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Investigation of the “*Locked-Unlocked*” Mechanism in Living Anionic Polymerization Realized with 1-(*Tri*-isopropoxymethylsilylphenyl)-1-phenylethylene (DPE-Si(O-*i*Pr)$_3$)

Pibo Liu, Hongwei Ma*, Li Han, Heyu Shen, Lincan Yang, Chao Li, Xinyu Hao, Yang Li

Abstract: We report an intriguing advance in living anionic polymerization (LAP) via a “Locked-Unlocked” mechanism, in which the living anionic species can be quantitatively locked by end-capping with 1-(*tri*-isopropoxymethylsilylphenyl)-1-phenylethylene (DPE-Si(O-*i*Pr)$_3$) and can be unlocked by adding the “key”, namely, sodium 2,3-dimethylpentan-3-olate (NaODP). These new insights into this mechanism were carefully confirmed by designing reactions involving sequential feeding of quantitative DPE-Si(O-*i*Pr)$_3$ and traditional monomers mixed with NaODP and subsequently characterizing the corresponding samples taken during the feeding process with GPC, NMR, and MALDI-TOF-MS techniques. The switch from the locked to unlocked state was clearly confirmed by these characterization techniques. MALDI-TOF-MS was especially illustrative, as the restarting of the propagation of the living anions capped with DPE-Si(O-*i*Pr)$_3$ by unlocking with NaODP can be clearly observed. Next, based on the significant differences between the normal ^{13}C and 135° DEPT-^{13}C NMR spectra of the locked and unlocked living species, the putative “Locked-Unlocked” mechanism in the LAP was simulated by the Gaussian method. This intriguing mechanistic finding of LAP reactions is expected to supplement the existing knowledge and facilitate the tailoring of specific structures for these polymerizations.

ON and OFF are two basic but highly significant logical states for controlling the transmission of both matter and nonmatter (such as information, energy, and force)[1]. Through controlled switching between locked (OFF) and unlocked (ON) states, technologies such as the transport of material between cells or supercomputing in information technology can be easily accomplished. Based on this basic understanding, molecular “switches”[2] and “motors”[3] have been synthesized and have revealed how switching between locked and unlocked states can be accomplished in inorganic or organic chemistry[4]. By controlling the facile transformation between locking and unlocking, elaborate behaviors such as moving, folding, repairing, and sensing have been achieved at the molecular level[5]. Furthermore, the ability to control the locked and unlocked states in chain growth polymerization has wonderful potential for the synthesis of advanced materials possessing specific structures or functions. Because a large number of living centers exists during chain propagation, if some portion of them can be controllably switched between the locked and unlocked states, the chain propagation reaction can insert specific monomer units or block structures at specific sites. More recently, photo-controlled radical polymerization (Photo-CRP) reactions have been explored, and the entire propagation can be locked and unlocked in a facile manner since the ON/OFF state can be controlled with light. Step chain propagation can be observed when the living centers go through cycles of locking and unlocking by controlling light exposure[6]. *Can some or all of the living centers be controllably locked and unlocked, and can this control be extended to other controlled chain polymerization methods?* This target is desirable but difficult to reach because there are many challenges in the quantitative locking of non-radical living centers, and other centers will continue to undergo chain propagation. Thus, novel chemical reactions or mechanisms are necessary to achieve this goal.

Living anionic polymerization (LAP) is a traditional example of living chain-growth polymerization, and this method offers great advantages in controlling molecular weights (M.W. values)[7] and polymeric architectures[8]. The mechanism of chain propagation in nonpolar solvents and at room temperature has been thoroughly investigated over the past 60 years[9]. The kinetic control can be used in block polymerization to effectively[10] cap polymers with functional end groups[11], and this knowledge has guided both industrial manufacturing and scientific research. As a typical methodology explored in LAP, 1,1-diphenylethylene (DPE) chemistry expands access to functionalized polymers due to the unique characteristics of DPE derivatives[12]. Because of the quantitative incorporation of the monomer and heterogeneity during copolymerization, sequence-controlled polymers have been synthesized with a variety of DPE derivatives[12-13]. Additionally, heteroatoms (such as N and O) can be successfully incorporated into DPE units, and copolymerization can be conducted without side reactions[14]. When they possess lone pair electrons, heteroatoms can serve as ligands for metal-centered catalyst[10, 15]. In LAP, polar heteroatom-containing additives, such as tetrahydrofuran (THF) or tetramethylethylenediamine (TMEDA), have been shown to have a significant impact on the kinetics of the reaction and the resulting microstructures[16]. Unlike the weak association formed when adding polar additives to living polymerizations, polar substituents in the DPE units form strong interactions with living anions especially when the polymers are end-capped. Such interactions have not been observed in copolymerizations with DPE derivatives until we synthesized a new DPE derivative with three oxygen-containing substituents, i.e., DPE-Si(O-*i*Pr)$_3$.

DPE-Si(O-*i*Pr)$_3$, possessing a siloxanyl group, was designed for polymeric grafting onto the surface of nanoparticles[17]. After successfully synthesizing molecular brushes, this compound was used in a copolymerization with styrene (St), and intriguing experimental phenomena were observed. The details of the

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syntheses are presented in Figure 1a, and the main discovery made during copolymerization was that when only sodium 2,3-dimethylpentan-3-olate (NaODP) was used as an additive, the copolymerization reaction generated polymers, while the use of other additives (i.e., conditions using TMEDA, THF or NEAT) generated living anions (dark red color that persisted until termination) but no product. This finding was different from what we observed in our copolymerization with DPE derivatives containing heteroatoms, such as DPE-NMe_2[14a], DPE-$(NMe_2)_2$[18], DPE-SiH/OMe[14b], and DPE-SiOEt[19]. Even though side reactions occurred when DPE-SiOEt, which possesses one siloxanyl group, was used, the copolymerization still provided the desired polymers. When NaODP was not used, no polymer was formed, and this phenomenon caused us to wonder if monomers containing heteroatoms could form strong interactions with living centers allowing extraordinary control in LAP.

Thus, sequential end-capping and monomer feeding strategies were designed, and the process of locking, unlocking and steady propagation could be observed simultaneously in one reaction. The corresponding routes are shown in Figure 1b.

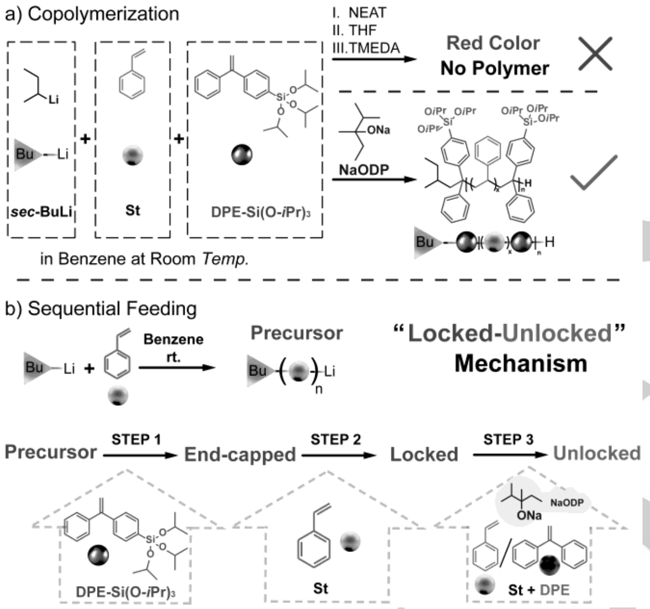

Figure 1. [a] Copolymerization of St and DPE-Si(O-*i*Pr)$_3$ via anionic polymerization (initiated by *s*-BuLi in benzene at room temperature) [b]. The sequential feeding routes.

All the samples taken at each step were terminated with methanol. First, the samples were analyzed by GPC. The remarkable variations between samples from sequential steps can be clearly observed in the GPC curves (see Figure 2). The differences between samples from different stages of the process are discussed below.

1. In STEP 1, to convert the living species to the locked state, the precursor PS-Li was end-capped with either 0.25 or 0.5 eqv. of DPE-Si(O-*i*Pr)$_3$.

2. In STEP 2, a new batch of 40 eqv. of St was added into the solution in which apportion of the living anions were end-capped. The end-capped living species, $St_{26}D_{SiO}$-Li, stopped propagating, while the non-end-capped living species (i.e., St_{26}-Li) continued to undergo chain growth and consumed the new batch of St. Thus, when 0.25 eqv. of the end-capping agent was used, an additional 60 monomers (40/0.75=53) were added to the noncapped chains, and a bimodal distribution can be clearly observed. The "locked" living species were formed by end-capping with DPE-Si(O-*i*Pr)$_3$.

3. In STEP 3, to verify that these living species were only locked and not terminated, confirming that these species could be "unlocked" was essential. Thus, 8.0 eqv. of NaODP, 15 eqv. of St and 16 eqv. of DPE were added simultaneously. Based on the results of copolymerization, NaODP may serve as the "key" that unlocks the locked living species. Both peaks in the GPC curves (see the locked state) shifted to higher M.W. values upon unlocking, and notably, the peak from the locked living species completely disappeared. The changes in M.W. reflected the two disparate outcomes caused by the pause in the propagation of the living species that were end-capped in STEP 2.

Taking 0.25 eqv. of end-capping agent as an example, the two peaks from species in the "unlocked" state can be attributed to St_{26}-St_{60}-$(St\text{-}D)_{28}$-Li and St_{26}-D_{SiO}-$(St\text{-}D)_{22}$-Li. Unlike what is seen with "locked" species, two types of living chain propagation can be observed upon introduction of NaODP, and propagation of both the "end-capped" and "locked" species is paused. Through the GPC characterization of products obtained from sequential feeding, locking and unlocking of the living species definitely occurred when DPE-Si(O-*i*Pr)$_3$ and NaODP were sequentially added into the LAP. Notably, equal amounts of St and DPE were used in STEP 3 to eliminate the crossover propagation of P-D_{SiO}-Li to St ($k_{DSiO\text{-}S}$ is much lower than k_{SS}), which had a dramatic impact on the splitting of the GPC curves between the "locked" and "unlocked" states.

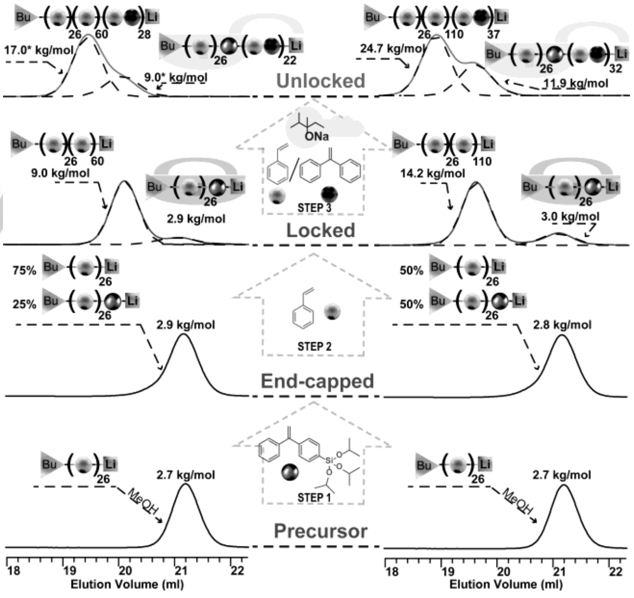

Figure 2. GPC curves of the samples taken from the polymerization. [a] The left-hand column shows the precursor, 25%-End-capped, 25%-Locked-HM, and 25%-Unlocked-HM species in the polymerization, and the right-hand column shows the precursor, 50%-End-capped, 50%-Locked-HM, and 50%-Unlocked-HM species in the polymerization. [b] In step one, the precursor, with a M.W. of 2 kg/mol, was end-capped by a certain amount of DPE-Si(O*i*Pr)$_3$; in step two, after removing an aliquot from the polymerization, 40 eqv. of St were added into the reaction mixture; in the final step, another aliquot of the mixture was taken, and then 15 eqv. of St, 16 eqv. of DPE and 8 eqv. of NaODP were added into the polymerization.

All the samples taken throughout sequential feeding process were also characterized by ^{1}H NMR, and the changes in signals of the protons at the chain ends shows that DPE-Si(O-*i*Pr)$_3$ could fully "*lock*" the living species and that NaODP can serve as the "*key*" and "*unlock*" them. Expansion of the region from 3.6 ppm to 2.9 ppm for each sample are shown in Figure 3, and the full ^{1}H NMR spectra are shown in Figure S6 in the ESI and are discussed in detail below. In particular, the variations of $A_{DSiO\text{-}H}$ (3.6~3.4 ppm) and $A_{D\text{-}H}$ (3.0~2.9 ppm) between the locked and unlocked states support the occurrence of a locking effect when DPE-Si(O*i*Pr)$_3$ was used to cap the living chains.

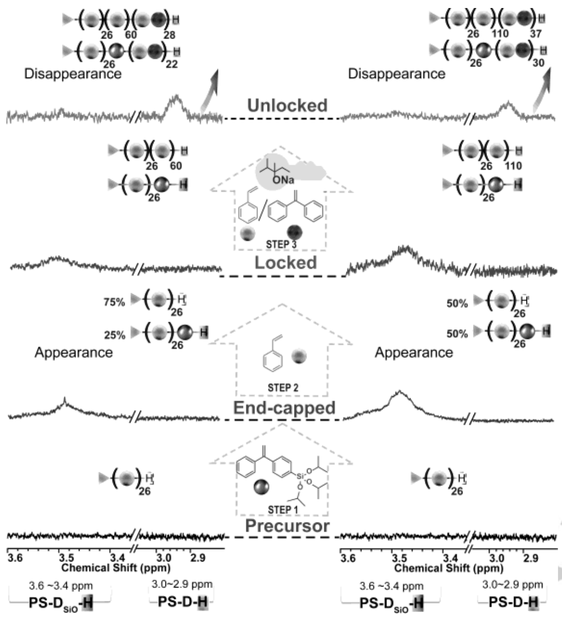

Figure 3. ^{1}H NMR spectra of the samples taken from the polymerization. [a] The left-hand column shows the precursor, 25%-End-capped, 25%-Lock-HM, and 25%-Unlocked-HM forms from the polymerization, and the right-hand column shows the precursor, 50%-End-capped, 50%-Locked-HM, and 50%-Unlocked-HM forms from the polymerization

The details of the variations in the M.W. as measured by GPC and signals for the protons in the end-caps as measured by ^{1}H NMR are listed in Table 1, and the corresponding spectra are shown in Figure S6. Additionally, all of the results acquired by GPC and ^{1}H NMR were further confirmed our understanding of this new mechanism. MALDI-TOF-MS can directly provide precise M.W. values of the polymers and elucidate the chain compositions, and therefore this technique was applied to characterize the samples taken during sequential feeding. However, for more precise characterization of the chain composition, samples with low M.W.s and narrow PDI values were necessary. Hence, samples with low M.W.s (samples of Locked and Unlocked-25%-LM, shown in Table 1) from the sequential feeding experiments were selected to carefully determine the chain compositions using the small signal variations caused by the locking and unlocking of living species end-capped with DPE-Si(O-*i*Pr)$_3$ unit insertion.

Table 1. The details of the variations in the M.W. and the integrations of the end-capped protons signals during the process of sequential feeding

Sample	M_n(kg/mol)		$A_{DR\text{-}H}$	
	Peak 1 (PDI)	Peak 2 (PDI)	$A_{DSiO\text{-}H}$	$A_{D\text{-}H}$
Precursor	/	2.7 (1.09)	-	-
End capped-25%	/	2.9 (1.12)	0.25	-
Locked-25%-LM	4.5*	2.9*	0.25	-
Unlocked-25%-LM	7.3*	4.0*	0.03	1.21
Locked-25%-HM	9.0 (1.10)	2.9 (1.12)	0.32	-
Unlocked-25%-HM	17.0*	9.0*	0.07	0.92
End capped-50%	/	2.8 (1.17)	0.70	-
Locked-50%-LM	5.5*	2.8*	0.62	-
Unlocked-50%-LM	9.8*	4.1*	0.09	0.78
Locked-50%-HM	14.2 (1.07)	3.0 (1.14)	0.78	-
Unlocked-50%-HM	24.7 (1.10)	11.9 (1.11)	0.10	0.61

[a] M.W.s were measured by GPC, and the asterisk indicates that the GPC curve showed two peaks using Origin software. [b] The number of end-capped protons for each sample was measured by ^{1}H NMR and calculated using the equation shown in Table S1, and the corresponding GPC spectra are shown in Figure S5. [c] Experiments were designed to generate HM (high M.W.) products. The monomer feeding in step 3 was 40 eqv. of St, and the monomer feeding at step 4 was 15 eqv. of St, 16 eqv. of DPE, and 8.0 eqv. of NaODP. [d] Experiments were designed to generate LM (low M.W.) products. The monomer feeding at step 3 was 10 eqv. of St, and the monomer feeding at step 4 was 5 eqv. of St, 6 eqv. of DPE, and 8.0 eqv. of NaODP..

The pivotal variations in the characteristics of the products according to MALDI-TOF-MS are shown in Figure 4 and discussed below (detailed descriptions are provided in the ESI):

1. In the end-capped state, a portion of the PS chains were clearly capped with one DPE-Si(O-*i*Pr)$_3$ unit, and this was confirmed by the changes in the characterization data from before and after end-capping.
2. Notably, in the locked state, the living species not end-capped by DPE-Si(O-*i*Pr)$_3$ units continue to undergo normal propagation when additional St monomers are added. The critical distinction in this state was that the pause in the propagation of the chains that were end-capped by DPE-Si(O-*i*Pr)$_3$ was clear. All the results were confirmed by the variations in the chain composition demonstrated by the MALDI-TOF-MS data.
3. The most significant and interesting discovery regarding species in the unlocked state was that the pause in the propagation for these living species end-capped with DPE-Si(O-*i*Pr)$_3$ was completely reverse and chain growth was restarted, and this can only be attributed to the addition of NaODP. Additionally, this result confirms that the living species end-capped with DPE-Si(O-*i*Pr)$_3$ underwent propagation (were not termination), and they remained in the locked state until the addition of the "*key*"-NaODP.

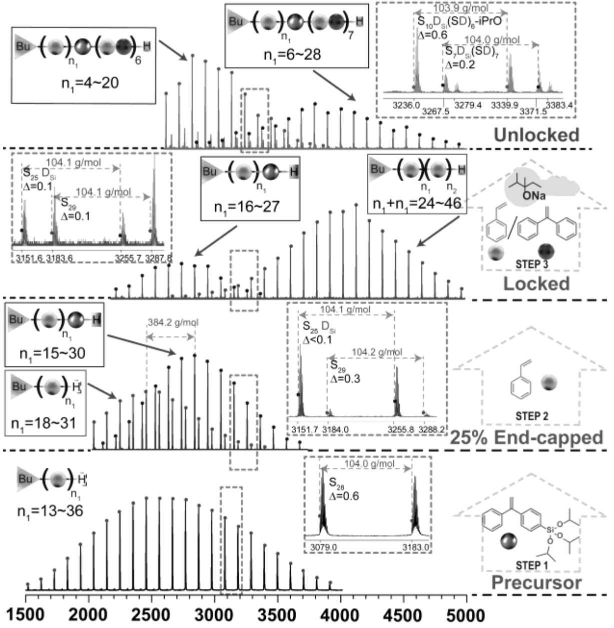

Figure 4. The MALDI-TOF spectra of the samples taken from the polymerization. [a] The left-hand column shows the precursor, 25%-End-capped, 25%-Locked-LM, and 25%-Unlocked-LM forms from the polymerization, and the right-hand column shows the precursor, 50%-End-capped, 50%-Locked-LM, and 50%-Unlocked-LM forms from the polymerization. [b] In step one, the precursor, with a M.W. of 2 kg/mol, was end-capped by a certain amount of DPE-Si(O-*i*Pr)$_3$; in step two, after taking an aliquot from the polymerization reaction, 40 eqv. of St were added to the reaction mixture; in the final step, another aliquot of the mixture was taken, and then 15 eqv. of St, 16 eqv. of DPE, and 8 eqv. of NaODP were added into the polymerization reaction..

Hence, based on careful characterization by MALDI-TOF-MS, the results thoroughly confirm the effects of locking and unlocking on living species can be controlled only through end-capping by DPE-Si(O-*i*Pr)$_3$ and the addition of NaODP (see Figure 5a). Although unlocking via NaODP is currently irreversible, the locking and unlocking of living species during LAP is truly a novel and intriguing finding. In addition to verifying our previously mentioned hypothesis, these results also demonstrate that what is currently known about LAP is only the tip of the iceberg. Additionally, to fully understand the “lock-unlock” phenomenon when using DPE-Si(O-*i*Pr)$_3$ and NaODP during LAP, some specific living species, DPE-Li, DPE-Si(O-*i*Pr)$_3$-Li and [(DPE-Si(O-*i*Pr)$_3$-Li)•NaODP], were synthesized and characterized by ^{13}C NMR and 135° DEPT-^{13}C NMR in benzene-d$_6$, and the corresponding spectra are shown in Figure S7 and Figure S8. These spectra directly show that the structures of these three living species are significantly different, and this is particularly obvious in the chemical shifts of (α)C. First, DPE is commonly used as an end-capping agent to stabilize active anionic centers[20]. Such effects are attributed to the delocalization of the negative charge between (α)C (C16 in Figure S7) and the two ipso carbons (C6 and C7 in Figure S7). The ^{13}C NMR spectra of the DPE-Li and DPE monomers showed that the resonances of the two (ipso)C atoms of the DPE monomer shift downfield by 1.9 ppm when *sec*-BuLi was added. The change in the chemical shift shows that the Li atom was η^3-coordinated to (α)C and the two (ipso)C atoms in DPE-Li. However, the resonances of the (ipso)C atoms of the phenyl rings exhibited little change between DPE-Si(O-*i*Pr)$_3$ and DPE-Si(O-*i*Pr)$_3$-Li, and the signal of the methyl groups connected to the O atoms split into two signals, one of which moved upfield by 2.5 ppm when DPE-Si(O-*i*Pr)$_3$ was mixed with *sec*-BuLi. The ^{13}C NMR data suggested that the alkoxysilyl group was involved in the Li coordination. Second, there were large differences between the chemical shifts of the (α)C atoms of DPE-Li, DPE-Si(O-*i*Pr)$_3$-Li and [(DPE-Si(O-*i*Pr)$_3$-Li)•NaODP]. The shifts of the (α)C atoms of DPE-Li and DPE-Si(O-*i*Pr)$_3$-Li were approximately 79.5 ppm and 100.4 ppm, respectively. However, the addition of NaODP to DPE-Si(O-*i*Pr)$_3$-Li caused the signal of the (α)C atom at 100.4 ppm to disappear. All of these results suggest that the chemical environment of the (α)C atoms changed upon addition of NaODP.

Overall, based on the ^{13}C NMR spectra, we assumed that the three oxygen atoms of the alkoxysilyl groups were η^3-coordinated to the Li atom. This preliminary binding model was evaluated by DFT with Gaussian 09 using the M062x/6-31+G(d) method to simulate the electronic structure of the locked living anion and potentially validate this structure. Surprisingly, the results reflected a complex coordination structure involving a Li atom and two O atoms of the alkoxysilyl group and one phenyl ring, as shown in Figure 5b. The Li atom was η^2-coordinated to the two O atoms, and natural bonding orbital (NBO) analysis showed that the Li atom, as an electron acceptor, and the two O atoms, as the donors, formed strong interactions, and the energies of the Li-O interactions were approximately 10.26 and 12.16 kcal/mol. In addition, the π-bonds of the phenyl ring were also coordinated with the Li atom, and the energy of this interaction was approximately 10 kcal/mol (the details are listed in Table S2). Hence, the Li atom was bound to the O atoms and a phenyl ring. This particular structure, with its substantial steric hindrance and electron delocalization, might prevent reactions with the added St monomers. In addition, when NaODP was added, the living species was converted from its initial compact structure to a four-membered ring. The four-membered ring was also evaluated by DFT with the same method, and the results shows that the O atoms of the alkoxysilyl groups were no longer coordinated with the Li atom, and instead, the Na and O atoms of the NaODP were coordinated with the Li. Four-membered rings of this type have been reported as a structural modifier that could be used to regulate living anionic copolymerizations[14a, 21]. Above all, the locked conformation of DPE-Si(O-*i*Pr)$_3$-Li could be converted into a classical four-membered ring-containing living center (Unlocked form) due to the effect of the key, NaODP, and this transition can reinitiate propagation with the monomers.

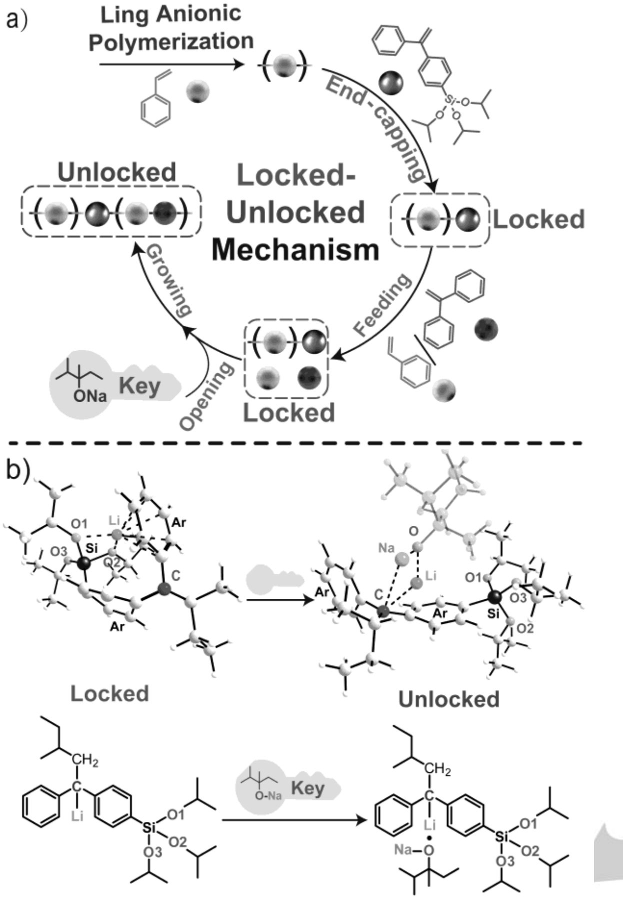

Figure 5. [a] Locked-unlocked mechanism. [b] DFT simulations of the locked and unlocked forms.

In conclusion, we elucidated a “locked-unlocked” mechanism in LAP in which living anionic species could be quantitatively locked by end-capping with DPE-Si(O-*i*Pr)$_3$ and then unlocked by adding the “key”, NaODP. These new mechanistic findings were carefully confirmed by designing experiments involving the sequential feeding of quantitative DPE-Si(O-*i*Pr)$_3$ and traditional monomers mixed with NaODP and characterizing the corresponding products generated throughout the feeding process by GPC, NMR, and MALDI-TOF-MS. The process of locking and unlocking the living species was clearly confirmed by these characterization techniques. Then, based on the significant differences between the normal ^{13}C and the 135° DEPT-^{13}C NMR spectra of the locked and unlocked living species, a reasonable “locked-unlocked” mechanism in the LAP was simulated by the Gaussian method. The data suggested that the strong coordination within the living species might result in the unlocking of further polymerization. The “key”, NaODP, can unlock the species by disrupting the coordination, forming a classical 4-membered ring-containing living center and restarting the polymerization. We believe that the new “locking-unlocking” mechanism could provide a new method for better controlling the composition or the sequence of polymers and provide new insight into the unknown attributes of LAP reactions.

Acknowledgements

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Keywords: Living anionic polymerization • 1-(*Tri*-isopropoxymethylsilylphenyl)-1-phenylethylene (DPE-Si(O-*i*Pr)$_3$) • Locked-Unlocked mechanism

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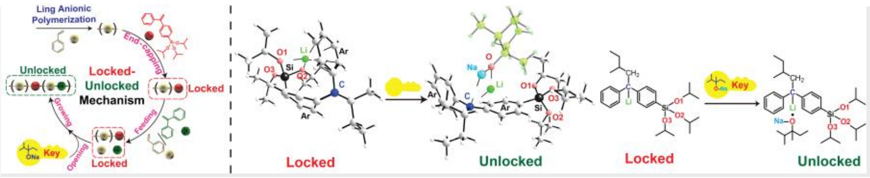

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