

Design and evaluation of improved magnetic stir bars for single-mode microwave reactors†

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 4949

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Magnetic stirring in sealed cylindrical vessels designed for use in single-mode microwave instruments is typically less than optimal, and is not comparable to the efficient agitation that can be generally obtained in a round-bottomed flask fitted with a suitable magnetic stir bar or using overhead mechanical stirring systems. A new “vertical blade” stir bar design that improves the stirring performance in the very narrow, flow-constricting microwave vessels has been developed and evaluated for several different transformations where stirring and efficient agitation are known to be of importance. The better performance of these novel stirrers compared to the traditional cylindrical stir bar design is not only due to the geometry of the stirrer but also to the utilization of a magnetic material with a stronger magnetic transmission force ($\text{Sm}_2\text{Co}_{17}$) compared to standard ferrite or AlNiCo alloys. For all three tested cases involving solid/liquid, liquid/liquid and highly viscous reaction systems, the new vertical blade stirrers showed a distinctively improved performance resulting in higher conversions and/or product yields.

Received 19th April 2013,
Accepted 4th June 2013

DOI: 10.1039/c3ob40790j

www.rsc.org/obc

Introduction

Heating chemical transformations utilizing microwave energy has been an increasingly popular theme in the scientific community over the past 25 years.^{1,2} The efficiency of this non-classical form of heating in dramatically reducing reaction times and in improving product yields are just two of the many advantages inherent to microwave chemistry. Not surprisingly therefore, many academic and industrial laboratories today utilize microwave-assisted organic synthesis in a routine manner, which undoubtedly is aided by the growing availability of carefully designed scientific microwave reactors, dedicated for use in chemical applications.³ While a variety of different microwave systems and processing options are available today, it can be estimated that more than 90% of all currently published microwave synthesis protocols rely on the use of single-mode microwave reactors typically employing a 10 mL sealed Pyrex reaction vessel.^{1,2} Sealed vessel microwave processing allows reaction mixtures to be heated very rapidly to temperatures far above the atmospheric boiling point of the reaction mixture. The elevated temperatures make it apparent that based on applying the Arrhenius law [$k = A \exp(-E_a/RT)$],

transformations that require several hours when performed in a solvent at reflux temperature may reach completion in a few minutes using superheated solvents in a sealed vessel, autoclave-type, microwave reactor (thermal microwave effect).⁴ State-of-the-art single-mode microwave instruments feature built-in magnetic stirrers, temperature monitoring of the reaction mixture with the aid of external infrared sensors (IR) recording the surface temperature of the reaction vessel and/or fiber-optic (FO) probes directly inserted into the reaction mixture, and software that enables online temperature control by regulation of microwave power output.^{3,5}

One key issue in performing microwave-heated transformations that is frequently overlooked is the importance of ensuring proper agitation of the reaction mixture. If efficient stirring/agitation cannot be ensured, temperature gradients may develop as a consequence of inherent field inhomogeneities inside single-mode microwave cavities.^{5–10} This in turn can lead to erroneous temperature measurements and therefore to incorrect interpretations of the results obtained from a microwave-heated experiment.^{8–10} Unfortunately, stirring in the standard 10 mL cylindrical microwave reaction vessels (internal vessel diameter ~10 mm) used in all of the commercially available single-mode reactors³ is less than optimal, and not comparable to the efficient agitation that can generally be obtained in a round-bottomed flask fitted with a suitable magnetic stir bar or using overhead mechanical stirring systems. While appropriate stirring using the built-in magnetic stirring system in single-mode reactors may be possible for pure solvents, this will not always be the case for strongly heterogeneous or viscous reaction mixtures.⁹ To complicate matters,

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†Electronic supplementary information (ESI) available: Images of stirring behavior and details of stir bar production. See DOI: 10.1039/c3ob40790j

the reaction mixture is typically not visible as for safety reasons the sealed microwave vessel is contained inside a steel cavity. The efficiency of the magnetic stirring system during a chemical transformation performed in a single-mode microwave reactor is therefore difficult to evaluate.

We have recently established that a camera incorporated into a single-mode microwave reactor is a very helpful tool for monitoring the stirring efficiency of the reaction system, in particular for strongly viscous reaction mixtures.^{9,11} Herein we present a new generation of magnetic stir bars that were specifically designed for use with cylindrical reaction vials inside single-mode microwave equipment. These types of stirrers are able to efficiently agitate even strongly heterogeneous mixtures, biphasic and viscous reaction mixtures in a far superior manner compared to the standard stir bars in use today.

Results and discussion

Magnetic transmission force

In response to the problem of the relatively weak magnetic transmission force of the typically used $\sim 10 \times 6$ mm (or similarly sized) cylindrical stir bars, we have looked for alternatives to the AlNiCo or ferrite alloys that are commonly employed. Rare-earth alloys based on SmCo_5 and $\text{Sm}_2\text{Co}_{17}$, or $\text{Nd}_2\text{Fe}_{14}\text{B}$ exceed the magnetic strength of both AlNiCo and ferrite considerably (Table 1) and have found increased application as permanent magnets in magnetic stir bars in recent years.¹² Apart from the magnetic transmission force, our practical experience with microwave reactors employing magnetic stirring has demonstrated that the strength of magnetic stir bars used at high temperatures in a microwave reactor continuously decreases during their estimated service life of several months, leaving only a fraction of the initial magnetic power. This effect is connected to the material's specific maximum service temperature, which in turn is correlated to its Curie temperature but also to the size of the magnet (smaller magnets are more easily demagnetized). Considering these facts, we have found that for the typical operating range of up to 300 °C of most microwave reactors, $\text{Sm}_2\text{Co}_{17}$ is a particularly attractive magnetic material having a maximum service temperature of 330–500 °C and an energy product BH that is several times higher than that for the above mentioned standard alloys (Table 1).¹³ For the experiments described below we have used nickel-coated $\text{Sm}_2\text{Co}_{17}$ magnets that were stacked to achieve a

Table 1 Energy product of some technically important magnetic alloys^a

Material	BH [kJ m^{-3}]	T_{max} [°C]	T_{Curie} [°C]
Ferrite	26–40	250	460
AlNiCo	13–69	450–550	810–900
$\text{Nd}_2\text{Fe}_{14}\text{B}$	240–400	60–180	320
SmCo_5	140–200	250	730
$\text{Sm}_2\text{Co}_{17}$	190–220	350–550	810

^a Data from ref. 13.

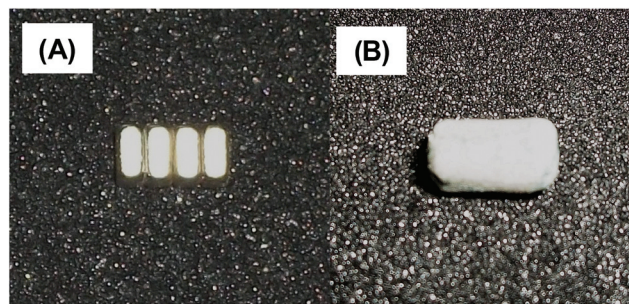


Fig. 1 $\text{Sm}_2\text{Co}_{17}$ stack ($8 \times 4 \times 4$ mm) before (A) and after coating (B) with PTFE (10×5.5 mm).

magnet core dimension of $8 \times 4 \times 4$ mm and protected with a layer of polytetrafluoroethylene (PTFE) using a simple dip-coating technique (Fig. 1, see Fig. S1 and S2 in the ESI† for a detailed description of the stir bar assembly).

Vessel geometry and mixing performance

Magnetic stir bar mixing strongly relies on the establishment of a liquid flow that is induced by centrifugal forces (tangential stirrer).¹⁴ The resulting flow in a stirred vessel has radial and tangential components, as well as an axial flow component which contributes most to liquid dispersion.¹⁴ In the case of microwave reaction vessels there is a hydrodynamic obstacle that is imposed by the high aspect ratio of the used 10 mL cylindrical pressure vials (typical dimensions: 11–12 mm inner diameter \times 80–90 mm height) which constricts the available cross section for the development of typical countercurrent flow patterns. These flow patterns are characterized in a downward liquid motion towards the center, and an upward liquid motion at the vessel wall.¹⁴ In fact, experiments show that with more viscous liquids, the flow is very often not fully developed and takes a “shortcut” (Fig. 2) because of the high friction within the liquid. In such a case, the upper part of the vessel is not agitated at all. As a consequence, the reaction mixture in the upper part of the vessel may overheat (owing to field inhomogeneities), or experiences lower conversion rates in the case

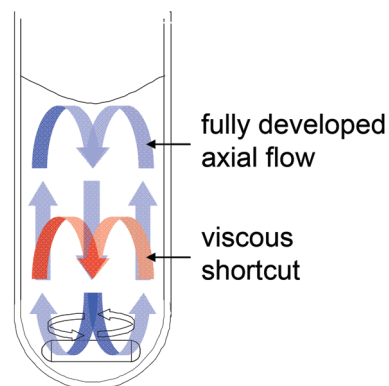


Fig. 2 Schematic drawing of the axial flow patterns observed with low- (blue arrows) and high-viscous (red arrows) reaction mixtures in a 10 mL microwave process vial agitated with a magnetic stir bar.

of biphasic or heterogeneous reaction conditions.^{5–10} As a further limitation, the maximum rotation speed in most microwave reactors is set to 400–1200 rpm, and the generally employed cylindrical magnetic stir bars (*e.g.*, 10 × 6 mm) have only a very small effective cross-sectional area. It was thus our goal to design a stirrer that is tailored to the peculiarities of small-scale mixing in a narrow pressure tube at the low stirring speeds employed in commercially available single-mode microwave reactors.

In order to improve the stirrers pumping ability (axial liquid movement) we have equipped the above described rare-earth magnet with vertical blade extensions (Fig. 3). As a first consequence, the cross-sectional area of the stirrer is significantly enlarged and the centrifugal forces responsible for the axial pumping motion are enforced. Viscous media can be agitated with high efficiency by virtue of the employed vertical blade extensions, which ensure agitation of the reaction medium also in the upper part of the vessel. With respect to the described countercurrent flow pattern, the center section of the tube should be free from rotating blade elements in order to guarantee liquid backflow and to allow the insertion of an internal temperature measurement probe. Small holes and cutouts on the paddles were incorporated to induce additional turbulence (mini-vortices).

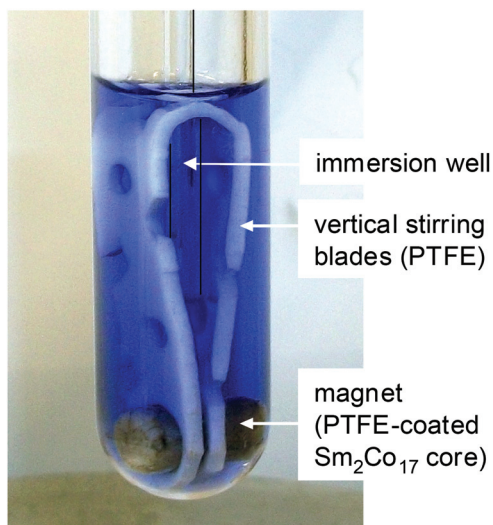
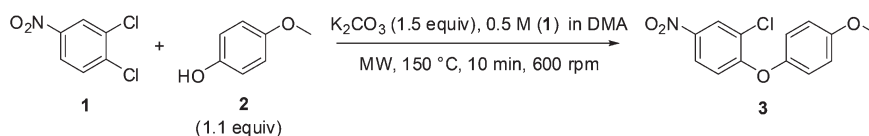


Fig. 3 Image of a double blade stirrer (30 × 10 × 2 mm) driven by a PTFE-coated Sm₂Co₁₇ magnet (dimension 10 × 5.5 mm). The stirrer is contained in a standard 10 mL Pyrex microwave vial (G10, Monowave 300) containing 3 mL of a liquid. The glass immersion well which houses the fiber-optic probe sensor is also shown.

Chemistry examples

The S_NAr reaction for the synthesis of diarylether **3** shown in Scheme 1 has proven to be a very suitable model transformation for the evaluation of stirring efficiency in single-mode as well as multimode microwave reactors in the past.¹⁵ As demonstrated by Moseley and co-workers under a variety of different processing conditions, insufficient agitation of the strongly heterogeneous reaction mixture (K₂CO₃/N,N-dimethylacetamide) will result in incomplete conversions.^{15a} This has also been confirmed by our own investigations into the scalability of this reaction, moving from single-mode to multimode microwave instrumentation.^{15b} Proper agitation under microwave conditions in this particular case is aggravated by the fact that the reaction temperature is kept below the boiling point of the solvent. Therefore, no solvent vapors (bubbles) are formed which significantly contribute to efficient agitation inside the reaction vial for experiments where the reaction temperature is above the boiling point of the reaction mixture.⁹ Not surprisingly therefore, better results for this transformation can generally be obtained using mechanical overhead stirrers,^{15a,b} which however are difficult to implement in a sealed vessel single-mode microwave reactor.

We anticipated that the stronger magnet in combination with the improved stirrer geometry would help to overcome the agitation problems typically experienced with this heterogeneous S_NAr reaction (Scheme 1) under sealed vessel microwave conditions. Therefore a set of experiments was performed where the reaction scale, and therefore the filling volume in the 10 mL cylindrical vessel, was continuously increased from 1.0 mmol (~2 mL filling volume) to 2.5 mmol (~5 mL filling volume) comparing the performance of the standard cylindrical with the new vertical blade stir bar at the identical stirring speed of 600 rpm. The experiments were performed using a standard 10 mL Pyrex microwave vial in combination with a Monowave 300 (Anton Paar GmbH) single-mode microwave reactor that allowed accurate temperature monitoring of the reaction mixture by an internal fiber-optic (FO) probe.^{7,9} Note that the stir bar was specifically designed in order to operate in conjunction with an internal temperature probe which provides additional stabilization to the stirring system (Fig. 3). The results quite clearly indicate that with increasing the filling volume in the vessel, the performance of the standard stirrer decreases significantly (Table 2). While at the 1.0 mmol scale an 85% HPLC conversion was reached, at 2.5 mmol the conversion dropped to only 52%. Notably, employing the vertical blade design not only provided a higher conversion at the 1.0 mmol scale (99%); the conversion remained almost unaffected by the scale of the reaction and therefore the filling



Scheme 1

Table 2 Comparison of HPLC conversions for the S_NAr reaction shown in Scheme 1 in dependence on the scale/filling volume using two different stir bar designs (10 mL Pyrex vessel, Monowave 300)^a

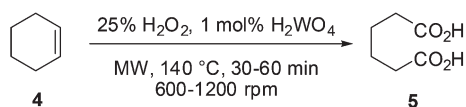
Scale (mmol)	DMA (mL)	Standard stir bar (conversion in %)	Vertical blade stir bar (conversion in %)
1	2	85	99
1.5	3	68	99
2	4	53	98
2.5	5	52	94 ^b (85)

^a HPLC conversion was determined by peak area integration at 215 nm. ^b Isolated yield.

volume in the vial (Table 2). These findings are supported by images of the stirred reaction slurry, demonstrating that the solid base is not dispersed longitudinally in the reaction tube, but rather remains at the bottom of the tube, when the standard stir bar was used. Contrary to this is observation that the vertical blade stirrer is able to disperse the solid base very effectively across the whole reaction volume (see Fig. S3 in the ESI†).

As an additional example to highlight the improved mixing characteristics of the vertical blade stir bar design introduced herein, a transformation that critically depends on the efficient mixing of two immiscible liquids was selected. We have recently described the oxidation of cyclohexene to adipic acid using 25% aqueous hydrogen peroxide in combination with catalytic amounts of tungstic acid under high-temperature microwave batch and continuous flow conditions (Scheme 2).¹⁶ During the preliminary microwave batch experiments using 10 mL reaction vessels we have noted that at 140 °C the biphasic reaction mixture (2.5 mL filling volume) cannot be properly agitated using the standard cylindrical stir bar (600 rpm).¹⁶ This apparently leads to selective heating of the aqueous hydrogen peroxide layer and thus to an often spontaneous and violent decomposition of hydrogen peroxide as indicated by a sharp increase in the reaction pressure and temperature inside the reaction vessel.¹⁶ Based on this premise, the application of an improved stirring system was expected to have beneficial effects on both conversion and controllability of this reaction.

Again, a set of different microwave experiments was designed to probe the different stirring efficiencies of both stirrers under otherwise identical conditions. Before the actual heating experiment was performed, the two stir bars were tested offline by visual inspection of the stirring efficiency of the reaction mixture. This preliminary test indicated that while the standard stir bar was unable to ensure efficient agitation of this biphasic reaction mixture, the vertical blade stir bar did lead to a noticeable improvement in mixing behavior and therefore provided a significant interfacial area between the



Scheme 2

two organic and aqueous phases required for a smooth oxidation process (for images of this set of experiments see Fig. S4 and S5 in the ESI†).

Encouraged by this observation, we conducted the oxidation of cyclohexene in a 10 mL microwave reaction vessel applying the conditions shown in Scheme 2. As experienced in our previous study,¹⁶ spontaneous decomposition of hydrogen peroxide accompanied by a rapid pressure increase to 30 bars was sometimes observed at 140 °C when the standard stir bar (600 rpm) was utilized. In our comparison experiments utilizing the vertical blade stirrer, the two phases were mixed much more efficiently, preventing unproductive (and uncontrolled) hydrogen peroxide decomposition as indicated by the corresponding temperature/pressure profiles (Fig. 4). Importantly, incomplete reaction was observed using the standard stir bar since after the heating experiment a phase of unreacted cyclohexene was clearly visible floating on top of the reaction mixture and only very small amounts of adipic acid product (7%) could be obtained by precipitation (Fig. S6 in the ESI†). Utilizing the vertical bladed stirrer, a homogeneous reaction mixture was obtained after 30 min at 140 °C followed by precipitation of adipic acid upon cooling (Table 3). After cooling at 0 °C for 2 h, 20% of pure adipic acid was isolated by filtration and washing with cold 1 N HCl (Table 3). The yield of

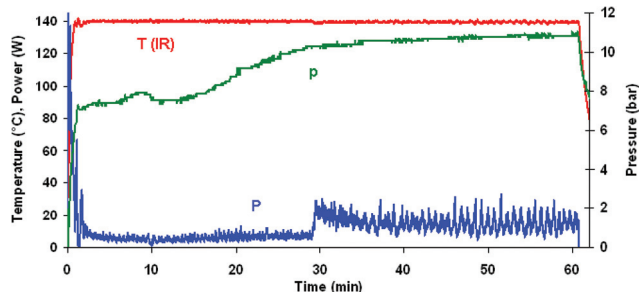


Fig. 4 Temperature (IR), pressure (p) and microwave power (P) profiles for the oxidation of cyclohexene to adipic acid (Scheme 2). Reaction conditions: a 10 mL Pyrex microwave vial, a vertical blade stirrer, 1200 rpm, 140 °C set temperature, 60 min reaction time. Because of the high explosion risk in this reaction, the external IR temperature sensor was used instead of the internal fiber optic probe.

Table 3 Oxidation of cyclohexene to adipic acid (Scheme 2) in a single-mode microwave reactor (10 mL Pyrex vessel, Monowave 300) utilizing different stir bar designs^a

Stir bar design	Stirring speed (rpm)	Heating time (min)	Adipic acid ^b (%)
Standard ^c	600	30	7
Vertical blade	600	30	20
Vertical blade	1200	30	42
Vertical blade	1200	60	60

^a Reaction conditions: 140 °C, 1 mol% tungstic acid, 25% hydrogen peroxide solution, 4.4 equiv. hydrogen peroxide. ^b Isolated yield after precipitation and filtration followed by washing with cold 1 N HCl. ^c Occasionally, vessel failure due to unproductive hydrogen peroxide decomposition caused by insufficient mixing occurred (see also ref. 16).

adipic acid could be further improved by increasing the stirring speed to 1200 rpm and/or extending the reaction time to 60 min (Table 3). While the isolated yields of adipic acid obtained using the vertical blade stir bar in combination with the 10 mL microwave vial cannot compete with the results obtained using a highly mixing intensive segmented flow microreactor approach (72% within 20 min),¹⁶ the results nevertheless demonstrate the considerably improved mixing behavior for liquid/liquid biphasic reaction mixtures compared to a standard cylindrical stir bar.

Finally, the stirring efficiency of the vertical blade stirrer was evaluated for viscous reaction systems using PEG 600 as an initial model solvent. We have recently demonstrated that the simultaneous use of an internal fiber-optic (FO) and an external IR temperature sensor can be used to monitor the temperature difference between the vessel wall (IR) and center (FO) inside a microwave reaction vessel.^{7–9} The recorded temperature difference between the external calibrated IR and internal FO sensors in turn can be used to judge temperature homogeneity within the irradiated sample. Only when no difference between the temperature recorded at the two different positions of the reaction vessel exists, the measured temperature can be considered homogeneous throughout the reaction mixture.⁹ For viscous samples this typically indicates efficient agitation of the reaction mixture, not leading to temperature inhomogeneities as a result of electromagnetic field inhomogeneities.^{8,9}

To demonstrate that magnetic stirring, and thus also the selection of a proper stir bar, plays an important role in achieving homogeneous temperature distributions within a cylindrical microwave process vial, a sample of 2 mL of PEG 600 was heated to 200 °C (FO temperature control) using both the improved vertical blade stirrer and the standard cylindrical stir bar. In addition to the FO temperature sensor controlling the magnetron output, the surface temperature (IR) of the reaction vessel was additionally recorded in both experiments.⁹ In our previous studies utilizing the standard cylindrical stir bar design we have found that the recorded difference between IR and FO sensor temperatures is critically dependent on the stirring speed. In general, the higher the stirring speed, the lower the observed difference.⁹ Applying a constant 100 rpm stirring speed for both experiments the measured temperature difference between the FO and IR probes was only 6–7 °C when using the vertical blade stirrer compared to 20–25 °C when the standard stir bar was employed. This again emphasizes the improved stirring characteristics of the vertical blade design (Fig. 5).

To demonstrate that the vertical blade stirrer is capable of agitating reaction mixtures of higher viscosity compared to the standard design, the ring-opening polymerization of ϵ -caprolactone (**6**) using tin(II)-2-ethylhexanoate as a catalyst to obtain ϵ -polycaprolactone was investigated (Scheme 3). Our previous studies involving this polymerization reaction applying dual IR/FO temperature monitoring in combination with a built-in camera (which allows a visual observation of the stirring efficiency) have confirmed that at a certain point during the

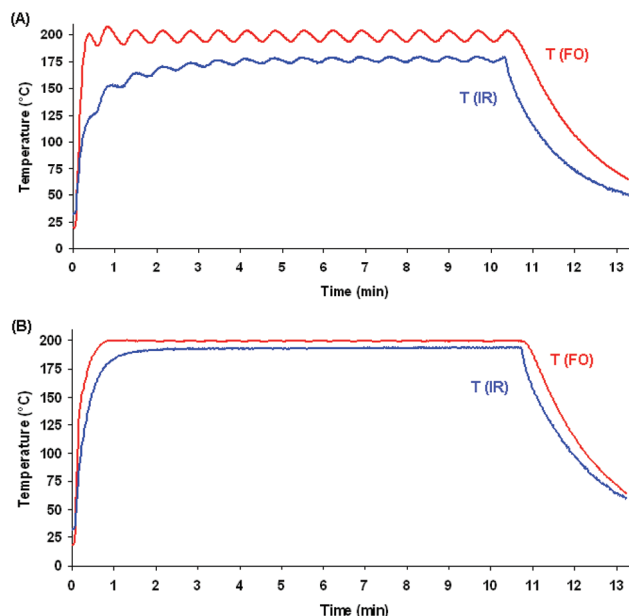
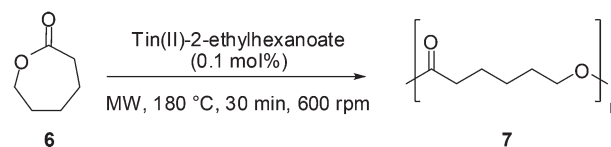


Fig. 5 FO and IR temperature profiles for a 2 mL sample of PEG 600 heated under microwave conditions using the internal FO temperature control as the lead sensor. Set temperature of 200 °C, 10 min hold time, stirring speed 100 rpm. (A) A standard cylindrical stir bar; (B) a vertical blade stirrer. Using the standard stir bar (A), it takes ~3 min until the IR sensor temperature equilibrates to a constant value which is differing by about 20–25 °C from the FO temperature. Because of mass and heat transfer issues an undesired oscillation of the target temperature can be observed. In contrast, the vertical blade stir bar (B) provides a much better mixing and thus leads to a rapid adjustment of the IR sensor to the FO temperature (~90 s).



Scheme 3

polymerization the stir bar gets “frozen” in the viscous polymer matrix, not being able to agitate the reaction mixture anymore.⁹ At this point the severe limitation of mass and heat transfer in the reaction mixture leads to significant deviations in the recorded IR and FO temperature profiles in the microwave experiments.⁹ For example, in an IR controlled experiment (180 °C target temperature, an FO sensor as slave) the standard stir bar stops agitating the reaction mixture after ~4 min at 180 °C, at which point the internal FO temperature starts to rise to ~240 °C (Fig. 6). Using the significantly stronger vertical blade stir bar, agitation of the very same reaction mixture is possible till ~7 min at 180 °C before the same effect occurs (Fig. 6). This indicates, although here not quantifiable, that by employing the improved stirrer, it is possible to stir reaction mixtures of higher viscosity compared to the standard design.

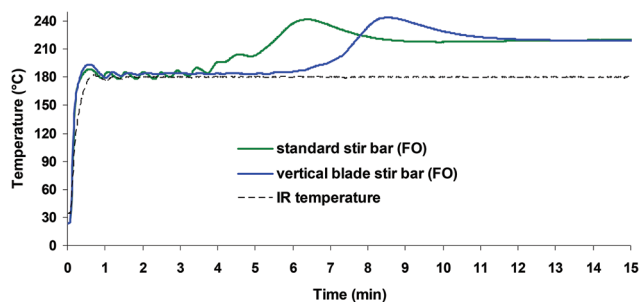


Fig. 6 Overlay of the FO/IR temperature profiles in the microwave-assisted polymerization of ϵ -caprolactone using cylindrical and vertical blade stir bar designs (Scheme 3). Conditions: 180 °C set temperature (IR control), hold time 30 min, ramp time 5 min (Monowave 300).

Conclusions

In summary, we have described the design and construction of a very simple to assemble small-scale magnetic stirrer that allows to significantly improve the stirring performance in the very narrow, flow-constricting process vials generally used in single-mode microwave reactors. The success of the new stir bar depends on both the use of a magnetic material with a stronger magnetic transmission force ($\text{Sm}_2\text{Co}_{17}$) compared to standard ferrite or AlNiCo alloys and a novel design concept that introduces vertical blades on the stirrer which significantly enlarge the cross-sectional area of the stirrer and enforces the centrifugal forces responsible for the axial pumping motion.

The successful use of this stirrer in improving reaction performance was demonstrated for a strongly heterogeneous slurry reaction, a biphasic liquid/liquid reaction mixture where intense mixing of the two immiscible phases is critical, and for a polymerization reaction leading to a viscous product. In all three cases an improved performance of the newly designed stir bar compared to the use of standard cylindrical stir bars was seen. Undoubtedly, this design which was specifically constructed for use in combination with the internal fiber-optic temperature measurement technique will be useful for many other transformations under microwave conditions where agitation is of relevance.

Experimental section

General

$^1\text{H-NMR}$ spectra were recorded on a Bruker 300 MHz instrument. Chemical shifts (δ) are expressed in ppm downfield from TMS as the internal standard. Analytical HPLC analysis (Shimadzu LC 20 AD) was carried out on a C18 reversed-phase analytical column (150 mm \times 4.6 mm, particle size 5 μm) using mobile phases A (water–acetonitrile, 90 : 10 (v/v) + 0.1% TFA) and B (acetonitrile + 0.1% TFA) at a flow rate of 1 mL min^{-1} . The following gradient was applied: a linear increase from 10% solution B to 100% solution B in 9 min, and a hold

at 100% solution B for 3 min. The conversion of the crude reaction mixture was determined by HPLC at 215 nm.

Microwave irradiation experiments

Microwave irradiation experiments were performed using a Monowave 300 single-mode microwave reactor from Anton Paar GmbH (Graz, Austria).⁷ The instrument uses a maximum of 850 W magnetron output power (2.45 GHz) and can be operated at 300 °C reaction temperature and 30 bar pressure. The reaction temperature is monitored by an external infrared sensor (IR) housed in the side-walls of the microwave cavity measuring the surface temperature of the reaction vessel, and/or by an internal fiber-optic (FO) temperature probe (ruby thermometer) protected by a borosilicate immersion well inserted directly into the reaction mixture. The magnetron output power can be controlled either by the FO probe (IR as slave) or by the IR sensor (FO as slave). Heating experiments can be performed in the temperature control mode (“as-fast-as-possible”, ramp mode) or using a constant power option. Pressure sensing is achieved by a hydraulic sensor integrated in the swiveling cover of the instrument. The reusable Pyrex vials (10 mL) are sealed with PEEK snap caps and standard PTFE coated silicone septa. In the case of FO temperature measurement, punched seals to insert the immersing tube are employed. Reaction cooling is performed by compressed air automatically after the heating period has elapsed. The required pressure of 6–8 bar is also used to pneumatically seal the vials tightly at the beginning to withstand 30 bar, and to ensure smooth release of potentially remaining pressure before opening the cover. Magnetic stirring is available at variable speed between 0 and 1200 rpm. The system used herein has been fitted with a built-in camera in order to visibly observe the reaction mixture during the microwave irradiation process.⁹

Synthesis of 2-chloro-1-(4-methoxyphenoxy)-4-nitrobenzene (3) at the 2.5 mmol scale (Scheme 1)

1,2-Dichloro-4-nitrobenzene (2.5 mmol, 478 mg) and 4-methoxyphenol (2.75 mmol, 341 mg) were dissolved in 5 mL DMA in a 10 mL Pyrex microwave vessel utilizing the vertical blade stir bar. After the addition of 3.75 mmol (518 mg) of K_2CO_3 (Sigma Aldrich 347825, –325 mesh) the vessel was sealed with a snap cap holding a PTFE-coated silicone septum equipped with a hole to be equipped with an immersion tube allowing the introduction of a fiber optic probe for internal temperature measurement. The reaction mixture was then heated in the single-mode microwave reactor to 150 °C holding the target temperature for 10 min (600 rpm stirring speed). Thereafter the reaction mixture was cooled to ambient conditions with compressed air and a drop of the reaction mixture was mixed with 1 mL of MeCN to allow HPLC monitoring, affording a conversion of 94% to the desired diarylether (3). The remaining crude mixture was slowly combined with 5 mL of water applying vigorous stirring. The mixture was then stirred for 1 h in an ice-bath and after that the product was filtered and washed with cold water to obtain the product 3 in 85% isolated

yield (593 mg), mp. 92–93 °C. lit.^{15c} mp. 88–89 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 8.44 (d, *J* = 2.75 Hz, 1H), 8.17 + 8.14 (dd, *J*₁ = 2.8 Hz, *J*₂ = 9.2 Hz, 1H), 7.21–7.15 (m, 2H), 7.08–7.03 (m, 2H), 6.92 + 6.89 (ds, 1H), 3.79 (s, 3H).

Synthesis of adipic acid (5) (Scheme 2)

A 10 mL Pyrex microwave vessel was equipped with the vertical blade stir bar, 10 mg tungstic acid (1 mol%), 1 mL of a 50% hydrogen peroxide solution, 1 mL of water, and 4 mmol of cyclohexene (405 μL) to obtain a 4.4 equiv. excess of hydrogen peroxide. The reaction vessel was sealed with a snap cap containing a PTFE-coated silicone septum and the reaction mixture was heated for 60 min at 140 °C utilizing a stirring speed of 1200 rpm (IR temperature control). After cooling to ambient conditions the reaction mixture was cooled for 2 h at 0 °C to allow precipitation of the desired product. Finally the adipic acid was filtered and washed with a small amount of cold 1 N HCl to obtain 351 mg (60% isolated yield) of pure product, mp. 151 °C (lit.¹⁶ mp. 151–152 °C); ¹H NMR (300 MHz, DMSO) δ 12.01 (s, 1H), 2.2 (t, *J* = 6.0 Hz, 1H), 1.64–1.38 (m, 1H).

Synthesis of ε-polycaprolactone (7) Scheme 3

A stock solution consisting of 17.1 g (0.15 mol) ε-caprolactone and 60.75 mg (0.15 mmol) tin(II)-2-ethylhexanoate was prepared to obtain comparable initiator to monomer ratios. For a typical reaction 3 mL of the prepared stock solution were filled in a 10 mL Pyrex vessel that was equipped with a vertical blade stir bar and closed with a snap cap holding a pierced PTFE-coated silicone septum to be equipped with an immersion tube that protects the utilized internal FO probe during the microwave run. The reaction mixture was heated for 30 min at 180 °C (IR control) using a stirring speed of 600 rpm and subsequently cooled to 70 °C with compressed air. High ¹H NMR conversions were obtained for both stir bar designs (93% for the standard stir bar as well as 94% for the vertical blade stir bar). The conversion rate was calculated from the relative intensities of the ¹H NMR signals of the ω-methylene protons (–CH₂OC(O)–) in the product (2H, 4.04 ppm) and the monomer (2H, 4.22 ppm) as previously reported.⁹

Acknowledgements

This work was supported by a grant from the Christian Doppler Research Society (CDG).

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