Styrene-terminated poly(vinyl alcohol) macromonomers: 1. Synthesis by aldol group transfer polymerization

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Aldol group transfer polymerization of t-butyldimethylsilyl vinyl ether initiated by an unsaturated compound, *p*-formylstyrene, and catalysed by zinc bromide allowed synthesis of styryl-silylated poly(vinyl alcohol) macromonomers bearing an aldehyde end-function. Various macromonomers with average degrees of polymerization up to 28 were prepared and characterized according to different analytical methods, such as ^{1}H and ^{13}C nuclear magnetic resonance and ultra-violet spectroscopy and gel permeation chromatography. In order to improve the stability of the end-group, the aldehyde function was reacted with a silylketene acetal compound, 1-methoxy-2-methyl-1-trimethylsiloxypropene, which leads to a β-hydroxy ester end-group, much more stable towards side-reactions. Afterwards, the silyl ether side-groups were hydrolysed with tetrabutylammonium fluoride in order to obtain hydrophilic styryl–poly(vinyl alcohol) macromonomers.

(Keywords: aldol group transfer polymerization; macromonomer; poly(vinyl alcohol); synthesis; characterization)

INTRODUCTION

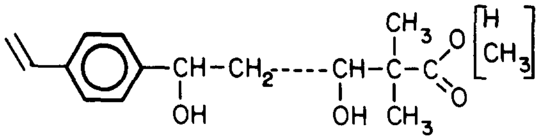
Macromonomers are macromolecular monomers synthesized by polymerization of a low-molecular-weight monomer. Living polymerization techniques, which allow good control of chain length together with a narrow distribution, are preferred, and functionalization with one polymerizable end-group per chain is necessary. The latter can be performed either by use of an unsaturated initiator or by direct or indirect deactivation of the growing chain with an unsaturated compound[1].

Anionic polymerization has been used extensively for the preparation of well characterized polystyrene, poly(ethylene oxide), etc., macromonomers[1], and group transfer polymerization of acrylic and methacrylic monomers[2,3] offers new developments in this direction, especially for the preparation of poly(methyl methacrylate) macromonomers[4–7].

On the contrary, aldol group transfer polymerization of trialkylsilyl vinyl ether monomers has not been studied so far, and only one paper has described the synthesis, by this method, of a styrene-terminated silylated poly(vinyl alcohol) (PVA) macromonomer[8].

The aldol group transfer polymerization (aldol GTP) technique has been pioneered and described in 1985 by Sogah and Webster[9,10] as a nucleophilic polyaddition method involving trialkylsilyl vinyl ether monomers, and was found to be efficient at room temperature. The initiator is an aldehyde compound (aromatic aldehydes are preferred) and the reaction is catalysed by Lewis acids (for instance, zinc bromide). This polymerization method leads to an aldehyde-terminated silylated poly(vinyl alcohol) chain, after which deprotection of hydroxyl side-groups can be carried out in order to recover a hydrophilic PVA chain.

Owing to its living character, this polymerization technique allows molecular-weight control through the monomer-to-initiator ratio (i.e. initial concentration ratio $[M]_0/[I]_0$) and the distribution is usually narrow, since it is governed by a Poisson law. This paper deals with the use of aldol group transfer polymerization of t-butyldimethylsilyl vinyl ether, catalysed by zinc bromide and initiated by an unsaturated compound, *p*-formylstyrene, for the synthesis of a functional hydrophilic styrene-terminated PVA macromonomer, the other end being functionalized with an ester or a carboxylic acid group:



MECHANISM AND KINETIC ASPECTS OF ALDOL GROUP TRANSFER POLYMERIZATION

The aldol GTP process can be described according to the scheme presented in *Figure 1*. As stated by Sogah and Webster[10,11], the first step of the mechanism consists of rapid and reversible initiator carbonyl double bond activation by zinc bromide catalyst, which makes the carbon electrophilicity increase. Then, nucleophilic addition of monomer is possible, which constitutes the initiation step (rate constant k_i). This addition is followed by silyl group transfer from monomer oxygen to initiator – or growing chain – aldehyde oxygen and, therefore, regeneration of an aliphatic terminal aldehyde function.

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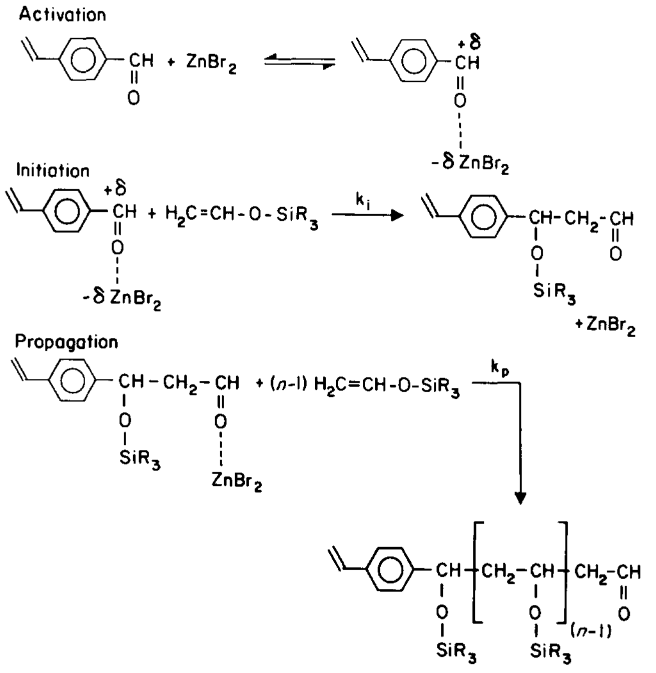


Figure 1 Aldol GTP reaction scheme and mechanism (n represents number-average molecular weight; k_i and k_p are respective initiation and propagation rate constants)

After zinc bromide activation, this species is able to carry on monomer polyaddition, i.e. the propagation step (rate constant k_p).

Considering that each aldehyde function is equally able to add a monomer molecule independently of the chain length, then addition follows a Poisson law, which allows calculation of the final molar fraction of each species as a function of the monomer-to-initiator initial ratio (see *Figure 2*). Two cases can be considered:

$$k_i = k_p \qquad \text{and} \qquad k_i \gg k_p$$

In the first case, where initiation and propagation rate constants are equal, monomer addition is not dependent upon the nature of the aldehyde. On the contrary, when the initiation rate constant is much higher than the propagation rate constant, then aromatic aldehyde is more reactive and addition to initiator is much more rapid than addition to any other aldehyde present in the medium. The following expressions can be given with respect to average degree of polymerization and molecular-weight distribution of the macromonomers:

First case, $k_i = k_p$

$$IM_i = \frac{v^i \mathrm{e}^{-v}}{i!}$$

where IM_i represents the final molar fraction of macromolecules with degree of polymerization equal to i, and v is the monomer-to-initiator ratio $[\mathrm{M}]_0/[\mathrm{I}]_0$,

$$\overline{DP_n} = v = \frac{[\mathrm{M}]_0}{[\mathrm{I}]_0}$$

is the number-average degree of polymerization,

$$\overline{DP_w} = v + 1$$

is the weight-average degree of polymerization, and

$$I_p = \frac{v+1}{v}$$

is the polydispersity index.

Second case, $k_i \gg k_p$

$$IM_i = \frac{v^{i-1} \mathrm{e}^{-v}}{(i-1)!} \qquad \text{where} \qquad v = \frac{[\mathrm{M}]_0}{[\mathrm{I}]_0} - 1$$

$$\overline{DP_n} = v + 1 = \frac{[\mathrm{M}]_0}{[\mathrm{I}]_0}$$

$$\overline{DP_w} = 1 + v + 1/v$$

$$I_p = 1 + 1/v - (1/v)^2$$

EXPERIMENTAL

Reagents

p-Bromostyrene (97% from Aldrich), magnesium, anhydrous dimethylformamide (DMF), n-butyllithium (1.6 or 2.0 M solution in hexane or pentane, from Aldrich), t-butyldimethylsilyl chloride (98% from Janssen), anhydrous zinc bromide (99.999% from Aldrich), 1-methoxy-2-methyl-1-trimethylsiloxypropene (95% from Fluka), dichloromethane and tetrabutylammonium fluoride (1 M solution in tetrahydrofuran (THF), from Janssen) were used as received; THF was distilled over sodium and benzophenone prior to use.

p-Formylstyrene (4-vinylbenzaldehyde) initiator was prepared from *p*-bromostyrene according to Dale's method[12] by reaction of DMF with *p*-vinylphenylmagnesium bromide followed by acidic hydrolysis. Purification was performed by column chromatography and vacuum distillation: the boiling point of the pure monomer is 36°C under 0.1 mbar. This compound was

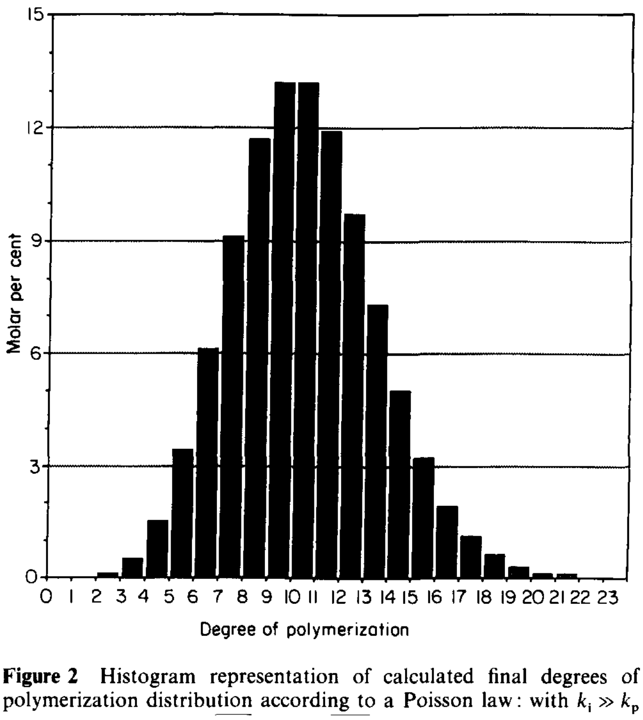
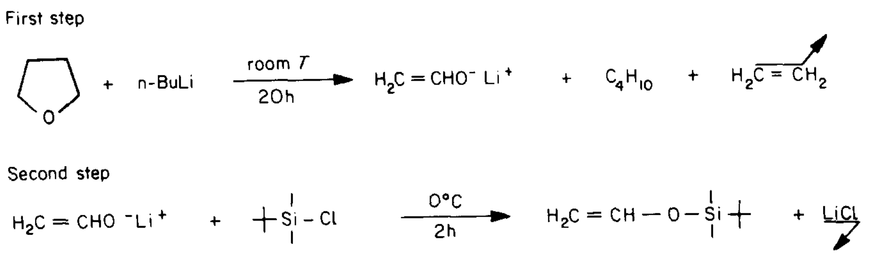


Figure 2 Histogram representation of calculated final degrees of polymerization distribution according to a Poisson law: with $k_i \gg k_p$ and $[\mathrm{M}]_0/[\mathrm{I}]_0 = 10$; $\overline{DP_n} = 10.0$, $\overline{DP_w} = 10.9$, $I_p = 1.09$



Scheme 1

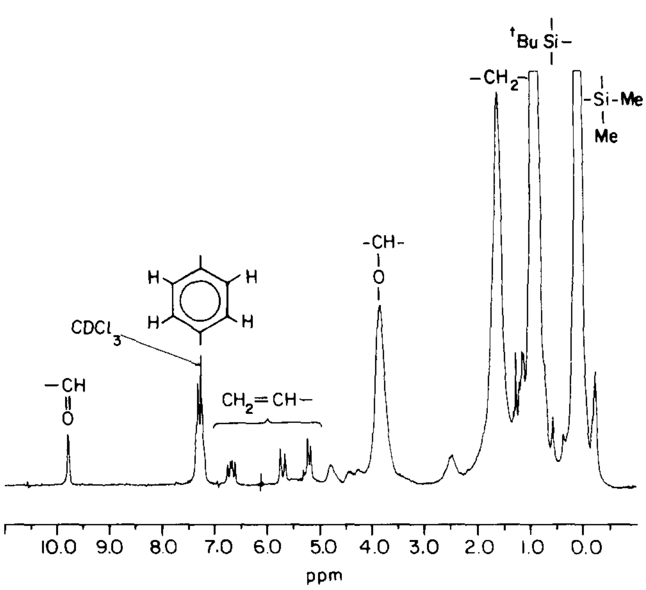
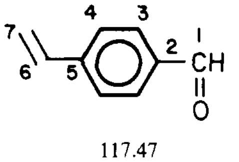


Figure 3 The 200 MHz ^1H n.m.r. spectrum of a styryl-silylated PVA macromonomer with an aldehyde end-group: P10 ($CDCl_3$ solution, TMS as internal standard)

analysed by high-resolution liquid n.m.r. spectroscopy (in $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference). For 200 MHz ^1H n.m.r. the chemical shift values δ (ppm) and coupling constants J (Hz) from high field to low field are:

vinylic protons	$\delta=5.410$	(dd; $J_{gem}=0.50$ and $J_{cis}=10.90$; 1 H)
	$\delta=5.885$	(dd; $J_{gem}=0.60$ and $J_{trans}=17.60$; 1 H)
	$\delta=6.745$	(dd; $J_{cis}=10.90$ and $J_{trans}=17.60$; 1 H)
aromatic protons	$\delta=7.815$	
	$\delta=7.515$	(AB spectra; 4 H)
aldehydic proton	$\delta=9.960$	(s; 1 H)

For 50.3 MHz ^{13}C n.m.r. the chemical shift values (ppm) from high field to low field are:

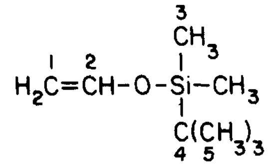


C_7	117.47
C_3 and C_4	126.75 and 130.10
C_2	135.70
C_6	135.90
C_5	143.47
C_1	191.74

The monomer, t-butyldimethylsilyl vinyl ether, was synthesized by reaction, at room temperature under inert atmosphere, of n-butyllithium with THF for about 20 h followed by slow addition at 0°C of t-butyldimethylsilyl chloride, according to *Scheme 1*[13]. The monomer was purified by vacuum distillation: its boiling point is 60–63°C under 80 mmHg. Most of the fractions still contained residual THF and hexane or pentane, which were not eliminated prior to further reactions when they represented less than about 15 wt%. Final yield was in the range 55–60%. This compound was analysed by high-resolution liquid n.m.r. spectroscopy (in $CDCl_3$ as solvent and TMS as internal reference). For 200 MHz ^1H n.m.r. the chemical shift values δ (ppm) and coupling constants J (Hz) from high field to low field are:

methyl protons	$\delta=0.130$	(s; 6 H)
t-butyl protons	$\delta=0.905$	(s; 9 H)
vinylic protons	$\delta=4.090$	(dd; $J_{gem}\simeq0.60$ and $J_{cis}=5.80$; 1 H)
	$\delta=4.415$	(dd; $J_{gem}\simeq0.60$ and $J_{trans}=13.65$; 1 H)
	$\delta=6.410$	(dd; $J_{cis}=5.80$ and $J_{trans}=13.65$; 1 H)

For 50.3 MHz ^{13}C n.m.r. the chemical shift values (ppm) from high field to low field are:



$H_2C=CH-O-Si(CH_3)_2-C(CH_3)_3$

C_3	−5.28
C_4	18.33
C_5	25.64
C_1	94.28
C_2	146.47

Characterization techniques

High-resolution liquid n.m.r. spectroscopy was carried out with a Bruker AC200 apparatus working at 200 MHz for protons and 50.3 MHz for carbon-13; $CDCl_3$, acetone-d_6 and D_2O were used as solvents. Chemical shift values were given in ppm with reference to TMS used as internal standard for organic solvents; in deuterium oxide solutions, sodium 3-trimethylsilylpropanoate-d_4 (TSP-d_4) was used as internal standard ($\delta = 0$ ppm for ^1H n.m.r. and $\delta = -1.7$ ppm for ^{13}C n.m.r., with reference to TMS). Integration of the different peaks of ^1H n.m.r. spectra of aldehyde-ended silylated macromonomers allowed calculation of number-average degree of polymerization n according to the characteristic features of the spectrum exhibited in *Figure 3*.

Gel permeation chromatography (g.p.c.) was carried out with Waters equipment using four columns: two Ultrastyragel with porosities 100 and 500 Å respectively and two Microstyragel with porosoties 10^3 and 10^4 Å respectively. THF was used as eluant at a flow rate of 1 ml min^{-1} and detection was performed by measurement of the optical density at 253 nm (u.v. spectrophotometer detector, Waters 484). Average molecular weight and dispersity index were derived from a calibration curve based on narrowly distributed polystyrene standards.

Table 1 Experimental conditions for the synthesis of styrenic silylated PVA macromonomers by aldol GTP

Reference code	CH_2Cl_2 (ml)	$ZnBr_2$ (mmol)	Initiator[a] (mmol)	Monomer[b] (mmol)	$[M]_0/[I]_0$
P37	$CDCl_3$ 3 ml	0.27	0.99	0.98	0.82[c]
P39	$CDCl_3$ 4 ml	0.37	1.01	2.02	1.58[c]
P16	10	3.9	3.97	21.1	5.3
P36	25	4.2	16.55	150.0	9.1
P35	40	2.88	11.77	117	9.9
P3	10	0.59	0.99	15.1	15.2
P7	11	0.56	0.99	20.2	20.4
P10	12	0.28	1.00	22.5	22.5
P11	20	1.5	1.47	42.0	28.6

[a] *p*-Formylstyrene
[b] t-Butyldimethylsilyl vinyl ether
[c] $[M]_0/[I]_0$ ratio was recalculated from zero-time ^1H n.m.r. spectra

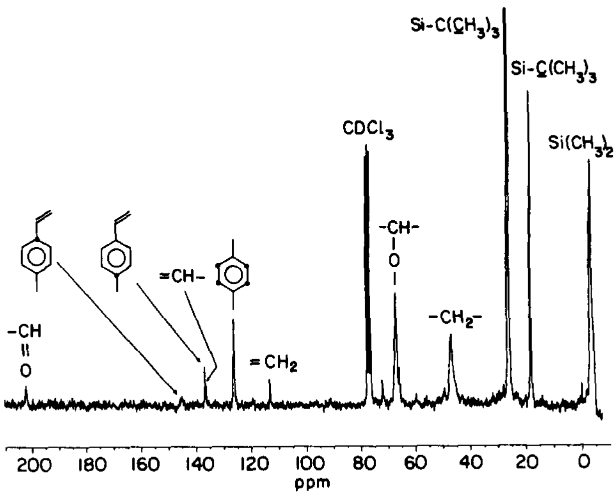


Figure 4 The 50.3 MHz ^{13}C n.m.r. spectrum of a styryl-silylated PVA macromonomer with an aldehyde end-group: P10 ($CDCl_3$ solution, TMS as internal standard)

U.v. analysis was realized in quartz cells with a Kontron 930 spectrophotometer. The optical density (*OD*) of a solution of macromonomer in THF was measured at a wavelength of 253 nm. From the *OD* value and weight concentration of macromonomer, *t* ($g\,l^{-1}$), and knowing the molar extinction coefficient, $\varepsilon = 1.80 \times 10^{-4}\,l\,mol^{-1}\,cm^{-1}$ (ref. 8), the number-average molecular weight of macromonomer $\overline{M}_n$ could be calculated according to the Beer–Lambert law:

$$OD = \varepsilon l c$$

with $l = 1.000$ cm (cell length) and *c* represents the molar concentration of macromonomer ($mol\,l^{-1}$):

$$c = t/\overline{M}_n$$

Therefore:

$$\overline{M}_n = \frac{\varepsilon l t}{OD}$$

Fourier-transform infra-red transmission spectroscopy (*FT*i.r.) was carried out with a Nicolet 5PC apparatus: solid macromonomers were mixed with KBr and pressed into pellets.

Synthesis of macromonomers

Aldol group transfer polymerization process. Reaction was performed at a temperature of 30°C under an inert atmosphere (argon). Zinc bromide catalyst was introduced into the reactor and purified by fusion under reduced pressure and very high temperature; then aldehyde initiator and dichloromethane solvent were added, followed by slow addition of monomer. At the end of reaction (2 or 3 h), the medium was evaporated and the weight of solid residue allowed one to estimate the monomer conversion and macromonomer average molecular weight. After resolubilization in dichloromethane, macromonomers with an average degree of polymerization higher than about 15 were purified by precipitation into methanol, filtered and dried at room temperature under reduced pressure; they looked like a white powder. Lower-molecular-weight macromonomers could not be easily precipitated, so they were simply isolated by evaporation of solvent. Different macromonomers were synthesized with ratio $[M]_0/[I]_0$ ranging between 0.82 and 28.6 (see *Table 1*).

Macromonomers were characterized by ^1H and ^{13}C n.m.r. (*Figures 3* and *4*), g.p.c. (*Figure 5*), *FT*i.r. (*Figure 6*) and u.v. so as to show the presence of one styrene and one aldehyde group per chain and also to determine the average degree of polymerization. Results concerning various characteristics of the macromonomers are presented in *Table 2*.

Aldehyde end-group transformation (compounds P11e, P35e, P36e and P29). In order to improve the stability

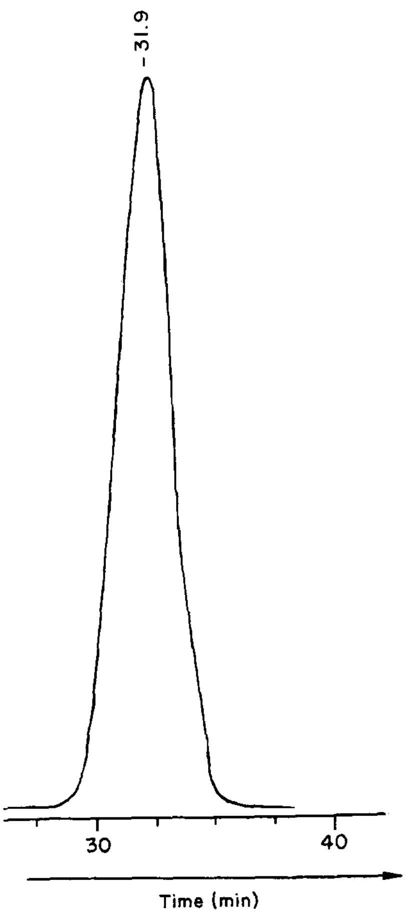


Figure 5 G.p.c. chromatogram of a styryl-silylated PVA macromonomer with an aldehyde end-group: P3

of the macromonomer's end-group, the aldehyde function of P11, P35 and P36 macromonomers was reacted with a silylketene acetal compound, 1-methoxy-2-methyl-1-trimethylsiloxypropene[14]. Such a reaction, also catalysed by zinc bromide, is known as the Reformatsky reaction and leads to a methyl ester, according to *Scheme 2*[15]. This reaction was realized under the same experimental conditions as aldol GTP: in CH_2Cl_2 solvent, 30°C and under an argon atmosphere, but with a shorter duration (reaction was instantaneous and exothermic). An excess of silylketene acetal was necessary to transform the terminal function completely, which was checked by ^{1}H and ^{13}C n.m.r. and *FT*i.r. spectrometry, showing the disappearance of aldehyde characteristic peaks. By ^{1}H n.m.r. analysis, $-O-CH_3$ ester protons appeared at 3.63 ppm and $-C(CH_3)_2$ protons at 1.06 and 1.13 ppm; by ^{13}C n.m.r. analysis, carbonyl carbon exhibited resonance at 177.5 ppm and $-O-CH_3$ at 51.8 ppm. By *FT*i.r., a shift of carbonyl absorption band was observed from 1729 cm^{-1} for aldehyde to 1742 cm^{-1} for ester.

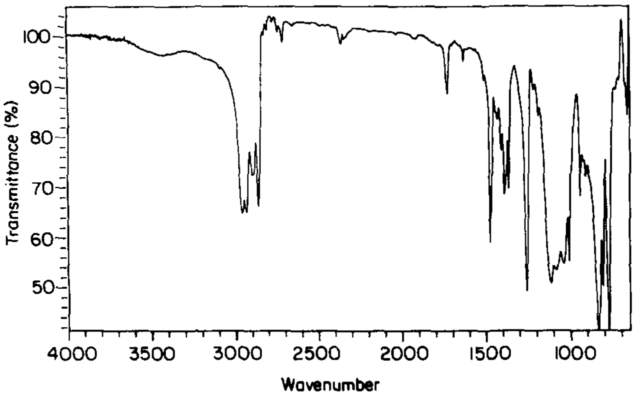
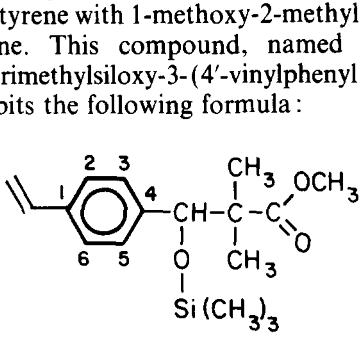
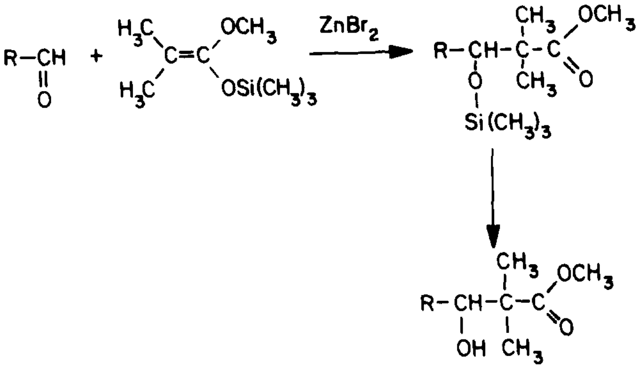


Figure 6 *FT*i.r. spectrum of a styryl-silylated PVA macromonomer with an aldehyde end-group: P10

A model compound was also synthesized by reaction of *p*-formylstyrene with 1-methoxy-2-methyl-1-trimethylsiloxypropene. This compound, named methyl 2,2-dimethyl-3-trimethylsiloxy-3-(4′-vinylphenyl)propanoate (P29), exhibits the following formula:



and it has been characterized by ^{1}H and ^{13}C n.m.r., with the following results. ^{1}H n.m.r. ($CDCl_3$): δ (ppm) = 7.295–7.190 (second-order spectra; 4 H, aromatic protons), 6.60–6.695, 5.518 (3 H, vinylic protons), 4.925 (s; 1 H, $-CH-O-$), 3.640 (s; 3 H; $-O-CH_3$), 0.165–0.055 (s; 3 H; $-C(CH_3)_2$), -0.070 (s; 9 H; $-Si(CH_3)_3$). ^{13}C n.m.r. ($CDCl_3$): δ (ppm) = 177.5



Scheme 2

Table 2 Characterization[a] of styrenic silylated PVA macromonomers bearing an aldehyde end-group

				U.v.	^{1}H n.m.r.	G.p.c.		
Code	$[M]_0/[I]_0$	ρ[b]	$\overline{DP_n}$[c]	$\overline{M_n}(\overline{DP_n})$	$\overline{DP_n}$	$\overline{M_n}(\overline{DP_n})$	$\overline{M_w}$	I_p
P37	0.82	1.0	–	–	$i = 0$:22 mol%[d]	$i = 0$	–	–
					$i = 1$: 78 mol%	$i = 1$		
P39	1.58	1.0	–	–	$i = 0$: 0 mol%[d]	$i = 0$	–	–
					$i = 1$: 62 mol%	$i = 1$		
					$i = 2$: 37 mol%	$i = 2$		
					$i = 3$: ?	$i = 3$		
P16	5.3	1.0	5	–	4–5	–	–	–
P36	9.1	0.93	8.5	–	6–7	1654 (9.6)	2608	1.58
P35	9.9	0.72	7.2	–	5–6	1267 (7.2)	1469	1.16
P3	15.2	0.98	15	2400 (15)	14–16	1672 (10)	1971	1.18
P7	20.4	0.73	15	2700 (16)	14–16	2067 (12)	2562	1.24
P10	22.5	0.78	18	2600 (16)	15–17	2022 (12)	2523	1.25
P11	28.6	1.0	28	4400 (27)	26–27	2967 (18)	3795	1.28

[a] With $\overline{DP_n}$ = number-average degree of polymerization
$\overline{M_n}$ = number-average molecular weight (g mol^{-1}), $\overline{M_n} = 132 + 156\ \overline{DP_n}$
$\overline{M_w}$ = weight-average molecular weight (g mol^{-1})
I_p = polydispersity index, $I_p = \overline{M_w}/\overline{M_n}$
[b] ρ = monomer conversion (from end reaction residue weight)
[c] Calculated $\overline{DP_n}$ from conversion results = $\rho\ [M]_0/[I]_0$
[d] Molar percentage of each species of degree of polymerization i

Table 3 P35eH and P36eH PVA macromonomer characteristics (from ^1H n.m.r. results), after precipitation of TBA

	P35eH	P36eH
$\overline{DP}_n$	6–7	8–9
Average molecular weight ($189 + 44\ \overline{DP}_n$)	500	560
Residual -O–CH_3 (mol%)	0	54
Molar percentage of macromonomer	37	33
Weight percentage of macromonomer	53	51

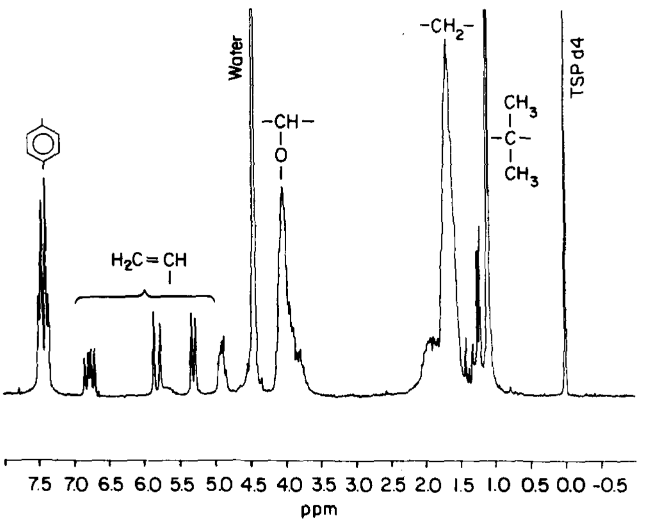


Figure 7 The 200 MHz ^1H n.m.r. spectrum of a styryl-PVA macromonomer with a carboxyl end-group: P35eH (in D_2O solution with TSP-d_4 as internal standard; temperature 330 K)

(carbonyl), 140.35 (aromatic C_1), 136.65 (–CH=), 136.5 (aromatic C_4), 127.9–125.25 (aromatic C_2, C_6–C_3, C_5), 113.5 (=CH_2), 79 (–CH–O–), 51.75 (–O–CH_3), 49.05 (–C–$(CH_3)_2$), 21.64–19.15 (–$(CH_3)_2$), –0.08 (–Si$(CH_3)_3$).

Hydrolysis of silyl ether side-groups (compounds P29H, P11eH, P35eH and P36eH). The desilylation reaction was carried out for P11e, P35e and P36e ester-ended macromonomers with 1.5–2 equivalents for tetrabutylammonium fluoride (TBAF) in THF for about 20 h at room temperature. After reaction, the crude medium was evaporated and the brown viscous residue was analysed by ^1H n.m.r. spectroscopy in deuterated acetone: disappearance of t-butyldimethylsilyl protons confirmed the reaction efficiency.

The residue was then solubilized in water: for low-molecular-weight macromonomers, an insoluble part appeared (degree of polymerization lower than 3), and only the soluble part was purified. TBA elimination was first performed by precipitation of this organic salt at low temperature (near 0°C) and filtration. This step led to a mixture of about 50 wt% of PVA macromonomer and TBA salt, which was soluble in water and polar organic solvents such as THF or acetone. At this step, the ester function appeared partially or totally hydrolysed as shown in ^1H and ^{13}C n.m.r. spectra by the disappearance of –O–CH_3 protons and carbon peaks and the shift of ^{13}C carbonyl resonance from 177.5 ppm for ester to 183.5 ppm for carboxylate. Further purification was performed on a silica gel column with a mixture of acetone and water (50 vol%) as eluant. Final mixtures contained more than 80 wt% macromonomer, but complete purification has not been reached. At this step, purified macromonomer was only soluble in water, so further purification could be improved by washing the precipitate with acetone.

PVA macromonomers were characterized by ^1H and ^{13}C n.m.r. analysis in deuterium oxide solutions and by g.p.c. (in THF eluant, before purification on the column) (see *Table 3* and *Figures 7*, *8* and *9*).

Desilylation of the ester model monomer (P29 gives P29H) was performed by reaction for 1 h with TBAF followed by water/ethyl ether extraction. The reaction product, named methyl 2,2-dimethyl-3-hydroxy-3-(4′-

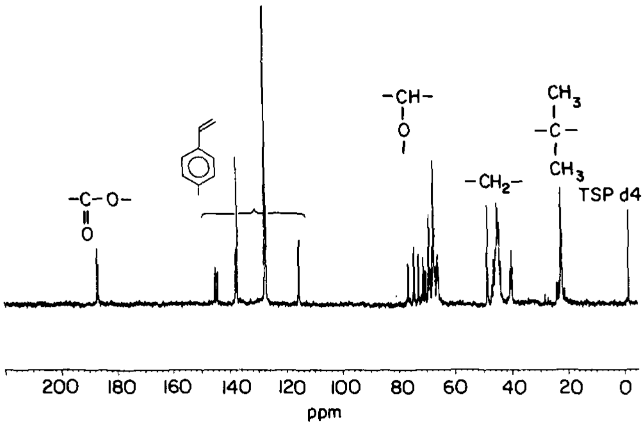


Figure 8 The 50.3 MHz ^{13}C n.m.r. of a styryl-PVA macromonomer with a carboxylic end-group: P35eH (in D_2O solution with TSP-d_4 as internal standard; temperature 330 K)

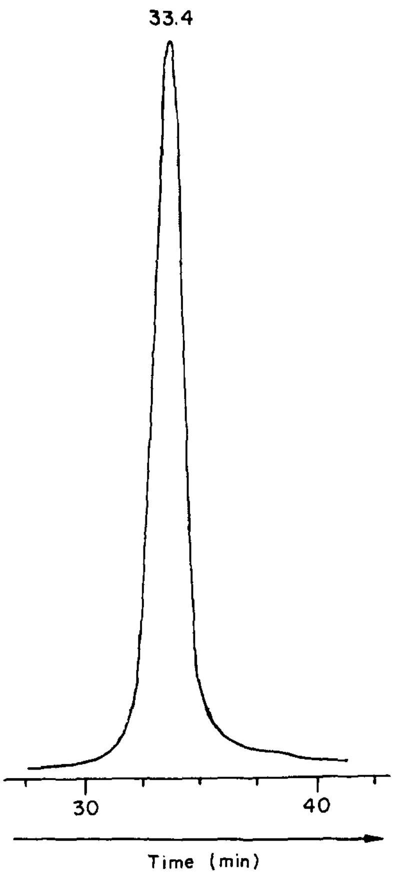
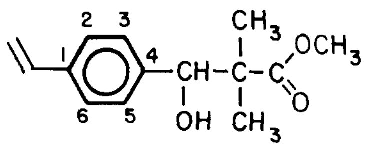


Figure 9 G.p.c. chromatogram of a styryl-PVA macromonomer with a carboxylic end-group: P35eH (before column purification)

vinylphenyl)propanoate, has the formula:



It looked like a white powder with a melting point around 53.5–54.0°C. This compound has been analysed by ^1H and ^{13}C n.m.r. with the following main features. ^1H n.m.r. (acetone-d_6): δ (ppm) = 7.41–7.305 (second-order spectra; 4 H, aromatic spectra), 6.740, 5.785, 5.205 (3 H, vinylic protons), 4.795 (d; $J = 4.35$; 1 H; -CH-O-), 4.525 (d; $J = 4.45$; 1 H), 4.525 (d; $J = 4.45$; 1 H; -OH), 3.635 (s; 3 H; $-O-CH_3$), 1.150–1.015 (s; 3 H; $-C(CH_3)_2$). ^{13}C n.m.r. (acetone-d_6): δ (ppm) = 177.35 (carbonyl), 142.3 (aromatic C_1), 137.55 (-CH=), 137.45 (aromatic C_4), 128.85–126.1 (C_2, C_6–C_3, C_5), 113.8 ($=CH_2$), 78.2 (-CH-O-), 51.85 ($-O-CH_3$), 48.95 ($-C(CH_3)_2$), 21.95–20.2 ($-C(CH_3)_2$).

RESULTS AND DISCUSSION

Owing to the nature of the polymerization process, the control of macromonomer molecular weight requires complete monomer conversion (ρ) and also total initiator efficiency. In this case, final average degree of polymerization equals $[M]_0/[I]_0$; but, when ρ is lower than 1, $\overline{DP}_n = \rho\ [M]_0/[I]_0$.

Experimental results showed that *p*-formylstyrene is a quite efficient initiator since it is completely depleted at the end of polymerization. On the contrary, monomer conversion has not always been complete: in the case of P35, P7 and P10 experiments, it was in the range 72–78%, which could not be explained by experimental conditions but perhaps by a too short duration of the reaction.

Experimental degrees of polymerization as determined by u.v. analysis and ^1H n.m.r. spectroscopy (see *Table 2*) were in good agreement with calculated values deduced from conversion and initial monomer-to-initiator ratio. On the contrary, g.p.c. results were quite different, which suggests that calibration with polystyrene standards is not suitable for the molecular-weight determination of silylated poly(vinyl alcohol) compounds. The polydispersity index, as calculated from g.p.c. results, was in most cases lower than 1.3, which is indicative of a narrow distribution, but was slightly higher than calculated values from Poisson statistics.

From experiments where $[M]_0/[I]_0$ ratio equalled 0.82 and 1.58, the final distribution was determined (see *Tables 1* and *2*) and confirmed the high reactivity of *p*-formylstyrene initiator: monomer addition onto this compound seems to be much more rapid than addition onto the growing chain aldehyde function. These results can assert that aromatic aldehyde functions are more reactive than aliphatic ones and also that the initiation step is much more rapid than the propagation step ($k_i \gg k_p$).

Low-molecular-weight macromonomers ($n < 5$) were found to be quite unstable when maintained in the reaction medium solution. The clear, colourless solution turned red or brown. The aldehyde function disappeared as revealed by ^1H n.m.r. spectroscopy; very high-molecular-weight species were observed by g.p.c. analysis, which could lead to an insoluble gel after a few days. This problem was less significant for higher-molecular-weight macromonomer solutions, perhaps because molar aldehyde concentration was much lower.

Purified and dried macromonomers were quite stable but, when desilylation with TBAF was performed without protecting the aldehyde function, very few PVA macromonomer molecules were recovered and the end-function had disappeared.

Such macromonomer instability was ascribed to aldol condensation, which is well known for an aliphatic aldehyde especially when bound to a methylene group. That explains why it was necessary to get rid of this type of end-group, whose sensitivity to side-reactions is too great.

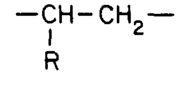
Reaction with a silylketene acetal in the presence of zinc bromide as a catalyst is an efficient way to achieve this transformation: first, reaction is instantaneous and complete; secondly, it leads to a more stable function; and thirdly, since ester is easily hydrolysed into an acid, end-group functionality is maintained.

p-Formylstyrene reaction with 1-methoxy-2-methyl-1-trimethylsiloxypropene was a good model not only to study reaction conditions but also to prepare a monomer representing a model macromonomer with a degree of polymerization equal to zero. Reaction with the macromonomer was performed under the same conditions as aldol GTP, but direct addition of the silylketene acetal at the end of polymerization did not appear to be a very reliable method because premature addition causes termination by deactivation of growing chains. So aldehyde-ended macromonomers were first isolated and analysed just at the end of polymerization; thereafter they were resolubilized in dichloromethane and reaction with silylketene acetal was then performed. Reaction leads to a stable compound that seemed to be insensitive to side-reactions, especially in the presence of tetrabutylammonium fluoride.

Desilylation with this compound was quite efficient and recovery of the macromonomer was quantitative. Shorter PVA macromonomers ($DP < 3$) were not soluble in water and thus were not studied because they are not very interesting for further applications. Water-soluble macromonomers were purified from TBA using different methods, but, in most cases, complete purification could not be reached easily. Those purification steps lead to a fractionation of the macromonomer and reduction of polymer chain dispersity as illustrated on a g.p.c. chromatogram (*Figure 9*); such an analysis was indeed possible when macromonomer was recovered with enough TBA to be still soluble in polar organic solvents such as THF.

Nevertheless TBA did not affect the characterization, especially by ^{13}C n.m.r., which allowed investigation of the PVA chain tacticity as was done for the highest-molecular-weight macromonomer (P11eH).

Actually, ^{13}C n.m.r. is indeed a powerful and suitable technique for studying vinylic homopolymer configuration[16], with a general formula such as:



$$\overset{\alpha}{-\underset{\displaystyle R}{\underset{|}{C}H}}-\overset{\beta}{CH_2}-$$

In the following, because carbons along such a chain are not truly asymmetric, Bovey's relative notation will

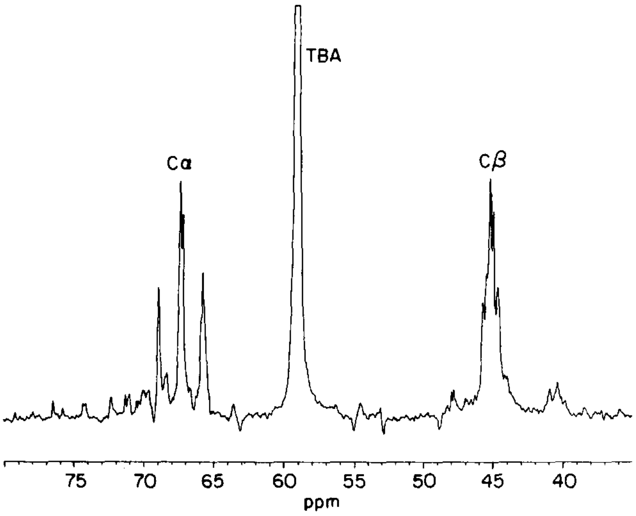


Figure 10 The 50.3 MHz ^{13}C n.m.r. spectrum of a styryl-PVA macromonomer with a carboxylic end-group: P11eH (in D_2O solution with TSP-d_4 as internal standard). Expanded C_α and C_β region, from 35 to 80 ppm

Table 4 50.3 MHz ^{13}C n.m.r. study of styryl-PVA macromonomer, P11eH (in D_2O solution): C_α chemical shifts and peak integration

δ (ppm)	Triad nature	Normalized peak area
68.70	mm	$I = 0.223$
67.25	$mr + rm$	$H = 0.482$
65.70	rr	$S = 0.295$

be used[17]: m for meso dyads and r for racemic ones. When monomer addition obeys Bernoullian statistics, only one parameter is useful to describe respective proportions of dyads and triads, P_m or P_r representing respective dyad existence probability:

Dyad proportions

$$m = P_m$$

$$r = P_r$$

Triad proportions

$$I = mm = P_m^2 \qquad \text{(isotactic)}$$

$$H = mr + rm = 2P_mP_r = 2P_m(1 - P_m) \qquad \text{(heterotactic)}$$

$$S = rr = P_r^2 = (1 - P_m)^2 \qquad \text{(syndiotactic)}$$

The C_β ^{13}C n.m.r. spectrum can provide information about dyads, when two peaks are visible; whereas the C_α ^{13}C n.m.r. spectrum gives information on triads, when three peaks are visible.

Silylated P11 macromonomer ($R = -O-Si-Me_2Bu^t$) was analysed by ^{13}C n.m.r. in $CDCl_3$ solvent: C_α and C_β carbons exhibit respectively only one large resonance peak so their chemical shifts are not influenced by chain tacticity. Desilylated P11eH macromonomer ($R = -OH$) was also analysed by ^{13}C n.m.r. in D_2O solvent: C_β exhibits six peaks in the region 43–47 ppm, characteristic of tetrad influence (*Figure 10*) but the peaks are not well separated enough to allow quantitative analysis. On the contrary, C_α exhibits three peaks in the region 65–70 ppm (*Figure 10*), individual integration of which can be easily performed (*Table 4*). Results allow the calculation of m (meso dyad proportion) and r (racemic dyad proportion) as follows:

$$m = I + H/2 = 0.464 = P_m$$

$$r = S + H/2 = 0.536 = P_r$$

Considering that propagation obeys Bernoullian statistics, the respective triad proportions can be calculated according to the formulae:

$$mm = P_m^2 = 0.215$$

$$mr + rm = 2P_mP_r = 0.497$$

$$rr = P_r^2 = 0.287$$

Those values do not differ drastically from experimental results (*Table 4*), and therefore monomer addition is actually mainly controlled by Bernoullian statistics, with, however, a tendency to block formation: $I > P_m^2$ and $S > P_r^2$. Nevertheless, propagation is not perfectly random (case where $P_m = P_r = 0.5$; $mm = 0.25$, $mr + rm = 0.5$ and $rr = 0.25$): $P_r = 0.536$ is slightly higher than $P_m = 0.464$, which indicates that the macromonomer poly(vinyl alcohol) chain is rather atactic with a tendency to syndiotacticity. This is quite similar to the case of a PVA sample (from radical-initiated poly(vinyl acetate), >98.5% hydrolysed) where $P_r = 0.531$ and $P_m = 0.469$[18].

CONCLUSIONS

Aldol group transfer polymerization of t-butyldimethylsilyl vinyl ether initiated by an unsaturated compound, *p*-formylstyrene, and catalysed by zinc bromide allowed the synthesis of well characterized styryl-silylated poly(vinyl alcohol) macromonomers bearing an aldehyde end-function. Various macromonomers with average degrees of polymerization ranging from 1 to 28 were prepared and characterized according to different analytical methods such as ^{1}H and ^{13}C n.m.r., u.v. and g.p.c. Results showed that n.m.r. and u.v. analyses were quite reliable for the molecular-weight determination; on the contrary, g.p.c. was quite unsuitable since column calibration was carried out with polystyrene samples. When using low monomer-to-initiator ratios, polymerization experiments confirmed the higher reactivity of *p*-formylstyrene as compared to aliphatic aldehyde compounds resulting from monomer addition. Moreover, the aldehyde end-function appeared to be very sensitive to side-reactions especially aldol condensation. Therefore, to improve stability, it was reacted with a silylketene acetal compound, 1-methoxy-2-methyl-1-trimethylsiloxypropene, leading to an ester end-group. Afterwards, silyl ether side-groups were hydrolysed with tetrabutylammonium fluoride in order to obtain hydrophilic styryl-poly(vinyl alcohol) macromonomers: the reaction was quite efficient, but purification was rather difficult and often incomplete. PVA chain tacticity has been studied by ^{13}C n.m.r.: it was found to be atactic, with a slight tendency towards syndiotacticity.

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