



Cite this: *Polym. Chem.*, 2024, **15**, 4364

Received 21st August 2024,  
Accepted 26th September 2024

DOI: 10.1039/d4py00913d

rs.c.li/polymers

# Comment on “Limonene as a renewable unsaturated hydrocarbon solvent for living anionic polymerization of $\beta$ -myrcene” by A. Dev, A. Rösler and H. Schlaad, *Polym. Chem.*, 2021, **12**, 3084

Akhil Dev, , Alexander Rösler and Helmut Schlaad \*

Addition and correction for ‘Limonene as a renewable unsaturated hydrocarbon solvent for living anionic polymerization of  $\beta$ -myrcene’ by Akhil Dev *et al.*, *Polym. Chem.* 2021, **12**, 3084–3087; <https://doi.org/10.1039/d1py00570g>.

We earlier reported on the living anionic polymerization of  $\beta$ -myrcene at room temperature using *sec*-butyllithium as the initiator and DL-limonene as a bio-sourced unsaturated hydrocarbon solvent.<sup>1</sup> First kinetic studies, based on three experiments conducted with constant monomer-to-initiator ratio, suggested that the reaction order with respect to initial initiator (not active chain end) concentration is  $0.9 \pm 0.1$ , and polymyrcenyllithium chains should therefore be present as single chains and not forming associates – this is not correct.

The results of additional kinetic experiments with 1 M or 2 M monomer solutions and different initiator concentrations of 10.0–39.6 mM are summarized in Table 1, #4–7 (the re-eval-

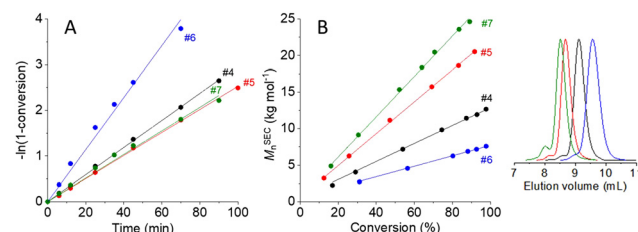
ated kinetic data of the original three experiments<sup>1</sup> are included in Table 1 as #1–3). Monomer conversions were determined by <sup>1</sup>H NMR spectroscopy,<sup>1</sup> and apparent rate constants of propagation ( $k_{app}$ ) were obtained from the slopes of the linear pseudo first-order time-conversion plots (Fig. 1A). Number-average molar masses of polymyrcenes were deter-

**Table 1** Anionic polymerization of  $\beta$ -myrcene (Myr) with *sec*-butyllithium (sBuLi) in DL-limonene at room temperature

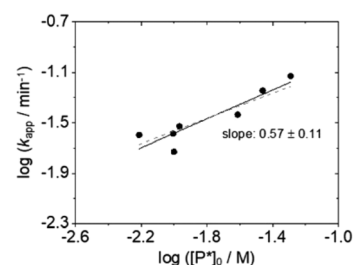
| # | [Myr] <sub>0</sub><br>(M) | [sBuLi] <sub>0</sub><br>(mM) | $x_p^a$<br>(%) | $M_n^{cal\ b}$<br>(kg mol <sup>-1</sup> ) | $M_n^{SEC\ c}$<br>(kg mol <sup>-1</sup> ) | $D^d$ | $[P^*]_0^e$<br>(mM) | $k_{app}^f$<br>(min <sup>-1</sup> ) |
|---|---------------------------|------------------------------|----------------|---|---|-------|---------------------|-------------------------------------|
| 1 | 2.79                      | 60.3                         | 92             | 5.86                                      | 6.91                                      | 1.07  | 51.1                | 0.0744                              |
| 2 | 1.22                      | 26.5                         | 92             | 5.83                                      | 6.34                                      | 1.05  | 24.4                | 0.0367                              |
| 3 | 0.64                      | 13.9                         | 89             | 5.64                                      | 7.80                                      | 1.05  | 10.1                | 0.0187                              |
| 4 | 1.02                      | 19.5                         | 98             | 7.04                                      | 12.70                                     | 1.04  | 10.8                | 0.0296                              |
| 5 | 1.00                      | 10.0                         | 92             | 12.59                                     | 20.50                                     | 1.04  | 6.1                 | 0.0253                              |
| 6 | 1.95                      | 39.6                         | 98             | 6.63                                      | 7.58                                      | 1.05  | 34.6                | 0.0570                              |
| 7 | 2.00                      | 19.7                         | 89             | 12.36                                     | 24.60                                     | 1.05  | 9.9                 | 0.0259                              |

<sup>a</sup> Monomer conversion for the last sample of the kinetic experiment, by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> Calculated number-average molar mass,  $M_n^{cal} = ([Myr]_0/[sBuLi]_0 \cdot x_p \cdot 136.2 + 58)/1000$  kg mol<sup>-1</sup>. <sup>c</sup> Number-average molar mass of the final polymyrcene sample, by SEC with 1,4-polyisoprene standard (PSS, Mainz, Germany) calibration. <sup>d</sup> Dispersity index of the final polymyrcene sample, by SEC. <sup>e</sup> Concentration of active chain ends,  $[P^*]_0 = [sBuLi]_0 \cdot M_n^{cal}/M_n^{SEC}$ . <sup>f</sup> Apparent rate constant of propagation,  $k_{app}$  = slope of linear pseudo first-order time-conversion plot.

University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany. E-mail: [schlaad@uni-potsdam.de](mailto:schlaad@uni-potsdam.de)



**Fig. 1** (A) Pseudo first-order time-conversion plots for the *sec*-butyllithium initiated anionic polymerizations of  $\beta$ -myrcene in DL-limonene at room temperature (Table 1, #4–7). (B) Evolution of the number-average molar mass,  $M_n^{SEC}$ , as a function of monomer conversion and SEC traces of the final polymyrcene samples #4–7.



**Fig. 2** Bilogarithmic plot of the apparent rate constant  $k_{app}$  vs. the concentration of active chains  $[P^*]_0$ ; slope of linear regression line (solid line):  $0.57 \pm 0.11$  (slope of dashed line: 0.5).



mined by size exclusion chromatography (SEC) with 1,4-polyisoprene calibration ( $M_n^{\text{SEC}}$ , Fig. 1B), and concentrations of active chain ends ( $[P^*]_0$ ) were calculated from the initial initiator concentrations times the ratio of calculated over experimental number-average molar masses ( $M_n^{\text{cal}}/M_n^{\text{SEC}}$ ) at a given monomer conversion  $x_p$ .

With this larger data set (Table 1) we obtain the bilogarithmic plot of  $k_{\text{app}}$  vs.  $[P^*]_0$  in Fig. 2, according to which the reaction order with respect to active chain ends is close to one half, suggesting that the polymyrcenyllithium chains are present as dimeric associates and not, as proposed earlier, as single chains.

We apologize for any inconvenience or debate this may have caused.

## Data availability

Data available upon request.

## Conflicts of interest

There are no conflicts to declare.

## References

- 1 A. Dev, A. Rösler and H. Schlaad, *Polym. Chem.*, 2021, **12**, 3084–3087.

