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Choose Your 1,3-Diene

Nopadiene

Myrcene

Farnesene

Cat

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Leaf

Spring

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Green perspective drives the renaissance of anionic diene polymerization

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Polymers based on 1,3-diene monomers play a pivotal role in many commercial elastomers and thermoplastic elastomers. This perspective summarizes the state of the art and recent developments in the living anionic polymerization of dienes, permitting to finely tune the properties of the resulting polymers. An emphasis is placed on novel biobased diene monomers (myrcene, farnesene, etc.) and polymerization solvents, which bear promise for more sustainable elastomers in the future. Furthermore, statistical copolymerization of dienes with vinyl monomers and the *in situ* monitoring of monomer gradients and formation of tapered di- and triblock copolymers due to disparate reactivity ratios is also reviewed. Thermoplastic elastomers based on tri- and multiblock architectures as well as recently reported diene-based polymer architectures are discussed as well. A summary of current challenges and future options for carbanionic diene polymerization concludes this short review article.

1. Introduction

Polymers based on 1,3-diene monomers played a pivotal role in the early days of macromolecular science, when Staudinger introduced the term “macromolecule” in 1920, specifically referring to polyisoprene (PI).^{1,2} Although the first anionic diene polymerization was observed already a decade earlier by Matthews,³ who stored isoprene in the presence of sodium, it was *IG Farben* that later commercialized the alkali metal-initiated polybutadiene (PB) based elastomers as “Buna”. This development was prompted by a substantial increase in demand for natural rubber.^{4,5} From a molecular perspective, natural rubber derived from *hevea brasiliensis* consists of 1,4-

cis (>98%) polyisoprene.⁶ Nowadays, synthetic rubber based on diene polymerization is produced on a megaton scale and is often combined or blended with natural rubber.⁷ Both synthetic polydienes and natural rubber possess a double bond per repeating unit, rendering them suitable for crosslinking *via* vulcanization. The resulting elastomers are used for applications as diverse as tires and medical gloves. The anionic polymerization of dienes continues to garner significant attention in today’s industrial and scientific research.⁸ This leads to continuous new insights also for the established dienes such as butadiene (B) and isoprene (I). Synthetic rubber offers advantages over natural rubber due to its versatile and adjustable properties, since the exact chemical nature of the polymer can be influenced during the polymerization process.⁹ The commercial importance also arises from the option to produce homo- and copolymers with controlled molar masses and the capability to precisely regulate the microstructure by so called “modifiers” that coordinate the counterion to tailor a variety of

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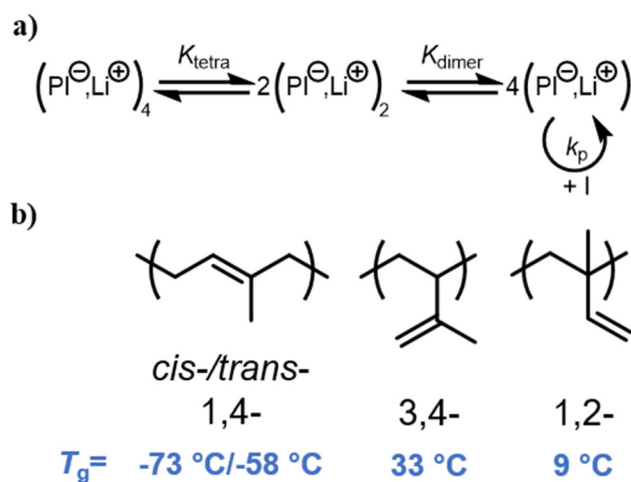
Moritz Rauschenbach was born in Bad Homburg v. d. Höhe (1996) and graduated in Chemistry (2021) from the Johannes-Gutenberg-University, Mainz in Germany. During his studies he spent 6 months in the labs of Rachel O'Reilly at the University of Birmingham working on the synthesis of antimicrobial hyperbranched polymer-complexes. In his PhD he focusses on the anionic polymerization of non-conventional 1,3-dienes. Hence, he is interested in the kinetics of those new monomers in comparison to established systems with the aim of elucidating their potential as thermoplastics or functional precursors.

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Fig. 1 Overview of a selection of 1,3-dienes discussed in this perspective, including recently introduced diene monomers. Reactive diene moieties are marked for each monomer.



Scheme 1 (a) Aggregation equilibrium of polyisoprenyl lithium in non-polar solvents in analogy to Müller and Matyjaszewski; (b) possible microstructures of PI and their respective glass temperatures.^{38,40}

counter ion,^{10,36,37} solvent,^{10,38} and the presence of a polar modifier.^{17,19} The formation of aggregates during the polymerization in nonpolar solvents and their suppression by the use of polar solvents or modifiers was found to be one of the key aspects of the propagation mechanism. The number of the aggregating chains evolves from the kinetic order, expressed by the following eqn (1):

$$\log(k_{\text{app}}) \sim \frac{1}{n} \log[\text{Ini}]_0 \quad (1)$$

k_{app} gives the apparent rate constant of the propagation, $[\text{Ini}]_0$ the initial concentration of the initiator and n the number of aggregating chains. Importantly, the aggregates are

in an equilibration with the unimers, which are considered to be the active species capable of sustaining the propagation mechanism, see Scheme 1. M. Szwarc already reported that the relative rates of propagation for isoprene and butadiene are ordered as isoprene > butadiene, while both exhibit a number of aggregating chains of $n = 4$.^{10,39} However, it was found that polyisoprenyl lithium aggregation also depends on the concentration of active chain ends. An overall equilibration between tetramers and dimers was observed, with n approaching ~ 2 with decreasing concentration.^{10,38} β -Myrcene and β -farnesene, although kinetically investigated under the assumption of tetramer formation, have not been explored with respect to their aggregation behavior.^{19,22} The observation that their propagation rate surpasses that of isoprene suggests the presence of an equilibrium solely between dimers and unimers. It should be noted that this assumption has not yet been empirically confirmed.

The coordination of the counterion to the incoming monomer and its spatial orientation mainly dictate the regioselectivity, see Scheme 2. In nonpolar media, it has been reported to undergo a six-membered transition state, where the diene is added in a *cis*-form, explaining overall high amount of 1,4-addition. The final *cis/trans* ratios have been extensively elucidated by Gebert *et al.* who suggested an isomerization of the *cis*-oriented chain end to a *trans*-form before the next monomer addition.^{38,41,42} Worsfold and Bywater further proposed that the isomerization occurs in competition with the monomer addition.^{10,43} Based on these fundamental studies, the final ratio of *cis* and *trans* 1,4-units can be explained.

By changing the counterion from Li^+ to Na^+ or K^+ , for instance, the interionic distance increases, which reduces the 1,4-content of polydienes.^{10,44} Based on the industrially most





Scheme 2 Proposed mechanism of the polymerization of isoprene with lithium as a counter ion in apolar or polar media, respectively; image is reproduced from Frey *et al.*⁴¹ with permission of the Royal Society of Chemistry, 2022.

popular diene representative 1,3-butadiene, Carlotti and co-workers have investigated the impact of bimetallic initiator systems with lithium and potassium or calcium, respectively. They studied the influence of the additional coordinative center on the microstructure. While the addition of potassium led to an expected increase of 1,2-units, the designed calcium-lithium initiators enabled high control towards *trans*-1,4-units.^{45,46} Reviewing the accessible microstructures of polybutadiene, Carlotti *et al.* also reported on the combined effect of both variation of the counterions as well as changing to polar solvents.⁹ The polymerization in polar solvents, *e.g.* THF, or the addition of polar modifiers are both associated with sup-

pression of the coordination between the chain end, the counterion and the diene. In consequence, the resulting increased vinyl content enhances the backbone rigidity of the polydiene, which is reflected by an increase of the glass temperature (Scheme 1b).^{38,41} The influence of solvents on the anionic polymerization will be discussed below in greater detail.

A rather new aspect in this field is the examination of the orientation of the double bonds with respect to each other in the 1,3-diene scaffold. In this regard, DFT calculations can give mechanistic insights beyond the mere conversion in a copolymerization. In a recent publication we investigated rotationally constrained dienes.⁴¹ Two model compounds were synthesized to obtain a *cisoid* and a *transoid* monomer as shown in Fig. 2a. DFT calculations identified deviations of the torsion angle in both monomers and allow for an assumption regarding the reactivity given by the electron densities. A crucial finding from the simulation is that if a fixed *transoid* geometry is present, only one of the double bonds can coordinate with the lithium counterion. This crucial step should prevent the polymerization. In contrast, the *cisoid* model compound coordinates with both double bonds, albeit a distortion of the ring is required. Consequently, only homopolymers with the *cisoid* 1,2-dimethylene-cyclohexane (DMCH) were obtained and copolymerization with isoprene was achieved. DFT calculations show that the energy required for the polymerization of DMCH is significantly increased compared to isoprene due to a required distortion of the ring, see Fig. 2b. Empirically, this was observed *via in situ* ¹H NMR kinetics. In the copolymerization with isoprene, isoprene is consumed predominantly, resulting in a gradient structure along the chain. The homopolymerization of DMCH itself required unusual conditions to keep the growing chain in solution: high temperatures of 140 °C were applied in the high-boiling solvent tetralin. Noteworthy, the analysis of PDMCH confirmed the exclusive formation of 1,4-units and a *T_g* of 53 °C. In contrast, no poly-

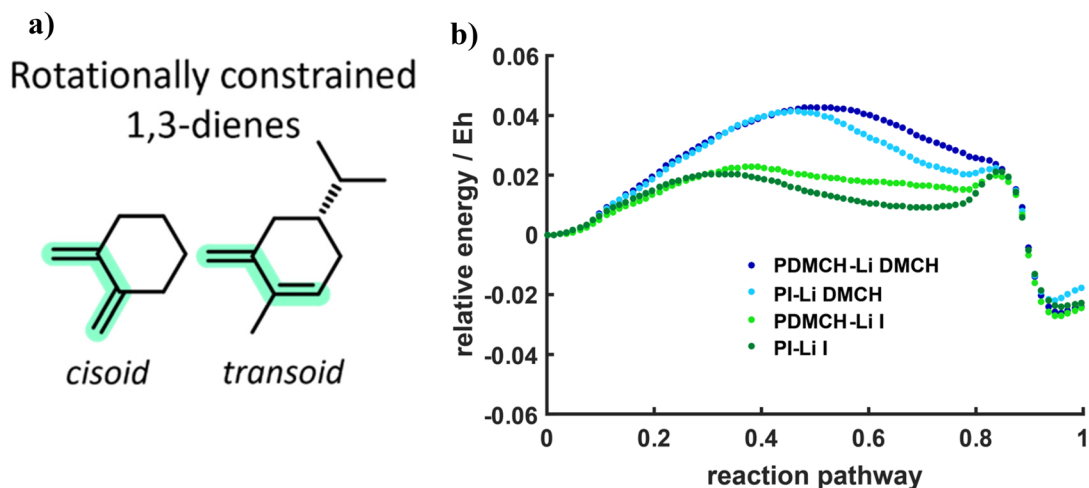


Fig. 2 (a) Rotationally constrained dienes with a *cisoid* (DMCH) and a *transoid* (IMMCH) geometry; (b) reaction pathways for the four possible propagation steps of the copolymerization of isoprene and DMCH (addition of DMCH, blue; addition of isoprene, green), image is reproduced from Frey *et al.*⁴¹ with permission of the Royal Society of Chemistry, 2022.



mers were obtained with the *transoid* monomer IMMCH. In 2015, Ishizone and coworkers described the anionic polymerization of the *transoid*-fixed benzofulvene in both polar and apolar media.^{47–49} This can be attributed to the conjugation with the aromatic ring that leads to a planar cross-conjugated π -system resulting in a higher reactivity. The removal of the aromatic ring, *e.g.*, in methylene cyclopentane resulted in the expected reduction of the reactivity. For this monomer 70 °C and a reaction time of 4 days were required to achieve full conversion.⁵⁰ Consequently, it can be concluded that *transoid* dienes are not suitable for the living anionic polymerization in nonpolar solvents at mild conditions.

Moreover, already a methyl group can interfere with the coordinative process and prevent the formation of a narrow molar mass distribution. This was shown for the two isomers *trans*- and *cis*-pentadiene. They exhibit rate constants in the order *cis* > *trans*, while only the *trans*-isomer gives well-defined polymers ($D \leq 1.09$).⁵¹ Surprisingly, the polymerization is gradually decelerated, if both isomers are mixed, leading to the order of the rate constants as follow: *cis* > *trans* > *cis/trans*.⁵²

Taking these recent results of geometrically constrained dienes together, one can tentatively answer the initially raised question: the classic anionic polymerization shows indeed many features of a coordinative process in apolar media. Various parameters can be changed to influence the coordination, either by relying on a solvent that coordinates the counter ion or by changing the substitution pattern of the diene, which was found to influence the mechanism drastically as in the diastereomers isoprene and *cis*-pentadiene. These strategies are being further pursued by various groups at present.

3. Controlling the microstructure of polydienes

The resulting microstructure is directly dependent on the propagation mechanism, as introduced previously. Primarily for rubber applications, 1,4-repeating units are favored because of the known low T_g of the polymers and lower entanglement molar mass.^{5,44} On the other hand, for specific post-polymerization modification reactions^{53,54} or to suppress crystallization as for hydrogenated polybutadiene,⁵⁵ an increased vinyl content is targeted. Polydienes, such as polyisoprene, were widely investigated to understand their microstructural changes with respect to solvent polarity. It is well-known that polymerization in polar solvents like THF results in significantly higher content of 3,4- (62%) and 1,2-units (24%).⁵⁶ However, the monomer incorporation mode can also be tailored by using small amounts of polar modifiers in nonpolar solvents. Morton and Fetters reported that for isoprene the addition of aliquots of THF initially increases the propagation rate.⁵⁷ Surprisingly, further addition leads to a subsequent decrease, as Bywater had previously demonstrated for styrene.⁵⁸ Recently, we have been able to give a detailed view of the

impact of THF on the statistical copolymerization of styrene and isoprene, relying on online NIR monitoring of the anionic copolymerization. When increasing the THF concentration the vinyl content of the isoprene-units increases.¹⁷ In other works based on online kinetics, polymerization of the analogous β -myrcene was investigated to compare the influence of ditetrahydrofuryl propane (DTHFP) and tetramethyl ethylene diamine (TMEDA) as polar modifiers with the established THF. As shown in Table 4, both DTHFP and TMEDA show a stronger impact on the microstructure than THF.^{19,59} The addition of 2 equivalents with respect to the lithium-ion concentration leads to predominant 3,4-units (>57%). Undesirably, this leads to an increase of the low glass temperature. Polydiene based elastomer chains usually exhibit a T_g below -60 °C. When gradually increasing the ratio of vinylic units, the T_g of polyisoprene can reach 0 °C.⁶⁰ Although the T_g of polydienes shows this correlation with the proportion of the different microstructures, polyfarnesene (PFar), discussed later in this perspective, shows a different behavior. Due to its long side chain in every repeating unit, the T_g remains nearly unaffected by increasing the vinyl content, as illustrated in Fig. 3.

In addition to altering the system's polarity, it is well-known that increasing bulkiness of the substituent results in an almost exclusive formation of *cis*-1,4-units. This was demonstrated for the anionic polymerization of 2-substituted 1,3-butadiene derivatives with a methyl, ethyl, *n*-propyl or isopropyl group.^{64–66} Pendant phenyl groups, as seen in 1-phenyl butadiene (PhB), 1-phenyl isoprene (1PhI) and 4-phenyl isoprene (4PhI), have demonstrated a predominant occurrence of 1,4-addition (>80%), even in the polar solvent THF.^{67–69} Furthermore, Ishizone and coworkers achieved control over the incorporation by designing rather unusual allylidene monomers.^{70,71} The reported butadiene-derivatives were 1,1-disubstituted with increasing bulkiness of the pendant group. Various substituents, ranging from two methyl groups to a bornane ring and even the bulky adamantyl group, were attached to the dienylic-unit. Hence, the sterically hindered 1,4-



Fig. 3 Correlation of glass temperature of polydienes with the vinyl content. The values are combined from several original works.^{60–63}



a) Increased vinyl-content



b) Predominant vinyl-content



Fig. 4 1,1-Disubstituted 1,3-dienes studied with respect to their behavior in the anionic polymerization, reported by Ishizone *et al.*^{70,71}

addition could be further prohibited with increasing bulkiness, which is underlined by the absence of 1,2-units. The structures shown in Fig. 4a were sufficiently effective to increase 3,4-units to more than 20% in apolar media. The bulky substituents of the structures in Fig. 4b result almost exclusively in 3,4-incorporation. As a result, these polymers turned out to be very rigid materials with high glass temperatures of nearly 200 °C in case of the pendant bornane-ring. In theory, this might allow for application in high temperature resistant thermoplastic elastomers (TPEs) as a hard segment, but on the other hand this will also necessitate extremely high processing temperatures.

The monomer 1-vinyl cyclohexene (VCH) serves as a model compound with one double bond that is sterically constrained within a cyclic structure. The key question is whether VCH behaves as a 1,3-diene or as a styrenic vinyl monomer in the anionic polymerization in nonpolar media. In analogy to other diene structures, the homopolymerization in cyclohexane (CHx) lead to a predominant formation of 64% 1,4-units.⁷² The extent of 1,4-incorporation is comparable to the allylidene cyclohexane with a reported 66% 1,4-units when polymerized in benzene.⁷¹ However, the added rigidity from the ring in the backbone increased the T_g to 78 °C. The microstructure of PVCH was adjusted to enhance the vinyl content, reaching up to 78% of 3,4-PVCH upon addition of the polar modifier THF. The resulting material properties, with a T_g of up to 89 °C, are much closer to those of PS ($T_g = 100$ °C).⁷³ Likewise, hydrogenation leads to a high amount of polyvinylcyclohexane (PVCH) segments, as obtained by hydrogenation of PS.

4. Bio-derived diene alternatives

The dwindling fossil resources evolved to be a major motivation in finding new substitutes for established systems such as polydiene-based (co)polymers. Wahlen and Frey presented a wide scope of terpene monomers that are amenable to the anionic polymerization.⁷⁴ Predominantly, β -myrcene (Myr) and β -farnesene (Far) have gained significant attention owing to their structural similarity to the 2-substituted isoprene frame-

work and their biobased origin from turpentine oil and sugar cane, respectively. Both monomers show similar dependencies of the polymer structures on the polymerization conditions and result in comparable polymer properties. A highly 1,4-dominated microstructure is obtained when polymerizing in apolar solvents, which results in a similarly low T_g as polyisoprene, with $T_g < -60$ °C (Fig. 3).^{60,62} This renders PFar and PMyr suitable for the application as soft phase in thermoplastic elastomers. Combinations with polystyrene or polylactide (PLA) as the vitrified plastic domains have also been reported. When polystyrene is used for the rigid phase, classical linear ABA-triblock copolymers can be synthesized. Sequential addition yields block architectures, whereas tapered structures are obtained by one-step statistical copolymerization.^{19,23,62} This will be discussed in greater detail in one of the following sections. By the combination with polylactide as the rigid phase even more complex architectures were realized, *e.g.*, graft polymers and H-shaped triblock structures, see Fig. 5.^{75–77}

Due to the increasing length of the side chains in PMyr and PFar that do not contribute to the polymer backbone length, the entanglement molar mass strongly increases from 7 kg mol⁻¹ for PI, 18 kg mol⁻¹ for PMyr to 50 kg mol⁻¹ for PFar.^{79–81} This effect has considerable consequences for elastic mechanical properties that are strongly dependent on the entanglements of the polymer chains. Therefore, higher molar masses compared to PI are required for PFar to obtain similar mechanical properties.

The first report on the anionic polymerization of β -myrcene by our group focused on the behavior in statistical copolymeri-



Fig. 5 Different copolymer architectures for TPEs based on block, tapered and branched triblock structures as well as graft-copolymers.^{22,75–78}



Table 1 Summary of a variety of polydienes accessible *via* carbanionic polymerization, listed with increasing glass temperatures

Polymer	1,4 [%]	T_g [°C]	Ref.	Polymer	1,4 [%]	T_g [°C]	Ref.
PB	72	-86	60	PDMNT	74	-30	—
PFar	91	-75	60	POc	15	-26	87
PFar	61	-73	60	PB	10	-21	60
PFar	48	-70	60	PI	15	0	60
PMyr	94	-67	61	PMyrDOL	67	11	89
PI	91	-67	60	P4PhI	94	48	69
PFar	37	-66	75	PDMCH	100	53	41
PMyr	72	-58	63	P1PhI	35	65	69
PMyrOSi	69	-53	61	PVCH	22	89	72
PB	30	-45	60	PNopa	51	158	88
PMyr	30	-39	62	PAad ^a	0.0	178	70
PI	44	-32	60	PATMC5 ^b	0.0	194	71

^a 2-Allylidene-adamantane (Aad). ^b 2-Allylidene-1,1,3,3-tetramethylcyclopentane (ATMC5).

tures, benzene, and toluene are established solvents. Toluene is less favored due to reported transfer reactions.⁹⁰ Cyclohexane is used for the industrial synthesis of thermoplastic elastomers by anionic polymerization.¹¹ For specific demands, *e.g.*, solubility of bifunctional initiators, functional initiators and monomers, tetrahydrofuran (THF) is primarily used to increase the polarity and to suppress aggregation. Proton abstraction at ambient temperatures restricts its use to low temperatures, usually -78 °C.^{91,92} However, the polymerization of dienes is thermodynamically hindered at these low temperatures. Gallei *et al.* took advantage of this to prepare block copolymers by using a one-pot synthesis of styrene/myrcene mixtures, applying a temperature change to polymerize the diene monomer. Only styrene polymerizes at low temperatures, whereas myrcene requires temperatures above -30 °C in THF to polymerize.⁹³

Further, the awareness of sustainability and a shift towards more biobased systems has led to a reconsideration of solvents, as they make up for a large proportion of a synthesis. Consequently, biobased, more sustainable solvents are currently under investigation, see Fig. 6.

Looking beyond butadiene and isoprene, other new and often biobased monomers may require the use of more polar solvents. As introduced above, PFar maintains a low T_g when

polymerized in a polar medium, whereas the syntheses of other polydienes require an apolar solvent to achieve similar material properties. Schlaad and coworkers investigated the polymerization of isoprene and β -myrcene in a variety of “green” solvents, *i.e.* limonene, 2-methyl tetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME).^{56,94} On the one hand, 2-MeTHF appeared to have almost the same impact on the microstructure as THF, affording a majority of 3,4-incorporation (54%). On the other hand, CPME yielded a major fraction of 1,4-units of 64%. The apolar solvent limonene strikingly resulted in 90% 1,4-incorporation. In all solvents, moderate to low dispersities below 1.15 were obtained. Recently, CPME has also been employed for the copolymerization of styrene with isoprene or 1,3-pentadiene, as well as for the copolymerization of isoprene and 1,3-pentadiene. Kinetic studies were conducted to assess its suitability for use in anionic polymerization.⁹⁵ Additionally, 2-MeTHF and CPME were both evaluated as additives in the anionic polymerization of 1,3-cyclohexadiene. Notably, CPME in a toluene system demonstrated promising results, with quantitative yields and successful achievement of targeted molar masses, while maintaining low dispersities of $D < 1.12$.⁹⁶ In addition, Haddleton *et al.* investigated the use of squalane, bearing a C₃₀ framework, in its unpurified form as a polymerization medium. Despite the high dispersity ($D = 1.84$), attributed to the avoidance of purification steps, the low polarity yielded 94% of 1,4-incorporation.³⁵ In one of our recent works we showed that the moderately polar solvent methyl *tert*-butyl ether (MTBE) is ideally suited to solvate the bifunctional initiator 1,3-diisopropenyl benzene (DIB). A synergy can be found, as MTBE enables a reliable bifunctional initiation, as it prevents aggregation, while the associated increase in vinyl content does not affect the properties of PFar.^{75,78} MTBE, besides being cheap due to industrial scale production for petrol-additives, can also potentially be obtained from renewable feedstocks, *i.e.* bio-methanol and bio-isobutylene.⁹⁷ It is therefore somewhat surprising that it has not received more attention in carbanionic polymerization to date. This can certainly be attributed to the prevalence of the “classical” solvents established over decades. Recently, we investigated MTBE in-depth as moderately polar solvent and additive in homo- and copolymerizations.⁹⁸

**Fig. 6** Established and emerging solvents for the anionic polymerization.

7. Behavior of 1,3-dienes in the statistical copolymerization

The statistical copolymerization of styrene and butadiene in apolar solvents, leading to so-called “tapered” block copolymers was patented as early as 1958 by Phillips Petroleum Company.^{111,112} Further development by Shell Co. resulted in gradient copolymers for commercial application.¹¹³ The statistical copolymerization is an efficient tool to form block-like, tapered structures that still retain microphase segregation like sequential block copolymers. Therefore, the investigation of the gradient formed in a statistical anionic copolymerization is of significant interest. In recent works, we compared tapered multiblock copolymers composed of isoprene and styrene with their respective analogues obtained *via* sequential monomer addition. SAXS patterns revealed weaker segregation, clearly attributed to a reduced effective Flory–Huggins parameter, χ_{eff} .¹⁴ Consequently, the order–disorder transition (ODT) temperature, T_{ODT} decreases, which is desirable for industrial applications targeting high-speed processing *via* melt extrusion.¹¹ The synthesis of tapered block copolymers relies on significantly different reactivity

ratios.^{114,115} In 2013, we reported on *in situ* ¹H NMR spectroscopy to track the individual comonomer consumption throughout the living carbanionic copolymerization. The decreasing integrals of the respective monomer signals can be used to determine the reactivity ratios of each system. By this means, one can directly monitor the copolymerization of isoprene and styrene in apolar media up to full monomer conversion, demonstrating the formation of a steep gradient. The associated reactivity ratios were determined to be $r_{\text{I}} = 11$ and $r_{\text{S}} = 0.053$. This can be attributed to a faster cross-propagation rate of S to I, compared to *vice versa* ($k_{\text{SI}} \gg k_{\text{IS}}$).^{16,116} Consequently, by initiation of a monomer mixture, two blocks, PI-*grad*-PS, linked by a short gradient structure are obtained. This can be repeated multiple times to generate multiblock copolymers with exceptional material properties, while minimizing the number of reaction steps required.^{5,13–15,117} Driven by the interest for biobased monomers, we also investigated the terpenes β -myrcene and β -farnesene in the copolymerization with styrene. Interestingly, both show an even steeper gradient when combined with styrene. Table 2 summarizes 1,3-dienes that have been investigated regarding their statistical copolymerization with styrene. First, butadiene and monosubstituted

Table 2 Summary of reported reactivity ratios for the copolymerizations of 1,3-dienes with styrene in cyclohexane, together with the resulting monomer gradients

Diene	Solvent	T [°C]	r_{diene}	r_{S}	Molar gradient	Ref.
Myr	CHx	20	40	0.024		19
β -Farnesene	CHx	23	27	0.037		22
Butadiene	CHx	25	15.5	0.04		10
Isoprene	CHx	20	10.1	0.013		16
4PhI	CHx	25	9.2	0.109		69
MyrDOL	CHx	25	5.2	0.19		89
1PhI	CHx	25	3.38	0.3		69
Nopadiene	CHx	25	3.26	0.31		88
<i>cis</i> -Ocimene	CHx	23	1.015	0.985		87
<i>trans</i> -Ocimene	CHx	23	0.62	1.59		87
VCH	CHx	25	0.39	2.56		72



1,3-dienes form very pronounced gradients. Secondly, the homopolymerization becomes less preferred when additional substituents are introduced to the monomer scaffold. For instance, VCH with a double bond captured in the ring is consumed slower than styrene, indicating that the cross-over reaction is highly dependent on the sterics of the respective 1,3-diene. Furthermore, the aforementioned ocimene and its two isomers reveal an impact of the configuration of the double bonds. While the *trans*-isomer is consumed first when both isomers are polymerized together, the reactivity order inverts when both are copolymerized with styrene. This observation was supported by ^1H NMR chemical titration, which revealed a surprising interaction between styrene solely with the *cis*-isomer.

The copolymerization of two 1,3-dienes, mostly with isoprene as a comonomer, has also been investigated, see Table 3. Generally, rather weak gradients in comparison to diene/S-systems are observed. The β -myrcene derivative MyrDOL has been found to form the steepest gradients when copolymerized with either isoprene or β -myrcene, respectively. However, this monomer can hardly be compared with other systems due to its increased polarity resulting from the functional side chain, which is expected to reduce the formation of aggregates, similar to a polar modifier. Noteworthy, the copolymerization of isoprene with the DMCH and VCH, which are both rotationally constrained, results in a favored consumption of isoprene.

More recently, we also implemented NIR-spectroscopy to track monomer consumption.¹⁶ The reactions can be monitored directly in the stirred polymerization solution in the reactor, which means that the product formed is directly characterized

with respect to its monomer gradient in the chains. Using *in situ* NIR spectroscopy, we studied the influence of polar modifiers, *i.e.* THF and DTHFP, in the copolymerizations of I/S and Myr/S. Gradually increasing the ratio of $[\text{THF}]/[\text{Li}]$ can be used as a tool to control the molar composition of the copolymer chains, as indicated by the profiles shown in Table 4. Both isoprene and β -myrcene are incorporated to a reduced extent, when the polarity of the system increases, resulting in the preferred consumption of styrene.^{17,19} In case of the copolymerization of β -myrcene and styrene, the chelating modifiers DTHFP and TMEDA were shown to have a much stronger impact compared to THF. Already 0.5 eq. of $[\text{DTHFP}]/[\text{Li}]$ influences the copolymerization stronger than 20 eq. of THF. Only 2 eq. of either DTHFP or TMEDA already lead to an enhanced incorporation of styrene, as indicated by reactivity ratios of $r_{\text{S}} \geq 17.5$ and $r_{\text{Myr}} \leq 0.15$, respectively.^{19,59}

8. Current challenges and perspective

Anionic polymerization is still the benchmark when it comes to high precision polymer synthesis. Since the polymer chains can be obtained with high uniformity, details of structure–property correlations can be determined and consequently tailored with great accuracy. The current shift towards more sustainable feedstocks has led to an increased diversity of diene structures and transforms the deemed “old-fashioned” and fossil fuel-based status of carbanionic diene polymerization. This also motivates fundamental works regarding carbanionic

Table 3 Reported reactivity ratios for the copolymerization of two 1,3-dienes in apolar media, together with the resulting monomer gradients

Diene 1	Diene 2	Solvent	T [°C]	r_1	r_2	Molar gradient	Ref.
MyrDOL	Isoprene	CHx	25	9.22	0.11		89
β -Myrcene		CHx	23	4.4	0.23		23
Butadiene		<i>n</i> -Hexane	20	2.82	0.42		118
1PhI		CHx	25	0.865	1.155		69
VCH		CHx	25	$\ll 1$	$\gg 1$		72
DMCH		CHx	25	0.087	11.51		41
MyrDOL	β -Myrcene	CHx	25	6.22	0.16		89
Nopadiene		CHx	25	0.13	7.49		88
Nopadiene	β -Farnesene	CHx	25	0.155	6.50		78



Table 4 Reported reactivity ratios for the copolymerization of dienes with styrene in the presence of polar modifier, together with resulting molar gradients of the chains

Diene	Polar modifier	eq.	T [°C]	r_{Diene}	r_{s}	Molar gradient	Ref.
Isoprene	THF	0.5	20	2.856	0.093		17
Isoprene	THF	2	20	1.06	0.262		
Isoprene	THF	20	20	0.374	0.925		
Isoprene	THF	240	20	0.148	4.196		
β -Myrcene	THF	0.5	20	12.3	0.082		19
β -Myrcene	THF	2	20	4.38	0.23		
β -Myrcene	THF	20	20	0.87	1.15		
β -Myrcene	THF	240	20	0.17	5.77		
β -Myrcene	DTHFP	0.5	20	0.41	2.42		
β -Myrcene	DTHFP	2	20	0.056	18.0		
β -Myrcene	TMEDA	2	—	0.15	17.52		59

polymerization to further investigate the mechanisms and eventually to develop high performance materials. As most products based on dienes are used as high-volume materials, the economy of scale is a key factor in this area.

An aspect not to be neglected is the responsibility of the industrialized countries to regulate the usage of the available farmland between the production of renewable raw materials and agriculture for food production. For this reason, many different feedstocks are under investigation to obtain dienes *via* truly sustainable pathways. One approach relies on utilizing bacteria in fermentation processes that are capable of turning waste streams into valuable resources.⁸⁴ Another approach addresses turpentine oil as a feedstock, which does not compete with food production. This shows that the future holds many challenges when fossil fuel-based isoprene and butadiene are to be replaced as standard diene building blocks. New routes are therefore mandatory to adapt the new monomers to specific material properties. Other aspects such as more sustainable solvents or more efficient processes are also driving current research.

A major challenge for the polymerization of novel dienes is the transfer of innovations from academia to industry, as this

sets the starting point for economic considerations of more sustainable solutions. This involves a shift from only three primarily used monomers, *i.e.*, styrene, butadiene, and isoprene at present towards a variety of biobased diene structures.

9. Conclusion

In this short review we have briefly described the significance of polydienes in the past and also highlighted recent developments. Capitalizing on the high precision of the anionic polymerization technique, a variety of 1,3-dienes have been successfully polymerized in a living manner. Besides matching the properties of fossil fuel-based PB or PI with biobased candidates, the synthesis of unprecedented rigid polydienes like PNopa was recently achieved. Nopadiene shows promising performance as a bio-based substitute for PS. This monomer permitted the first synthesis of fully diene-based TPEs. The flexibility of polydienes can be either tuned by the addition of different polar modifiers or by changing the substitution pattern of the monomer. This has great impact on the reactivity ratios when copolymerized with



styrene. While monosubstituted 1,3-dienes showed a block-like polymer composition, disubstituted 1,3-dienes reacted almost randomly with styrene in apolar media. The increase in steric demand is directly correlated to the resulting microstructure of the polydiene. Further, if the degrees of freedom are reduced to a minimum *via* constrained 1,3-dienes of a *cisoid* or *transoid* structure, respectively, the requirement of a *cisoid*-state was revealed. A large variety of copolymerizations and their respective reactivity ratios within the field of dienes in the carbanionic polymerization was presented, alongside with insights into new emerging fields including new and often biobased monomers, solvents and modifiers. We emphasize that the findings of the past years, summarized in this overview, are crucial for creating innovations in the future and are of general relevance for the field of carbanionic polymerization and polydienes.

Author contributions

The manuscript was conceptualized by all authors and the original draft was written by equal contributions of Moritz Rauschenbach and Moritz Meier-Merziger. Both contributed to the visualization, data curation and formal analysis of the work. The supervision was carried out by Prof. Holger Frey as well as validation, reviewing and editing of the final work.

Data availability

Since this is a review article, there are no research data available that would have to be disclosed.

Conflicts of interest

The authors declare no conflict of interest.

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