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Limonene as a renewable unsaturated hydrocarbon solvent for living anionic polymerization of β-myrcene†

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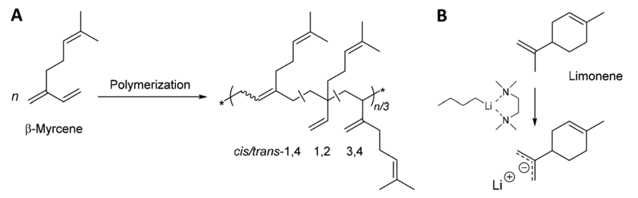
The acyclic monoterpene β-myrcene is polymerized by anionic polymerization at room temperature using *sec*-butyllithium as the initiator and the cyclic monoterpene DL-limonene as an unsaturated hydrocarbon solvent. The polymerization is a living process and allows production of polymyrcenes with narrow molar mass distribution ($Đ \sim 1.06$) and high content of 1,4 units (~90%) as well as block copolymers.

Polymer chemistry is progressing towards a more sustainable future by exploring renewable feedstocks and environmentally friendly processes.[1–3] A considerable amount of effort is put on biorefinery of waste biomass to produce new (or old) monomers or building blocks for sustainable materials as well as renewable solvents.[4,5] One of these 'old' monomers is β-myrcene, which is an unsaturated acyclic monoterpene predominantly produced in plants, or – more precisely – a 1,3-conjugated diene hydrocarbon monomer, like butadiene, isoprene, or β-farnesene.[6–8] β-Myrcene can be directly converted into a fully bio-based elastomer by either free-radical,[9,10] controlled radical,[11,12] anionic,[13–22] cationic,[23] or coordination polymerization.[24–26] Depending on the used polymerization method and reaction conditions, the polymyrcenes exhibit different microstructures (from highly *cis*-1,4, resembling natural rubber, to isotactic 3,4, see Scheme 1A) and thermal properties (glass transition temperatures from −70 °C to −40 °C). Alternatively, β-myrcene can be converted into a cyclic diene monomer, that is, 3-methylenecyclopentene, and polymerized *via* radical, anionic, or cationic polymerization.[27,28]

Among all polymerization methods, the anionic polymerization technique offers some outstanding advantages. The anionic polymerization of diene monomers is a 'living' process,[29,30] which proceeds in the absence of termination and chain transfer reactions, and which can be driven to complete monomer consumption without risking branching or chain coupling reactions. The resulting polymers exhibit predictable molar masses and narrow molar mass distributions as well as, depending on the chosen reaction conditions (temperature, counterion, additive, and solvent), tuneable microstructures.

Earlier we reported the anionic polymerization of β-myrcene, initiated by *sec*-butyllithium in bulk and in 'green' ether solvents, *e.g.*, 2-methyltetrahydrofuran (2-MeTHF), at room temperature.[21] As expected, the polymyrcene prepared in bulk exhibited a high content of 1,4 units while those obtained in ether solvents were rich in 3,4 units. Other than in bulk, 1,4-polymyrcenes are only obtained with nonpolar hydrocarbon solvents like *n*-hexane or cyclohexane. Aiming at avoiding the use of (cyclo)hexane, we decided to explore the cyclic monoterpene limonene as a renewable – albeit not 'green'[31] – hydrocarbon solvent. Actually, limonene contains two isolated double bonds and can serve as a monomer in radical copolymerizations[6] or as a platform chemical for new monomers (*e.g.*, limonene oxide).[32–34] Other than that, metalation of limonene can occur on reaction with a strong metalation agent, for example a mixture of *n*-butyllithium and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (Scheme 1B) or potassium *tert*-amyloxide[35,36] – but not with alkyllithium alone.[37]

The β-myrcene (95%, stabilized, Sigma Aldrich) was dried over molecular sieves (3 Å) and destabilized by filtration through basic alumina, DL-limonene (≥95%, Sigma Aldrich) was dried over calcium hydride and distilled in vacuum, and



Scheme 1 (A) Polymerization of β-myrcene and general chemical structure of polymyrcene. (B) Tentative metalation of limonene.

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sec-butyllithium (*s*BuLi, 1.4 M solution in cyclohexane, Sigma Aldrich) was used as received. Monomer and solvent were filled into a Schlenk flask, put under an argon atmosphere, and then the initiator was added *via* a syringe. At the end of the polymerization, the reaction was terminated by the addition of degassed methanol. The polymyrcene was isolated simply by evaporation of the solvent (residual solvent traces were removed in a vacuum oven at 100 °C).

The anionic polymerizations of β-myrcene in limonene were performed at room temperature with a fixed initial monomer-to-initiator ratio of 50 (targeted M_n 6.9 kg mol^{-1}) and varying monomer concentrations of 45.7 wt% (2.74 M), 19.2 wt% (1.18 M), and 9.8 wt% (0.60 M). For kinetic studies, samples were taken out of the reaction flask (which was immersed in a water bath for better heat transfer) at predetermined times, quenched with degassed methanol, diluted with chloroform-*d* or tetrahydrofuran (THF), and analyzed by ^{1}H NMR spectroscopy‡ and size exclusion chromatography (SEC)§.

As seen in Fig. 1A and B, the anionic polymerization of β-myrcene in limonene follows a pseudo first-order kinetics and the apparent number-average molar mass (M_n^{app}, by SEC) of the polymyrcene increases linearly with monomer conversion. Accordingly, the polymerization proceeds in the absence of termination and chain transfer reactions (which also excludes a metalation of limonene and re-initiation by limonenyllithium, Scheme 1B), hence it is indeed a living polymerization. The obtained polymyrcenes exhibit monomodal and narrow molar mass distributions (*Đ* ~ 1.06), however their apparent molar masses are higher than the targeted molar masses (attributable to the SEC calibration with polystyrene standards and/or an initiator efficiency of less than 100%).

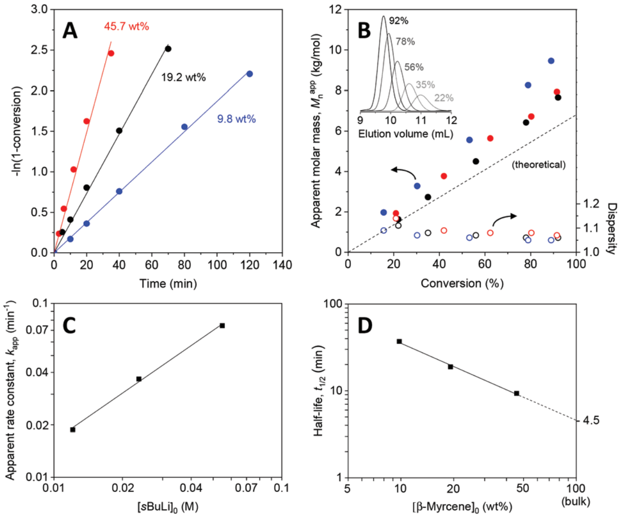

Fig. 1 (A) Pseudo first-order time-conversion plots for the *sec*-butyllithium initiated anionic polymerizations of β-myrcene ([β-myrcene]$_0$/[*s*BuLi]$_0$ = 50) in limonene ([β-myrcene]$_0$ = 45.7 wt%, 19.2 wt%, and 9.8 wt%) at room temperature (monomer conversions were determined by ^{1}H NMR spectroscopy, ESI). (B) Evolution of the apparent number-average molar mass (M_n^{app}) and dispersity (*Đ*), as determined by SEC, as a function of monomer conversion and SEC-RI traces of polymyrcenes obtained at different monomer conversions in limonene ([β-myrcene]$_0$ = 19.2 wt%) (ESI). (C) Bilogarithmic plot of the apparent rate constant k_{app} (as determined from the slope of the pseudo first-order time-conversion plot, A) *vs.* the initial initiator concentration [*s*BuLi]$_0$; slope: 0.9 ± 0.1 = reaction order with respect to initiator (propagating chain) concentration. (D) Dependence of the half-life $t_{1/2} = \ln 2/k_{app}$ of the polymerization on the initial monomer concentration [β-myrcene]$_0$.

The kinetic studies further indicate that the polymerization is close to first order (Fig. 1C, slope = 0.9 ± 0.1) with respect to the initiator concentration, suggesting that the propagating polymyrcenyllithium chains are present as single chains without forming associates. Association occurs with the sterically less hindered polybutadienyl- or polyisoprenyllithium in *n*-hexane solution (as indicated by a fractional order with respect to the concentration of propagating chains) but not in polar ether solvent such as THF (first-order).[29,38,39] Despite the seeming absence of associates, however, the anionic polymerization of β-myrcene in limonene is slower than the ones in cyclohexane, THF, or 2-MeTHF.[21] The half-life of the polymerization decreases from $t_{1/2} \approx 37$ min ([β-myrcene]$_0$ = 9.8 wt%) to 19 min (19.2 wt%) to 9 min (45.7 wt%); hence, the half-life of the polymerization of β-myrcene in bulk (*i.e.*, 100 wt% or 5.84 M) is estimated to be <5 min (Fig. 1D).

The polymyrcenes prepared in limonene solution contain a high content of 1,4 units (~90%) and some 3,4 units (~10%) but no 1,2 units, as revealed by ^{1}H NMR analysis¶ (Table 1). The 1,4 content is thus very similar as for the polymyrcenes produced in bulk or in cyclohexane solution (91–94%).[21] Since the microstructure changes with the polarity of the solvent used during polymerization,[40] we also examined the effect of 2-MeTHF (99%, anhydrous, Acros Organics) as a renewable polar additive or co-solvent. An increasing volume fraction of 2-MeTHF results in a significant decrease of the 1,4 content and increase of the 3,4/1,2 content; the polymyrcene produced in limonene/2-MeTHF 85 : 15 (v/v) exhibits virtually the same microstructure as the one obtained in pure 2-MeTHF (1,4 40% and 3,4/1,2 60%) (Table 1).

We also explored styrene as a common vinyl monomer. The *sec*-butyllithium initiated polymerization of styrene (99.5%, Acros Organics) at 20.7 wt% in limonene solution came to completion within less than 10 min to yield a polystyrene with

Table 1 Microstructures of the polymyrcenes obtained by anionic polymerization in limonene and in limonene/2-MeTHF mixed solvents[a]

[β-Myrcene]$_0$ (wt%)	Limonene/2-MeTHF (v/v)	Microstructure (%) 1,4	1,2	3,4
100	—[b]	91	—	9
45.7	100/0	92	—	8
19.2	100/0	89	—	11
9.8	100/0	88	—	12
20.3	99/1	56	2	42
19.7	95/5	45	5	50
20.6	85/15	41	5	54
22.5	0/100[b]	40	6	54

[a] Polymerizations were performed at room temperature for 24 h. [b] Ref. 21.

M_n 6.4 kg mol^{-1} (targeted M_n 5.2 kg mol^{-1}) and $Đ$ 1.05 (SEC). The polymerization of styrene is thus faster than that of β-myrcene in limonene solution (*cf.* Fig. 1A), which is opposite to the observed relative polymerization rates of styrene and dienes in cyclohexane.[17,41] In the copolymerization of an equimolar mixture of β-myrcene and styrene, however, the reactivities are reversed and the β-myrcene is consumed faster than the styrene to produce a gradient copolymer (Fig. S7, ESI†).[17] Furthermore, a polymyrcene-polystyrene diblock copolymer was prepared successfully by sequential monomer addition (Fig. S8, ESI†), further demonstrating the livingness of this anionic polymerization system.

Conclusions

Limonene as an unsaturated hydrocarbon can serve as a solvent for the living anionic polymerization of β-myrcene (and styrene) at room temperature, making this process potentially more sustainable. The polymyrcenes, which are isolated simply by evaporation of the solvent, exhibit a low dispersity ($Đ \sim 1.06$) and a high content of 1,4 units (~90%). The microstructure can be tuned, *i.e.*, decreasing the 1,4 content and increasing the 3,4/1,2 content, by using 2-MeTHF as a renewable additive or co-solvent. Also copolymers can be prepared in limonene solution, for example polymyrcene-polystyrene block copolymers.

However, the kinetic studies seem to suggest, by the first order with respect to propagating chain concentration and the relative polymerization rates of β-myrcene and styrene, that limonene is not just a simple replacement for cyclohexane as a hydrocarbon solvent. Further studies will be needed to fully understand the mechanism of the anionic polymerization in limonene solution or, more generally, in unsaturated hydrocarbons.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ ^{1}H NMR spectra were recorded on a Bruker AVANCE Neo 400 MHz spectrometer at room temperature; signals were referenced to the solvent peak at δ 7.26 ppm ($CHCl_3$). The initial monomer/solvent compositions and monomer conversions were determined from the characteristic olefinic proton signals of β-myrcene (δ 6.42–6.35 ppm, $=C\underline{H}-C=$) and limonene (δ 5.41 ppm, $=C\underline{H}-$ endocyclic, 1H, and δ 4.71 ppm, $=C\underline{H}_2$ exocyclic, 2H); the limonene signal at δ 5.41 ppm was used as the internal reference (Fig. S1–S4, ESI†).

§ SEC with simultaneous UV and RI detection was performed with THF as the eluent (flow rate: 0.5 mL min^{-1}) at room temperature. The stationary phase used was a 300 × 8 mm^2 PSS SDV linear M column (3 μm particle size, molar mass range 10^2–10^6 Da). Solutions containing ~0.15 wt% polymer were filtered through 0.45 μm filters; the injected volume was 100 μL. Polystyrene standards (PSS, Mainz, Germany) were used for calibration.

¶ The microstructure of polymyrcene was determined by ^{1}H NMR spectroscopy, as described previously.[21] The integrals of the olefinic proton signals of 1,2 units (δ 5.65 ppm, 1H), 1,4 units (δ 5.13 ppm, 1H, and $-C\underline{H}=(CH_3)_2$ side chain, 1H), and 3,4 units (δ 4.76 ppm, 2H) were referenced to the integral of the methyl proton signals of the side chain (δ 1.68 and 1.62 ppm, 6H) (*cf.* Scheme 1A) (Fig. S5 and S6, ESI†).

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