesis of oligopeptides and oligonucleic acids using the well-known Merrifield chemistry. More recently, 'combinatorial chemistry' techniques based on the same kind of solid-phase synthetic approach have been introduced in medicinal chemistry, with possible extensions to other area of chemistry and physics.[2] As this new and rapidly growing field does require a large array of possible reactive groups attached to the polymeric support, additional efforts have been directed recently towards the introduction of new reactive groups into styrenic or acrylic materials, adding to the impetus already provided by more traditional applications.[3,4]

Even if in theory any new reactive group has some potential, some specific groups offer a much more defined interest. For example, of particular importance from a practical point of view would be the capability to introduce reactive groups able to react with electrophiles of low-to-medium reactivity under mild experimental conditions. Most groups introduced so far are indeed electrophilic in nature, benzyl halides or epoxide being the most typical examples.[3,4] Versatile reactivity of the reactive moiety, easy introduction into the polymer, and possibility to maintain reasonable costs are also points to carefully consider when analyzing the perspectives offered by a potential new reactive group.

Silyl enol ethers should constitute interesting candidates from all these points of view. Extensively used in organic synthesis, they can react under mild experimental conditions with a large number of electrophiles, even those of low reactivity.[5-6] Furthermore the large amount of available literature allows to rapidly figure out what kind of modification reactions should be theoretically possible.

This paper describes the reactivity towards typical electrophiles of trimethylsilyl and tert-butyldimethylsilyl enol ethers incorporated into soluble styrene (St) or methyl methacrylate (MMA) polymers. The aim of the study was to map the possibilities offered by these two groups, the tert-butyldimethylsilyl group having been selected for its known superior stability towards moisture. In the present study, soluble polymers rather than insoluble gels were investigated in order to obtain reliable and quantitative information on the functionalization efficiencies as they can be easily analyzed by quantitative ^{1}H- and ^{13}C-NMR.

Experimental

Materials

THF and toluene were dried by distillation over sodium benzophenone ketyl. Methyl alcohol and benzaldehyde were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. Tetrabutylammonium fluoride (TBAF, 1.1 mol.L^{-1} in THF), bromine, and potassium iodide were obtained from Aldrich. Concentrated hydrochloric acid (37%) was obtained from Lab Chemistry. All commercially available reagents described above were used as received. 2-Trimethylsiloxybutadiene (TMSBD)[7] and 2-(*tert*-butyldimethylsiloxy)butadiene (TBMSBD)[8] were synthesized from methyl vinyl ketone, using the procedures previously reported in the literature. Trimethylsilyl triflate was synthesized following a reported procedure.[9]

Synthesis of the Polymers

Polymers used in this study were obtained by copolymerizing TMSBD or TBMSBD with styrene or MMA as described in our previous publications (polymerization conditions : bulk, 60 °C, AIBN 1-2 nmol-%).[10]

Functionalization

General Procedure. Modification reactions were carried out as described below under the different subheadings. Flame-dried glassware and classical precautions to avoid interference with moisture were used for the aldol condensations and the reaction with benzaldehyde dimethyl acetal. The polymer was then precipitated into a large amount of cold methanol refrigerated at about -45 °C, was filtered off, washed with a large amount of methanol, and dried overnight at 60 °C under vacuum (0.1-0.5 mmHg).

Hydrolysis. The appropriate amounts of catalyst and solvent were added to a solution of 0.2 g of the (co)polymer dissolved in 20 mL of acetone (conditions I) or 3 mL of THF (conditions II) : conditions I: 0.3 g of a 9 $mol.L^{-1}$ solution of HCl ; conditions II: 0.5 mL of deionized water, 2.5 mL of a 1.1 $mol.L^{-1}$ solution of TBAF in THF. The solution was then stirred at room temperature for 24 hours.

[2+2] Cycloaddition with p-Toluenesulfonyl Isocyanate (p-TSI). The appropriate amount of p-TSI (1.5 to 15 equivalents, see Table I) was slowly added via a cannulla and under argon to a solution of the copolymer (0.2 g, about 5.10^{-4} mol of silyl enol ether) in 4 mL of toluene. The solution was then stirred at room temperature for the appropriate period of time.

Aldol Condensation. 0.2 g of polymer (about 5.10^{-4} mol of silyl enol ether) dissolved in 6 mL of CH_2Cl_2 were added dropwise into a mixture of the aldehyde, $TiCl_4$ (see Table II for the appropriate amounts), and dry CH_2Cl_2 (12 mL) at -78°C under argon. The mixture was stirred for 1 h. 6 mL of methanol were then added and the mixture was stirred for an additional 30 minutes period.

Bromination. A 0.1 $mol.L^{-1}$ bromination reagent was prepared by mixing 0.5 mL of bromine in a 100 mL-volumetric flask containing 50 mL of the appropriate solvent and adding more solvent to obtain a final volume of 100 mL. The final solution was titrated with a 0.1 $mol.L^{-1}$ sodium thiosulfate solution under standard conditions. 6 mL of this brominating reagent were added to a stirred solution of polymer (0.10-0.15 g) in the appropriate solvent (toluene, benzene or carbon tetrachloride). The resulting mixture was placed in the dark during the appropriate amount of time. An excess of potassium iodide in 2-3 mL of water was added and the solution was immediately titrated with standardized 0.1 mol.L^{-1} sodium thiosulfate aqueous solution until final disappearance of the yellow color.

Condensation with Benzaldehyde Dimethyl Acetal. Benzaldehyde dimethyl acetal (0.075 mL, 5.10^{-4} mol) and 0.2 µL (about 10^{-5} mol) of trimethylsilyl triflate were subsequently added at -78°C under argon into a solution of 0.2 g of polymer (about 5.10^{-4} mol of silyl enol ether) in 3 mL of CH_2Cl_2. The mixture was stirred for one hour. 3 mL of methanol were added and the mixture was stirred for an additional 30 minutes period.

Measurements. ^{1}H- and ^{13}C-NMR spectra were recorded on a Gemini 200 spectrometer at 200 MHz and a Gemini 300 at 300 MHz. $CDCl_3$ (99.8 atom % D), C_6D_6 (99.5 atom-% D) and CD_2CL_2 (95.6 atom-% D) were purchased from Janssen Chimica (now Acros). Infrared spectra were measured on a Nicolet 205 FT-IR and a Perkin-Elmer 1710.

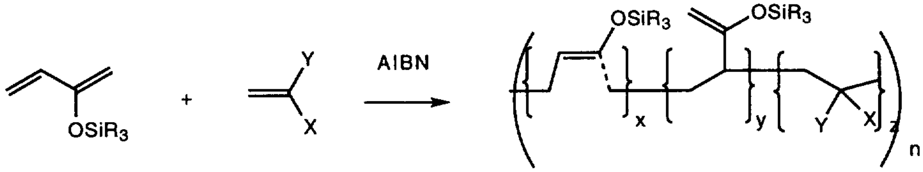
Results And Discussion

More than a hundred different electrophiles are known to react with silyl enol ethers, and many experimental variables have been tested for the most classical reactions, in particular the aldolization.[5,6] As this project was focused on determining the reactivity pattern of silyl enol ethers groups incorporated into styrenic or methacrylic polymers, five different sets of electrophilic reagents were selected for that particular purpose, namely water, p-toluenesulfonyl isocyanate, aldehydes, bromine, and benzaldehyde dimethyl acetal. These reagents were chosen to cover a broad range of electrophilicities and geometries adopted in the transition state, allowing us to map as effectively as possible the scope offered by the reactive group using the smallest possible set of electrophilic reagents.

Preparation of the Polymers

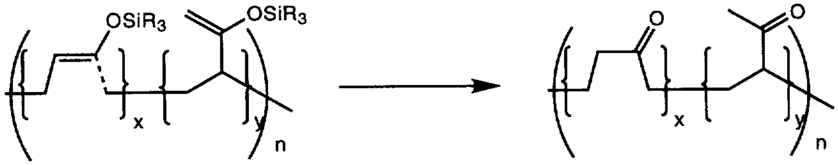
Silyl enol ether groups were introduced into the polymer by the simple method described and analyzed by Nagai *et al.* and ourselves.[10-12] This method, which is based on the free-radical copolymerization of 2-trialkysiloxybutadienes with a vinyl comonomer, is schematically depicted in Scheme 1. It allows full incorporation of the butadienes as silyl enol ether functionalities since no 1,2-incorporation of the butadiene monomer occurs during the polymerization. Four copolymers were used in this project, corresponding to the four possible combinations corresponding to the copolymerization of 2-trimethylsiloxybutadiene (TMSBD) or 2-(*tert*-butyldimethylsiloxy)butadiene (TBMSBD) with styrene (St) or methyl methacrylate (MMA). Experimental conditions were selected to allow copolymers containing 24 ± 4 mol-% of butadiene to be obtained. The exact content was determined each time by quantitative ^{1}H-NMR. Resulting colorless polymers exhibited reasonable stability when kept under anhydrous conditions. As expected, TBMSBD copolymers showed a much better hydrolytic stability than the TMSBD analogs.

Scheme 1. Synthetic procedure used to introduce the silyl enol ether functionality into the MMA or St polymer



Our previous studies had shown that only 3,4- and 1,4-microstructures are formed under the experimental conditions used in this study.[10,11] The 1,4 microstructure amounts to 82 and 77 mol-% of the two microstructures, for the TMSBD-St and TMSBD-MMA copolymers respectively. This ratio, which was determined by quantitative ^{13}C-NMR, was very similar to the one observed previously for the corresponding homopolymer (83 mol-%), indicating that the comonomer does not seem to drastically influence the incorporation pattern of the butadienic monomer. TBMSBD-St and TBMSBD-MMA copolymers were not analyzed by quantitative ^{13}C-NMR. For the TBSMD homopolymer, 1,4-microstructures amounted for 85 mol-% of the total, indicating that the nature of the alkyl groups on the silicon does not influence strongly the incorporation pattern either. It was not possible to determine the E-Z ratio of the 1,4-microstructures.

Hydrolysis

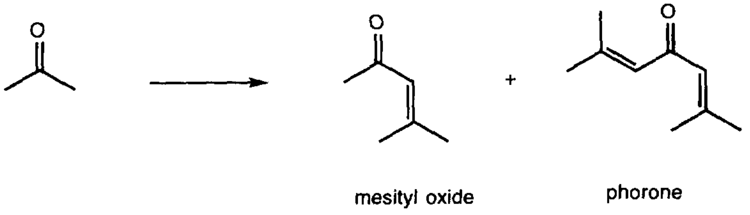


(1)

Reaction with water to yield an aldehyde or a ketone is the most common reaction of silyl enol ethers, even if generally of poor practical utility in organic synthesis. In the present case however, hydrolysis offers an indirect way to introduce keto groups into a vinyl polymer (equation 1), which in turn can lead to superior photodegradability or allow hydrophilic group to be introduced into the polymer matrix.[13,14] Also, further chemical modification of the keto group can be accomplished using classical chemistry and will be reported at a later date.

Hydrolysis is also the only modification reaction that has already been reported for polymers containing silyl enol ether units. Nagai *et al* reported the easy hydrolysis of TMSBD homopolymers and copolymers with St, MMA and acrylonitrile using three different catalysts: concentrated hydrochloric acid, tetrabutylammonium fluoride (TBAF) in tetrahydrofuran, and acetic acid.[12] It was speculated by the authors that side reactions had occurred under the investigated conditions (see discussion below). A short note appeared more recently on the photodegradability of styrenic polymers containing keto groups that were synthesized by hydrolysis of TMSBD-containing styrene copolymers.[13] No mention was made on the structure of the polymer, nor on the experimental conditions utilized.

Reinvestigation of homo(TMSBD) hydrolysis in the presence of 9 mol.L^{-1} hydrochloric acid in acetone (Experimental Part, conditions I) gave in our hands deeply colored solution from which a sticky dark brown solid was recovered by precipitation in methanol. With the possible exception of the hydrochloric acid solution whose exact concentration was not mentioned, these conditions are identical to the conditions described previously.[12] A 300 MHz ^{1}H-NMR spectra was reasonably identical with the provided 60 MHz ^{1}H-NMR except for the presence of an additional tiny peak at 5.7-5.8 ppm. Evaporation of the acetone solution in which the reaction had been carried out, and analysis of the residue by ^{1}H-NMR showed - as expected - the presence of mesityl oxide and phorone resulting from acetone self-condensation under acidic conditions (equation 2).

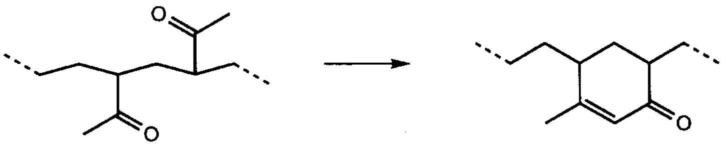


(2)

TMSBD copolymers with styrene and MMA had also been hydrolyzed by the same authors using TBAF solution in THF as the catalyst.[12] It was not clear whether the authors had added acetone in the reacting mixture, the table reporting the data and the experimental part being in conflict on that particular point. In our case, the modified polymer recovered by precipitation in methanol (conditions II in

Experimental Part) was slightly yellow, possibly due to the presence of small amounts of TBAF contaminating the polymer and identified by both 300 MHz ^{1}H- and ^{13}C-NMR spectra. NMR spectra showed the complete disappearance of peaks due to the silyl enol ether structure (at 0.0-0.5 and 4.0-5.0 ppm in ^{1}H-NMR and at 0.0-5.0 and 80.0-170.0 ppm in ^{13}C-NMR) and the appearance of peaks due to the new carbonyl structure (complex spectra in the 2.0-3.0 ppm area in ^{1}H-NMR due to the methyl, methylene and methyne groups adjacent to the carbonyl and a broad peak included between 205 and 215 ppm in ^{13}C-NMR). No signal possibly resulting from an α,β-unsaturated ketone substructure was detected in the ^{1}H-NMR spectrum nor in the ^{13}C-NMR spectrum (around 200 ppm for the C=O and 140 ppm for the vinyl carbon). The FT-IR was similar to the one reproduced by the authors, including a strong absorption band at 1710 cm^{-1} (lit. 1720 cm^{-1}) and a shoulder at 1660 cm^{-1} (lit. 1650 cm^{-1}). Quantitative ^{1}H-NMR confirmed the quantitative transformation of the silyl enol ether groups into keto groups, with about 70-80 % of these groups introduced as expected in the main chain and the residual ones being present as pendant acetyl group.

In order to take into account the additional signal at 1650 cm^{-1}, the authors had proposed that a cyclohexenone unit can possibly result from intramolecular aldol condensation of two adjacent hydrolyzed 3,4-subunits (equation 3). Our results however do not support this suggestion as no signal that might possibly be assigned to this structure was found in the NMR spectra. It is quite possible however that under the first conditions investigated, i.e. in the presence of hydrochloric acid and acetone, this cyclic structure or other acyclic α,β-unsaturated ketone substructures resulting from the condensation of acetone with a carbonyl on the chain might be produced and are responsible for the more complicated ^{1}H-NMR spectrum. This presence alone however cannot explain the shoulder at 1660 cm^{-1} as the relative ratio between the signals at 1710 and 1660 cm^{-1} is identical for the two samples.

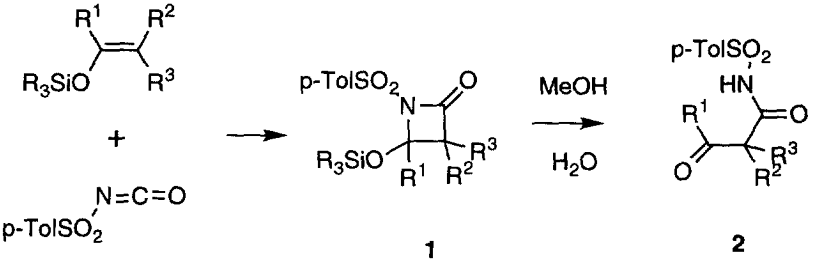


(3)

TBMSBD homopolymer and copolymers of TMSBD and TBMSBD with styrene and MMA were hydrolyzed using TBAF as the catalyst under the experimental conditions described above for poly(TMSBD). Results identical to those obtained for poly(TMSBD) were obtained, except for the color of the copolymers (entirely white instead of slightly yellow), and of the FT-IR spectra of the copolymers on which no shoulder at 1660 cm^{-1} could be noticed anymore. The first observation probably results from a lower contamination of the precipitated polymers by TBAF as no signal arising from TBAF could be found on the ^1H-NMR spectra. Analysis of the hydrolyzed TMSBD-St copolymer by non-quantitative ^{13}C-NMR and APT confirmed the final structure of the polymer and the absence of any noticeable side reaction.

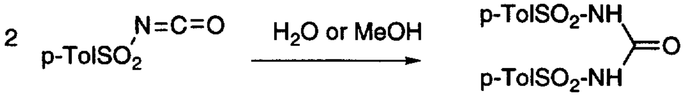
[2+2]-Cycloaddition with p-Toluenesulfonyl Isocyanate (p-TSI)

[2+2]-Cycloaddition of low-molecular weight silyl enol ethers with p-TSI yields β-lactams **1** that can react further in the presence of moist methanol to give β-ketoamides **2** via ring-opening of the β-lactam cycle (equation 4). It is not clear whether the second transformation results from a reaction with water or methanol, both pathways being theoretically possible. The reaction has been investigated by Ojima *et al.* on several silyl enol ethers in the absence of any solvent, and gave isolated yields in β-ketoamides in the 80-98 % range.[15] The reaction was described as extremely rapid, almost instantaneous.



(4)

For our experiments, a solvent was needed in order to dissolve the solid reactant and the polymer. Toluene was selected for its inertness and its ability to dissolve both p-TSI and the whole range of polymers under study. The rapid hydrolysis-methanolysis reaction was ensured by precipitating the polymer at the end of the reaction into a large excess of methanol. When excess amounts of p-TSI were used, N,N'-bis(p-toluenesulfonyl)urea resulting from the reaction of residual p-TSI with water or methanol (equation 5) coprecipitated with the polymer, and only extensive washing with cold methanol allowed to remove the contaminant.



(5)

Experimental conditions for the reactions with TMSBD and TBMSBD copolymers are summarized in Table I. Conversions were determined by quantitative ^{1}H-NMR by comparing signals from aromatic protons of styrene and tolylsulfonamide groups, centered at 6.8 and 7.95 ppm respectively, or from MMA MeOOC- group (3.4-3.8 ppm) and aromatic protons of tolylsulfonamide group (7.95 ppm).

Table I. [2+2] Cycloaddition with p-TSI (0.2 g copolymer, 4 mL toluene, room temperature)

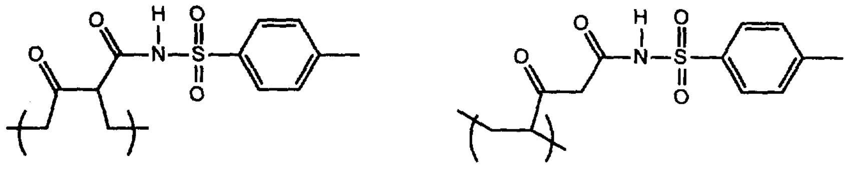
Exp.	copolymer	p-TSI equivalents	reaction time (h)	functionalization[a] (%)
1	TMSBD-St	15.0	24.0	99
2	TMSBD-St	3.0	24.0	97
3	TMSBD-St	1.5	3.5	93
4	TMSBD-St	1.5	24.0	97 - 93 - 93[b]
5	TMSBD-St	1.5	216	quantitative[d]
6	TMSBD-MMA	1.5	24.0	98 - 91[c]
7	TBMSBD-St	1.5	24.0	75 - 78[c]
8	TBMSBD-MMA	1.5	24.0	77

a) determined by quantitative ^{1}H-NMR (see text) ; b) result of three separate experiments ; c) results of two separate experiments ; d) complete disappearance of IR and ^{1}H-NMR signals arising from the silyl enol ether structure

FT-IR spectra of the recovered polymers exhibited a broad absorption band centered at 3250 cm^{-1} (N-H) and a typical C=O vibration at 1730 cm^{-1}. Almost complete disappearance of absorptions at 840 (Si-CH$_3$), 1250 (Si-CH$_3$) and 1670 cm^{-1} (C=C) was also observed. Complete disappearance of peaks corresponding to the olefinic protons was observed by ^{1}H-NMR, and an additional large decrease in the intensity of signals corresponding to alkylsilyl groups was also observed, amounting to about 97 % of the starting signal. New peaks can be observed in the aromatic region (7.15, 7.95, and 9.8 ppm for MMA copolymers, and 7.95 and 9.6 ppm for St copolymers) was also observed. ^{13}C-NMR spectra of the TMSBD-ST and TMSBD-MMA copolymers showed a large decrease in the intensity of olefinic and trialkylsilyl carbons. Spectra exhibited additional peaks at 60, 120-150, 164-167, and 205-215 ppm, which were assigned to the carbons of the two new structures depicted in Figure 1 (60 ppm $[(\mathrm{C{=}O})\underline{\mathrm{C}}\mathrm{H}(\mathrm{C{=}O})$

and (C=O)CH$_2$(C=O)], 120-150 ppm [aromatic ring], 164-167 ppm [(C=O)NHSO$_2$], and 205-215 ppm [ketone]).

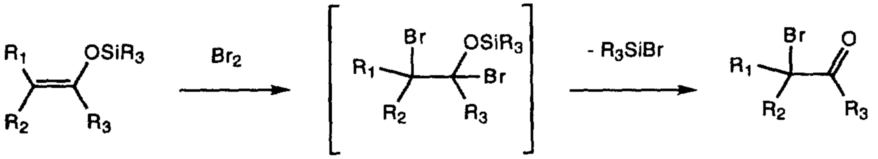
Figure 1. New structures appearing on p-TSI-modified copolymers



Results in Table I show that full conversion can be obtained either by using very large amounts of p-TSI (exp. 1) or longer reaction times (exp. 5), suggesting that conversion is limited by the kinetics of the reaction rather than by possible side reactions. Spectroscopic analysis of the transformed copolymers showed only the expected structure and supports the same idea. Very reasonable conversions (higher than 90 % for the TMSBD copolymers) can be obtained under less stringent reaction conditions as shown by experiments 3, 4 and 6. *tert*-Butyldimethylsilyl enol ethers demonstrated a slightly lower reactivity under the same experimental conditions, conversions of about 70% being obtained instead of the 90 %+ observed for the trimethylsilyl-based copolymers (exp. 8 and 9 vs. 4 and 6).

Bromination

Treatment of a silyl enol ether with bromine yields an intermediate 1,2-dibromoalkyl silyl ether that converts spontaneously at room temperature to the corresponding β-bromo carbonyl compounds and trimethylsilyl bromide (equation 6).[16,17] Yields are good to excellent for silyl enol ether derived from ketones, and the reaction is almost instantaneous as expected for such an electron-rich olefin. In some cases, isomerization and multiple bromination have been reported as well.



(6)

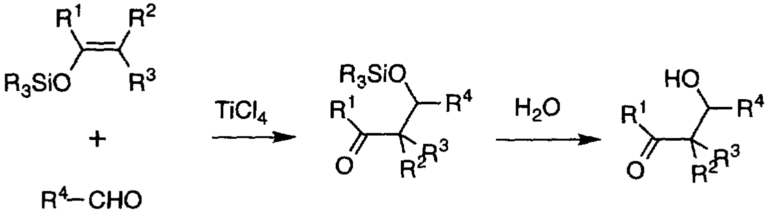
Preliminary experiments were carried out on PSt-TMSBD copolymers dissolved in toluene or CCl_4 using a large excess of bromine, typically about two equivalents of bromine per silyl enol ether function. The excess of bromine was then titrated at different times using the classical KI-$Na_2S_2O_3$ reaction. The titrations indicated that slightly more than one equivalent of bromine had been consumed in a few minutes. The reaction did not evolve any more in CCl_4 even after 24 hours. In toluene on the contrary, bromine continued to be consumed but at a much lower rate due to slow bromination of the solvent. Polymers recovered by precipitation in methanol displayed strictly identical IR and NMR spectra whatever the solvent of the reaction was, indicating that the side reaction is independent of the polymer itself and is not due to further bromination of the α-bromoketone that had been formed. A blank experiment confirmed that toluene was responsible for the slow side reaction. All samples included in this particular study contained 19 mol-% of TMSBD units as determined by quantitative ^{1}H-NMR. Assuming that the reaction of the silyl enol ether with bromine is quantitative, the actual content as determined by titration is a little bit higher. Six identical samples titrated in Ccl_4 provided an average value of 23.4 mol-%. This number however is still compatible with the result provided by the NMR analysis, considering typical analytical errors attached to both analytical methods, and supports the quantitative character of the bromination.

FT-IR spectra of the brominated TMSBD-St copolymers exhibit new peaks at 1117 cm^{-1} and at 1718 cm^{-1} (carbonyl). Complete disappearance of the absorptions at 840 (Si-CH_3), 1 250 (Si-CH_3) and 1670 cm^{-1} (C=C) typical of the starting silyl enol ether function was also observed. Disappearance of the vinyl peaks and of the alkyl groups on the silicon and emergence of a small peak at 3.1 ppm can be noticed on the ^{1}H-NMR spectra as well. The new peak can be assigned to the proton on the same carbon than the bromine. ^{13}C-NMR spectrum of the TMSBD copolymer isolated after 24 h of reaction showed the disappearance of all peaks corresponding to olefinic carbons and alkyl groups on the silicon and exhibited new peaks at 52.5-57.0 ppm ($\underline{C}$HBr(C=O)) and 201- 206 ppm (C=O) that did not appear on the spectrum of the hydrolyzed polymer.

The three other copolymers were brominated using the same experimental procedure, except that benzene was substituted to CCl_4 for the MMA-based copolymers as precipitation did occur in CCl_4. A blank experiment using benzene did not allow to detect any reaction of bromine with benzene even for much longer reaction time than the 15 minutes that were used for the experiments. Bromination of the TMSBD-MMA copolymer indicated - as in the TMSBD-St case above - that the actual content in TMSBD units is slightly higher than what is measured by ^{1}H-NMR (22.7 rather than 19 mol-%), indicating once again that the reaction is almost quantitative. For TBMSBD copolymers however, further incorporation of bromine was observed. After 15 minutes, 1.5 equivalents of bromine has been consumed (with respect to the amount of silyl enol ether present in the copolymer as determined by ^{1}H-NMR), and after 3 hours, most of the bromine initially present in the solution had disappeared. Unfortunately, we don't have at present any explanation for the difference in reactivity displayed by the trimethylsilyl- and *tert*-butyldimethylsilyl enol ethers, respectively.

Aldol Condensation

Aldol condensation of a silyl enol ether with an aldehyde in the presence of a Lewis acid yields a β-siloxy ketone that can be converted under mild hydrolytic conditions to the corresponding β-hydroxyketone (equation 7). Numerous experimental conditions have been proposed in the literature for this reaction. In this study, experimental conditions were restricted to those described by Mukaiyama *et al.* ($TiCl_4$, CH_2Cl_2, -78 °C).[18] Mechanistic studies on the aldol reaction carried out under these conditions have been provided by several authors and showed *inter alia* that the reaction is very rapid.[19-21]



(7)

Reactivities of St- and MMA-copolymers were investigated using 7-methoxy-3,7-dimethyloctanal (MDMO) and benzaldehyde respectively as the co-reactant. This choice was made to allow the extent of functionalization to be measured easily by quantitative ^{1}H-NMR. Signal intensities were compared for the phenyl groups and the MeO- group centered at 6.8 and 3.1 ppm respectively in the case of the St-based copolymers, and of the aromatic protons and -COOMe groups centered at 7.3 and 3.6 ppm respectively in the case of the MMA-based copolymers.

Results are included in Table II and show that the efficiency of functionalization is far from quantitative, extent of functionalization ranging from almost zero to 57 %. This observation contrasts with results obtained for low-molecular weight analogs for which the reaction was almost quantitative after 1h.[18] Analysis of the recovered TMSBD copolymers by NMR showed that the only other observable substructure is the hydrolyzed structure previously studied at the beginning of this study. For the TBMSBD copolymers however, about 20 % of the silyl enol ether groups present at the beginning of the reaction were recovered unchanged at the end of the reaction. Curiously enough, increasing the amount of $TiCl_4$ introduced in the reaction medium did not improve the efficiency of the functionalization (exp. 1, 3, and 4). On the contrary, when 5 equivalents were used, the extent of functionalization dropped to zero (exp. 4). This result can be rationalized on the basis of a rapid complexation of the first equivalent of $TiCl_4$ with the aldehyde present in the reaction mixture, and the subsequent transformation of part of the silyl enol ether functions with the remaining $TiCl_4$ to yield trichlorotitanium enolates unable to react with the aldehyde. This Ti-Si exchange reaction had been observed by Kuwajima et al. under conditions similar to ours.[22]

Table II. Aldol condensation of TMSBD and TBMSBD copolymers (CH_2Cl_2, 1 equivalent of aldehyde, -78 °C)

N°	copolymer	aldehyde	$TiCl_4$ (equivalent)	reaction time (h)	functionalization[c] (%)
1	TMSBD-MMA	PhCHO	1	1	36 - 30[a]
2	TMSBD-MMA	PhCHO	1	5	57
3	TMSBD-MMA	PhCHO	2	1	29
4	TMSBD-MMA	PhCHO	5	1	<2 - <2[a]
5	TBMSBD-MMA	PhCHO	1	1	26 - 19[a]
6	TMSBD - St	MDMO[b]	1	1	35 - 41[a]
7	TBMSBD-St	MDMO[b]	1	1	22 - 25[a]

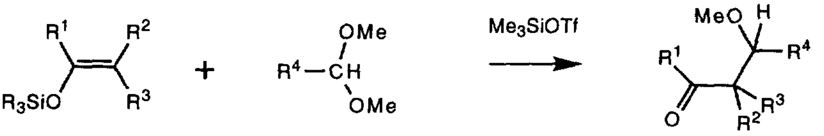
a) results of two different experiments ; b) 7-methoxy-3,7-dimethyloctanal ; c) as determined by NMR (see text)

Polymers were extensively analyzed by ^{1}H- and ^{13}C-NMR. Spectra showed partial or complete disappearance of the peaks previously assigned to olefinic protons and alkylsilyl protons. For MMA-copolymers functionalized with benzaldehyde, new peaks at 4.6 and 7.3 ppm in the ^{1}H-NMR spectra were assigned to C$\underline{H}$-OH and aromatic protons, respectively. ^{1}H-NMR spectra of the St-copolymers functionalized with MDMO showed the expected signal at 3.1 ppm (terminal MeO). ^{13}C-NMR spectra of the TMSBD-MMA copolymers showed a large decrease in intensity for the peaks previously assigned to olefinic carbons and alkyl groups on the silicon, as well as new peaks at 74 ($\underline{C}$-OH), 120-145 (aromatic ring) and 205-215 ppm (carbonyl). ^{13}C-NMR spectra of the TMSBD-St functionalized new peaks at 68.5 ppm ($\underline{C}$-OH), 206-218 ppm (C=O). An APT experiment confirmed the assignment. FT-IR spectra of the different copolymers were very similar to those observed for hydrolyzed polymers.

Attempts were made to functionalize the TMSBD-MMA copolymer with MDMO, and the TMSBD-St copolymer with acetaldehyde and benzaldehyde (same experimental conditions as in exp. 1, 5, 6 or 7). NMR analysis of the resulting polymers are compatible with some incorporation of the aldehyde moiety into the polymer, but it was impossible to measure the exact extent of functionalization.

Condensation with Benzaldehyde Dimethyl Acetal

Condensation of silyl enol ethers with dimethyl acetals can yield β-methoxy ketones (equation 8). Under the conditions described by Noyori *et al.* (trimethylsilyl triflate, 1-5 mol-%, CH_2Cl_2, -78 °C, 4-10 h), yields in the 80-90 % range can usually be obtained.[23]



(8)

In order to obtain an idea on the efficiency of this particular reaction, TMSBD-MMA copolymer was reacted with one equivalent of benzaldehyde dimethyl acetal in the presence 2 mol-% trimethylsilyl triflate (-78 °C, 1h). A functionalization of about 31 % was determined by quantitative ^1H-NMR using signals of the aromatic ring and of the methyl ester at 7.3 and 3.6 ppm, respectively. This result is disappointingly lower than the 80%+ expected on the basis of the reaction with low molecular-weight analogs. The ^1H-NMR spectrum was similar to the one observed after aldolization with benzaldehyde, except for the appearance of new peaks between 2.9-3.4 ppm and at 4.0 ppm that can be assigned to the methoxy group and the $PhC\underline{H}(OMe)$- proton, respectively. The ^{13}C-NMR spectrum showed new peaks at 82-88 ($Ph\underline{C}H(OMe)$), 120-145 (phenyl), and 205-215 ppm (carbonyl).

Conclusion

Trimethylsilyl enol ethers incorporated into vinyl polymers were found to react with several electrophilic reagents that were already known to react with low-molecular weights analogs. A summary table is provided below. Experimental conditions allowing a quantitative transformation were found for water, p-toluenesulfonyl isocyanate, and the reaction of bromine with trimethylsilyl enol ether. In the last case, a competitive reaction of yet unknown nature was observed for the reaction with *tert*-butyldimethylsilyl enol ether. Aldolization with aldehydes and condensation with benzaldehyde dimethyl acetal allowed to incorporate aldehyde derivatives into the polymer, but incorporation yields were much lower than reaction yields obtained with low-molecular weight analogs under similar reaction. Preliminary results indicate that better yields can be obtained by increasing reaction times.

Table III. Summary of the modification reactions investigated during this study (maximum % functionalization obtained)

Polymer	TMSBD			TBMSBD		
Electrophile	-	St	MMA	-	St	MMA
H_2O	> 97	> 97	> 97	> 97	> 97	> 97
p-TSI	-	> 99	98	-	78	77
Aldehyde-$TiCl_4$	-	57^a	26^a	-	41^b	25^b
Br_2	-	> 97	> 97	-	0^c	0^c
$PhCH(OMe)_2$	-	-	31	-	-	-

a) with benzaldehyde ; b) with 7-methoxy-3,7-dimethyloctanal ; c) side reactions occured

This study confirmed that silyl enol ethers constitute a interesting reactive groups to consider when analyzing possible groups to introduce into a vinyl polymer matrix. The vast choice of possible reactions and the easiness with which the group can be introduced into the polymer make silyl enol ethers suitable candidates for numerous applications.

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