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# Microwave-assisted polymer chemistry: Heck-reaction, transesterification, Baeyer–Villiger oxidation, oxazoline polymerization, acrylamides, and porous materials

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**Abstract**—Several questions are still open concerning the different effects of microwave (MW) irradiation in organic and macromolecular chemistry. Analyzing experimental results on a relatively broad investigation area, we came to elucidate three main effects of microwave irradiation: efficient non-contact heating, an accelerating effect, and what we term a special effect. In this paper, we report the first MW-assisted synthesis of poly(2,5-dibutoxy-1,4-phenylenevinylene) via Heck-polycondensation as an example for efficient heating. The facile synthesis of the higher lactones 1-oxa-2-oxocyclooctanone and 1-oxa-2-oxocyclononanone via Baeyer–Villiger reaction offers indeed an example for the MW-accelerating effect. A survey of our recent work is also given to explain the effects more in detail and to provide examples of the special MW effect.

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## 1. Introduction

Besides the fact that commercially available microwave (MW) reactors provide a comfortable, safe, and clean way of working, MW irradiation shows remarkable advantages in chemical reactions. It accelerates many syntheses providing selective activation with short start-up phase and allows fast optimization of reactions. In macromolecular chemistry as well, the application of microwaves opens up many opportunities<sup>1,2</sup> to improve monomer and polymer preparation and enhances polymer analogue reactions.

In this work we want to report some examples of chemical reactions that allow us to define three main aspects of MW effect. We found that the Heck-polycondensation or the synthesis of  $\epsilon$ -caprolactone based macromonomers<sup>3</sup> are reactions that can be performed with comparable results under MW irradiation and under normal conditions (thermal heating in oil bath). In this case the MW effect can be defined just as a convenient non-contact heating.

Investigating the lactone synthesis via Baeyer–Villiger reaction or the polymerization of 2-phenyl-2-oxazoline,<sup>4</sup> we

could recognize an improvement, under MW irradiation, in terms of higher yield or shorter reaction time. Accordingly, we like to delineate the MW effect as a way to accelerate the monomer and polymer synthesis. Finally, we provide examples of synthetic pathways not accessible under normal conditions. It is the case of the acrylamide formation<sup>5</sup> or the preparation of channel-containing materials that can be described invoking a special MW effect.<sup>6</sup>

## 2. Results and discussion

### 2.1. Convenient non-contact heating

Heating in oil bath and in microwave shows different temperature gradients.<sup>7</sup> In the case of heating with external heat sources as hot oil, for example, the heat comes from the outer environment and becomes less in the inner reaction solution. Otherwise, microwaves directly heat up the reactive centers of the reagents and the solvent, if a dipole moment exists. The reaction vessels used are, in general, transparent to microwaves. In this way the most effective energy transfer can be provided.

### 2.2. Heck-polycondensation

Although many reactions show different behavior under microwave irradiation, there also exist reactions, which

**Keywords:** Microwave; Heck-reaction; Macromonomer; Poly-oxazoline; Baeyer–Villiger oxidation; Acrylamide; Coating.

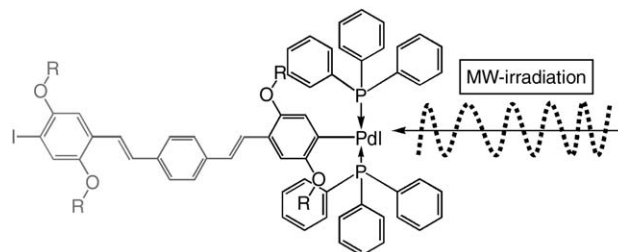
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show the same progression in oil bath and in microwave without differences in yield or reaction time. Homogeneous transition metal catalyzed reactions provide an abundance of possibilities for carbon–carbon or carbon–heteroatom bond formation with high yields and stereo- and/or regioselectivity. One example for this kind of reactions is the investigated synthesis of poly(phenylene vinylene) via Heck-polycondensation. According to literature, the employment of MW reactors in organic metal catalysis may reduce the reaction time up to tenfold.<sup>8</sup> MW-assisted Stille and Suzuki cross-coupling reactions have been used to prepare semiconducting polymers within 10 min without affecting the yield, molecular weight or the quality of the material.<sup>9</sup> Low molecular weight Heck-reactions were also reported to be accelerated via MW-assisted synthesis.<sup>8,10</sup>

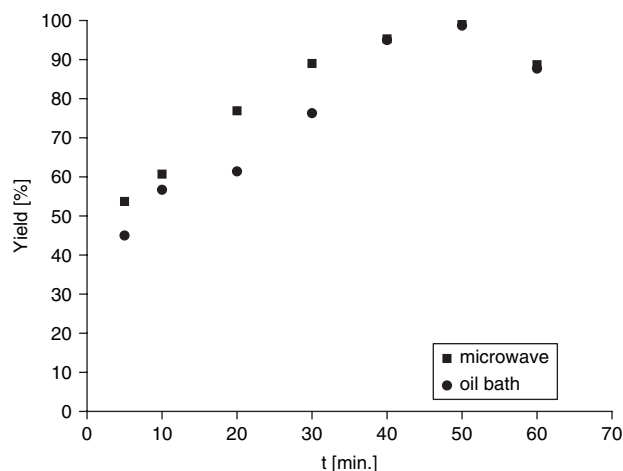
Up to now, the synthesis of poly(2,5-dibutoxy-1,4-phenylenevinylene) via Heck-reaction by using MW irradiation has not been studied. Thus, the following section deals with the kinetics of Heck-reactions focusing on the preparation of poly(phenylene vinylene) (Scheme 1).

In this type of metal catalyzed reaction the polymer is formed stepwise. Thus, the kinetics can be correlated to the molecular weight  $M_n$ . To compare the kinetics, the reactions must be performed at exactly defined temperatures. To avoid inaccuracies in determination of temperatures, the reactions were carried out in boiling solvent. It turned out that refluxed solutions of 1,4-dioxane were suitable for the Heck-reaction and therefore, should offer a constant bulk temperature of 102 °C both for MW and oil bath assisted synthesis, respectively. Thus, a direct comparison between the kinetics of both is possible. As 1,4-dioxane is a poor MW absorber (low dipole moment), a simple and instantaneous heating effect of the solvent was excluded. MW irradiation is normally highly effective in the case of polar structures.<sup>4,5,11</sup> It was predicted that the MW field interacts with the dipolar metal complex at the chain end (Fig. 1).

Surprisingly, the results obtained in boiling 1,4-dioxane showed almost equal yields (Fig. 2) and that there was only a minor acceleration effect for MW-assisted Heck-polycondensations (Fig. 3). Within 1 h reaction time, MW-promoted reactions always yielded polymers with  $M_n$  values



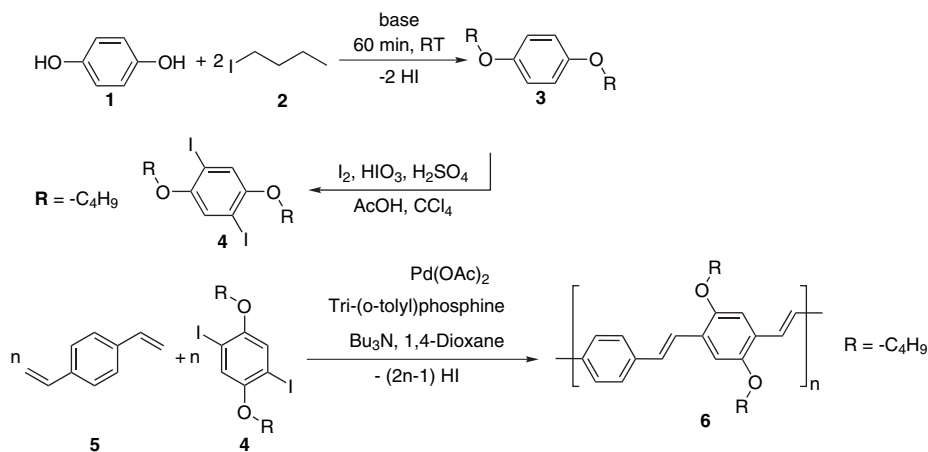
**Figure 1.** Schematic illustration of the postulated interaction of MW with the chain end.



**Figure 2.** Dependence of yield (%) on reaction time in boiling 1,4-dioxane.

of about 1000 g/mol higher molecular weight on an average than the corresponding polymer samples obtained from classical oil bath heating. This low effect is clearly in contrast to some earlier published papers, dealing with MW-accelerated low molecular weight Heck-reactions.<sup>8,10</sup>

In conclusion, our results show that reactions in boiling solvents are a good method to compare precisely the kinetics of the Heck-reaction in MW and oil bath. Only a small effect of MW irradiation on the kinetics of the Heck-polycondensation of PPV (**6**) could be detected.



**Scheme 1.** Synthesis of poly(2,5-dibutoxy-1,4-phenylenevinylene) (PPV) (**6**).

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