

Anionic ring-opening polymerization of cyclic organosiloxanes using phosphorus ylides as strong non-ionic bases

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Dedicated to Professor Robert Corriu.

Abstract

Phosphonium alcoholates obtained by treatment of dimethylmethylene-[tris(dimethylamino)]phosphorane (**1**) with an excess of alcohol polymerize cyclic siloxanes (D_4) at room temperature. The thermal lability of this system permits simplifies polymer purification.

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1. Introduction

Polymeric siloxanes are widely employed in industry for a broad variety of applications [1]. Among different methods for their production, ring-opening polymerization of cyclic organosiloxanes is particular significant due to the low cost of the necessary monomers and the simplicity of the polymerization processes, something that may be accomplished by either cationic or anionic initiators. Indeed, the materials produced using the anionic approach have been used for the manufacturing of silicon rubber gum stocks [2]. Such initiator systems have been the subject of much recent research since many of their potential advantages are still waiting to find industrially interesting applications.

Initiation for this process consists of nucleophilic attack at the silicon atom of a cyclic monomer molecule by the initiator's anion, resulting in ring-opening and the formation of a new active center, which itself becomes involved in chain propagation. The reactions of polysilanolates with a monomer molecule give rise to

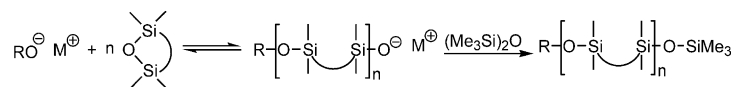
a propagation–depropagation equilibrium, which requires a chain-capping agent in order to regulate the molecular weight of the polymer. Hexamethyldisiloxane (M_2) or acid reagents are common terminating agents (Scheme 1).

Kinetic studies have shown that the rate of polymerization of cyclic oligosiloxanes depends not only on the nature of the initiator's anion, but also on its counter cation. Since these reactions are often bulk polymerizations, the cyclic oligosiloxanes present an apolar medium for the active ionic, polymerization initiator, which exists as a tight ion-pair that is in equilibrium with inactive aggregates of polysilanolates. Thus, the nature of the cation has a great influence on the polymerization rate and properties of the resulting polymers. The larger and softer the counter cation, the more rapid the reaction proceeds affording enhanced yields of the desirable linear polymers. For example, the activity of metal hydroxides increases in the series: $Li^+ < Na^+ < K^+ < NR_4^+ < PR_4^+$ [3].

The rate of polymerization also directly depends upon the solubility of the initiator in the bulk monomer material. Indeed, the use of KOH to initiate polymerization requires the reaction to be carried out under drastic conditions due to its poor solubility in the

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Scheme 1.

reaction medium. One would expect that bulky, soft counterions, such as quaternary phosphonium derivatives, should be more soluble in apolar media, and therefore, better initiators. Indeed, in the 1950s, it was shown that such compounds were in fact efficient initiators, but that they were not likely to be of any practical use due to their instability and difficult preparation [4]. In the 1990s, interest in these types of phosphorus derivative was reawakened following the discovery of non-ionic phosphazene bases by Schwesinger [5]. These strong bases react readily with water or methanol to generate the necessary hydroxide or methoxide, respectively, possessing a very soft counterion that has an inherent low tendency for ion-pair association. Thus, systems combining an alcohol and a phosphazene base were shown to be extremely fast initiators in the ring-opening polymerization of cyclic siloxanes [6]. However, the high molecular weight and cost of phosphazene bases are drawbacks for their industrial applications.

Recently, we have shown that readily available phosphonium ylides can be conveniently used as strong non-nucleophilic bases, in place of phosphazene bases [7]. In this work we address the question of whether such ylides, in the presence of alcohols, are suitable initiators for the anionic ring-opening polymerization of cyclic siloxanes.

2. Results and discussion

One would expect that an active initiator system could be obtained by mixing phosphorus ylides with acids, as is the case of phosphazenes [6]. However, phosphonium ylides are more nucleophilic compared with phosphazenes, and it is well-known that their hydrolysis and methanolysis usually lead to phosphine oxides instead of the corresponding hydroxides and alkoxides [8]. Thus, initially we were interested in finding a combination of ylide and acid, which would give stable ionic derivatives; dimethylmethylenetrakis(dimethylamino)phosphorane (1) [7] was chosen as a base for this study.

2.1. Hydrolysis and alcoholysis of ylide 1

Ylide 1 reacts with water so swiftly that it must be synthesized under a strictly inert atmosphere. However, phosphine oxide 3 is formed rapidly under these conditions (Scheme 2), making it impossible to detect the intermediate hydroxide 2a by ^{31}P -NMR spectro-

scopy. Thus, water cannot be used as an acid component in the initiator system. Similarly, the reaction of ylide 1 with one equivalent of MeOH in pentane also rapidly forms phosphine oxide 3. Even in the case of sterically hindered *t*-BuOH, the phosphonium alkoxide 2c is not stable, a mixture of the oxide 3 and the bis(dimethylamino)(*i*-propyl)phosphine (4) being obtained.

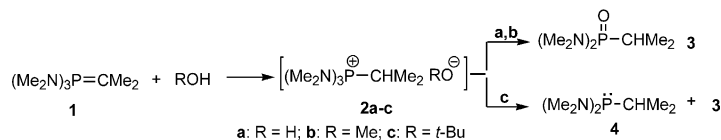
The formation of phosphine oxide 3 can be rationalized by nucleophilic attack of hydroxide or alkoxide anion at the phosphorus center of 2 (Scheme 3). The resulting pentavalent phosphorane 5 then decomposes by elimination of the most stable anion. The more basic *t*-butylate anion causes the formation of phosphine 4 by deprotonation of one of dimethylamino groups. Under these experimental conditions, we failed to detect any phosphonium alkoxide 2b or 2c.

It is noteworthy that an excess of alcohol may have a great influence on the product structure in the alcoholysis of trialkylphosphonium ylides since the stabilization of ionic intermediates like 2b, c can be achieved by using an excess of alcohol [9]. Indeed, when the reaction of ylide 1 was carried out in the presence of five equivalents of MeOH or *t*-BuOH, the alcoholates 2b, c were the main products after 10 min. These compounds slowly decomposed giving the same products that were obtained in the presence of one equivalent of alcohol. Contrastingly, in neat alcohol solutions (MeOH or *t*-BuOH) alcoholates 2b, c are remarkably stable, with the degree of decomposition not exceeding 25% even after 5 days. We can assume that solvation of the alkoxide anions by excess alcohol results in a decrease in their nucleophilicity and basicity, stabilizing the phosphonium alcoholates 2b, c (Fig. 1).

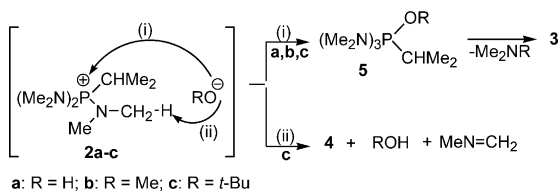
2.2. Polymerization of cyclic siloxanes

Octamethylcyclotetrasiloxane (D_4) was used as a model monomer compound in the study of ring-opening polymerization. Polymerization reactions were carried out in the presence of hexamethyldisiloxane (M_2) as a chain-capping agent with a view to obtaining polymers with molecular weights in the range 10 000–30 000.

The bulk polymerization of D_4 using the [ylide 1–MeOH (five equivalents)] initiator system occurred readily at room temperature, a polymer with an M_w of 9800 being obtained after only 10 h in 36% yield (Table 1, entry 1). The rate of the reaction is relatively high considering that with *t*-BuOK (entry 11) no polymerization was detected after 24 h at room temperature. Increase of MeOH amounts had no effect on



Scheme 2.



Scheme 3.

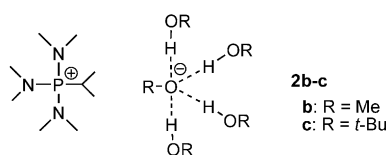
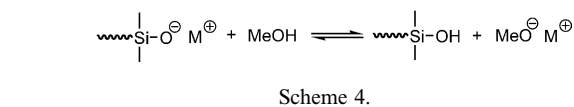


Fig. 1. Stabilization of phosphonium alcoholates by solvation.

the monomer conversion but led to a significant decrease in polymer molecular weights (entries 1 and 2). This observation can be explained taking into account an acid–base equilibrium between MeOH and polymeric phosphonium silanolates, which led to a chain termination (Scheme 4).

Moreover, similar polymer molecular weights were observed when the D_4 polymerization was carried out in the presence or in the absence of M_2 (entries 3 and 4).



Scheme 4.

This fact demonstrated a quite negligible role of M_2 in the terminating step under these conditions.

Thus, the mixture [ylide **1**–MeOH] is an efficient initiator system. However, the polymerization is slow and methanol is a chain-capping agent; so we decided to replace MeOH by *t*-BuOH, which is a less acidic alcohol.

A significant change in polymer yield and molecular weight was observed with the system [ylide **1**–*t*-BuOH]. Using 0.5 mol% of ylide **1** (relative to D_4) the polymerization was faster, 87% yield of an oily polymer being obtained after 1 h at room temperature. Under these conditions the molecular weight of the polymer was much higher than that observed using methanol ($M_w = 17800$) (entry 5), the cyclic oligomers amount was less than 3%. The initiator system [ylide **1**–five equivalents of *t*-BuOH] is remarkably stable and can be stored under an inert atmosphere for 7 days. Experiments carried out using 0.5 mol% initiator systems that were either freshly prepared or that had been kept for 1 week gave similar results. It was observed that the reaction rate dramatically depended upon the amount of

Table 1
Results for D_4 polymerization^a

Entry	Initiator (mol%) ^b	ROH (equivalents) ^c	M_2 (mol%) ^b	Time (h)	Yield ^d (%)	M_w	M_w/M_n
1	Ylide 1 (1.0)	MeOH (5)	2.5	0.5	36	9800	1.24
				150	67	11 400	1.25
2	Ylide 1 (1.0)	MeOH (50)	2.5	150	70	3900	1.16
3	Ylide 1 (2.0)	MeOH (50)	2.5	75	80	5400	1.22
4	Ylide 1 (2.0)	MeOH (50)	–	75	80	4900	1.22
5	Ylide 1 (0.5)	<i>t</i> -BuOH (5)	2.5	1	87	17 800	1.29
6	Ylide 1 (0.5)	<i>t</i> -BuOH (40)	2.5	20	61	39 700	1.27
7	Ylide 1 (0.5)	<i>t</i> -BuOH (40)	25	20	50	12 000	1.37
8	Ylide 1 (2.5)	<i>t</i> -BuOH (5)	25	12	89	2700	1.45
9	Ylide 1 (2.5)	<i>t</i> -BuOH (5)	2.5	12	87	13 700	1.28
10	Ylide 1 (2.5)	<i>t</i> -BuOH (100)	2.5	18	73	12 200	1.29
				75	77	10 900	1.26
11	<i>t</i> -BuOK (1.0)	–	2.5	24	NR ^f	NR	NR
12 ^e	<i>t</i> -BuOK (1.0)	–	2.5	24	86	28 700	1.28

^a T = 25 °C.

^b Relative to D_4 .

^c Relative to **1**.

^d GPC amount of polymer oil.

^e T = 70 °C.

^f No reaction.

t-BuOH present. Thus, when 40 equivalents of *t*-BuOH were used, the polymerization proceeded 20 times slower, resulting the oily polymer being obtained in 61% ($M_w = 39\,700$) yield after 20 h (entry 6). On the contrary to a ylide **1**–MeOH system (entries 1 and 2), the decrease in alcohol amounts in this system led to a lower polymer molecular weight (entries 5 and 6). In fact, solvation of *t*-BuO[−] and polysilanolates anions by the excess of *t*-BuOH in non-polar monomer medium has a great influence on their nucleophilicity. More solvated anions are less reactive and this effect is much more pronounced for less active M_2 . So decreasing of polymerization rate and increasing of polymer molecular weights were observed when the amount of *t*-BuOH was increased.

Since the nature of terminating groups has a great influence on polymers properties, it was important to compare the reactivity of *t*-BuOH and M_2 in the terminating step. This information is inferred from a comparison of the influence of their quantity on molecular weights of the silicon oil. When we increased M_2 amounts tenfold, polymer molecular weights decreased threefold when the polymerization was conducted in the presence of 40 equivalents of *t*-BuOH (entries 6 and 7), or even fivefold in the presence of only five equivalents of the alcohol (entries 8 and 9). This confirms that M_2 reacted with polymeric chains and that enhanced reactivity was observed in the presence of only slight excess of *t*-BuOH. On the contrary, increasing *t*-BuOH amounts in 20 times failed to produce any significant change in the polymer composition (entries 9 and 10). Nevertheless, we cannot exclude a slow reaction of *t*-BuOH with polymeric chains since polymer molecular weights were lower in the presence of 100 equivalents of *t*-BuOH and decreased when the reaction mixture was allowed to stand for several days (entry 10).

An additional advantage of [ylide **1**–*t*-BuOH] initiator system comes from its comparatively low thermal stability, a feature that can be exploited in terminating the polymerization reactions. Quenching of the anionic polymerization is a very important operation as the properties of the polymer, in particular its thermal behavior, depend to a considerable extent upon how exhaustively living ends were decomposed. Initiators producing thermolabile onium polysilanolates simplified the polymer separation and improved polymer properties [1,4,10]. In our case active centers can be destroyed in a few hours by moisture from the air or by heating the polymer–initiator mix. In the latter case, the termination of the polymeric chains and removal of by-products (macrocyclic siloxanes, D_4 , M_2 , and *t*-BuOH) can be carried out simultaneously by heating the reaction mixture at 100 °C under vacuum, a procedure that resulted in the isolation of colorless polymers.

3. Conclusion

We have shown that the basic properties of phosphorus ylides can be used in ring-opening polymerization of cyclic siloxanes. Phosphonium alcoholates, obtained by the treatment of ylide **1** with an excess of MeOH or *t*-BuOH, polymerize monomer D_4 even at room temperature. The rate of the polymerization is dramatically dependent on the nature and amounts of the alcohol employed. The efficiency of initiator system [ylide **1**–five equivalents of *t*-BuOH] is comparable to that of phosphazene–water (or MeOH) systems [6] and much more superior to that of *t*-BuOK, which needs to be heated to 70 °C in order to induce polymerization (Table 1, entry 5). Moreover, the use of ylide initiators simplifies polymer separation/isolation. As a result, it would seem particularly interesting to test this system in the polymerization of less active cyclic cyclosiloxanes such as 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotrasiloxane (D_4^{Ph}) and for the kinetic polymerization of D_3 .

4. Experimental

All experiments were carried out under dry argon using standard Schlenk or drybox techniques. THF was distilled under argon from sodium benzophenone. MeOH, *t*-BuOH were dried under Ar by distillation following sodium addition. D_4 was dried by azeotropic distillation with small amounts of benzene. M_2 and pentane were purified by distillation over CaH₂. Dimethylmethylene tris(dimethylamino)phosphorane (**1**) was prepared according to the literature procedure [7a]. D_4 and M_2 were obtained from Rhodia Silicones. Other chemicals were obtained from Aldrich and used as received.

¹H- and ¹³C-NMR were recorded on a Bruker AC250 and ³¹P-NMR spectra recorded on a Bruker WM200 instrument. Chemical shifts are reported in ppm downfield from Me₄Si and were referenced to solvent peaks (¹H, ¹³C) or external 85% H₃PO₄ (³¹P). Coupling constants are given in Hz.

The degree of conversion and molecular weight distributions were obtained from gel-permeation chromatography (GPC) using a Waters 746 instrument. The instrument was fitted with three Waters Styragel HR GPC columns (7.8 × 300 mm; two columns HR 5E and one column HR1) heated to 35 °C. Toluene was used as the eluent. Sample detection was performed by a Waters 410 differential refractometer. A calibration was made by using a set of narrow molecular weight distribution silicon oils supplied by Rodia Silicones.

4.1. Reaction of ylide **1** with methanol

Freshly prepared ylide **1** was used in the alcoholysis reactions. To a solution of 272 mg (1.33 mmol) of ylide **1** in 5 ml of pentane was added 268 μ l (6.65 mmol) of MeOH. The reaction mixture was monitored by ^{31}P -NMR spectroscopy. After 15 min at room temperature (r.t.) the signal of phosphonium methylate **2b** ($\delta = 66.1$) was detected. After 24 h only the signal of phosphonium oxide **3** ($\delta = 41.5$) was observed.

4.2. Bis(dimethylamino)(*i*-propyl)phosphine oxide (**3**)

^1H -NMR (C_6D_6): 1.02 (dd, $J_{\text{H-P}} = 16.8$, $J = 7.0$, 6H, Me-CH), 1.76 (dq, $J_{\text{H-P}} = 18.5$, $J = 7.0$, CH-P), 2.36 (d, $J_{\text{H-P}} = 8.8$, Me-N). ^{13}C -NMR (C_6D_6): 16.8 (s, Me-CH), 25.1 (d, $J_{\text{C-P}} = 115.8$, P-CH), 36.4 (s, Me-N). ^{31}P -NMR (C_6D_6): 40.2.

Our attempts to isolate bis(dimethylamino)(*i*-propyl)phosphonium methylate (**2b**) were unsuccessful due to its fast decomposition to phosphine oxide **3**. In order to obtain ^1H - and ^{13}C -NMR spectra of this compound we prepared its deuterated analogue.

4.3. Bis(dimethylamino)(2-deuterioprop-2-yl)phosphonium methylate- d_3 (**2b**)

^1H -NMR (CD_3OD): 1.05 (bd, $J_{\text{H-P}} = 18.25$, 6H, Me-CD), 2.46 (d, $J_{\text{H-P}} = 9.5$, Me-N). ^{13}C -NMR (CD_3OD): 19.2 (d, $J_{\text{C-P}} = 23.0$, Me-C), 25.2 (dt, $J_{\text{C-P}} = 103.1$, $J_{\text{C-D}} = 20$ Hz, P-CD), 37.9 (d, $J_{\text{C-P}} = 22.0$ Hz, Me-N). ^{31}P -NMR(CD_3OD): 68.3.

4.4. Reaction of ylide **1** with *t*-BuOH

To a solution of 272 mg (1.33 mmol) of ylide **1** in 5 ml of pentane was added 150 μ l (1.57 mmol) of *t*-BuOH. The reaction mixture was monitored by ^{31}P -NMR spectroscopy. After 30 min at r.t. the signals of phosphine **4** ($\delta = 106.4$), ylide **1** ($\delta = 58.9$), phosphine oxide **3** ($\delta = 41.5$), and intermediate pentavalent phosphorane ($\delta = -27.7$) were detected in the ratio 2:2:1:1. After 5 h only signals due to phosphine **4** and phosphine oxide **3** (in the ratio 2:1) could be observed.

When 155 mg (0.75 mmol) of ylide **1** was dissolved in 3 ml of *t*-BuOH only phosphonium *t*-butylate (**2c**) ($\delta = 67.2$) was detected after 15 min. After 5 days at r.t. the formation of phosphine oxide **3** was observed to have occurred in 25% yield.

4.5. Typical procedure for D_4 polymerization reactions

Alcohol was added to the pure ylide **1**, with stirring, at r.t. in a Schlenk. After 2 min a mixture of D_4 and M_2 was added. The reaction mixture was stirred at r.t. The

polymerization was monitored by GPC. The reaction conditions and the results are summarized in Table 1.

Acknowledgements

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