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SYNTHESIS OF POLY(ETHYLENE OXIDE) MACROINITIATORS WITH A VIEW TO THE PREPARATION OF BLOCK COPOLYMERS BY RADICAL POLYMERIZATION

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Abstract—Poly(ethylene oxide) radical macroinitiators with built-in benzopinacolate groups were prepared by two different methods: the first one involves a hydrosilylation reaction between α, ω-difunctional polylethylene oxide (PEO) precursors and a difunctional benzopinacolate; due to the presence of a spacer group on the benzopinacolate compound the resulting segmented PEO is rather close to a block-copolymer. The second method is based on the general duplication reaction of benzophenone groups fitted at both chain ends of a PEO precursor.

INTRODUCTION

After the discovery of the stable triphenylmethyl radical [1], several investigations were devoted to substituted tetra- and hexaphenyl ethanes and their radical dissociation [2–11]. It was established that tetraphenylethanes and related compounds can undergo homolytic cleavage of the central ethane bond. Until quite recently the radical species formed by such strongly hindered ethanes were supposed to be too stable to initiate radical polymerization of vinyl monomers and only a few of them have attracted the interest of polymer chemists. In fact the characteristics of these products are rather different from those of traditional radical initiators such as azobisisobutyronitrile, benzoyl peroxide and many others.

Tetraphenylethanes exhibit rapid dissociation but delocalization of the single electron within the aryl system of the diphenyl radicals is considerable. Thus the primary radicals formed are relatively stable resulting in slow initiation of radical polymerization. The simultaneous presence of growing oligomeric radical species and the primary radicals in the reaction medium is a drawback in the use of these compounds; on the other hand the stability of the latter could also be an advantage in practical applications. For instance 1,1,2,2-tetraphenyldicyanoethane (NC—CPh_2—CPh_2—CN) is able to initiate methyl methacrylate polymerization. Tetraphenylethanes with other substituents (OCH_3, OPh,) have been used as polymerization initiators for styrene or methyl methacrylate [12, 13].

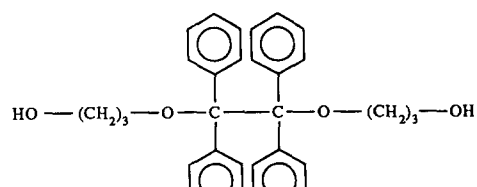
A tetraphenylethane group can also be fixed to a polymer chain, either as an end-group or as a hinge in a segmented chain. Like the above compounds, these species can act as macroinitiators for the radical polymerization of vinyl monomers and can be incorporated as blocks in the resulting copolymer. Of course the first case is not favourable since half of the radicals formed do not carry the polymer chain and so generate only homopolymer.

The present investigation deals with the synthesis of poly(ethylene oxide) (PEO) macroinitiators by two methods with a view to incorporating a PEO chain in a copolymer or in a polymer network by radical polymerization.

Preliminary efforts to prepare these compounds showed that most of the straightforward syntheses do not lead to the expected macroinitiators, generally as a consequence of predominating side reactions which probably involve the PEO chain. Thus the deactivation of a "living" PEO (alcoholate) with 1,2-dichlorotetraphenylethane did not produce the expected chain coupling which would yield a PEO with twice the initial molecular weight.

A possible approach to link two PEO chains to a tetraphenylethane was the ring-opening reaction of tetraphenylethylene oxide with PEO potassium alcoholate and to initiate the polymerization of ethylene oxide with the resulting PEO tetraphenylethylene oxanion. This method also failed, since the latter was not formed. The steric hindrance due to the phenyl groups of the oxirane compound could explain its low reactivity [14–16].

Attempts to obtain tetraphenylethylene dialcoholates by the attack of benzopinacolate with an organopotassium reagent were unsuccessful because of the scission of the tetraphenylethylene bond, a behaviour which can be explained by investigations reported by Hirota [17]. An alternative procedure to prepare a dioxanion was based on the duplication reaction of diphenylketone with potassium. To reduce the interaction between oxanions and the tetraphenylethane bond, a spacer group was introduced (compound A).



(compound A)

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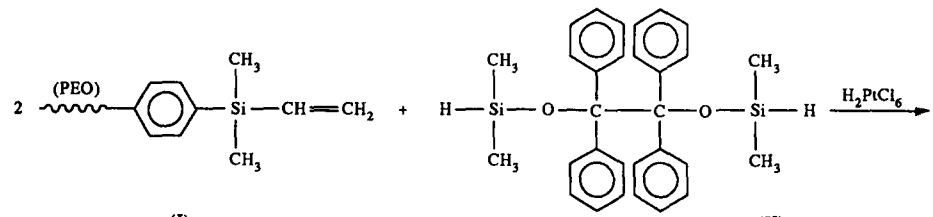
This product was obtained but in very low yield. Other methods used to prepare type A compounds, based on coupling reactions reported in the literature for diacetonitrile [18, 19], also failed. The most significant approaches summarized above did not lead to the synthesis of the expected PEO macroinitiators. They clearly indicate that the problems originate mainly in the marked weakness of the tetraphenyl-ethane bond, still pronounced in the presence of the PEO chain. They also show the difficulty in forming such a bond by a coupling reaction of diphenyl reagents. Other less direct methods are required to prepare these macroinitiators.

SYNTHESIS OF PEO MACROINITIATORS BASED ON THE HYDROSILYLATION REACTION

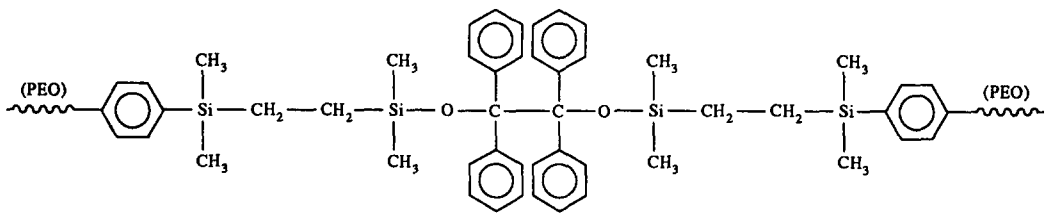
The addition reaction of a silane function on an unsaturated bond has been used in many synthetic purposes. It was applied also to the particular case of copolymers with PEO blocks [20] prepared by the "condensation" of functional precursor poly-mers. The synthesis of a PEO macroinitiator by hydrosilylation requires a precursor polymer with either vinyl or silane end-groups and benzopinacolates fitted with the corresponding antagonist functions.

PEO with unsaturated functional end-groups can easily be prepared by anionic deactivation of "living" oxanionic chain-ends with a suitable electrophile. On the contrary, it is rather difficult to fix silane functions at PEO chain-ends. The preparation of benzopinacolates is rather general and offers the possibility to synthesize dimethylvinylsilane as dimethylsilane derivatives [21].

The hydrosilylation coupling reaction between α-functional PEO(I) and pinacolate (II) according to the scheme below should produce a segmented PEO of approximately twice the initial molecular weight.



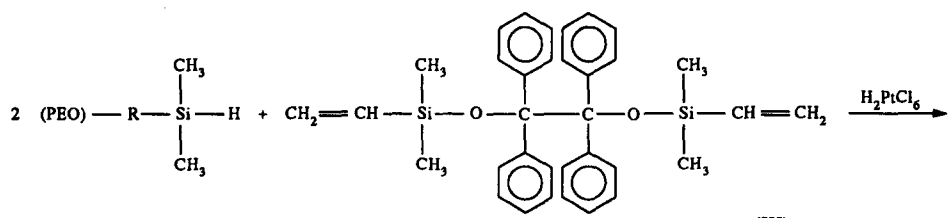
(I) (II)



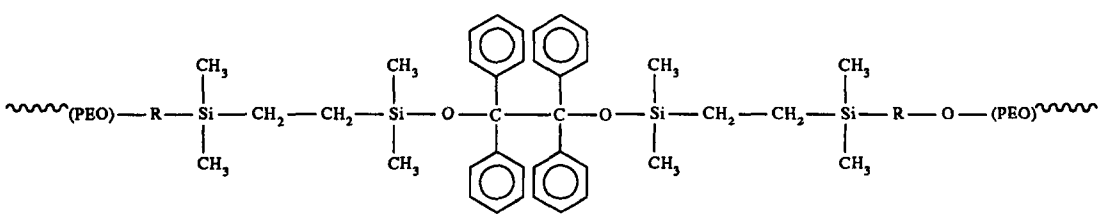
This type of synthesis, successfully applied to the reaction between polydimethylsiloxanes with endstanding dimethylsilane functions and a pinacolate with dimethylsilvinylic groups [21], failed completely in the present case. No hydrosilylation coupling was observed, but degradation of the benzopinacolate occurred with formation of benzophenone, the presence of which was clearly demonstrated by thin-layer chromatography.

This result shows that the proximity between the central linkage of the benzopinacol and the dimethylsilane function represents a major difficulty in these syntheses. In addition, the PEO chain also seems to play a role, due to a possible complexing activity.

A logical approach to overcome this problem related to the neighbourhood of the dimethylsilane function and the tetraphenylethane linkage would be the symmetrical procedure as indicated below:

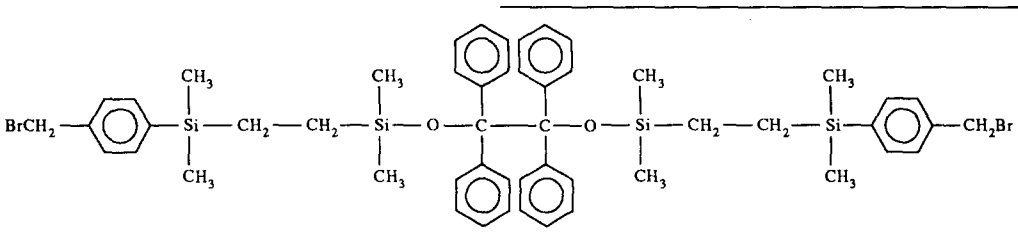


(III)



The disilvinylic benzopinacolate (**III**) can easily be prepared according to the general reductive duplication method (*cf* Experimental Procedures) [21, 22]. On the other hand, to attach a dimethylsilane function directly to a PEO chain-end was extremely difficult because of side reactions resulting in chain coupling, without introduction of the tetraphenylethane group.

An alternative way seemed to be the use of the dibromomethyl benzopinacolate (**IV**) (*cf* Experimental Procedures) usable as a coupling agent for PEO potassium alcoholate:



(IV)

However the yield of the coupling reaction between alcoholate chain-ends and compound **IV** was very poor, since the resulting polymer contained only a small fraction of aromatic constituent, probably as a consequence of a predominant side reaction involving the Si—O—C linkage.

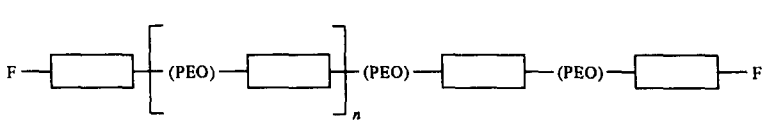
In spite of the considerable fragility of the benzopinacolic derivatives, hydrosilylation syntheses are possible but it must be pointed out that, in the examples reported in the literature, vinyl and not silane functions are located on the benzopinacolate molecule [21].

Since it proved to be practically impossible to attach a silane function at PEO chain-end, we had to link it to the benzopinacol but we decided to introduce a spacer group between the benzopinacolic and silane functions. For this purpose, we prepared a compound in which these functions are separated by a dimethylphenylsilyl unit (**V**) (*cf* Experimental Procedures). The hydrosilylation reaction between **V** and α,ω-dimethylsilvinylic PEO ($\bar{M}_n = 2000$ g/mol) was carried out in toluene solution at 70° as shown overleaf.

The expected "condensation reaction" between pinacolate and functional PEO occurs and a segmented PEO is obtained.

When heated at *ca* 80° in toluene, a solution of this polymer shows the characteristic red colour of the macroradical species formed by the thermal dissociation of the tetraphenylethylene segment.

In fact, rather than a segmented polymer, the resulting product is a block copolymer, since the intermediate segment, which contains the pinacolate unit, represents a molecular weight of the same order of magnitude as that of the PEO precursor chain. The following scheme represents such a copolymer:

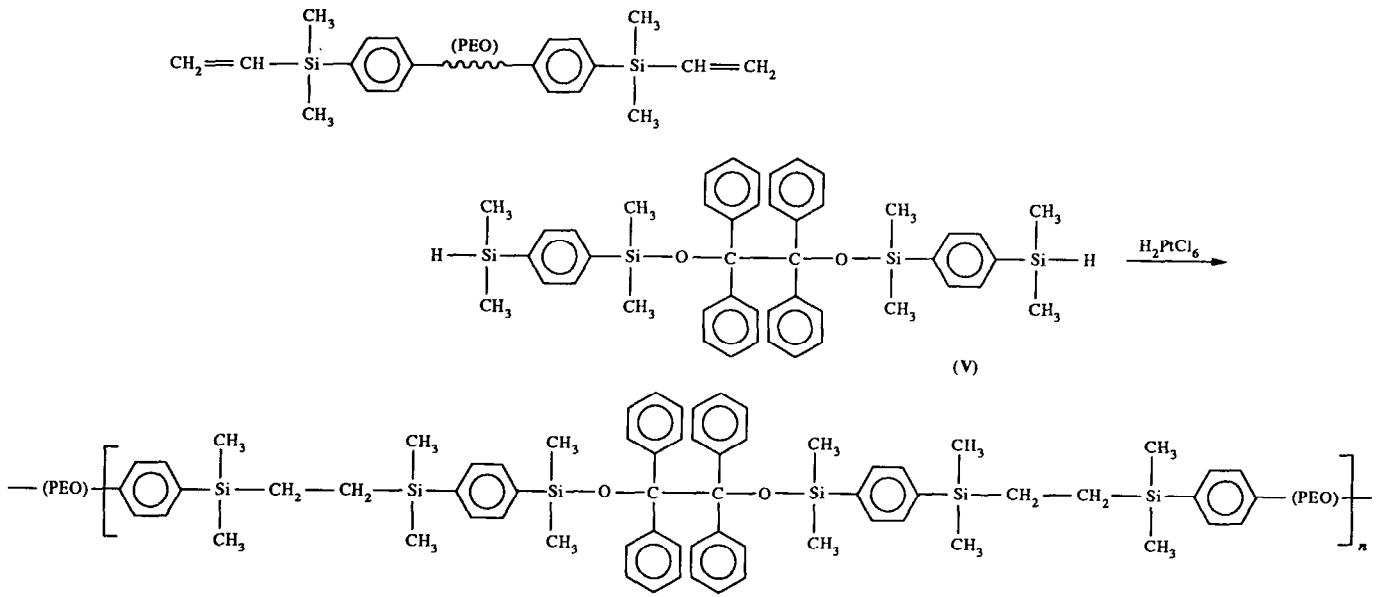


The rectangles represent the organosilicic blocks with tetraphenylethylene units and F indicates unreacted silane or vinylsilane functions.

The present synthesis, based on hydrosilation, is comparable to a condensation reaction where stoichiometric conditions are essential. It requires a good knowledge of the functionality of the PEO precursor and high purity of the benzopinacolate. A second factor to be considered is the reaction temperature. A compromise has to be made between the benzopinacolate dissociation temperature and the temperature required for the hydrosilylation.

To establish the optimal experimental conditions, we carried out a first series of hydrosilylations at 70° in toluene solution at various molar ratios. The results (Table 1) show that the maximal number of blocks is obtained at the 1/1 stoichiometry, an indication that the number of functional groups in the starting compounds is close to the experimentally determined value. A second series of experiments was performed under these stoichiometric conditions but at 100, 80, 70 and 40°.

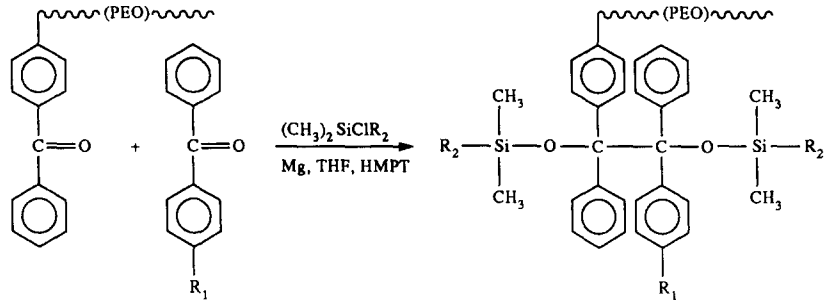
At 100° the hydrosilylation takes place but is accompanied by thermal cleavage of the tetraphenylethylene bond, as indicated by the slight red colour of the solution. Though this dissociation is reversible, it is preferable to avoid it, thus excluding any possible side reaction involving the cetyl radicals. On the other hand, at 40° no significant reaction occurs; after 3 hr, only a very slight increase of the average molecular weight is observed. Satisfactory results were obtained at 80 and 70°. At these temperatures, the hydrosilylation is rapid and the contribution of thermal cleavage can be neglected. A PEO macroinitiator containing several tetraphenylethylene groups can thus be prepared (5–6 blocks). A typical example of a SEC curve of such samples is shown in Fig. 1. One drawback of the compounds obtained and of the block copolymers resulting from radical polymerization initiated by these macroinitiators is the presence of hydrolysable Si—O—C links in the polymer chain. In a hydrophobic copolymer, these groups are protected and the probability of chain scission by hydrolysis is low but, in the present case, the environment of hydrophilic PEO chains could favour such degradation.



Scheme V

SYNTHESIS OF PEO MACROINITIATORS BY THE REDUCTIVE DUPLICATION REACTION OF BENZOPHENONE END-GROUPS

In the case where a possible hydrolysis represents a serious drawback, the previous synthesis is not adequate. Therefore we have developed a method based on the general reductive duplication reaction used for the synthesis of bis trialkylbenzopinacolates [22–24], where the Si—O—C bond is not situated in the main chain but is part of a pendant group. The principle of this method is shown in the scheme:

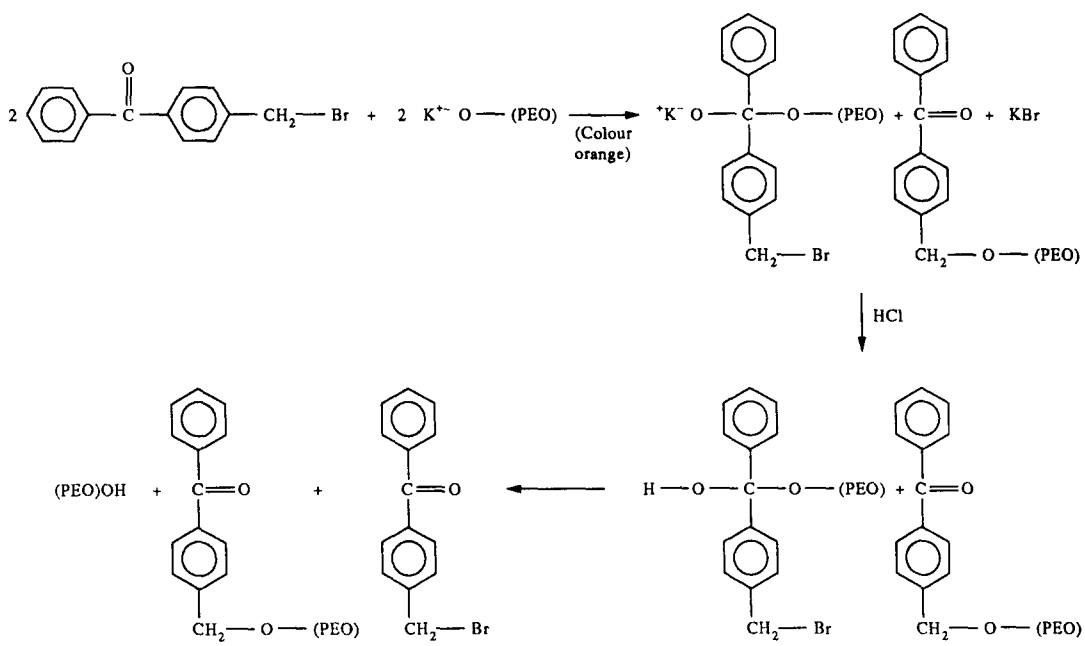


R_1 = H, CH_3, (PEO)

R_2 = CH_3, CH_2 — $CH_2Si(CH_3)_2Cl$

Of course, it still requires the preparation of the functional PEO but it avoids the preliminary synthesis of benzopinacolate. Indeed, the macroinitiator and the benzopinacolate are formed in the same reaction step. Another advantage is that the benzopinacolate is directly fixed to the PEO chain. A consequence of the absence of a spacer group is the higher PEO content in the macroinitiator.

Direct functionalization of PEO by reacting *p*-bromomethyl benzophenone with PEO potassium alcoholate was found to be an unsatisfactory method. Functionalization yields below 50% were obtained, as a consequence of a side reaction involving the highly conjugated carbonyl group according to the scheme:



To avoid this reaction, we protected the carbonyl function by acetalizing before reacting the bromomethyl compound with the above alcoholate (*cf* Experimental Procedures). The expected PEO is then obtained in very good yield by hydrolysis of the acetal function.

Table 2 shows the characteristics of difunctional PEO prepared by this method. These samples were used in subsequent synthesis of macroinitiators by "pinacolization".

Preliminary experiments were carried out on a monofunctional PEO with molecular weight $\bar{M}_n = 2000$ g/mol and showed that the pinacolization is hindered by the bulkiness of the polymer chain, the

Table 1. Synthesis of PEO macroinitiators by hydrosilylation

Experimental conditions				Results		
$\bar{M}_n^{PEO}$	r	T(°C)	Time (hr)	$\bar{M}_n^{COP}$	$\bar{M}_w^{COP}/\bar{M}_n^{COP}$	n
1400	1.00	70	3	3000	1.6	2.9
1400	1.05	70	3	2300	1.5	2.2
1400	1.20	70	3	1500	1.5	1.4
1400	1.00	100	2	3000	1.8	2.9
1900	1.00	80	3	7000	2.1	5.4
3750	1.00	80	3	8600	1.25	3.8
1400	1.00	40	3	No significant reaction		

Number-average molecular weights determined by SEC (g/mol): $\bar{M}_n^{PEO}$ = difunctional PEO precursor, $\bar{M}_n^{COP}$ = macroinitiator, r = [—SiH]/[—SiCH=CH_2].
Initial PEO precursor concentration: 0.125 mol/l; n, average number of blocks $[\bar{M}_n^{COP}/(\bar{M}_n^{PEO} + 750)] \times 2$.
Solvent: toluene.

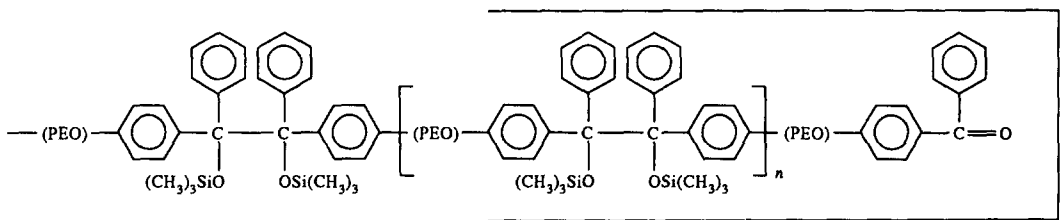
Table 2. Characteristics of PEO samples fitted with benzophenone end-groups

$\bar{M}_n^{PEO}$[a]	Functionalization yield % (u.v.)	$\bar{M}_n^{PEOF}$[b]
1900	95.0	2500
1500	93.5	1600
1500	96.0	—
1000	90.0	1200
1000	84.7	—
3400	88.3	3000

[a] Initial number-average molecular weight (g/mol).
[b] Number-average molecular weight of functionalized PEO determined by SEC (g/mol).

quite low concentration of functional groups and the heterogeneity of the reaction medium. Therefore, only difunctional polymers with low molecular weight were used (Fig. 2). It is evident that, even when the above mentioned factors are taken into account, the chain extension resulting from the pinacolization is rather limited, since the increase of polymer chain length implies an increase of its bulkiness and a decrease of the concentration of benzophenone groups.

The expected segmented PEO (R_1 = PEO and $R_2 = CH_3$) corresponds to the following structure:



Under the conditions used for the pinacolization, as described in Experimental Procedures, a segmented polymer with an average of four precursor chains is obtained. A characteristic SEC diagram of such a sample is shown in Fig. 2. However, this is the case only when the molecular weight of the PEO precursor does not exceed $\bar{M}_n$ = 1500 g/mol. Figure 3 shows the SEC chromatogram of a segmented polymer prepared with a higher molecular weight PEO precursor: only a small fraction of the polymer has reacted (20%) yielding some polymer with twice the initial molecular weight, but no higher molecular weight species. We know that, under comparable conditions, transformation of micromolecular benzophenone is almost complete but is accompanied by side reactions. In the present case, it is difficult to conclude whether the pinacolization is very incomplete or

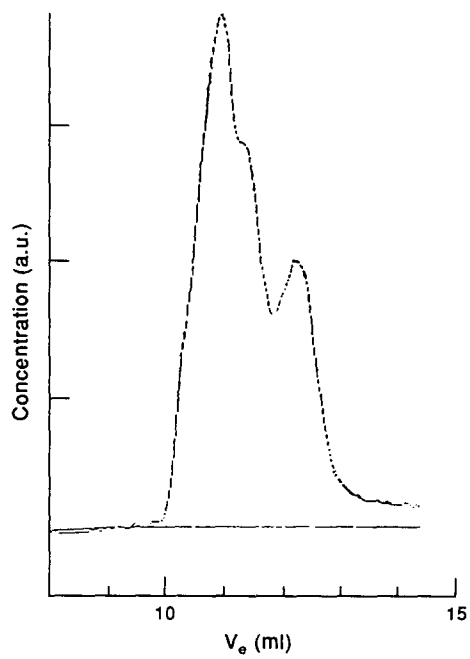


Fig. 1. SEC chromatogram of a PEO macroinitiator prepared according to the hydrosilylation method. Difunctional PEO precursor: $\bar{M}_n$ = 1400 g/mol.

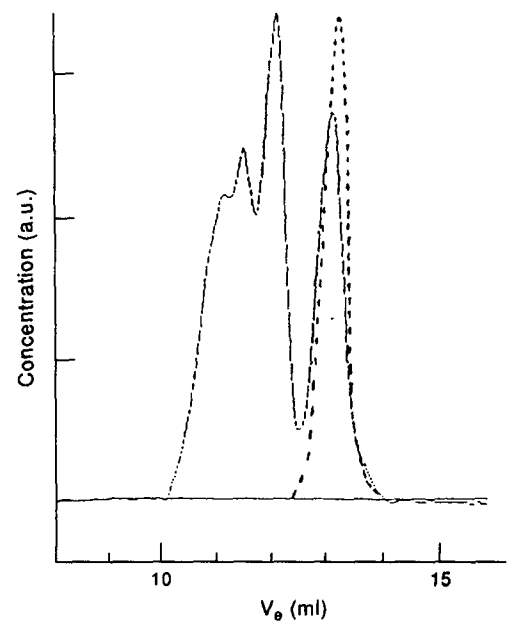


Fig. 2. SEC chromatogram of a PEO macroinitiator prepared by the pinacolization reaction of a difunctional PEO precursor with molecular weight $\bar{M}_n$ = 1400 g/mol.

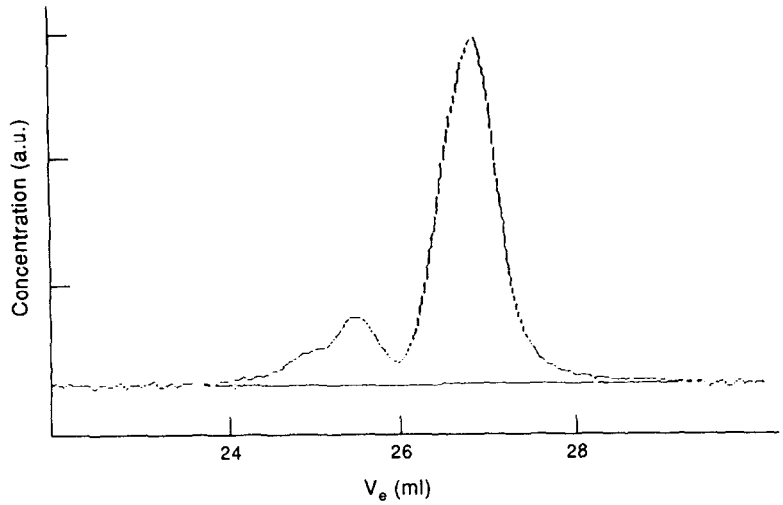


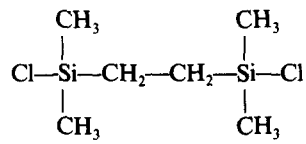
Fig. 3. SEC chromatogram of a PEO macroinitiator prepared by the pinacolization reaction of a difunctional precursor polymer with molecular weight $\bar{M}_n = 3800$ g/mol.

whether the side reactions predominate. Ultraviolet spectrometry does not allow determination of the reacted benzophenone since the benzopinacolate absorption is at the same wavelength.

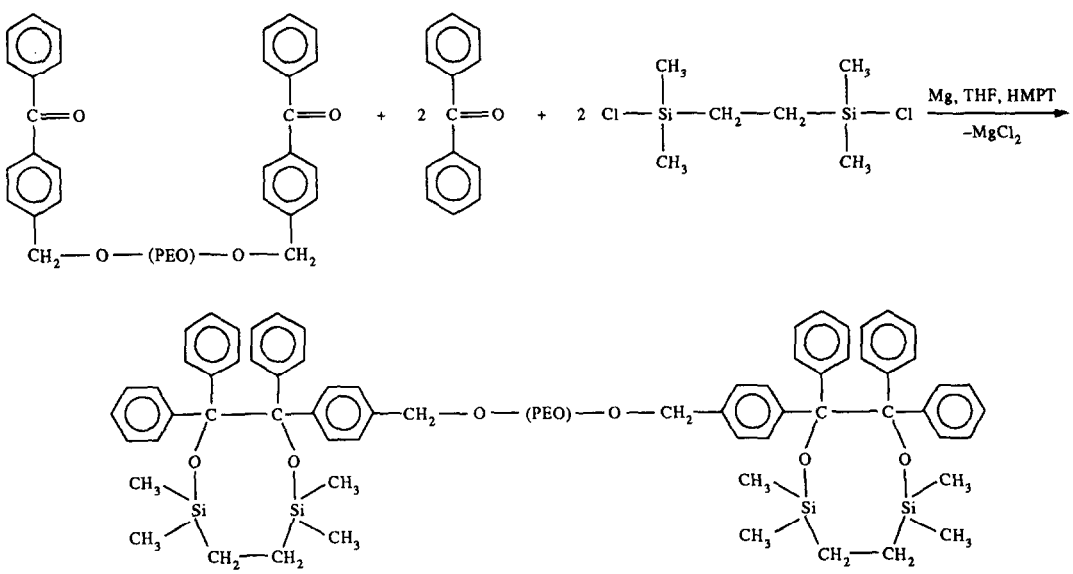
An extension of the pinacolization to higher molecular weight precursors was tried using blends of precursors with molecular weights $\bar{M}_n = 1400$ and 3800 g/mol but without substantial improvement.

We also reacted the functional PEO ($\bar{M}_n = 3800$ g/mol) in the presence of excess free benzophenone. As expected, PEO with benzopinacolate end-groups at both chain-ends is obtained in very high yield. However some coupled PEO is also formed.

A further alternative procedure applied to the pinacolization is the use of 1,4-dichloro-1,1,4,4-tetramethyldisilethylene:



instead of the previous chlorotrimethylsilane. This bifunctional reagent should produce the cyclic ether derivatives of benzopinacols or a short benzopinacolate block. To carry out this synthesis, we reacted a mixture of α,ω-difunctional PEO, benzophenone and 1,4-dichloro-1,1,4,4-tetramethyldisilylethylene according to the reaction below but using the molar ratio 1–10–6 in order to reduce the chance of intramolecular reaction or cyclization of the PEO.



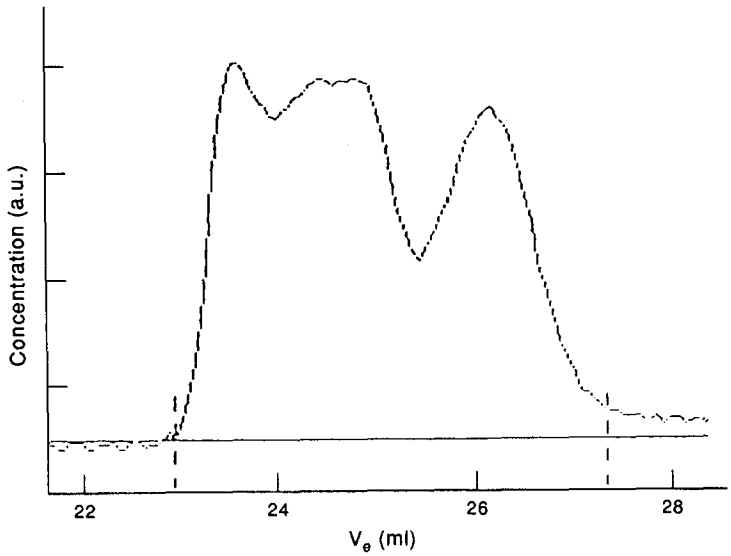
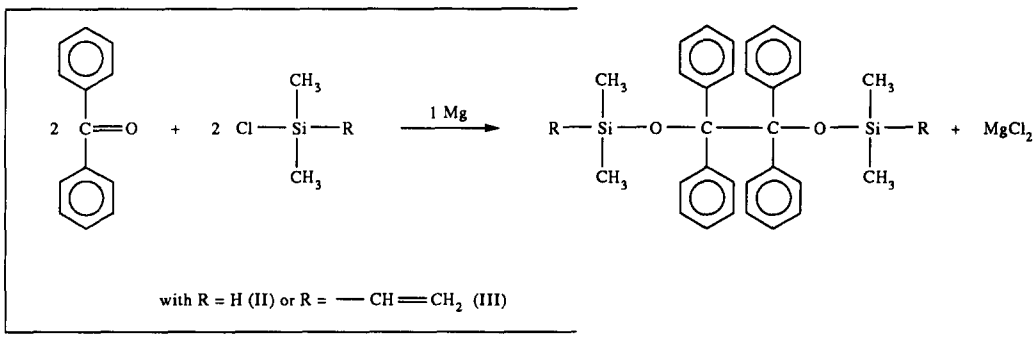


Fig. 4. SEC chromatogram of a PEO macroinitiator resulting from the pinacolization reaction of difunctional PEO with 1,4-dichloro-1,1,4,4-tetramethyldisilethylene.

The molecular weight of the resulting polymer is noticeably higher than that of the expected species shown in the scheme. Elemental analysis, ^{1}H-NMR spectroscopy and SEC characterization of this polymer indicate that it contains on average two to three precursor chains and four benzopinacolate groups, i.e. twice the expected number. Neither chain-end functionalization nor chain extension by pinacolization can produce such a high benzopincolate content; consequently the above result must imply the presence of short pinacolate blocks. Formation of this type of pinacolate oligomer was observed in the reaction between benzophenone and the above dichloride in the absence of PEO. Thus one could expect that this method yields many different benzophenone-containing polymer species of a very large structural variety, viz. linear, branched, cyclic and even tridimensional. However, the absence of real gel formation and the low fraction PEO chains linked together indicate that the degree of branching of these species is rather low. Figure 4 shows a SEC diagram of such a complex macroinitiator prepared by this method.



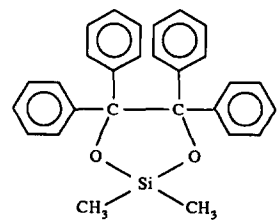
EXPERIMENTAL PROCEDURES

(a) Solvents and reagents

Tetrahydrofuran (THF) was distilled on Na wire, treated with sodium benzophenone and, after distillation from the organometallic solution, stored under argon. Hexamethylphosphoric triamide (HMPT): on treatment with Na wire, the characteristic blue solution of radical-anions was formed. The dry HMPT recovered by distillation was kept under argon. Toluene and benzene were distilled and stored on sodium wire. Chlorotrimethylsilane (Aldrich) was distilled on molecular sieve and collected in a burette. 1, 4-Dichloro-1, 1, 4, 4-tetramethyldisilethylene (Petrarch) and 4-methylbenzophenone (97%, Aldrich) were used without further purification. *1-Bromomethyl-4-dimethylvinylsilylbenzene* was prepared as described earlier [20]. Magnesium powder (Merck): particle size = 0.1–0.3 mm. Hydrosilylation catalyst: H_2PtCl_6, 6 H_2O (Prolabo) in isopropanol solution, concentration: 1.9×10^{-2} mol/l.

Bis dimethylsilylbenzopinacolate (II) and bis dimethylvinylsilylbenzopinacolate (III). Both compounds were prepared using the general reductive duplication reaction of benzophenones [22–24] according to the scheme:

Cazeau [23] established that the mole ratio magnesium/benzophenone must be $\leqslant 0.5$. The white crystalline compound **III** is obtained pure in high yield but only small amounts of **II** can be obtained because of a predominant cyclization yielding 2, 2-dimethyl-4, 5-tetraphenyl-1, 3-dioxa-2-silol [25]:



Bisdimethyl [dimethyl (4-bromomethyl) phenylsilyl] ethylene silyl benzopinacolate (IV). 5.34 g (0.010 mol) **III** and 4.81 g (0.021 mol) 1-bromomethyl-4-dimethylsilylbenzene were dissolved in 50 ml toluene and heated at 60°; 0.25 ml of the chloroplatinic acid solution were added (0.5×10^{-2} mol H_2PtCl_6 per mole silane). After 18 hr, the mixture was cooled to room temperature and washed with an aqueous $NaHCO_3$ solution. The organic layer was poured off and dried on Na_2SO_4. After elimination of the toluene under reduced pressure, the remaining product was dissolved in boiling ethanol. Phase separation on cooling yielded a supernatant alcoholic phase which was eliminated and 4.1 g of an oily compound. The latter was purified by liquid chromatography on silica gel using a 20/80 ratio benzene–cyclohexane mixture as elution agent: 1.4 g of pure compound **IV** were collected and stored at low temperature. The final yield was only 14%.

^{1}H-NMR (CCl_4) $\delta = -0.20$ (s; —O—Si CH_3) 0.15 (s; Ar—Si CH_3) 0.33 (m; —CH_2—CH_2) 4.21 (s; Ar—CH_2 Br) 7.05–7.28 (m; ArH).

Elemental anal. $C_{52}H_{64}Br_2O_2Si_4$ (993.3). Th %: C 62.9 H 6.5 Br 16.1 Si 11.3; exp %: C 64.3 H 7.0 Br 15.2 Si 11.0.

The discrepancy between theoretical and experimental values results from retained cyclohexane which cannot be eliminated. ^{1}H-NMR leads to a mole ratio cyclohexane/pinacolate close to 0.75. Taking into account the presence of this solvent, the calculated elemental composition of this product is: $C_{52}H_{64}Br_2O_2Si_4$, 0.75 C_6H_{12} (1.056, 4). Th %: C 64.2 H 7,0 Br 15,1 Si 10.6.

1-Chlorodimethylsilyl-4-dimethylsilylbenzene [26]. A mixture of 41.5 g (0.27 mol) carbon tetrachloride, 50.0 g (0.26 mol) 1, 4-bisdimethylsilylbenzene and 0.40 g (17×10^{-4} mol) benzoyl peroxide was heated at 80° for 18 hr. The volatile products were then removed under reduced pressure. A Widmer column fitted with an analyser was used to distil the remaining fraction: 19.4 g 1-chlorodimethyl-4-dimethylbenzene were recovered, corresponding to 33% yield; b.p. 52–54° (0.15 mbar).

^{1}H-NMR (CCl_4): $\delta = 0.25$; 0.30 (d; —SiH—CH_3) 0.58 (s; —SiCl—CH_3) 4.4 (m; —SiH—CH_3) 7.45 (ArH).

Bisdimethyl (4-dimethylsilyl) phenylsilyl benzopinacolate (V): A solution of 7.81 g (0.042 mol) benzophenone and 9.50 g (0.042 mol) 1-chlorodimethylsilyl-4-dimethylsilylbenzene in a mixture of 20 ml THF and 2 ml HMPT was reacted with 0.50 g (0.021 mol) Mg powder. After one night at 50°, the solvent was evaporated under reduced pressure leaving 18.2 g of a viscous oil.

Purification was achieved by liquid chromatography on silica gel in a benzene–heptane mixture (20/80), the elution agent. 6.0 g of the pure pinacolate were obtained. Yield: 38%.

^{1}H-NMR (CCl_4): $\delta = 0.04$ (s; —SiCH_3) 0.30; 0.38 (d; —SiH—CH_3) 4.38 (m; —SiH) 6.80–7.65 (m; ArH).

Elemental anal. $C_{46}H_{54}O_2Si_4$ (751.3). Th %: C 73.5 H 7.2 Si 15.0; exp %: C 73.7 H 7.1 Si 13.0.

4-Bromomethylbenzophenone was prepared as described in the literature [27, 28]. Yield: 25%.

^{1}H-NMR (CCl_4): $\delta = 4.39$ (s; CH_2Br) 7.2–7.8 (m; ArH).

Elemental anal. $C_{14}H_{11}BrO$ (275.2). Th %: C 61.1; H 4.0; Br 29.0; O 5.8; exp %: C 61.1; H 4.0; Br 29.1; O 5.9.

2-(4-Bromomethyl)phenyl-2-phenyl-1,3-dioxolane: A solution of 9.31 g (0.034 mol) 4-bromomethylbenzophenone, 2.3 g (0.37 mol) ethylenediol and 20 mg *p*-toluenesulphonic acid in 80 ml dry benzene was introduced into a flask equipped with a Dean Stark separator. The mixture was heated to its boiling temperature. The water produced in the reaction was eliminated by azeotropic distillation and collected in the separator siphon. After *ca* 60 hr, when no more water was formed, the mixture was cooled, washed with an aqueous $NaHCO_3$ solution and dried on Na_2SO_4. The reaction product was purified by liquid chromatography on silica gel using dichloromethane as elution solvent. Pure dioxolane (5.1 g) was obtained (yield: 45%).

^{1}H-NMR (CCl_4): $\delta = 3.9$ (s; —CH_2—O—) 4.3 (s; —CH_2Br) 7.25 (m; ArH).

Elemental anal. $C_{16}H_{15}BrO_2$(319.2). Th %: C 60.2; H 4.7; Br 25.0; O 10.0; exp %: C 60.3; H 4.7; Br 25.2; O 9.9.

(b) Functional poly(ethylene oxides)

Functionalization of PEO samples was achieved by reaction of the macromolecular potassium alcoholates with the appropriate bromomethyl compounds. The alcoholates were prepared by reacting hydroxyl end-groups of PEO with diphenylmethylpotassium. The experimental procedures are illustrated by the following examples:

α,ω-(4-Dimethylvinylsilyl) benzylpoly(ethylene oxide) precursors. In a glass reactor, under a slight argon pressure, 15 g (4.4×10^{-3} mol) PEO ($\bar{M}_n = 3400$ g/mol) were dissolved in 135 ml THF at 40°. To this solution was added dropwise a THF solution of diphenylmethyl potassium ([C] = 0.5 mol/l). After addition of 17.2 ml (8.6×10^{-3} mol) of the organometallic solution, orange colouring was observed, indicating that all the hydroxyl groups had been transformed to alcoholates, corresponding to 97.7% of the theoretical value, calculated on the molecular weight quoted by the supplier (Hoechst). 2.48 g (9.7×10^{-3} mol) 1-bromomethyl-4-dimethylvinyl silylbenzene in 5 ml THF were then introduced. After 14 hr, two drops of HCl were added to facilitate rapid precipitation of KBr. The solution of the modified PEO was filtered and precipitated in 1500 ml ether. The polymer was recovered in 97% yield. Molecular weight of the functionalized PEO(SEC): $\bar{M}_n = 3750$ g/mol.

^{1}H-NMR(CCl_4): $\delta = 0.37$(s; —SiCH_3) 3.55 (s; —O—CH_2—CH_2—) 4.5(s; Ar—CH_2—O—) 6.05 (m; —CH=CH_2) 7.38 (m; ArH).

Several PEO precursors used for the synthesis of macroinitiators by hydrosilylation were thus prepared.

α,ω-Dibenzophenone poly(ethylene oxide) precursors. The experimental conditions were the same as in the previous example. PEO dipotassium alcoholate was prepared with 18.8 g (5.5×10^{-3} mol) PEO ($\bar{M}_n = 3400$ g/mol) in 40 ml THF and reacted with 2.2 g (6.9×10^{-3} mol) 2-(4-bromomethyl)phenyl-2-phenyl-1, 3-dioxolane in THF solution. The reaction mixture was treated with HCl to regenerate the ketone and to facilitate KBr precipitation. After 48 hr the solution was filtered and the functional polymer recovered by precipitation in dry ether. The functionalization yield was determined by u.v. spectroscopy using, as absorption coefficient of the chromophoric group, the value determined for the model compound 4-ethoxymethylbenzophenone: $\epsilon_{(257\,nm)} = 19{,}200$ l/mol cm.

Functionalization yield (u.v.): 90%.

^{1}H-NMR (CCl_4): $\delta = 3.4$(s; —CH_2—O—) 4.5 (s; —CH_2—Ar) 7.5(m; ArH).

(c) Example of PEO macroinitiator synthesis by hydrosilylation

A solution was prepared with 3.28 g (4.4×10^{-3} mol) **V** and 8.07 g (4.4×10^{-3} mol) α,ω-(4-dimethylvinylsilyl)benzyl PEO ($\bar{M}_n = 1850$ g/mol) in 24 ml toluene. This mixture was heated to 80° before addition of 0.14 ml of the chloroplatinic acid solution in isopropanol corresponding to 3×10^{-4} mol catalyst per functional chain-end. After 3 hr reaction, the solution was cooled to room temperature and centrifuged; the polymer was precipitated in 800 ml heptane, recovered by decantation, washed twice with heptane and redissolved in benzene. After lyophilization of this solution, 10.6 g dry PEO macroinitiator was obtained in 93% yield.

Molecular weights (SEC/THF): $\bar{M}_n = 6900$ g/mol; $\bar{M}_w = 14{,}600$ g/mol; $M_{pic} = 13{,}700$ g/mol; $\bar{M}_w/\bar{M}_n = 2.12$.

^{1}H-NMR (CCl_4): $\delta = 0.01$–0.23(m; —SiCH_3) 0.51(s; —Si—CH_2—) 3.4(s; —CH_2—O—) 4.39 (s; Ar—CH_2—O—) 6.81–7.24(m; ArH)

Elemental anal. $C_{136}H_{220}O_{37}Si_6$ (repetitive unit: 2.615.8). Th %: C 62.5; H 8.5; O 22.6; Si 6.4; exp %: C 61.7; H 8.6; O 23.6; Si 6.1.

(d) Example of PEO macroinitiator synthesis by the "pinacolic" duplication reaction

A typical "pinacolization" reaction between a PEO precursor with benzophenone end-groups, in the presence of free benzophenone and 1,4-dichloro-1,1,4,4-tetramethyldisilethylene, follows. In a flask, under argon atmosphere, 4 g (1.1×10^{-3} mol) functional PEO with molecular weight $\bar{M}_n = 3800$ g/mol, 1.91 g (10.5×10^{-3} mol) benzophenone and 1.41 g (6.5×10^{-3} mol) 1,4-dichloro-1,1,4,4-tetramethyldisilethylene, dissolved in 15 ml THF, were reacted in the presence of 0.15 g (6.3×10^{-3} mol) Mg powder. The reaction, which started after addition of 1 ml HMPT with a temperature rise to 40°, was continued at room temperature for 12 hr. The resulting polymer was precipitated in dry ether, washed, dissolved in benzene and dried by lyophilization.

SEC characterization (THF): Plurimodal curve; $\bar{M}_n =$ 8900 g/mol; $\bar{M}_w = 11{,}600$ g/mol.

^{1}H-NMR (CCl_4): $\delta = 3.4$(s; CH_2—CH_2—O)4.5(s; CH_2-Ar) 7.5(m; ArH).

CONCLUSION

The principal target of our investigation was the synthesis of PEO samples having built-in benzopinacolate groups, suitable as macroinitiators for radical polymerization. Two methods were developed. The first, involving a hydrosilylation reaction, yields "segmented" PEO. These macroinitiators are rather similar to multiblock copolymers since the size of the pinacolate-containing "segments" is of the same order of magnitude as that of the PEO precursor chains, a consequence of the presence of bulky spacer groups in these molecules.

The second method is based on the general duplication reaction used in benzopinacolate synthesis. An advantage of this preparation over the hydrosilylation method is the small number of steps in the synthesis.

We have checked that both types of macroinitiators are able to initiate radical polymerization of styrene to form PEO–polystyrene block copolymers. This subject will be reported in a later publication.

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