Phosphazene-promoted anionic polymerization

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Dedicated to Professor Stanisław Penczek on the occasion of his 80th birthday

Abstract: In the recent surge of metal-free polymerization techniques, phosphazene bases have shown their remarkable potential as organic promoters/catalysts for the anionic polymerization of various types of monomers. By complexation with the counterion (*e.g.* proton or lithium cation), phosphazene base significantly improve the nucleophilicity of the initiator/chain-end resulting in rapid and usually controlled anionic/*quasi*-anionic polymerization. In this review, we will introduce the general mechanism, *i.e. in situ* activation (of initiating sites) and polymerization, and summarize the applications of such a mechanism on macromolecular engineering toward functionalized polymers, block copolymers and complex macromolecular architectures.

Keywords: controlled anionic polymerization, metal-free polymerization techniques, phosphazene bases, mechanism *in situ* activation.

Polimeryzacja anionowa katalizowana fosfazenami

Streszczenie: Fosfazeny stosowane w technikach polimeryzacji przebiegającej bez udziału metalu, jako organiczne zasady wykazywały dużą zdolność do inicjowania reakcji polimeryzacji anionowej różnego typu monomerów. Dzięki kompleksowaniu przeciwjonu (kationu wodoru lub litu), zasady fosfazenowe znacznie zwiększały nukleofilowość końca łańcucha, co przyspieszało przebieg kontrolowanej polimeryzacji anionowej lub *quasi* anionowej. W niniejszym przeglądzie literaturowym omówiono ogólny mechanizm aktywacji *in situ* centrów aktywnych oraz przebiegu polimeryzacji z udziałem fosfagenów, zastosowanie takiego mechanizmu w inżynierii makrocząsteczek pozwalającej na wytworzenie polimerów funkcjonalnych, kopolimerów blokowych oraz polimerów o skomplikowanej złożonej architekturze, takich jak: polimery gwieździste, dendrytyczne itp.

Słowa kluczowe: kontrolowana polimeryzacja anionowa, metody polimeryzacji bez udziału metalu, zasady fosfazenowe, mechanizm aktywacji *in situ*.

INTRODUCTION

Metal-free, *i.e.* organocatalytic, polymerization/depolymerization techniques are among the most appealing topics in polymer chemistry, not only for the inherent merit that the products formed are free from residual metal-based catalysts/promoters but also for the opportunities they have opened for sophisticated macromolecular engineering [1—3]. Through the activation of monomer, initiator/chain-end, or simultaneous activation of both, polymerization from substrates containing the initiating sites can be conducted, usually in a fast and controlled manner, giving rise to polymers with low dispersity, high-level chain-end functionality, and/or designated macromolecular architectures [1—4].

Phosphazene superbases (PBs), a family of extremely strong but non-nucleophilic Brönsted bases [5—8], have been employed as effective organic catalysts or promoters for the polymerizations of various types of monomers, including epoxides [9—15], cyclosiloxanes [16—20], lactams [21, 22], cyclopropane derivatives [23—25], cyclic esters [26—30], cyclic carbonates [31—33], and alkyl (meth)acrylates [34—38]. Formulas (I)—(V) show the chemical structures and p*Ka* values (in parenthesis) of PBs that have been used for polymer synthesis.

Due to their high basicity, non-nucleophilic nature, good solubility in a wide range of solvents (hexane, benzene, toluene, tetrahydrofuran, dimethyl sulfoxide, *etc.*), and easy handling, PBs can be readily used to turn protic moieties into nucleophilic initiating sites through deprotonation or activation of weak nucleophiles. Hydroxyl has been the most commonly employed protic moieties in cooperation with PBs, probably due to the wide variety and high availability. However, some recent reports have also demonstrated the feasibility of using other protic functionalities, *e.g.* thiol [23—25] and amide [39, 40], and the polymerizations appear to be similarly effective. The use of such unusual initiating sites is of great interest, as it provi-

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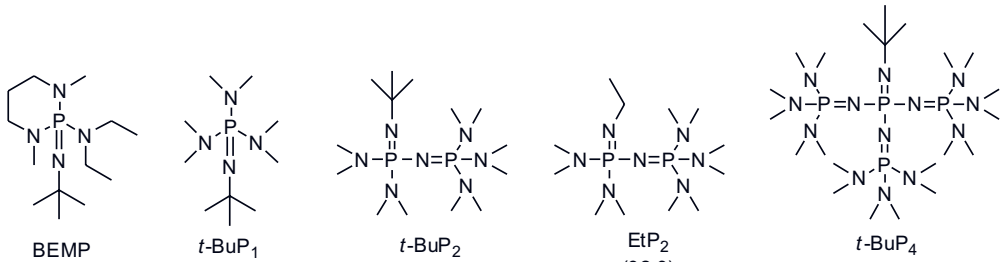


(I) (II) (III) (IV) (V)

BEMP: 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine;

t-BuP_1: *tert*-butylimino-tris(dimethylamino)phosphorane;

t-BuP_2: 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene);

EtP_2: 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene);

t-BuP_4: 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethyl-amino)phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)

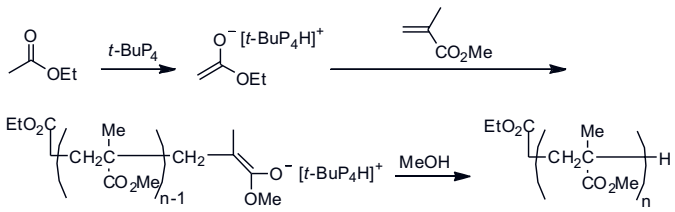
des the chance to develop new methodologies toward facile macromolecular engineering on some desirable substrates, such as bio(macro)molecules and carbon materials, containing these chemical functionalities. In addition, the complexation/coordination of PB with lithium cation (Li^+) [41—43] or trimethylsilyl group [37, 38] provides alternative ways to activate the initiating sites (alkoxides or enolates) and conduct the polymerization.

Although higher bacisity can lead to higher polymerization rate, it is not always ideal to use the strongest PB, as undesirable amount of side reactions (*e.g.* chain transfer to polymers) can occur and broaden the dispersity of the polymer formed. Therefore, choosing PB with the right basicity becomes important when a new type of monomer is to be polymerized. In the first part, we are going to introduce the general methods of conducting PB promoted/catalyzed polymerization for different types of monomers; and in the second part, we are going to introduce the application of these methods on macromolecular engineering.

GENERAL MECHANISMS FOR DIFFERENT TYPES OF MONOMERS

Methacrylates and acrylates

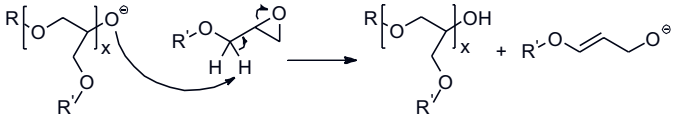
As the strongest and the mostly used one shown in Formula V, *t*-BuP_4 is capable to polymerize a wide range of monomers. Fast polymerization (30 min) is firstly achieved for methyl methacrylate (MMA), with ethyl acetate as initiator (Scheme A). Broadly distributed products are obtained in apolar solvents (hexane, toluene) at room temperature and tetrahydrofuran (THF) at low temperature (-78 °C); while in THF at 60 °C, low dispersity and targeted molecular weight are achieved, and the product formed contains 80 % syndiotactic diads [34]. Butyl acrylate is polymerized in a similar manner (THF, -40 °C). The polymerizations is complete in less than 15 min, however, the products have high dispersity ($\overline{M}_w/\overline{M}_n \geq 2$) due to the side reactions [35]. Recently, *t*-BuP_4 has been used as catalyst for the group transfer polymerization of MMA [38]. Due to its desirable silicon activation ability, the use of 1 % of *t*-BuP_4 allows the achievement of fast polymerization (30 min), targeted molecular weight as well as low dispersity. The activation of silicon-based compounds through the interaction between organic superbases and silyl groups has opened new pathways for the development of metal-free polymerization techniques [44—46].



Scheme A. Mechanism of *t*-BuP_4-promoted anionic polymerization of methyl methacrylate using ethyl acetate as initiator

Epoxides

t-BuP_4 is probably the only PB (see Formulas I—V) that has been used for the ring-opening polymerization (ROP) of epoxides, due to the high basicity needed in this case. *t*-BuP_4 generates active alkoxide initiator by either deprotonating an alcohol [9, 10] or coordinating with Li^+ of a organolithium compound [47—51], controlled polymerization of ethylene oxide (EO) can be achieved in either way resulting in poly(ethylene oxide) (PEO) with low dispersity [9]. Higher temperature seems to accelerate the polymerization and favor the achievement of complete monomer conversion without affecting the quality of the product. In the case of organolithium compound, the presence of *t*-BuP_4 breaks up the association of Li^+ with alkoxide and therefore enables the polymerization to proceed. Kinetic studies reveals the existence of an induction period in this case, which is affected by factors like the reaction temperature, *t*-BuP_4 concentration



Scheme B. Mechanism of the chain transfer to the monomer in the anionic ROP of alkyl glycidyl ether involving alkoxide as active species

and the structure of initiator [48]. Such reactions have been used extensively in EO and other epoxide-based macromolecular engineering, as will be discussed in detail later.

The anionic ROP of alkylated epoxide, especially propylene oxide (PO), suffers from the chain transfer to monomer (Scheme B), which limits the achievable molecular weight, especially in the case of *t*-BuP_4 since it gives rise to high basicity of the alkoxide chain ends [49, 52]. The combination of *t*-BuP_4 and triisobutylaluminum (Lewis acid) is proven to induce a faster polymerization and favor propagation over chain transfer, and hence the high molecular weight of the product (80 000 g/mol) [15].

Cyclosiloxanes

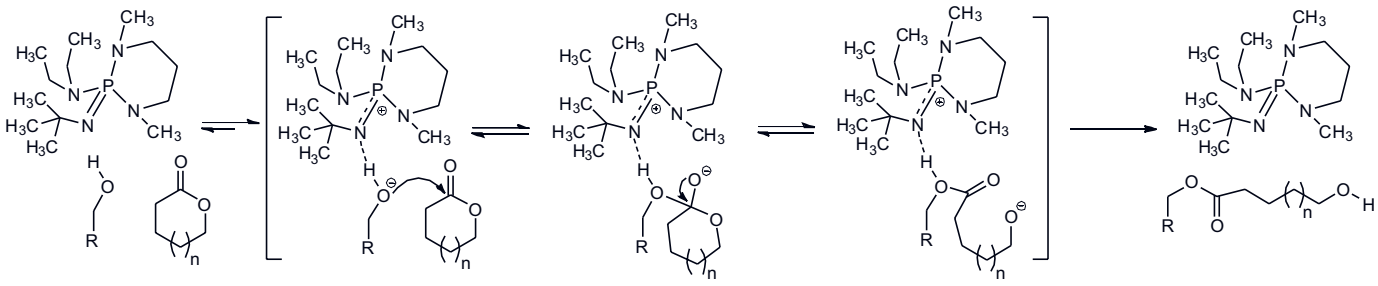
Similarly to epoxide, extremely rapid polymerizations of cyclosiloxanes are readily achieved at room temperature with the assistance of *t*-BuP_4 starting from either alcohol or organolithium initiator [9, 16—19, 53]. The polymerization of octamethylcyclotetrasiloxane (D4) with methanol/*t*-BuP_4 initiating system reaches equilibrium in 1 min. The product, which shows high molecular weight as well as high dispersity, appears to be a mixture of high polymer and small cycles due to the extensive occurrence of backbiting reaction [9, 16]. Lower monomer concentration results in lower molecular weight and higher cycle fraction. The use of *t*-BuP_4 in combination with water is proven to be efficient initiating system as well, for the polymerization of D4 and decamethylcyclopentasiloxane (D5) [18, 19].

The use of a weaker PB, EtP_2 (Formula IV), in combination with *sec*-BuLi for the ROP of hexamethylcyclotrisiloxane ($D3^{Me}$) in toluene solution or hexaethylcyclotrisiloxane ($D3^{Et}$) in bulk gives much better results [9]. Polydimethylsiloxane and polydiethylsiloxane with high molecular weight and low dispersity ($\overline{M}_w/\overline{M}_n \leq 1.15$) can be obtained when the monomer conversion is lower than 80 %. Higher monomer conversion leads to elevated dispersity of the polymer. The polymerization rate depends on the ratio between EtP_2 and Li^+. When the EtP_2/Li^+ ratio is lower than 1, every Li silanolate molecule still leads to a polymer chain. This observation points to the existence of a dynamic equilibrium and not a strong complex as in the case of the EtP_2/Li^+ system, which is quite similar to the case of *t*-BuP_4/H^+ and *t*-BuP_4/Li^+ systems for the ROP of EO, as will be discussed later.

Obviously EtP_2 is a better choice for cyclicsiloxanes, when controlled molecular weight and low dispersity are targeted at. The lower basicity slows down the polymerization, while also suppresses the undesired side reactions (*e.g.* backbiting reaction). This concept can be extended to other types monomers (*e.g.* cyclic esters, see below), in the case that high chain-end basicity leads to extensive chain transfer to polymer and inflicts poor quality to the product.

Cyclic esters

PBs with relatively lower basicity, *i.e.* BEMP, *t*-BuP_1 and *t*-BuP_2 have shown their excellent activity as organocatalysts for the ROP of cyclic esters, including L-lactide (LLA), *rac*-lactide (*rac*-LA), δ-valerolactone (VL) and ε-caprolactone (CL) [26, 27]. Polyesters prepared through this organocatalytic route possess predictable molecular weights, narrow dispersities, and high end-group fidelity. An intermolecular activation of alcohol by the PB is suggested (Scheme C) [27]. Polymerizations proceed slowly in the case of BEMP and *t*-BuP_1 (at room temperature) even with more strained monomers (LLA, VL and *rac*-LA). The polymerization of a less strained monomer (CL) results in only 14 % conversion in 10 days. Higher loading of the BEMP brings about a higher polymerization rate, which, however, results in an increased dispersity of the product. The use a more basic PB (*t*-BuP_2) leads to an extremely fast polymerization of LLA. Full conversion can be achieved in less than 1 min at a monomer concentration of 0.32 M [26], while the dispersity of the PLLA product is relatively high (1.23). Dilution of the monomer

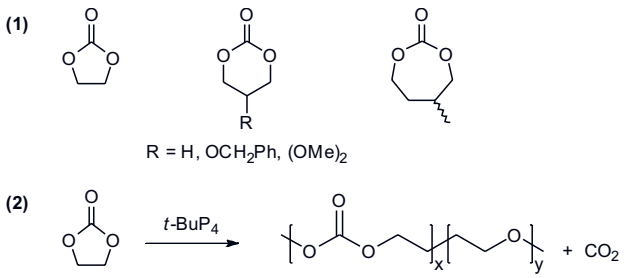


Scheme C. Postulated mechanism for the ROP of cyclic esters using BEMP as catalyst

(to 0.08 M) slows down the polymerization and favors a low dispersity (< 1.1). More importantly, excellent stereocontrol is exhibited for the ROP of *rac*-lactide. Highly isotactic polymers with high melting point and high crystallinity are obtained due to the effective cocrystallization between PLLA blocks and PDLA blocks. A chain-end control with stereoerror mechanism is postulated.

Similar to the case of cyclosiloxanes, weak PBs lead to slower kinetics but better control over the polymerization, as chain transfer to polymer (transesterification in the case of cyclic esters) occurs less extensively*) Important information is now available before choosing the most appropriate PB for the polymerization of a certain type of monomer.

The ROP of β-lactone derivatives (*e.g.* [R,S]-4-benzyloxycarbonyl-3,3-dimethyl-2-oxetanone) has been investigated with PBs (*t*-BuP_1, *t*-BuP_2 and *t*-BuP_4) as catalysts and carboxylic acids as initiators [28, 54]. A mechanism selectively involving the "*O*-alkyl" scission of the β-lactone monomer is proposed, which results in a complete absence of transesterifications and therefore favors a very good control over the polymerization in terms of polyester molecular weights and end-groups fidelity even in the case of *t*-BuP_4. A clear dependence of the overall polymerization kinetics on the PB basicity has been observed where the most basic *t*-BuP_4 brings about the highest ion-pair activity, and accordingly, allows for the synthesis of higher molecular weight (> 1.5×10^6 g/mol) samples.



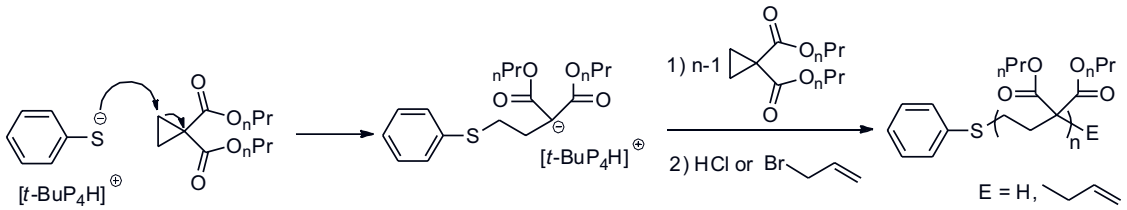
Scheme D. (1) Chemical structures of cyclic carbonates that have been polymerized by PBs; (2) Synthesis of poly[(ethylene carbonate)-*co*-(ethylene oxide)] by *t*-BuP_4-catalyzed ROP of 3-dioxolan-2-one

Cyclic carbonates

PB-catalyzed ROP of 5, 6, 7-membered rings carbonates (Scheme D) has been reported [31—33]. *t*-BuP_4-catalyzed ROP of 1,3-dioxolan-2-one is conducted at higher temperature (> 100 °C) resulting in an amorphous product with mixed monomeric units, *i.e.* poly[(ethylenecarbonate)-*co*-(ethylene oxide)], due to the release of CO_2 (Scheme D) [33]. ROP of 6,7-membered rings carbonates are carried out in bulk with catalytic amount of BEMP also at elevated temperature (from 60 to 150 °C) [31, 32]. High molecular weights, accompanied with higher dispersities, can be achieved in a relatively short reaction time (< 1 day).

Cyclopropane derivatives

The activation of thiol (Scheme E), phenol, amine (carbazole) or malonate precursors with *t*-BuP_4 generates effective initiating species for the polymerization of cyclopropane derivatives, *e.g.* di-*n*-propyl cyclopropane-1,1-dicarboxylate [23—25]. The polymerization proceeds in a well-controlled manner in either THF or toluene, while toluene is believed to be a better solvent since higher reaction temperature is achievable in it. Full monomer conversion is reached in a reasonable reaction time scale, leading to product with low dispersity and targeted molecular weight. The use of *t*-BuP_4 favors much higher reactivity compared to the alkali metal thiophenolate initiator, which has been used previously in dimethyl sulfoxide at high temperature.

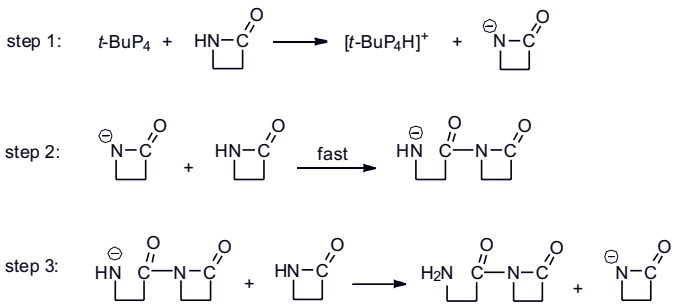


Scheme E. Postulated mechanism for the ROP of dipropyl cyclopropane-1,1-dicarboxylate using thiophenol as initiator and *t*-BuP_4 as catalyst

Lactams

High-molecular-weight (> 10^5 g/mol) nylon 3 has been prepared *via* the *t*-BuP_4-promoted ROP of 2-azetidinone (β-lactam) [22]. Rapid polymerization can be achieved at room temperature through an activated monomer mechanism even in the absence of any co-initiator (*e.g.*

*) ROP of CL in the presence of *t*-BuP_4 and *t*-BuP_2 has been investigated recently in our group. *t*-BuP_4 leads full monomer conversion in less than 1 min but high dispersity (> 1.5) of the product; while *t*-BuP_2 leads to much slower polymerization (85 % convertion in 8 h in toluene) and much lower dispersity (< 1.15).



Scheme F. Initiation process of the *t*-BuP$_4$-catalyzed ROP of β-lactam

N-acetyllactam). Unlike the case of metal catalysts, the high activity of *t*-BuP$_4$ leads to the immediate transformation of lactamate anion into an aminic anion (Scheme F), so that no apparent induction period is observed. An increase in temperature or *t*-BuP$_4$ concentration tends to increase the polymerization rate, but decreases the molecular weight and yield, probably due to the fast precipitation of the poorly soluble nylon 3.

t-BuP$_4$ also shows an excellent catalytic effect on the ROP of larger lactams such as ε-caprolactam in bulk at high temperature (220—270 °C) [21]. The reaction can be speeded up appreciably when *N*-acetyl-ε-caprolactam is added. EtP$_2$, though less active, also gives polymers.

Hybrid copolymerization of two different types of monomers

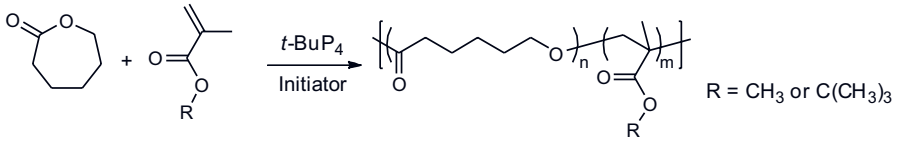
The high activity of *t*-BuP$_4$ allows the copolymerization of two different types of monomers, *i.e*. CL and methacrylates (Scheme G), with either alcohol or ethyl acetate being the initiator [30, 55]. This new type of polymerization is termed as hybrid copolymerization. Characterization data demonstrate random structure of the copolymer and that the molar fractions of the two monomers in the copolymer are approximately equal to the feed ratio. The copolymer exhibits a decomposition temperature higher than those of the homopolymers. Although the dispersity of the products is relatively high, this polymerization method is still very interesting since a new type of polymer can be created from two "old" monomers. This method has been extended to other monomer combinations such as CL with ethylene carbonate [56], LLA with methacrylates, cyclic carbonates with methacrylates [57].

MACROMOLECULAR ENGINEERING

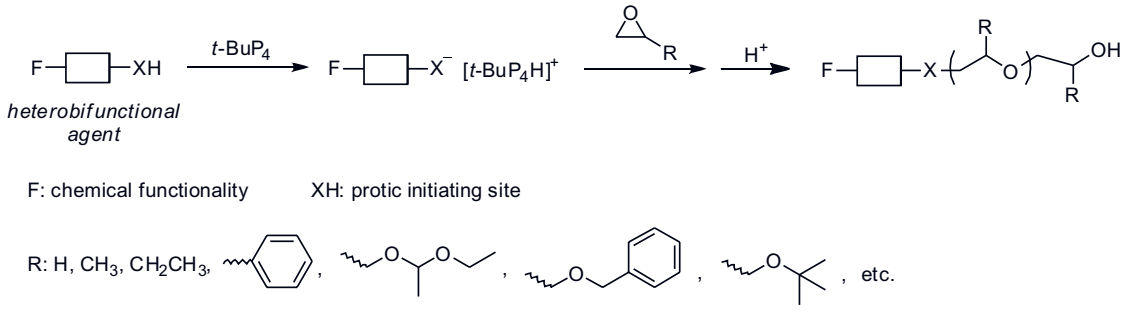
Owing to the simplicity of the mechanism, *i.e*. activation of initiating sites on the substrate *via* deprotonation/delithiation followed by polymerization therefrom, and the remarkably enhanced polymerization efficiency, PB-promoted polymerization techniques have been applied for macromolecular engineering toward chain-end (chemical/bio-) functionality and macromolecular architectures (*i.e*. block/star/graft/hyperbranched polymers). So far, a few types of monomers have been involved in such studies, in which epoxides are still mostly seen reported.

End-functionalized polymers

End-functionalized polyether can be easily achieved by the employment of a heterobifunctional agent (Scheme H), *i.e.* a small molecule containing a protic moiety acting as the initiating site and another chemical functionality which stays unreactive during the polymerization while allows the polyether to undergo further chemical modification (*e.g*. "click" chemistry, polymerization as macroinitiator or macromonomer, *etc*.). Due to the coexistence of the functional group and hydroxyl at two chain ends, such polyethers have also been referred to as

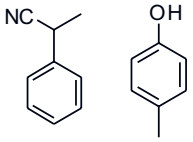
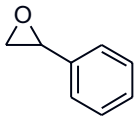
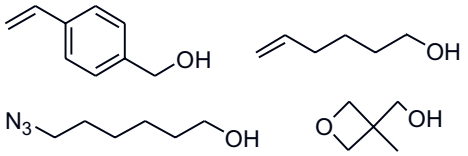


Scheme G. Illustration of *t*-BuP$_4$-catalyzed hybrid anionic copolymerization of CL with methacrylates



Scheme H. General synthetic mechanism toward end-functionalized polyethers *via* *t*-BuP$_4$-promoted ROP

T a b l e 1. Heterobifunctional initiator used for different epoxide monomers in *t*-BuP_4-promoted anionic ROP

Monomers	Initiators	Ref.
		[11]
		[12]
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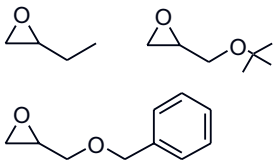
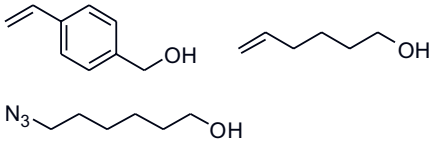
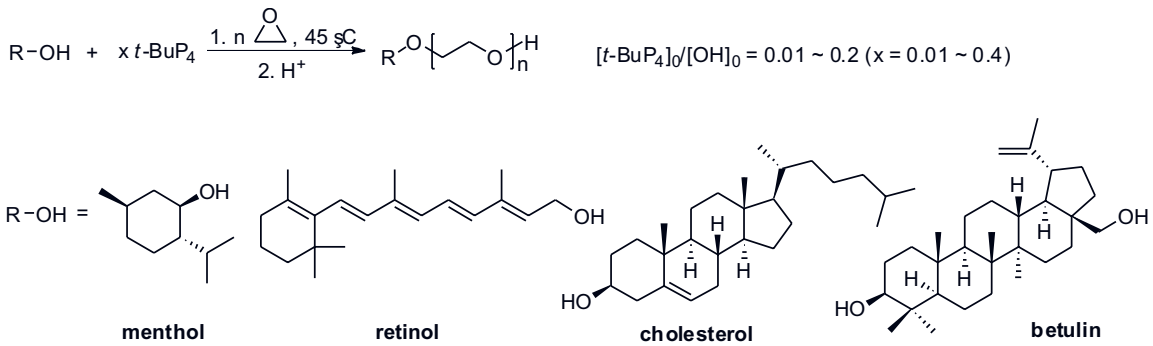
		[14]

α,ω-heterobifuntional or heterotelechelic polymer. Table 1 lists the heterobifunctional initiator used for different epoxide monomers. Usually, 1 equiv. of *t*-BuP_4 is used with regard to the initiator, leading to high polymerization rate as well as high chain-end functionality. However, some results have indicated that reducing the amount of *t*-BuP_4 to a certain extent (*e.g.* from 1 to 0.6) does not cause much influence to the polymerization of 1,2-butylene oxide [14]. Further decrease (to 0.3) slows down the polymerization, but a high initiation efficiency is still preserved owing to the rapid proton exchange between alkoxide and alcohol. Chain transfer to substituted epoxide monomers is not detected in this case, probably due to the low reaction temperature and relatively low targeted degrees of polymerization.

The same synthetic strategy has been used to control the chain end of poly(cyclopropane-1,1-dicarboxylates) [24]. Different types of initiator (thio, alcohol, carbazole, malonate) are used to control the end group at α-position. 1 equiv. of *t*-BuP_4 is used to promote the polymerization (high temperature is needed to ensure high monomer conversion), and finally halogenated capping agents are used to introduce functional group (*e.g.* allyl or propagyl) to the ω-position (Scheme E). Excess of capping agent is used resulting in quantitative functionalization.

Terpene alcohols, including cholesterol, menthol, retinol and betulin, are used as initiator for the anionic ROP of EO to introduce biological component at the end of PEO (Scheme I). Very low amount of *t*-BuP_4 is used (0.01—0.2 equiv. of hydroxyl groups) and nearly complete initiation efficiency can be achieved, as revealed by macromolecular characterization, indicating that the proton transfer between active and dormant chain ends during the polymerization is much faster than the chain growth.

Although not precisely documented, it can be presumed that low amounts of *t*-BuP_4 should lead to reduced



Scheme I. Synthesis of terpene-PEO conjugates by *t*-BuP_4-promoted anionic ROP of EO

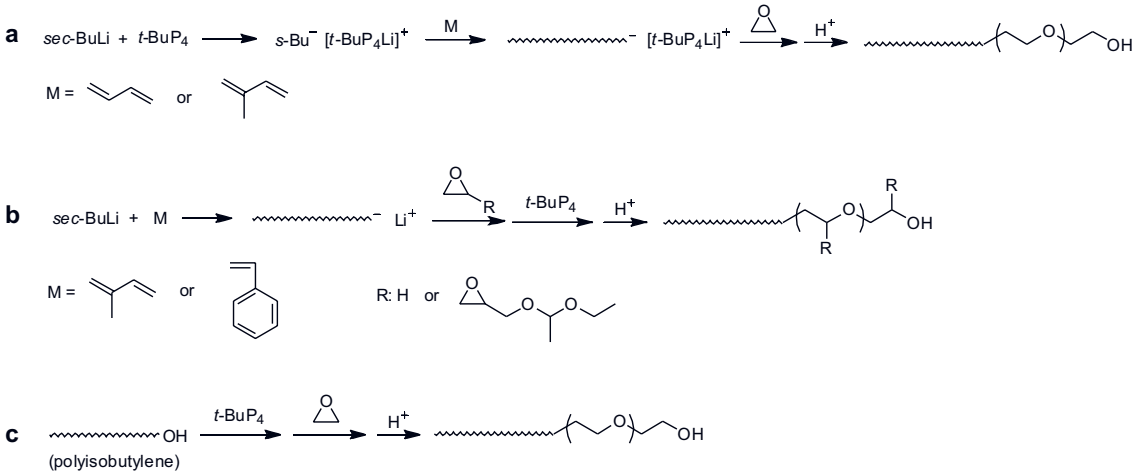
polymerization rate. In order to better reveal the influence of terpene entities, low molecular weights of PEO were targeted at in that study. However, on a chemical point of view, it would be interesting to study the limitation of the achievable molecular weight with different amount of *t*-BuP_4 (different percentage of activated chain ends). The different terpene entities have been demonstrated to affect the thermal and solution properties of these terpene-PEO conjugates [58]. The successful synthesis of bioconjugate polymers in this manner should also be attributed to the simplicity of chemical structure of the involved terpene alcohols, which stay intact during the anionic ROP. It would be also interesting to investigate the tolerance of such metal-free polymerization systems toward other types of biological entities.

Block copolymers

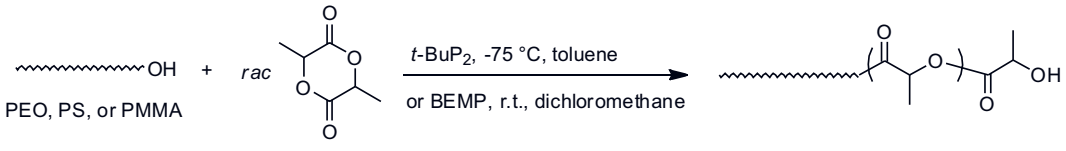
Polyether-based block copolymers have been synthesized by performing anionic ROP of epoxide monomers from "living" macro-initiators. The chain end of the macro-initiator is activated by *t*-BuP_4 *via* either deprotonation or complexation with Li^+ (Scheme J). The combination with organolithium-initiated anionic polymerization of dienes and styrene is mostly employed. Usually *t*-BuP_4 is added after the completion of the growth of the first block and the addition of epoxide monomer (Scheme J b) [42, 43, 59—61]. Adding *t*-BuP_4 for a direct complex with *sec*-BuLi has also been reported (Scheme J a) [41]. No side reaction is observed between active carbanions and *t*-BuP_4 probably due to the very low temperature used (-110 to -78 °C). In all these studies, an equal molar ratio of [*t*-BuP_4]/[Li^+] (0.9 ~1.05) is used, to ensure quantitative blocking efficiency in all cases. The polymerization of epoxides is conducted at elevated temperature (40 to 50 °C) for 2 to 4 days to ensure complete conversion. Triblock copolymers have been achieved by sequential polymerization of two diene monomers and an epoxide monomer [43], or styrene and two epoxide monomers [60].

Hydroxyl-terminated macro-initiator *(i.e.* polyisobutylene) has also been used in combination with *t*-BuP_4 to polymerize EO toward the preparation of diblock copolymer (Scheme J c) [62]. 0.5 equiv. of *t*-BuP_4 is used to activate the macro-initiator, resulting in pure diblock copolymer (free of homopolymer). A similar strategy has been applied for the preparation of polyester-based block copolymers, for which PBs with lower basicity are used [26—28]. BEMP and *t*-BuP_2 are used to catalyze the ROP of *rac*-LA from hydroxyl-terminated macro-initiators, *i.e.* PEO-OH, PS-OH (PS = polystyrene) and PMMA-OH, as is shown in Scheme K [26, 27]. Despite the high molecular weight of the initiators and relatively low monomer concentration, high yields are achieved with quantitative initiation efficiency and low dispersity. A low temperature is used in the case of *t*-BuP_2 and is believed to suppress the transesterification on polyester chains, as *t*-BuP_2 has a higher basicity than BEMP. Carboxyl-terminated PEO has been used as macroinitiator for the polymerization of a β-lactone [28], with *t*-BuP_1, *t*-BuP_2 or *t*-BuP_4 as catalyst.

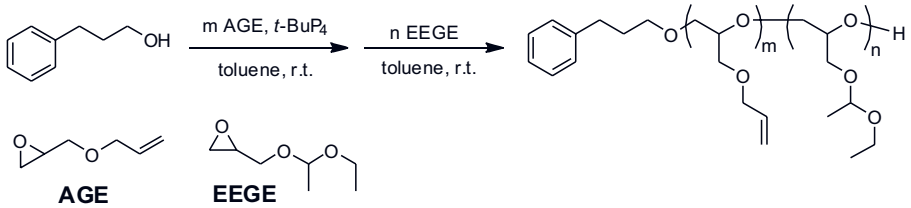
Block copolymers are prepared by sequential polymerization of two functional epoxide monomers, allyl glycidyl ether (AGE) and ethoxyethyl glycidyl ether (EEGE), from a hydroxyl-based initiator (Scheme L) [13]. Homopolymerization of EEGE undergoes side reaction (*i.e.*



Scheme J. Synthesis of polyether-based block copolymers *via* *t*-BuP_4-promoted anionic ROP



Scheme K. Synthesis of polylactide-based block copolymers *via* phosphazene-catalysed ROP from macro-initiators



Scheme L. Synthesis of poly(allyl glycidyl ether-*b*-ethoxyethyl glycidyl ether) by *t*-BuP$_4$-promoted sequential anionic ROP

chain transfer to monomer), while the sequential polymerization of AGE followed by EEGE is believed to be free from side reaction at room temperature. Selective deprotection of the two blocks allows further chemical modification toward novel polyether-based materials.

Attempt has also been made to polymerize a methacrylate monomer (*N*, *N*-dimethylaminoethyl methacrylate, DMAEMA) using PEO$^-$[*t*-BuP$_4$Li]$^+$ as macroinitiator (one-pot synthesis of diblock copolymer) [51]. High blocking efficiency is achieved, while the block copolymer formed entails a relatively high dispersity (1.4), which is attributed to the slow initiation of DMAEMA from PEO$^-$[*t*-BuP$_4$Li]$^+$. Polymerization using hydroxyl-terminated PEO as macroinitiator resulted in an even higher dispersity and a lower blocking efficiency (0.8).

As discussed above, PB-promoted polymerization of epoxides, cyclic esters, methacrylates benefits from a relatively high polymerization rate, but it can be accompanied by side reactions due to the high basicity of the initiator/chain-end, *e.g*. chain transfer to monomer (in the case of substituted epoxide) or to polymer chains (in the case of cyclic esters). Such side reactions may lead to some undesirable effects on the synthesis of block copolymers, such as low blocking efficiency, high dispersity, contamination with homopolymer. Therefore, further attempts need to be made to find the optimized synthetic condition for each specific system.

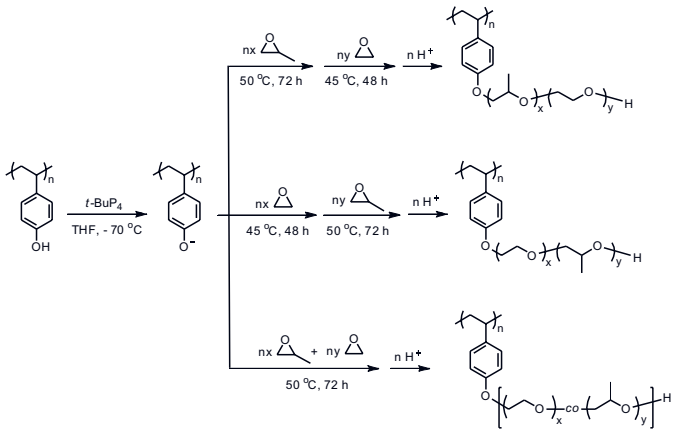
Graft copolymers

With the employment of multifunctional backbones, *i.e*. (co)polymer containing multiple protic groups (initiating sites), *t*-BuP$_4$-promoted anionic graft (co)polymerization of epoxides has been realized. This "graft from" technique has allowed the achievement of various complex comb-like macromolecular architectures including graft copolymer with side chains being homopolymers [10, 39, 63], block copolymers [64], and statistical copolymers [65].

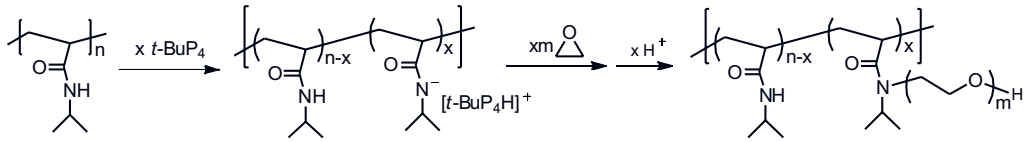
The first reported *t*-BuP$_4$-promoted graft polymerization of EO is performed on a poly[ethylene-*co*-(vinyl alcohol)] backbone [10]. The poor solubility of the backbone copolymer does not affect the graft polymerization as the solution becomes homogeneous after a certain reaction time (25 % monomer conversion). The number of hydroxyl groups that initiate polymerization leading to a PEO side chain (*i.e*. graft density) is found to correspond to the initial ratio of *t*-BuP$_4$ to hydroxyl groups, indicating that there is no effective proton exchange between active (alkoxide) and inactive (hydroxyl) sites present on the backbone. This is quite different from the case of polymerization from mono-alkoxide or di-alkoxide, as discussed above, which, however is seemingly the case for all graft polymerizations as further discussed below.

Amphiphilic block-graft copolymers are achieve by conducting graft polymerization of EO from polystyrene-*b*-poly(*p*-hydroxystyrene) backbones [63]. Different ratios of *t*-BuP$_4$ to phenol are used. Direct analysis for the proportion of the incorporated phenol moieties on the backbone is not performed, however, crystallinity (different length of the PEO side chains) indicates, at least qualitatively, a controlled graft density. Sequential or statistical copolymerizations of PO and EO from poly(*p*-hydroxystyrene) backbone have resulted in the preparation of graft copolymers with densely grafted block copolymer or statistical copolymer side chains (Scheme M) [64, 65]. The poor solubility of the highly charged backbone ([*t*-BuP$_4$]/[phenol] = 0.9) does not affect the results (products have low dispersity) as the solutions become homogeneous after a certain reaction time.

In addition to hydroxyl, amide moieties, in combination with *t*-BuP$_4$, have also been utilized to perform graft polymerization. Thermoresponsive graft copolymers, poly(*N*-isopropyl acrylamide)-*g*-poly(ethylene oxide) have been prepared in this manner (Scheme N) [39]. It is found that the graft density is indeed controlled by the initial ratio of *t*-BuP$_4$ to secondary amide moieties, which is consistent with the previously discussed results. Steric



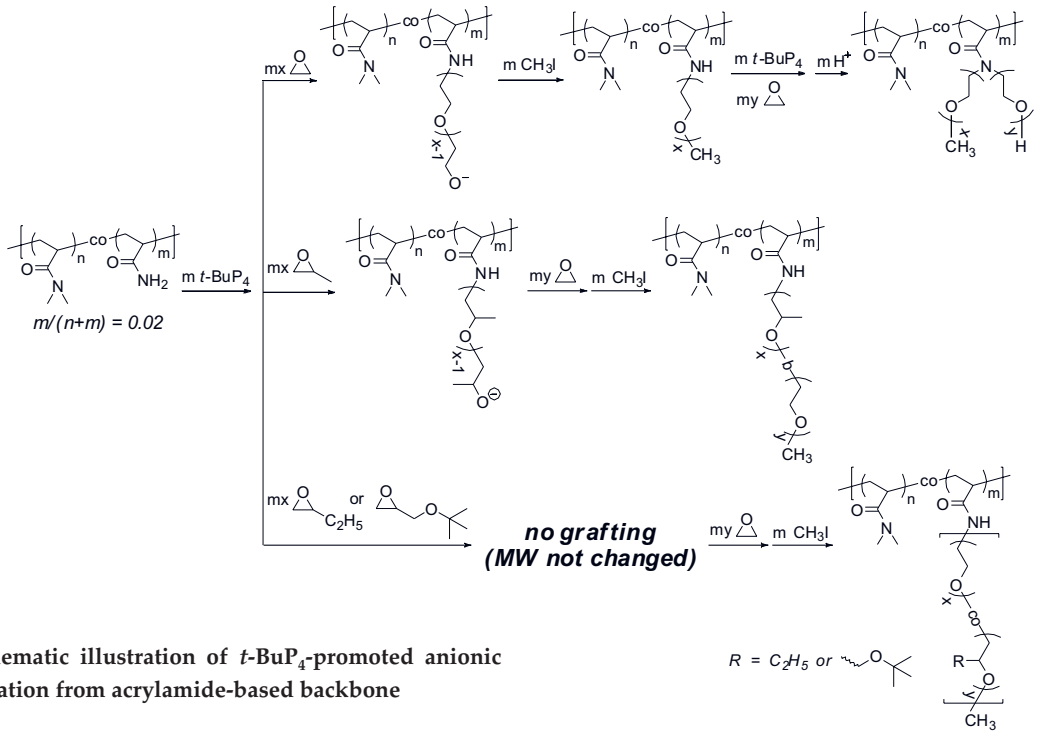
Scheme M. *t*-BuP$_4$-promoted graft (co)polymerization of PO and EO from poly(*p*-hydroxystyrene)



Scheme N. *t*-BuP$_4$-promoted graft polymerization of EO directly from poly(*N*-isopropylacrylamide)

hindrance, which inhibits proton transfer from the unreacted protic moieties carried by the backbone to the growing side chains, may be the explanation. However, more investigations need to be performed toward kinetic details.

High-molecular-weight poly(*N*, *N*-dimethylacrylamide-*co*-acrylamide)s have been used as a model functional substrate to investigate *t*-BuP$_4$-promoted graft polymerization utilizing primary amide moieties as initiating sites. The (co)polymerization of epoxides is shown to be effective, leading to macromolecular combs with side chains being single or double-graft homopolymers, block copolymers and statistical copolymers (Scheme O) [40].



Scheme O. Schematic illustration of *t*-BuP$_4$-promoted anionic graft polymerization from acrylamide-based backbone

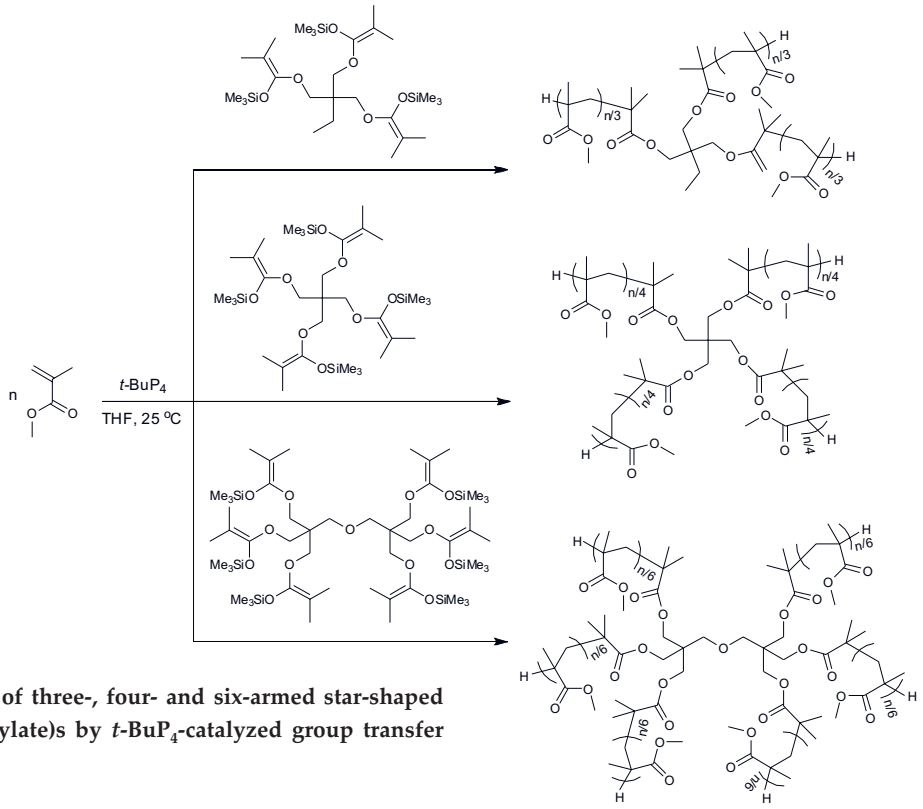
Star-shaped polymers

The synthesis of star-shaped polyether through *t*-BuP$_4$-promoted anionic ROP has scarcely been reported, which, however, should be normally successful *via* the so-called "core-first" protocol. Pentaerythritol has been used to generate a four-armed star-shaped PEO in this manner [10]. Regardless of its poor solubility in the solvent (THF), homogeneous solution is obtained at *ca.* 30 % monomer conversion and the final product has a low dispersity (1.1). A polylithiated carbosilane dendrimer has been used to prepare multi-arm star-shaped PEO [66], aided by the formation of *t*-BuP$_4$/Li$^+$ complex. Such initiating system benefits from the dendritic structure, which prevents the multifunctional (multi-charged) initiator from undergoing intermolecular association.

Group transfer polymerization catalyzed by *t*-BuP$_4$ has been used to prepared star-shaped polymethacrylates (Scheme P) [37]. Despite the fact that the ratio between *t*-BuP$_4$ and the initiating sites (silyl enolate) is mostly kept below 1, star-shaped polymer with desired number of arms are obtained in all cases. The polymerization/catalysis mechanism is still awaiting further evidence and discussion, however, the utilization of silicon activation ability of PB toward star-shaped polymethacrylates has definitely opened a new pathway toward macromolecular engineering based on metal-free polymerization techniques.

Hyperbranched polymers

Hyperbranched polysiloxanes have been prepared by *t*-BuP$_4$ promoted anionic ROP of hydroxyl-functionalized pentamethylcyclotrisiloxane monomers (Scheme R) [67, 68]. Rapid proton transfer between deprotonated and protonated hydroxyl groups is believed to facilitate the

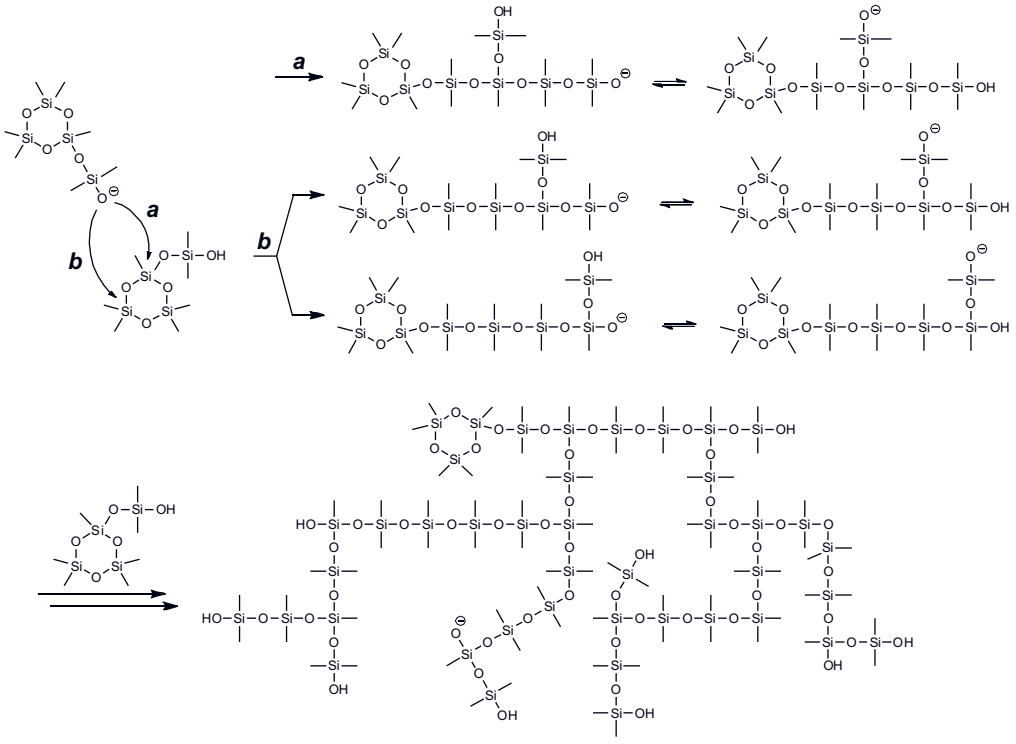


Scheme P. Synthesis of three-, four- and six-armed star-shaped poly(methyl methacrylate)s by *t*-BuP$_4$-catalyzed group transfer polymerization

formation of the hyperbranched structure, since in this case the reaction with monomer can occur at any of the six silanolate/silanol centers. Low reaction temperature is also needed to depress the occurrence of cross-linking (base-catalyzed silanol condensation).

SUMMARY

Although still in the preliminary stage of employment and exploitation, PBs have already manifested their remarkable potential as catalyst/promoter in metal-free



Scheme R. *t*-BuP$_4$-promoted anionic ROP of 1-(hydroxydimethylsiloxy)pentamethyl-cyclotrisiloxane toward hyperbranched polysiloxane

polymerization techniques for a wide range of monomer types. Upon association with the counterion (proton, lithium cation, *etc*.) and thus enhancing the nucleophilicity of the initiator, such organic superbases have permitted significant improvement of polymerization rate and, in many cases, the achievement of high molecular weight with narrow dispersity. Moreover, the simplicity and efficiency of the catalysis/promotion grants *in situ* growth of (co)polymer chains from substrate containing initiating sites (mono- or multifunctional small molecules, biomolecules, macromolecules), which provides new strategic concept for sophisticated macromolecular engineering in a metal-free manner toward end-functionalized polymers, bioconjugate polymers and complex macromolecular architectures. So far there is still a lot, concerning the activation/polymerization mechanism and kinetics, which remains to be investigated and understood. It would be also of great interest to further investigate the applicability of other monomer/initiator types, to optimize the conditions for each specific system in terms of *e.g*. basicity and quantity of PB used, co-catalyst, polymerization solvent/concentration/temperature, *etc*., and to exploit the potential of this technique for more applications in macromolecular engineering such as the modification of biomacromolecules and polymeric/carbon materials.

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