BAYESIAN OPTIMIZATION OF VALEROLACTONE POLYMERIZATION: EFFECTS OF ALGORITHM AND DATA SET

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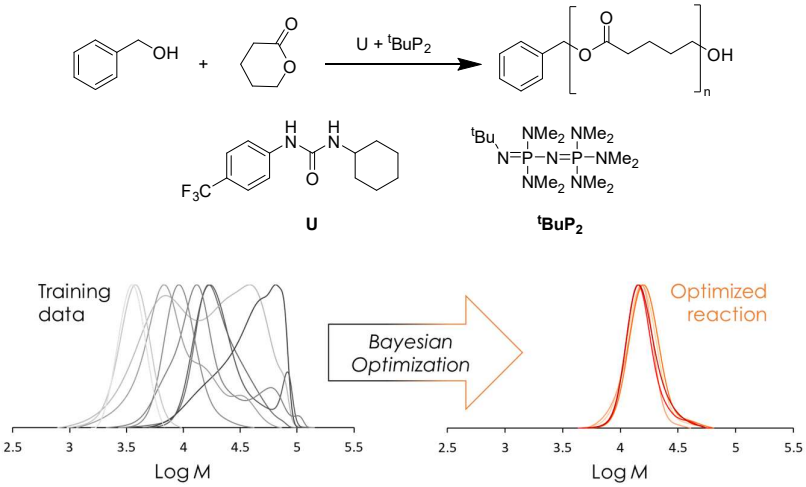
Résumé :

The ring-opening polymerization (ROP) of cyclic esters is attractive due to the degradability of the resulting polyesters, potential for biosourced feedstocks, and unique material properties.[1] These reactions are often difficult to control, however, due to side reactions including transesterification and competing initiation pathways.[2] In this work, which was supported by the AMETHYST project of the PEPR DIADEM, we investigated the dual organocatalyzed ROP of δ-valerolactone (VL) using a urea in conjunction with a phosphazene base (^{t}BuP$_2$).[3] This polymerization is highly reactive, reaching full conversion in less than 5 minutes at room temperature, but prone to undesirable side reactions. Continuous flow polymerization[4] was used to generate a poly(VL) library by varying residence time, initiator concentration, and catalyst concentration. Most initial conditions produced poorly controlled polymers, highlighting the need for systematic optimization.

The data were used to construct two training sets: a sparse 9-point set and a dense 35-point set, to which Bayesian optimization was applied using either an Expected Improvement (EI) or Thompson Sampling (TS) acquisition function. All methods successfully identified conditions yielding narrow-dispersity poly(VL) with a target molecular weight of 15 kDa. The dense data set converged within 1-5 iterations, while the sparse data set required 10-15. Despite this, the total number of experiments (training + optimization) was lower for the sparse data set. EI converged more smoothly and rapidly, while TS promoted broader exploration, reducing the risk of trapping in local maxima.

Optimal conditions favored short residence times (≤ 90 s) to limit transesterification and moderate catalyst concentrations (3.9-7.0 mM) to provide adequate kinetics while limiting branching. These results demonstrate that Bayesian optimization, integrated with high-throughput flow chemistry, is a powerful tool for exploring complex polymerization spaces and achieving controlled polymer synthesis with limited experimental cost.



Bayesian optimization of organocatalyzed valerolactone polymerization (EI algorithm, sparse training set, target M_n = 15 kDa, target Đ = 1.0)

Références :

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