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

Carsten Koopmans, Mauro Iannelli, Patrick Kerep, Michael Klink, Sarah Schmitz, Sebastian Sinnwell and Helmut Ritter*

Institut fuer Organische und Makromolekulare Chemie OCII, Heinrich-Heine-Universitaet Duesseldorf, Universitaetsstrasse 1, D-40225 Duesseldorf, Germany

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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.

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[1,2] 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 ε-caprolactone based macromonomers[3] 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,[4] 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[5] or the preparation of channel-containing materials that can be described invoking a special MW effect.[6]

2. Results and discussion

2.1. Convenient non-contact heating

Heating in oil bath and in microwave shows different temperature gradients.[7] 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

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

* Corresponding author. Tel.: +49 211 81 11 508; fax: +49 211 81 15 840; e-mail: h.ritter@uni-duesseldorf.de

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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.[8] 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.[9] Low molecular weight Heck-reactions were also reported to be accelerated via MW-assisted synthesis.[8,10]

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.[4,5,11] It was predicted that the MW field interacts with the dipolar metal complex at the chain end (Fig. 1).

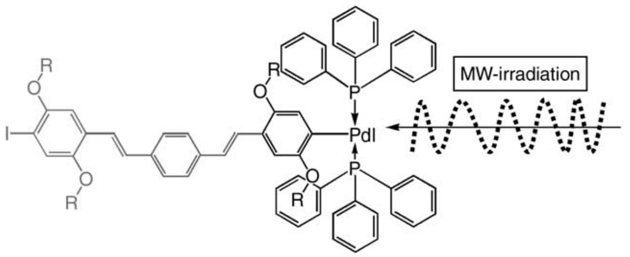


Figure 1. Schematic illustration of the postulated interaction of MW with the chain end.

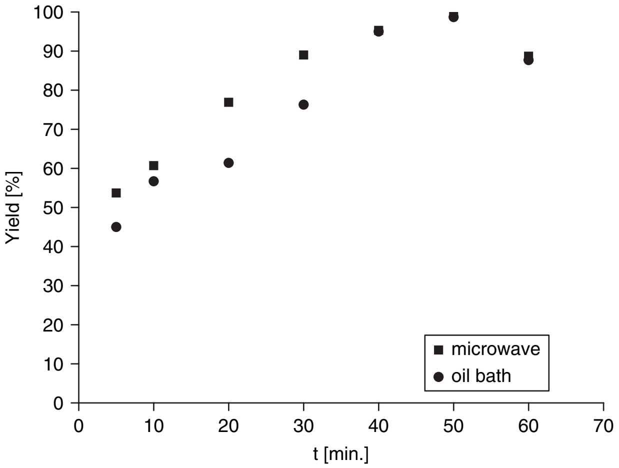
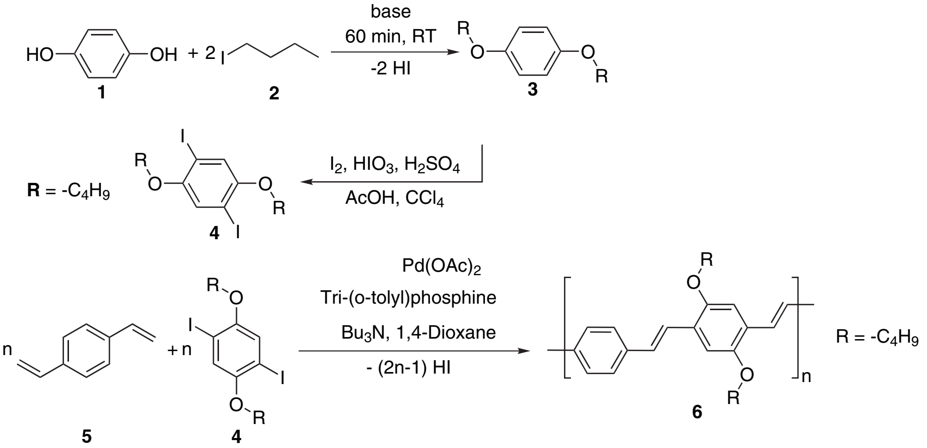


Figure 2. Dependence of yield (%) on reaction time in boiling 1,4-dioxane.

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 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.[8,10]

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**).

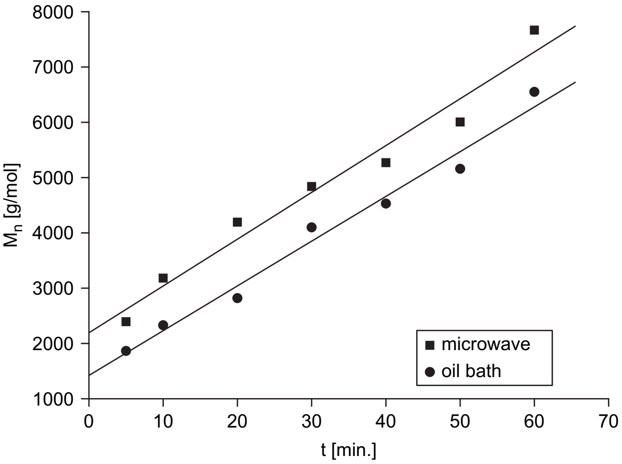
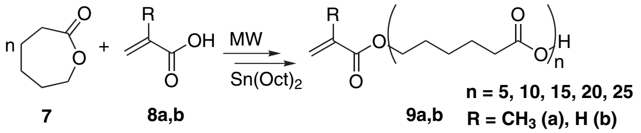


Figure 3. Dependence of molecular weight (M_n) on reaction time in boiling 1,4-dioxane.

2.3. Synthesis of macromonomers

The synthesis of macromonomers is another interesting field in polymer chemistry. In the investigated system of ε-caprolactone (**7**) in presence of (meth)acrylic acid (**8a** and **8b**) and tin octoate as catalyst we used microwave irradiation as a powerful energy source for the ring-opening polymerization and functionalization of the polyester in a single step (Scheme 2).[3] Due to the rapid non-contact heating under microwave conditions, fast optimization of the synthesis applying short reaction times was possible. However, comparison with classical thermal activation showed no significant acceleration effect under microwave conditions.



Scheme 2. Preparation of macromonomers (**9a**,**b**).

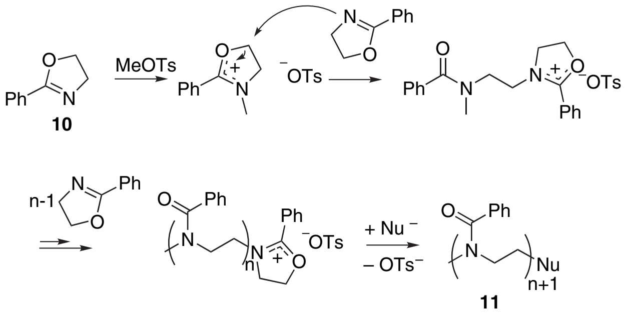
Polyester macromonomers can principally be prepared by two procedures: end-capping of polylactones with vinylic derivatives[12,13] or by initiation of the lactone polymerization by a vinylic derivative with a suitable initiation group.[14] Both methods require mostly two steps and often the addition of activation reagents. In contrast to common syntheses, we found a fast access to polyester macromonomers with high degree of functionalization and defined chain length using microwave irradiation. All reactions were carried out in a mono-mode microwave apparatus under temperature control at 180 °C (measured using a fiber optic device inserted directly into the reaction mixture) with a reaction time of 90 min starting from unpurified reagents and working in air. It is interesting to note that even at such high temperatures the spontaneous free radical polymerization of the (meth)acrylic derivates can be prevented. We polymerized different molar ratios of ε-caprolactone (**7**) and (meth)acrylic acid (**8a** and **8b**) to yield the macromonomers **9a** and **9b** with accordant chain length as shown in Scheme 2.

2.4. Accelerated monomer and polymer synthesis

In many cases using the microwave can accelerate the reaction procedure. This phenomenon of course can be connected to the fast and uniform heating profile. But it is obvious, that especially in case of existing dipolar moments in the reacting molecules the reaction occurs in an unexpected way. The presence of the alternating electric field seems to play an important role in microwave chemistry. The following examples should confirm this fact.

2.5. Polymerization of 2-phenyl-2-oxazoline

Kinetics of the cationic ring-opening polymerization of 2-phenyl-2-oxazoline (**10**) under microwave irradiation shows enhancement of reaction rate in comparison to normal heating.[4] The cationic ring-opening polymerization of 2-substituted 2-oxazolines has been intensively studied since the mid 1960s by several groups.[15–18] It is known that the polymerization of 2-phenyl-2-oxazoline takes place by treating the monomer with strong electrophiles (e.g., methyl tosylate) yielding poly(*N*-benzoylethylenimine) (**11**) (Scheme 3).



Scheme 3. Mechanism of the cationic ring-opening polymerization of 2-phenyl-2-oxazoline (**10**) via methyl tosylate.

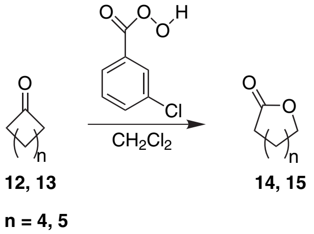
2-Phenyl-2-oxazoline (**10**) has been polymerized under microwave conditions both in closed and open reaction vessels. It is interesting to note that, synthesis in open and closed systems show nearly the same enhancement of reaction rate if the reaction is performed using microwave irradiation (Table 1).

Table 1. Reaction rate coefficient of the polymerization of (**10**) in closed vessel (CV) and open vessel (OV) under different conditions

	Rate coefficient (10^{-2}/min)	
	CV	OV
Microwave	4.17	3.55
Oil bath	1.08	1.11

2.6. Synthesis of lactones via Baeyer–Villiger oxidation

Ionic species are found as intermediates in all redox processes. Since microwaves strongly interact with polar species, especially with ions, redox reactions may be expected to proceed much faster under MW irradiation. As an example the Baeyer–Villiger rearrangement was investigated. Starting from ketones, reaction with peroxide species such as peroxybenzoic acid or *m*-chloroperoxy benzoic acid yields esters. Using cyclic ketones this method represents a convenient pathway to lactones (Scheme 4), which are common monomers for ring-opening polymerization.



Scheme 4. Synthesis of lactones (**14**, **15**) via Baeyer–Villiger oxidation.

Higher cyclic ketones with $n>3$ and their derivatives usually require reaction times up to several days or even weeks for high conversion.[19] We investigated the lactone formation with cycloheptanone (**12**) and cyclooctanone (**13**) as substrates for microwave-promoted Baeyer–Villiger oxidation. The experiments were performed under reflux in CH_2Cl_2 in open vessels using microwave irradiation as well as comparison studies in an oil bath. Calculating the ketone conversion by ^1H NMR from the ratio of the OCH_2– and the $COCH_2$– signals of the lactone and the $COCH_2$– signal of the ketone the kinetics displayed in Figure 4a and b were obtained. We could observe acceleration of the reaction rate for both cycloheptanone (**12**) and cyclooctanone (**13**). Especially in case of the latter, the formation of the lactone **15** proceeded significantly faster.

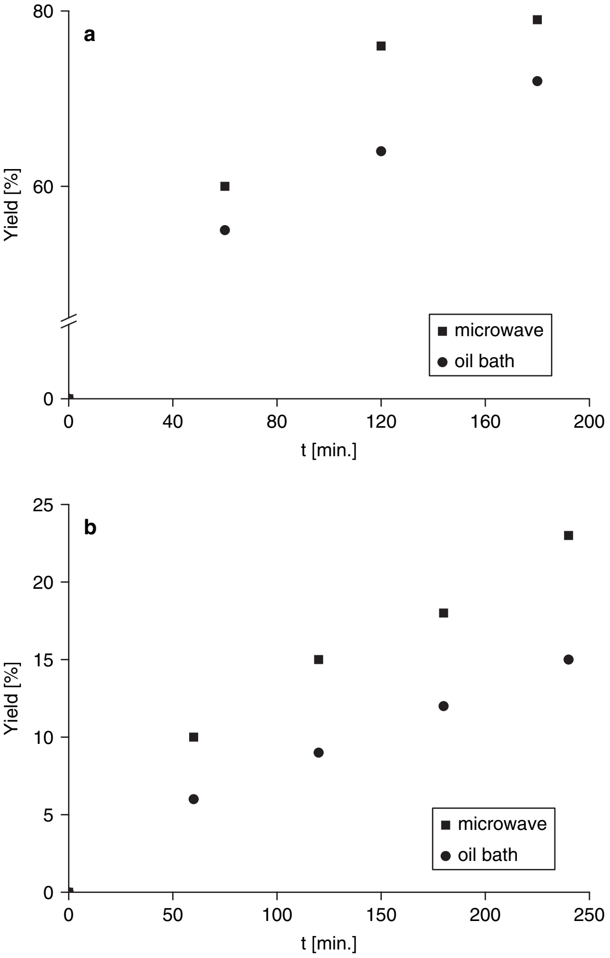


Figure 4. Kinetics of the Baeyer–Villiger oxidation of (a) cycloheptanone (**12**) and (b) cyclooctanone (**13**) in boiling CH_2Cl_2.

2.7. Special microwave effects and application

A special focus should be directed on the synthetic pathways that are not achievable under conventional heating conditions but can easily be realized using MW irradiation.

2.8. Direct synthesis and one-pot polymerization of acrylamide

Efficient synthetic routes towards acrylamides are through the conversion of acid chlorides, essentially in the presence of bases like triethylamine or pyridine, or directly, from acid and amine using activating agents like *N*,*N*′-dicyclohexylcarbodiimide. We previously investigated the MW-assisted reaction between (meth)acrylic acid and a chiral amine in the presence and in the absence of a radical initiator.[11] Focusing on the behavior of acrylic acid and (*R*)-1-phenylethylamine, we found that MW irradiation accelerates considerably the process of acrylamide formation with high selectivity.[5] After irradiation for only 15 min with a microwave power of 50 W, the amide **18** was synthesized in 93% yield (GC/MS). The reaction was performed in bulk without any activation reagents (Scheme 5).

Numerous attempts to perform the same synthesis by conventional thermal heating in an oil bath led to almost complete polymerization of the acrylic acid–amine salt (**17a**) after only 2 min of reaction time.

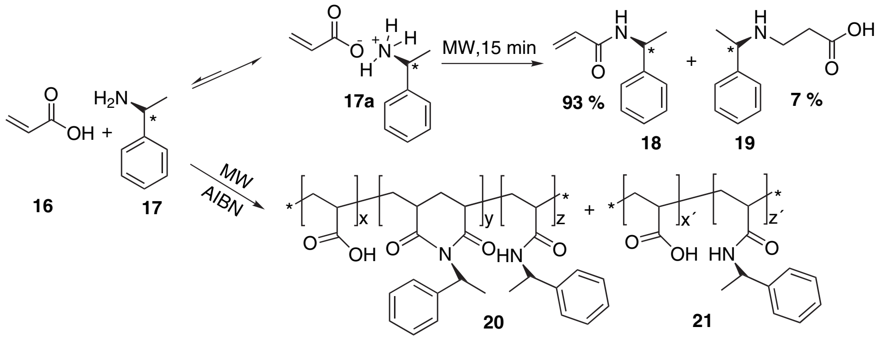
The MW-assisted reaction, carried out in the presence of AIBN, afforded optically active polymers in a single step. The ^1H NMR and DSC analyses suggest the presence of blends containing two different polymeric structures: a terpolymer containing imide moieties (**20**) and a copolymer containing acrylic acid and acrylamide units (**21**) (Scheme 5). The applied irradiation power and the average molecular weight of the polymers were inversely related. On the other side, the yield was observed to increase with power.

In conclusion, MW irradiation accelerates considerably the acrylamide formation with exceptional selectivity. The same results are not achievable by conventional thermal heating in an oil bath. The MW-assisted one-pot polymerization offers a good method for the synthesis of optically active polymers. These materials are possible candidates as chiral stationary phases for applications in chiral resolutions.

2.9. Coatings

Coatings, channel containing polymeric materials and the way to produce them play an important role, for example, in industry as protection against corrosion or in medical research for bone replacement.[6] Often the question rises, how to prepare materials, which contain ordered and defined structures.

It is well known that metals show fast heat development under MW irradiation.[20,21] This property, based on electrical resistance, was used to develop a new technique for the



Scheme 5. MW-assisted bulk amidation and one-pot polymerization.

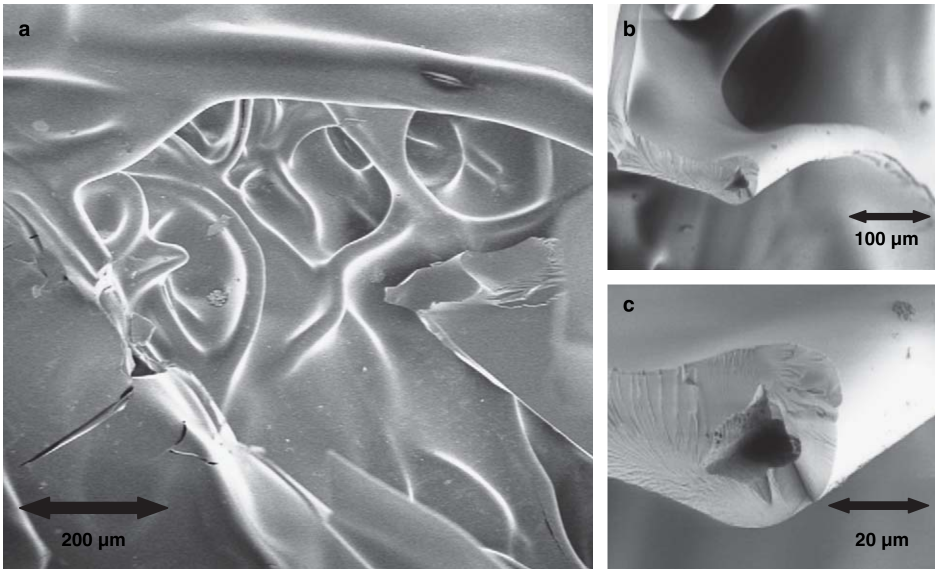


Figure 5. (a) SEM picture of channels in the polymer network synthesized by MW irradiation. (b) A tube opening of a channel after dissolving the iron component in HCl. The surface of the polymer cover is smooth. (c) Close up view of the tube opening in Figure 5b. The angular outlines of the metal fibers due to the production process can be recognized.

coating of metal fibers and the preparation of polymeric materials with defined channel structures.

MW irradiation of iron fibers, which are located in a monomer solution consisting of methyl methacrylate (MMA), ethylene glycol dimethacrylate as cross-linker, *N*,*N*′-azoisobutyronitrile (AIBN) as free radical initiator and toluene as solvent and weak MW absorber led to the formation of polymeric material on the iron surface. The thermal decomposition of the initiator predominantly took place close to the heated metal surface whereas the solution temperature outside the iron fibers was too low.[6] In contrast to MW irradiation, classical thermal heating leads to a temperature gradient in the opposite direction. As expected the polymerization reaction started first at the wall of the flask and then in the solution. Thus, it was not possible to adjust the reaction conditions in the way that polymer is formed only at the iron surface.

By dissolving the covered iron component in hydrochloric acid after polymerization it was possible to obtain polymeric materials with defined structures in the form of iron fibers. Scanning electron microscopy (SEM) elucidated the structure and distribution of the channels in the polymer matrix. The exterior surface of these tubes was smooth in contrast to the interior structures, which showed a rough surface. This fact can be attributed to the roughness of the metal fiber surface (Fig. 5).

This method represents a cheap, fast, and convenient pathway to defined porous materials and coatings, which was not possible to reproduce in an oil bath.

3. Conclusion

It can be concluded from the above described results that MW activation is in general a convenient method to carry out chemical reactions on a laboratory scale. However, in some cases it may not only accelerate certain chemical conversions but also influence the course of reactions. MW irradiation provides fast and convenient access to chiral (meth)acrylamides and their polymers in a one-pot synthesis. We could also show that it is possible to obtain well defined channel-like structures in a polymer matrix by focused heating of metals under MW irradiation in a monomer solution. Moreover, this method allows fast and effective excess to a multitude of other interesting monomers and macromonomers. Also the generation of selected polymers as polyoxazoline and poly(phenylene vinylene) under usage of metal catalysts can be provided.

4. Experimental

4.1. Materials and methods

p-Divinylbenzene was synthesized and purified according to literature procedures.[22,23]

All reagents used in our experiments were of analytical grade and were used without further purification.

The identity of the synthesized compounds was confirmed by mass spectrometry, NMR, and IR measurements. ^{1}H NMR and ^{13}C NMR were performed using a Bruker Advance DRX 500 spectrometer at 500.13 and 200.13 MHz for proton and 125.77 MHz for carbon in $CDCl_3$ as solvent. The δ-scale relative to TMS was calibrated to the deuterium signal of the solvent as internal standard. Infrared spectra were recorded on a Nicolet 5SXB FTIR spectrometer. Size exclusion chromatography (SEC) was performed on a SEC-system consisting of a Waters 486 tunable absorbance detector at 275 nm and a Waters 410 differential refractometer, using THF as eluent. The system was calibrated with polystyrene standards with a molecular weight range from 580 to 1,186,000 D. The flow rate was 1 mL/min. Polymer solution [100 μL of a 0.125% (w/w)] was injected to a HEMA-column-combination consisting of a pre-column of 40 Å and main columns of 40, 100, and 300 Å porosities. For MW-assisted synthesis a monomodal microwave (CEM-Discover) equipped with an infrared pyrometer with maximum operation power of 300 W was used.

4.2. Synthesis

4.2.1. 1,4-Diiodo-2,5-dibutoxybenzene (4). 1,4-Diiodo-2,5-dibutoxybenzene was synthesized according to literature procedures shown in Scheme 1.[24]

4.2.2. Poly(2,5-dibutoxy-1,4-phenylenevinylene) (6). Tributylamine (0.53 mL, 2.2 mmol) was added to a solution of 1,4-diiodo-2,5-dibutoxybenzene (**4**) (474 mg, 1 mmol), *p*-divinylbenzene (144 μL, 1 mmol), Palladium-(II)-acetate (9 mg, 0.04 mmol), and tri-(*o*-tolyl)phosphine (61 mg, 0.2 mmol) in 5 mL 1,4-dioxane. For a series of kinetics 5 mL samples were taken from a 70 mL stock solution. MW-assisted reactions were irradiated to reflux at 300 W in a mono-mode microwave reactor under nitrogen atmosphere. Reaction mixture in oil bath was heated up to reflux under nitrogen atmosphere. The reaction mixture (5 mL each) was poured into 20 mL of methanol. The precipitated orange polymer was collected by filtration, washed several times with 20 mL of methanol, and dried for 12 h under vacuum.

FTIR (diamond): 2955 ($\nu_{C–H}$), 2929 ($\nu_{–CH_3}$), 2867 ($\nu_{–CH_2–}$), 1594 (ν_{Ar}), 1495 (ν_{Ar}), 1466 ($\delta_{CH_2–CH_3}$), 1420, 1200 ($\nu_{–C–O–C}$), 1027, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=7.47 (Ar), 7.10 (vinyl), 4.03 ($–OCH_2$), 0.93–1.81 ppm (polymer backbone); ^{13}C NMR ($CDCl_3$): δ=151.57 (O–C–Ar), 138.74 (vinyl), 124.22–129.37 (Ar), 111.23 (vinyl), 69.69 ($O–CH_2$), 32.02 ($CH_2–CH_2–CH_2$), 19.91 ($CH_2–CH_3$), 14.42 ppm (CH_3).

4.2.3. 1-Oxa-2-oxocyclooctanone (14) and 1-oxa-2-oxocyclononanone (15). *m*-Chloroperoxy benzoic acid with 30% water content (5.2 g, 20 mmol) was added to a solution of the cyclic ketone (**12** or **13**) (20 mmol) in 20 mL methylene chloride. The mixtures were refluxed for 3 and 4 h, respectively. For kinetic measurements samples were taken every hour. MW-assisted reactions were performed under 100 W irradiation and else same conditions.

Compounds **14**: ^{1}H NMR (500.13 MHz, $CDCl_3$): δ=4.45–4.32 (t, 2H, OCH_2), 2.65–2.55 (t, 2H, $COCH_2$), 1.95–1.54 ppm (m, 8H); **15**: ^{1}H NMR (200.13 MHz, $CDCl_3$): δ=4.38–4.29 (t, 2H, OCH_2), 2.38–2.28 (t, 2H, $COCH_2$), 2.00–1.32 ppm (m, 6H).

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