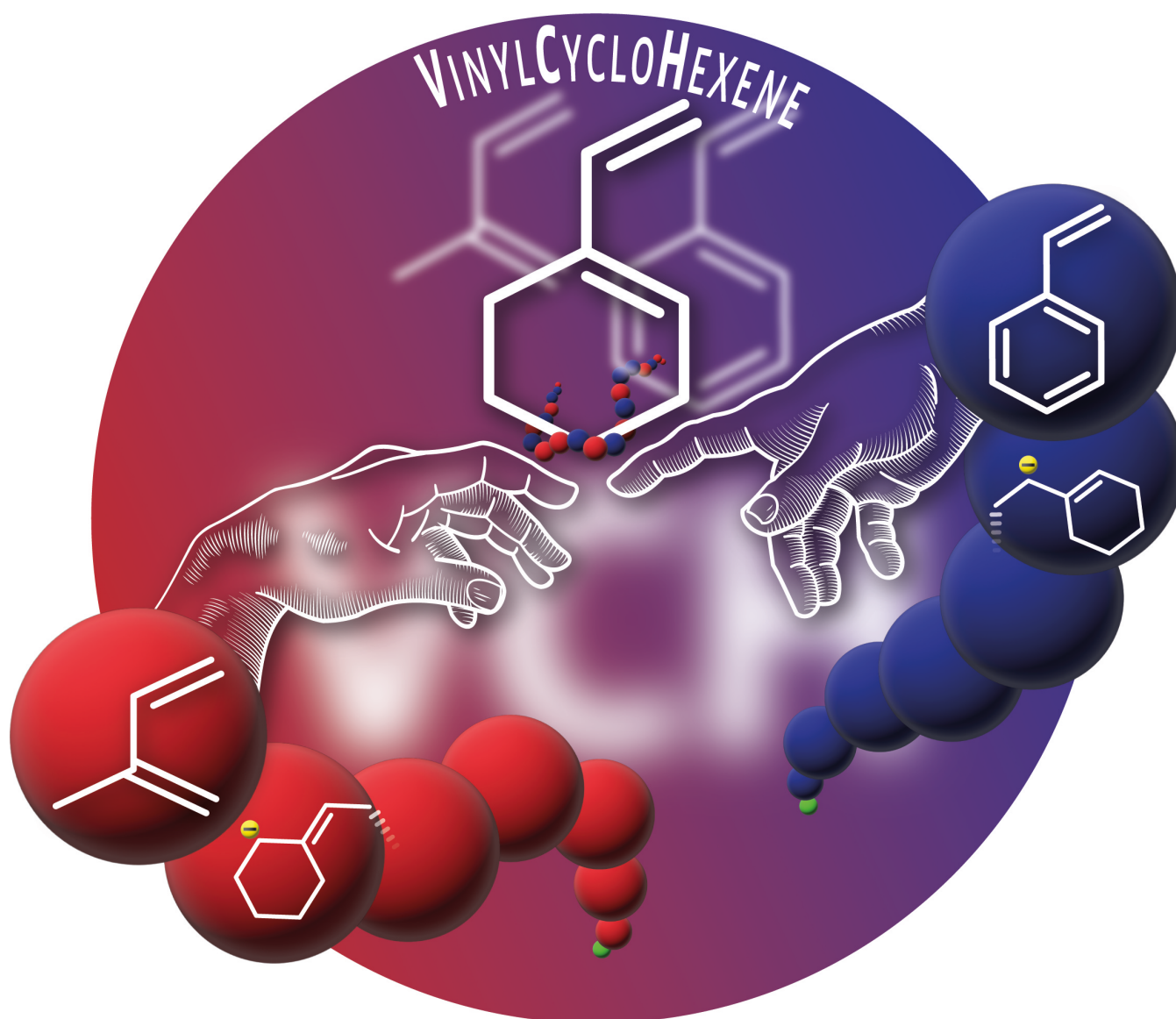


Polymerization

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# Merging Styrene and Diene Structures to a Cyclic Diene: Anionic Polymerization of 1-Vinylcyclohexene (VCH)

*Christoph Hahn<sup>+</sup>, Moritz Rauschenbach<sup>+</sup>, and Holger Frey\**Angewandte  
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**Abstract:** We report the first anionic polymerization of 1-vinylcyclohexene (VCH). This structure may be considered as an intermediate between dienes and styrene. The polymerization of this cyclic 1,2-disubstituted 1,3-diene proceeded quantitatively in cyclohexane at 25 °C with *sec*-butyllithium as an initiator. The obtained polymers have well-controlled molecular weights in the range of 5 to 142 kg mol<sup>-1</sup>, controlled by the molar ratio of monomer and initiator, with narrow molecular weight distributions ( $\mathcal{D} < 1.07$ –1.20). In situ <sup>1</sup>H NMR kinetic characterization revealed a weak gradient structure for the copolymers of styrene and VCH, ( $r_{\text{Sty}} = 2.55$ ,  $r_{\text{VCH}} = 0.39$ ). P(VCH) obtained in cyclohexane with *sec*-BuLi as an initiator showed both 1,4- and 3,4-incorporation mode (ratio: 64:36). It was demonstrated that the microstructure of the resulting P(VCH) can be altered by the addition of a modifier (THF), resulting in increasing 3,4-microstructure (up to 78 %) and elevated glass-transition temperature up to 89 °C. Thus, the monomer VCH polymerizes carbanionically like a diene, however leading to rigid polymers with high glass transition temperature, which provides interesting options for combination with other dienes to well-defined polymer architectures and materials.

Linear 1,3-dienes can be polymerized by various polymerization techniques such as emulsion polymerization, controlled and free radical polymerization, living anionic polymerization and catalytic or insertion polymerization.<sup>[1]</sup> Linear dienes play a key role for highly flexible polymers for manifold elastomer applications. However, cyclic 1,3-dienes with one vinyl double bond have been explored only to a limited extent. The first report on the polymerization of 1-vinylcyclohexene (VCH) was published in 1971 by Hara et al.<sup>[2]</sup> They polymerized VCH by cationic initiators and reported both 3,4- and 1,4-propagation mode, albeit no SEC measurements were conducted. Bonnans-Plaisance investigated the polymerization of VCH by cationic or radical initiators.<sup>[3]</sup> In 1997 Longo et al. reported that VCH polymerized exclusively in 3,4-addition mode in the presence of methylaluminumoxane (MAO) and *rac*-[ethylene-bis(1-indenyl)]-ZrCl<sub>2</sub>.<sup>[4]</sup> However, the poor catalytic activity resulted in extremely low monomer conversion (0.1 %). On

the contrary, the (Flu)(Cp)<sup>3</sup>PrZrCl<sub>2</sub>-MAO system afforded polymers with 1,4-*trans* microstructure.

In general, it was demonstrated that cyclic 1,3-dienes with different substitution pattern can undergo living anionic polymerization. Following the definition of Szwarc, no transfer and termination reactions occur during polymerization.<sup>[5]</sup> Ishizone et al. reported anionic polymerization of a series of extremely sterically hindered allylidene monomers. 1,1-disubstituted 1,3-butadiene derivatives were polymerized in a living manner, using *sec*-BuLi either in cyclohexane at 40 °C or in THF at 0–30 °C.<sup>[6]</sup> The substituents in 1,1-position studied were dimethyl, cyclohexyl, cycloheptyl, 2,2,5,5-tetramethylcyclopentyl, and bornyl. It is noteworthy that less bulky substituents resulted in polymers, wherein the 1,4-*trans* microstructure was predominant, whereas bulkier substituents resulted in an exclusive 3,4-microstructure under the very same conditions.<sup>[6]</sup> Selective hydrogenation of PI in PS-*b*-PI-*b*-PS triblock copolymers is employed to enhance thermal stability and induces altered mechanical properties, such as pronounced strain hardening.<sup>[7,8]</sup> Furthermore, the hydrogenation of polymers can increase the Flory-Huggins parameter ( $\chi$ ) and the order-disorder-transition temperature ( $T_{\text{ODT}}$ ). The key challenge lies in the selective hydrogenation of the PI block, retaining PS without saturation and without chain scission under the harsh conditions of the procedure.<sup>[9]</sup> For full saturation of all double bonds in PI-PS copolymers (olefinic and aromatic), heterogeneous palladium catalysts supported on calcium carbonate can be utilized. The hydrogenated 3,4-microstructure of VCH is identical with a fully hydrogenated PS, i.e. formally polyvinylcyclohexane.<sup>[4,10]</sup>

In this work, we report on the polymerization of VCH by anionic polymerization in order to evaluate the behavior of a conjugated cyclic 1,3-diene, possessing one cyclic and one vinyl double bond. We aim at understanding, whether the polymerization behavior is comparable to a conjugated diene (as isoprene) or to styrene due to the related molecular structure. In terms of the resulting polymer materials, the cyclic 1,3-diene structure should provide sufficient rigidity to result in a high glass-transition temperature polymer comparable to PS. Additionally, the cyclic 1,3-diene may be viewed as a less delocalized styrene analog with a partially hydrogenated aromatic ring. In contrast to the catalytic polymerization mentioned above, we aimed at quantitative monomer conversion and a living polymerization mechanism.

The monomer 1-vinylcyclohexene (VCH) was synthesized according to literature, starting from 1-ethynylcyclohexene by partial hydrogenation of the terminal alkyne with Pd/CaCO<sub>3</sub>, deliberately contaminated with Pb(OAc)<sub>2</sub>.<sup>[11]</sup>

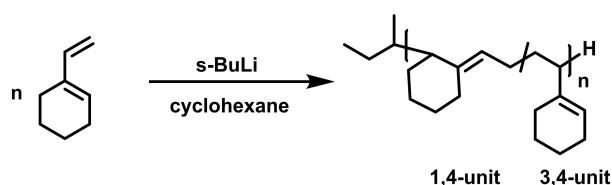
To the best of our knowledge, living anionic polymerization of VCH in apolar media with organo-lithium initiators (Scheme 1) has not been reported to date. The onset of the living polymerization was accompanied by an intense yellow color (Figure S21) upon initiation with *sec*-butyllithium, demonstrating the delocalization of the living carbanion. The living nature of the polymerization is demonstrated by the linear plot of  $\ln(M_0/M)$  vs. polymerization time (Supporting Information Figure S20).

[\*] C. Hahn,<sup>†</sup> M. Rauschenbach,<sup>†</sup> H. Frey  
Department of Chemistry, Johannes Gutenberg University  
Duesbergweg 10–14, 55128 Mainz (Germany)  
E-mail: h.frey@uni-mainz.de

C. Hahn<sup>†</sup>  
Max-Planck Graduate Center, MPG  
Staudingerweg 9, 55128 Mainz (Germany)

[†] These authors contributed equally to this work.

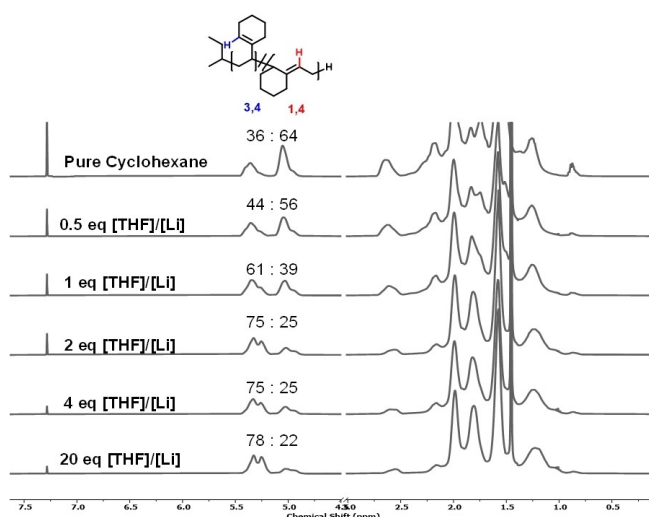
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**Scheme 1.** Anionic polymerization of VCH in cyclohexane. For reasons of clarity we exclude the cis-1,4 microstructure in the scheme. (For details regarding characterization of the microstructures see Supporting Information).

We synthesized a series of homopolymers with targeted molecular weights in the range of 5 to 48 kg mol<sup>-1</sup>, as summarized in Table 1 (SEC, THF, PS calibration). The resulting dispersities were in the range of  $\bar{D}$  = 1.07–1.20. In addition, the absolute molecular weight of low molecular weight polymer was determined via MALDI-ToF MS, confirming the narrow distribution and incorporation of 1-vinylcyclohexene (108.18 g mol<sup>-1</sup>). The MALDI-ToF spectrum (Figures S6,S7) shows the different species assigned to the respective distributions with different cations. The relative molecular weight (GPC, 5130 g mol<sup>-1</sup>) and absolute molecular weight according to MALDI-ToF MS (4800 g mol<sup>-1</sup>) are in good agreement.

DSC measurements reveal that the  $T_g$  values of the PVCH homopolymers are in the range of 62 to 78 °C, reaching a plateau value with constant  $T_g$  at 18.000 g mol<sup>-1</sup>, i.e. somewhat lower than for polystyrene. The polymerization of VCH was investigated regarding the addition of modifiers with respect to their influence on the microstructure. The microstructure was determined by integration of the allylic protons (5.1 ppm and 5.3 ppm) in the <sup>1</sup>H NMR spectra of the resulting polymer (Figure 1).



**Figure 1.** Stacked NMR spectra (CDCl<sub>3</sub>, 25 °C, 400 MHz) of P(VCH) with different equivalents (from top to bottom: pure cyclohexane, 0.5 equiv, 1 equiv, 2 equiv, 4 equiv, 20 equiv) of THF as a modifier.

Poly(vinylcyclohexene) (P(VCH)) obtained in cyclohexane by anionic polymerization with *sec*-BuLi as an initiator resulted in 64 % 1,4-microstructure (36 % 3,4-microstructure, respectively). The determination of the 1,4- and 3,4-units by NMR spectroscopy was carried out in agreement with literature.<sup>[4]</sup> Figure 1 shows the change of the structure of P(VCH) as a consequence of an increasing amount of the modifier THF towards 3,4-incorporation in <sup>1</sup>H NMR spectroscopy. Further investigation of the polymer structure by NMR spectroscopy is illustrated in the Supporting Information (Figure S9–S12).

As seen in other studies based on catalytic polymerization, no 1,2-microstructure of VCH was observed (see Supporting Information (Figure S11)). Polar additives such as THF are known to alter the microstructure of 1,3-dienes towards higher 3,4-microstructure (and 1,2-microstructure) content.<sup>[12]</sup> We utilized small quantities of polar modifiers to obtain a high content of 3,4-microstructure PVCH. This microstructure is comparable to a (semi)-hydrogenated polystyrene. Via NMR spectroscopy it was observed that the polymers possess an increasing amount of 3,4-units with increasing ratio of THF/Li. Upon the addition of more than 20 equiv of THF, no further increase of 3,4-units was observed. As a result of the modified microstructures, we observed significantly higher glass-transition temperatures upon addition of THF, compared to polymers obtained in cyclohexane ( $T_g$  = 74 to 89 °C).

We further investigated VCH with respect to statistical copolymerization with styrene and isoprene, since it is structurally related to both monomers. We were interested in understanding the behavior of the VCH monomer, particularly whether it is comparable to a 1,3-diene or rather to a vinyl monomer, such as styrene.

The results of the online kinetics of VCH with styrene and isoprene as well as a description of the method are shown in the Supporting Information. The reactivity ratios of styrene and VCH were determined to be  $r_{\text{sty}}=2.55$  and  $r_{\text{VCH}}=0.39$ . The crossover of PS–Li to P(VCH)–Li is indicated by a significant color change in the block-copolymerization of P(S-*b*-VCH) (see Supporting Information Figure S21).

To our surprise, we observed inverse reactivity ratios of VCH and styrene in comparison to those known from conventional diene/styrene copolymers.<sup>[13]</sup> In general, copolymerization of styrene and 1,3-dienes (e.g. isoprene and butadiene) results in pronounced gradient or tapered structures due to the slow crossover of PI–Li to styrene. The online NMR data show that styrene is consumed preferentially in the statistical copolymerization of styrene/VCH. This finding suggests fast crossover from P(VCH)–Li to styrene, in contrast to linear dienes, such as isoprene or myrcene.<sup>[14]</sup> Generally, the reactivity of styrene derivatives can be estimated from their  $\beta$ -carbon shift in <sup>13</sup>C NMR spectroscopy. The reactivity of the monomer is mainly based on the electron charge density of the reactive vinyl bond, which correlates with the chemical shift of the  $\beta$ -carbon. VCH shows a significantly decreased, low  $\beta$ -carbon shift (109.72 ppm) compared to styrene (113.36 ppm).<sup>[15]</sup> Based on these observations, we conclude a lower reactivity of

VCH compared to styrene. This is tentatively explained by the vinyl bond in the 1,3-diene being considerably less delocalized than the vinyl group at an aromatic ring in case of styrene. In other words, reduced stabilization is assumed compared to styrene.

Sequential block copolymerization of VCH with isoprene resulted in bimodal distributions with rather high dispersity of  $>1.35$ . We attribute this to the high reactivity difference between isoprene and VCH, resulting in a very low crossover rate to the less favored monomer. To further elucidate the slow crossover rate, we initiated VCH with living poly(isoprenyl)-lithium and vice versa. The results reveal that irrespective of the first monomer, the SEC traces show bimodal distributions (Figure S23). Consequently, the condition of fast initiation for a controlled polymerization is not fulfilled, leading to the observed bimodal molecular weight distribution. Surprisingly, the living chain ends of isoprene and VCH both showed incomplete initiation of the respective other monomer, leading to bimodal distributions in both cases. Moreover, increasing polymerization temperature to  $40^{\circ}\text{C}$  did not improve the resulting molecular weight distributions (Figure S23). The online kinetics study of the statistical copolymerization of isoprene and VCH showed full consumption of isoprene. However, the integrals of the respective signals of VCH remained nearly unchanged, and propagation of VCH only started, when no isoprene was left. This indicates highly disparate reactivity ratios of  $r_1 \gg 1$  and  $r_{\text{VCH}} \ll 1$  confirming the unfavorable crossover reaction (Figures S24–S27) and a very steep gradient, as known from the system isoprene/4-methylstyrene.<sup>[16]</sup>

P(VCH) generated by polymerization in cyclohexane (P3, 36 % 3,4-addition) and P(VCH) obtained with 20 equiv of THF modifier (P11, 78 % 3,4-addition) were hydrogenated, using palladium on carbon (10 wt %) as a catalyst under 30 bar  $\text{H}_2$  pressure at  $130^{\circ}\text{C}$  in a Parr reactor. The hydrogenation led to full saturation of the polymer, confirmed by  $^1\text{H}$  NMR spectroscopy (Figures S28, S29). Poly(vinylcyclohexane) P(CHE) has been prepared previously by coordination polymerization of vinylcyclohexane or by complete catalytic hydrogenation of PS. In comparison to literature, we found identical shifts in  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals to P(CHE) for hydrogenated P(VCH).<sup>[4]</sup>

For Sample P11, we observed an increase in  $T_g$  from  $89$  to  $114^{\circ}\text{C}$  after hydrogenation. The hydrogenated polymer consists of 78 % poly(vinylcyclohexane) moieties with a  $T_g$  of  $140^{\circ}\text{C}$ .<sup>[7]</sup> No evidence of any chain scission or degradation of the polymer backbone after hydrogenation (see SEC traces, Figure S30) was found. A lowered  $T_g$  of  $70^{\circ}\text{C}$  was observed after hydrogenation of Sample P3 (Figure S31), which is tentatively explained by the increased freedom of rotation of the saturated polymer backbone.

The living anionic polymerization of VCH, which has not been reported to date, affords polymers with good control over molecular weights and moderate to narrow molecular weight distributions. Compared to the catalytic approach<sup>[4]</sup> full conversion was always obtained due to the living character of the anionic polymerization. The results show that the microstructure of P(VCH) can be altered by

the addition of THF, leading to a higher extent of 3,4-incorporation.<sup>[17]</sup> A rigid polydiene with a tunable  $T_g$  in the range of  $77$ – $89^{\circ}\text{C}$  is obtained.

Initially, the question whether the monomer acts as a 1,3-diene or as a styrenic monomer was raised. Based on this study, VCH acts comparable to established dienes in the anionic polymerization, however, the final material properties are similar to polystyrene, with similar rigidity. The hydrogenation of P(VCH) resulted in polymers containing poly(vinylcyclohexane) segments, causing an increase in  $T_g$  to  $114^{\circ}\text{C}$  with a monomodal molecular weight distribution without any evidence of chain degradation.

This work demonstrates the significant effect of one double bond in a 1,3-diene being sterically constrained on the anionic polymerization behavior. It is important to emphasize that VCH represents a model system for a variety of biobased 1,3-dienes, derived from natural terpenes. VCH itself shows intriguing potential to produce fully hydrogenated high  $T_g$  materials, with improved phase separation behavior and access to complex polymer architectures via living anionic copolymerization.

### Author Contributions

*Christoph Hahn*\*: Investigation, synthesis, data curation, methodology, conceptualization, writing. *Moritz Rauschenbach*\*: Investigation, data curation, methodology, writing. *Holger Frey*: supervision, conceptualization, writing – review and editing. \* contributed equally to this work.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** 1,3-Dienes • Copolymerization Kinetics • Living Anionic Polymerization • Polyisoprene • Polystyrene

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