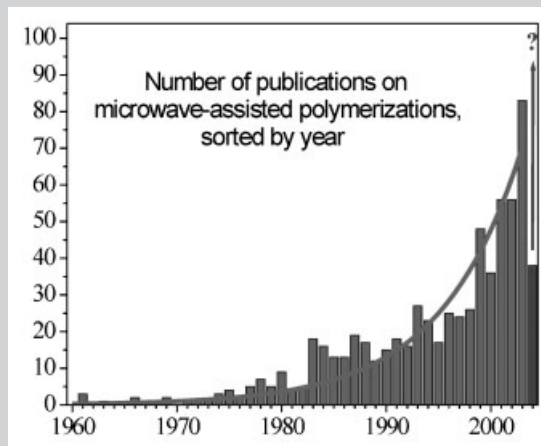


**Summary:** Monomodal microwaves have overcome the safety uncertainties associated with the precedent domestic microwave ovens. After fast acceptance in inorganic and organic syntheses, polymer chemists have also recently discovered this new kind of microwave reactor. An almost exponential increase of the number of publications in this field reflects the steadily growing interest in the use of microwave irradiation for polymerizations. This review introduces the microwave systems and their applications in polymer syntheses, covering step-growth and ring-opening, as well as radical polymerization processes, in order to summarize the hitherto realized polymerizations. Special attention is paid to the differences between microwave-assisted and conventional heating as well as the “microwave effects”.



Results of search on number of publications on microwave-assisted polymerizations, sorted by year.

# Microwave-Assisted Polymer Synthesis: State-of-the-Art and Future Perspectives

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## 1. Introduction

Microwave irradiation is a well-known method for heating and drying materials and is utilized in many private households and industrial applications for this purpose. It offers a number of advantages over conventional heating, such as noncontact heating (circumventing the decomposition of molecules close to the walls of the reaction vessel), instantaneous and rapid heating (resulting in a uniform heating of the reaction liquor), and highly specific heating (with the material selectivity emerging from the wavelength of microwave irradiation that intrinsically excites dipolar oscillation and induces ionic conduction).<sup>[1,2]</sup>

Microwave ovens operate with electromagnetic non-ionizing radiation with frequencies between 300 GHz and 300 MHz. The corresponding wavelengths span a range from 1 mm to 1 m, exhibiting the medial position of micro-

waves between infrared and radio waves. Most commercial microwave systems, however, utilize an irradiation with a frequency of 2 450 MHz (wavelength  $\lambda = 0.122$  m) in order to avoid interferences with telecommunication devices. The corresponding electric fields oscillate  $4.9 \times 10^9$  times per second and consequently subject dipolar species and ionic particles (as well as holes and electrons in semiconductors or metals) to perpetual reorientation cycles. This strong agitation leads to a fast noncontact heating that is (approximately) uniform throughout the radiation chamber.

A large number of reactions, both organic and inorganic, undergo an immense increase in reaction speed under microwave irradiation compared with conventional heating. Apart from this main advantage, significant improvements in yield and selectivity have been observed as a consequence of the fast and direct heating of the reactants themselves. Furthermore, high-pressure synthesis is easily

accessible for reactions performed in closed vessels, facilitating the use of low boiling solvents and thereby paving the way to environmentally benign reaction conditions.

It should be mentioned, however, that these ameliorations might be mainly ascribed to the one main characteristic of reactions performed under microwave irradiation: a combination of the large increase in reaction speed (caused by the high temperatures utilized) and the selective excitation that circumvents the formation of by-products or the exhaustion of catalysts and reduces the time available for the desired product to decompose.<sup>[2]</sup> In the literature, on the other hand, a controversial discussion has arisen as to whether the increase in reaction speed not only emerges from thermal effects, but also from (nonthermal) “microwave effects”.<sup>[2–5]</sup> These days, a strong tendency to dismiss microwave effects is discernible, benefiting from the observations made during reactions performed in monomodal microwave systems as reaction devices. This new class of reactors<sup>[6]</sup> was introduced to a large group of scientists at the beginning of the millennium and has

received broad interest in all branches of chemistry ever since then.

Monomodal microwave systems (Figure 1) heat only one reaction vessel at a time. Consequently, the volume of the reaction (heating) chamber is diminished, and the resulting homogenous irradiation field uniformly heats the reaction liquor. Most of these microwave reactors operate with standardized reaction vessels that are closed by septa, allowing for accurate control of the pressure (by the bowing of the septum) as well as the temperature inside the reaction vial (detected by an IR sensor that is directed towards the walls of the vessel). Depending on this online monitoring, the irradiation power may be adjusted (“dynamic field tuning”, DFT) to maintain the desired reaction conditions (like a fixed temperature and a threshold for maximum pressure), or be switched off, when the chosen parameters are exceeded. This way, a powerful tool is provided for minimizing the risk of hazardous explosions that are associated with reactions performed in domestic microwave ovens;<sup>[3]</sup> furthermore, exothermic reactions may be



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Figure 1. Microwave reactors for chemical syntheses. A: Emrys Liberator (Biotage, Sweden, [www.biotage.com](http://www.biotage.com)); B: CEM Discover BenchMate (CEM, USA, [www.cem.com](http://www.cem.com)) Copyright CEM Corporation; C: Milestone Ethos TouchControl (Milestone, Italy, [www.milestonesci.com](http://www.milestonesci.com)); D: Lambda MicroCure2100 BatchSystem (Lambda, USA, [www.microcure.com](http://www.microcure.com)).

subjected to analogous supervision, preventing them from running out of control.

The online measurement of temperature and pressure not only shifts the reliability of microwave reactors from hazardous to safe, it also allows for the determination of the reaction conditions inside the vials. This way, it has been elucidated for the majority of reactions that temperature effects or the selectivity in heating are solely responsible for the advantages experienced by using microwave irradiation. Furthermore, a high degree of reproducibility and a potential for optimization results from high-pressure syntheses. The ease of access to superheated reaction conditions facilitates the way to short reaction times, low-boiling solvents and, additionally, to halogen-free solvents (“green chemistry”), the latter as a consequence of the improved solubility at higher temperatures. In this respect, preliminary findings for polymerizations carried out in domestic microwave ovens might be taken into critical account as far as the measurement of the reaction conditions or reproducibility and up-scaling issues are concerned.

With their intriguing properties, monomodal microwave reactors have started a new era in several branches of organic chemistry, such as library synthesis<sup>[7–10]</sup> or solid-phase synthesis,<sup>[11–14]</sup> overcoming the long reaction times previously associated with these fields. A similar breakthrough seems to be at the outset for polymer science, as indicated by the almost exponential increase of publications on microwave-assisted polymerizations (Figure 2).<sup>[15]</sup>

With this background, the present review aims at summarizing the hitherto realized polymerizations under microwave assistance. In contrast to previous reviews,<sup>[1,16–18]</sup> the preparation of dental materials, polymer modification reactions, and curing processes are excluded. Instead, the focus of this review is directed towards microwave-assisted polymer synthesis, including step-growth, free and controlled radical, as well as ring-opening polymerizations.

## 2. Step-Growth Polymerization

These days, step-growth polymerizations are the most extensively investigated polymerization reactions under microwave irradiation. This is not accidentally because of the nearness of polymer and organic chemistry most discernible with this reaction type. A plethora of data has been collected, in particular for polyamides and polyimides. Polyethers and polyesters, as well as phase transfer and C–C coupling reactions, will be presented later in this section.

### 2.1. Polyamides

Amide linkages are most abundant in nature because of their involvement in peptides, proteins, and enzymes. In order to simulate the evolution of life from the assembly of nondirected amino acid sequences to extrinsically directed ones, Yanagawa et al. subjected amino acid amides to repeated hydration–dehydration cycles in a domestic

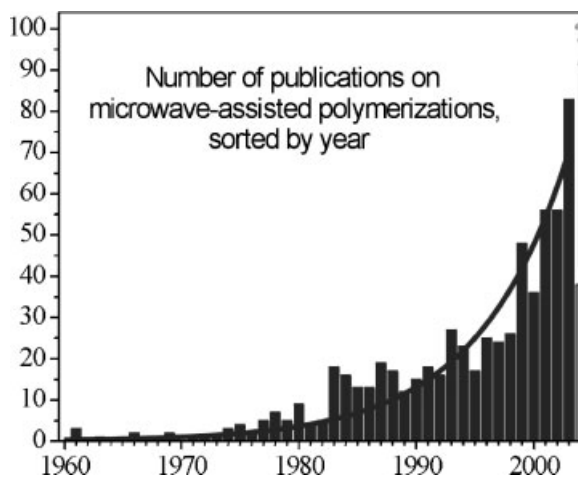


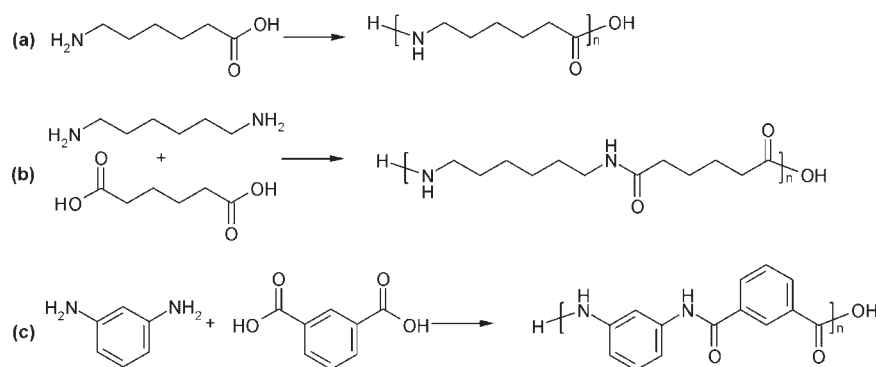
Figure 2. Number of publications on microwave-assisted polymerizations, sorted by year (updated on June 23, 2004).<sup>[15]</sup>

microwave oven.<sup>[19]</sup> The stock mixture was composed of equimolar amounts of glycylamide, alaninamide, valinamide, and aspartic acid  $\alpha$ -amide as model substances for molecules formed at an early stage of the chemical evolution. Continued solvation in aqueous solution and subsequent evaporation of the water in a microwave oven resulted in the formation of polypeptides with molecular weights of up to 4 000 Dalton. The molecular weights were found to be independent of the number of hydration–dehydration cycles; a saturating yield of 10% was obtained after ten cycles. Comparison experiments with conventional heating showed that the microwave did not affect the maximum molecular weight attainable, but it improved the yield of the polypeptides by a factor of 100. The authors ascribe this success to the shortness of the heating periods, keeping undesired side reactions, such as the hydrolysis of the terminal active amide groups, to a minimum.

Artificial polyamides have been derived from amino acids as well as nylon salts (for the synthesis of polyamides from caprolactam, see Section 3). Utilizing a domestic microwave oven, Imai et al. polymerized amino acids of the composition  $\text{H}_2\text{N}(\text{CH}_2)_x\text{COOH}$  ( $x = 5, 6, 10, 11, 12$ ) (Scheme 1a).<sup>[20,21]</sup> As a result of the incapability of the monomers to absorb microwave irradiation, the polymerization reactions were carried out in solution with the solvent additionally acting as absorber. Solvents with high boiling points and high dielectric constants, like *m*-cresol, *o*-chlorophenol, ethylene glycol, sulfolane, and *N*-cyclohexyl-2-pyrrolidone, proved to be most successful. As expected, diphenyl ether, with a high boiling point but a low dielectric constant, failed to support the polymerization. The syntheses of the polyamides were carried out in open reaction vials that allowed for the evaporation of the solvents; within five minutes, polymers with large inherent viscosities of around  $0.5 \text{ dL} \cdot \text{g}^{-1}$  were obtained. Average molecular weights and their distributions, however, were

not determined. The type of solvent did not influence the inherent viscosity (therefore, neither the molecular weight) of the polymers. The amount of solvent, however, played a (minor) role, as the use of a smaller amount of solvent resulted in a higher final temperature in a shorter reaction time, affording polymers with higher inherent viscosities.

Similar observations have been made for the polymerization of equimolar amounts of diamines and dicarboxylic acids, the “nylon salts”. Imai et al. investigated the polymerizations of aliphatic diamines and dicarboxylic acids for the preparation of polymers of the composition  $[-\text{NH}(\text{CH}_2)_x\text{NHCO}(\text{CH}_2)_y\text{CO}-]_n$  (with the combinations  $x/y = 6/4, 6/6, 6/8, 6/10, 8/4, 12/4, 12/6, 12/8, 12/10$ )<sup>[20–22]</sup> as well as the polymerizations of aromatic diamines (like 4,4'-methylenedianiline, 4,4'-oxydianiline, 1,3- and 1,4-phenylenediamine) and dicarboxylic acids (like isophthalic acid and terephthalic acid) to yield polymers of the structure  $[-\text{NH}-\text{Ar}-\text{NHCO}-\text{Ar}'-\text{CO}-]_n$  after a Yamazaki phosphorylation reaction (Scheme 1b and c).<sup>[23]</sup> For the polymerizations involving aromatic monomers, a domestic microwave reactor was additionally supplied with a Teflon insulated thermocouple (Figure 3). Like the polymerizations of amino acids, these reactions were also carried out in high-boiling solvents with high dielectric moments. The products were obtained after short reaction times (less than one minute) in high yields (85–96%), and the polyamides exhibited medium to high inherent viscosities (up to  $0.86 \text{ dL} \cdot \text{g}^{-1}$ ). For one series of aliphatic diamines and dicarboxylic acids ( $x = 6, 8, 12; y = 4$ ), the difference between continuous and periodic microwave irradiation was investigated.<sup>[22]</sup> In final consequence, the polymerizations carried out under periodic microwave irradiation allowed for easier temperature control and gave polymers with a higher inherent viscosity (compared with continuous heating). These findings are taken into account in the monomodal microwave systems available today in dynamic field tuning (see Section 1).



Scheme 1. Polyamides derived from microwave-assisted polymerizations: (a) nylon 6 from  $\epsilon$ -amino caproic acid as an example of polymers of the composition  $[-\text{NH}(\text{CH}_2)_x\text{CO}-]_n$  ( $x = 5$ ); (b) nylon 6,6 from adipic acid and hexamethylenediamine as an example of polymers of the structure  $[-\text{NH}(\text{CH}_2)_x\text{NHCO}(\text{CH}_2)_y\text{CO}-]_n$  ( $x = 6, y = 4$ ); (c) Nomex from isophthalic acid and 1,3-methylene diamine as an example of aromatic polyamides.

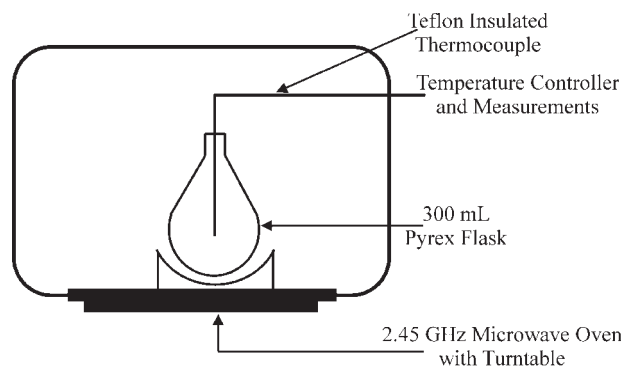


Figure 3. Experimental setup for the measurement of temperature in a domestic microwave oven (according to reference [23]).

Mallon and Ray, moreover, showed that the increase in reaction rates (for nylon 6,6) was determined by the enhanced diffusion rates under microwave irradiation (Figure 4; cf. Section 2.2).<sup>[24]</sup>

The high-pressure synthesis of polyamides was investigated by Pourjavadi et al. for the Yamazaki phosphorylation reaction of aliphatic dicarboxylic acids ( $x = 2, 4, 6, 8$ ) and aromatic diamines (like 1,4-phenylenediamine and 2,5-bis-(4-aminophenyl)-3,4-diphenylthiophene).<sup>[25]</sup> The educts were dissolved in *N*-methylpyrrolidone (NMP) and transferred to the (domestic) microwave oven in a polyethylene screw-capped cylinder. With this reaction, polymers with

high inherent viscosities were also obtained in (medium to) good yields after short reaction times (below one minute).

## 2.2. Polyimides

A large number of the presented polyimides contain the pyromellitoyl unit in their polymer chains. Imai et al. investigated the step-growth polymerization of aliphatic diamines  $H_2N-(CH_2)_x-NH_2$  ( $x = 6-12$ ) with both pyromellitic acid and its diethyl ester (Scheme 2a).<sup>[21,26,27]</sup> Analogously to the synthesis of polyamides (Section 2.1.), the reactions were performed in solution in a domestic microwave oven. Among the investigated solvents, all of them with high boiling points and high dielectric constants, 1,3-dimethyl-2-imidazolidone (DMI) proved to be best suited as primary microwave absorber and solvent for the monomers and polymers. Polyimides with inherent viscosities of  $0.7 \text{ dL} \cdot \text{g}^{-1}$  (for  $x = 12$ ) were obtained within two minutes from pyromellitic acid as starting material. Especially for pyromellitic acid diethyl ester as monomer, the microwave-assisted polymerization proved its virtues by producing a series of polyimides with inherent viscosities of up to  $1.6 \text{ dL} \cdot \text{g}^{-1}$ . For the reaction of dodecamethylene diamine with pyromellitic acid, a direct comparison between microwave irradiation and conventional heating was made by control experiments. The solution polymerization in the microwave was shown to proceed much faster than the corresponding solid-state synthesis under

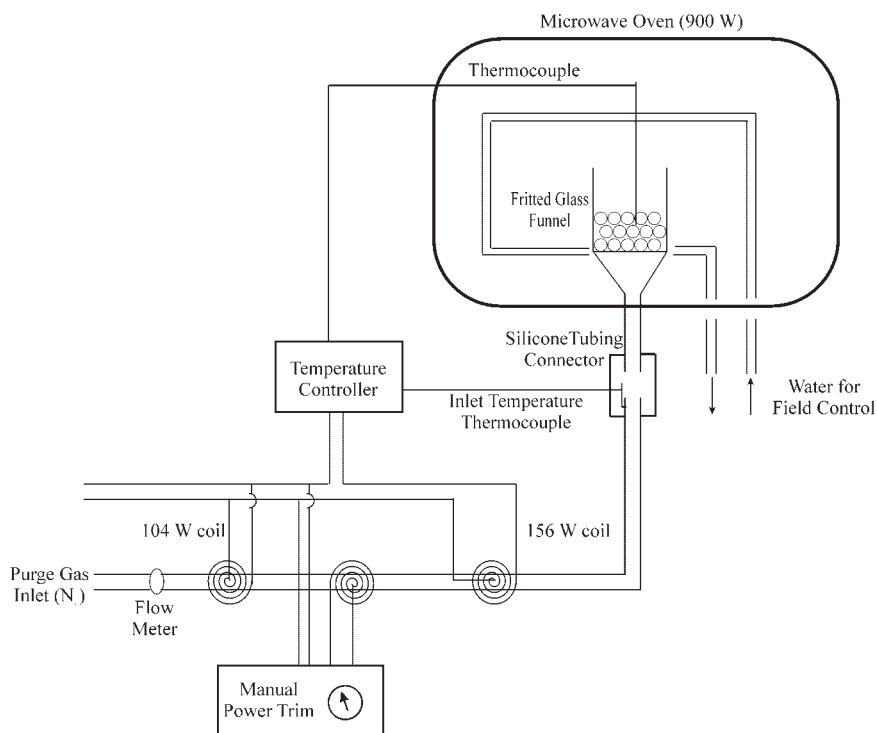
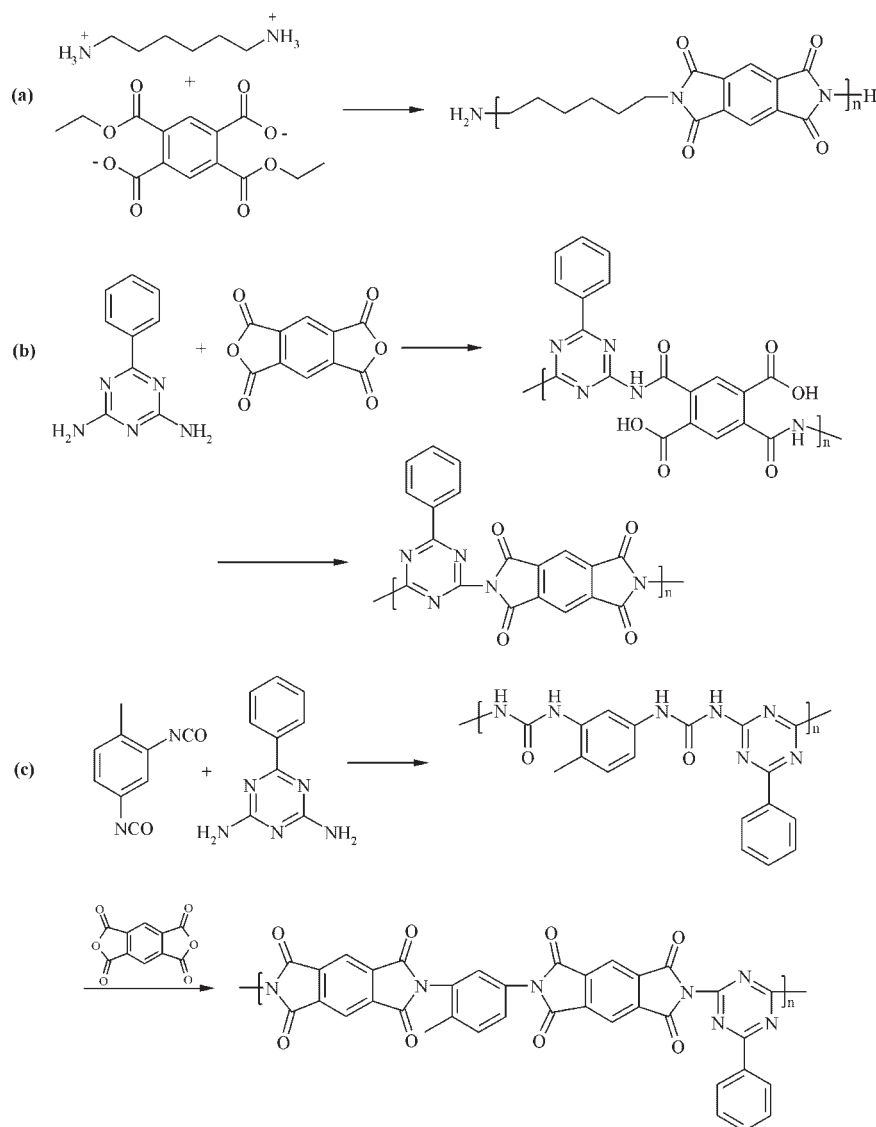


Figure 4. Setup for the determination of the diffusion rates in the course of the polymerizations of nylon 6,6 and poly(ethylene terephthalate) (according to reference [24]).



Scheme 2. Types of polyimides synthesized in microwave reactors: (a) polyimide synthesis from the reaction of hexamethylene diamine with pyromellitic acid diethyl ester; (b) preparation of rigid polyimides with third-order nonlinear optical properties from pyromellitic acid and benzoguanamine in a two-step procedure (by polyamic acid); (c) polyimides derived from the reaction of polyurea precursors and pyromellitic acid dianhydride.

conventional heating during the initial five minutes. After these five minutes and with concomitant inherent viscosities of around  $1 \text{ dL} \cdot \text{g}^{-1}$ , however, the inherent viscosities of the polymers that were prepared in the microwave oven only slightly increased with prolonged irradiation times, while those from the polymers that were synthesized with conventional heating still increased to values of up to  $2 \text{ dL} \cdot \text{g}^{-1}$ . No explanation was provided for these observations; instead, Imai et al. emphasized the microwave's superiority to conventional heating during the first five minutes.

In order to provide a new series of polymers with third-order nonlinear optical properties, Lu et al. synthesized

polyimides with rigid structures from pyromellitic acid dianhydride and aromatic diamines (such as benzoguanamine or 3,3'-diaminobenzophenone) or polyurethane-prepolymers prepared from benzoguanamine and toluene-2,4-diisocyanate (Scheme 2b and c).<sup>[28–32]</sup> The preparation of the polymers followed a two-step procedure, the first step of which was aimed at the microwave-assisted synthesis of a polyamic acid precursor under reflux conditions (in methanol or tetrahydrofuran). This precursor polymer was recovered from the reaction liquor, mixed with pyromellitic acid dianhydride, and was subjected to a solid-phase polymerization in a domestic microwave oven. The imidization reaction strongly profited from microwave

irradiation and the reaction time was decreased from 5 h to 8 min.<sup>[30]</sup> Furthermore, increased inherent viscosities and, hence, improved third-order nonlinear optical properties of the polymers were observed and referred to the reduced reaction times.

The use of polyamic acid prepared under microwave irradiation for grafting procedures has been also described by Lu et al.<sup>[33]</sup> For that reaction, a domestic microwave oven was supplied with an external voltage controller to allow for the modulation of the power. In this way, the temperature inside the reaction vial could be manually maintained at a favored value (Figure 5).

Kinetic measurements were performed for the imidization reaction under microwave irradiation. For the polyamic acid derived from 3,3',4,4'-benzophenone-tetracarboxylic acid and diaminodiphenylsulfone, Ward and co-workers showed that the increase in reaction rates and the concomitant decrease of the apparent activation energy was a consequence of the microwave irradiation's selectivity to excite dipoles.<sup>[34]</sup> According to that theory, a temperature enhancement of 50 K in the vicinity of the excited dipole moment was predicted. Mallon and Ray also ascribed the increase in reaction speed [for nylon 6,6 and poly(ethylene terephthalate)] to the selectivity of the microwave irradiation, based on findings from a specially designed microwave reactor setup (Figure 4).<sup>[24]</sup> However, they proposed that enhanced diffusion rates (of small molecules involved in the ring-closing imidization reaction) were responsible for the observable increase of reaction rates and the decrease of the apparent activation energy. This increase in the reaction speed was found to be most pronounced for water molecules that are known to optimally absorb microwave irradiation, a phenomenon

that was assessed as further proof for the postulated mechanism. A direct comparison of microwave irradiation and conventional heating for the synthesis of poly(ethylene terephthalate) was carried out by Gilmer et al. at 140 °C.<sup>[35]</sup> They reported that microwave irradiation did not enhance the reaction speed in the case of identical temperatures and reaction times.

Currently, with a major debate concerning the existence or nonexistence of microwave effects, all three reports should be taken into critical account. A steadily growing number of experiments gives rise to the last of the presented theories and predicts the microwave to be a fast and efficient heating device with no further influence on most of the reactions performed. For the other two theories, however, it should be mentioned that the observed ameliorations may originate from the selective excitation of dipoles (which is characteristically most pronounced for water molecules).

### 2.3. Poly(amide imide)s

Mallakpour et al. synthesized optically active pyromellitoyl polymers as model substances for column materials in enantioselective chromatography.<sup>[36,37]</sup> The polymerization reaction was proceeded by the preparation of optically active pyromellitoyl derivatives (under conventional heating), namely *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride and the corresponding *L*-leucine compound. Starting from these monomers, two series of optically active poly(amide imide)s were investigated: The bis-*L*-phenylalanine compound was reacted with six differently 5,5-disubstituted hydantoin compounds (Scheme 3a) and a bis-*L*-leucine derivative with six aromatic diamines, respectively. The polymerizations were carried out in a domestic microwave oven in *o*-cresol solution because of the low absorbance of the monomers. Polymers with inherent viscosities of up to 0.5 dL · g<sup>-1</sup> were obtained within 10 min. Longer exposure times led to partial degradation of the polymers.

Another library of poly(amide imide)s was prepared by Mallakpour et al. from the reactions of optically active *N,N'*-(4,4'-carbonyldiphthaloyl)-bis-*L*-phenylalanine diacid chloride and the corresponding *L*-alanine and *L*-leucine compounds, with eight aromatic diamines, all of them with a rigid scaffold (Scheme 3b).<sup>[38–40]</sup> The two monomers were dissolved in *o*-cresol and exposed to microwave irradiation for 7 to 10 min in a domestic microwave oven to yield polymers with large inherent viscosities in the range of 0.22 to 0.85 dL · g<sup>-1</sup>. A comparison of microwave-assisted polymerization in a Teflon vessel with that in a porcelain dish showed that (for identical reaction times) the polymers recovered from the porcelain dish had larger inherent viscosities.<sup>[38]</sup> Furthermore, for two series of compounds, the microwave-assisted polycondensation was compared with a solution polymerization supported by trimethylsilyl chloride (for the activation of the

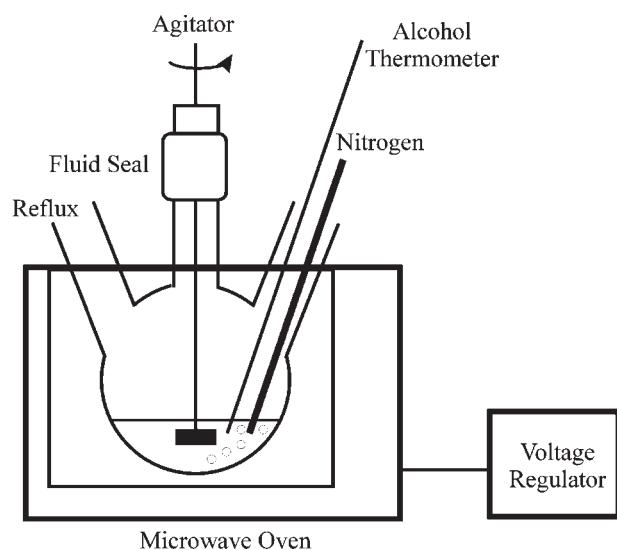
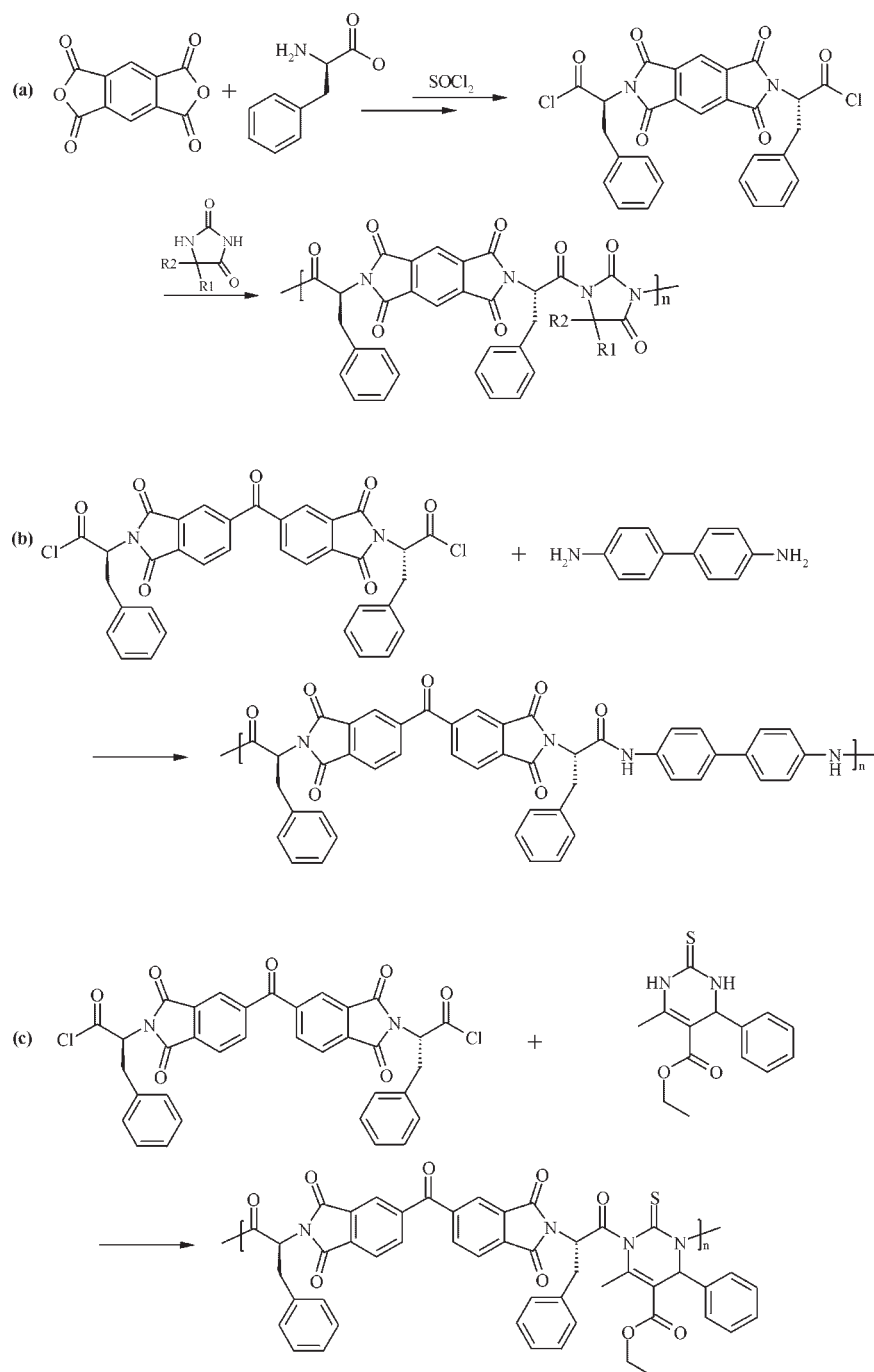


Figure 5. Modification of a domestic microwave oven in order to maintain the favored reaction temperatures by adjusting the supplied power (according to reference [33]).



Scheme 3. Poly(amide imide)s prepared in microwave reactors, Part I: (a) optically active poly(amide imide)s from pyromellitic diacid anhydride, L-amino acids, and 5,5-disubstituted hydantoin derivatives; (b) polymers containing a carbonyldipthaloyl unit; (c) poly(amide imide)s with tetrahydro-2-thioxopyrimidines in the main chain.

diamines).<sup>[38,39]</sup> These reference experiments were performed under a nitrogen blanket, followed by a subsequent increase of the temperature to ambient conditions. From the properties of the polymers, it could be concluded that the microwave irradiation was superior to the catalyzed solution polymerization. In a more recent publication, these findings were repeatedly observed for the corresponding

step-growth polymerizations of *N,N'*-(pyromellitoyl)-bis-L-isoleucine diacid chloride and six aromatic diamines (cf. beginning of this Section).<sup>[41]</sup>

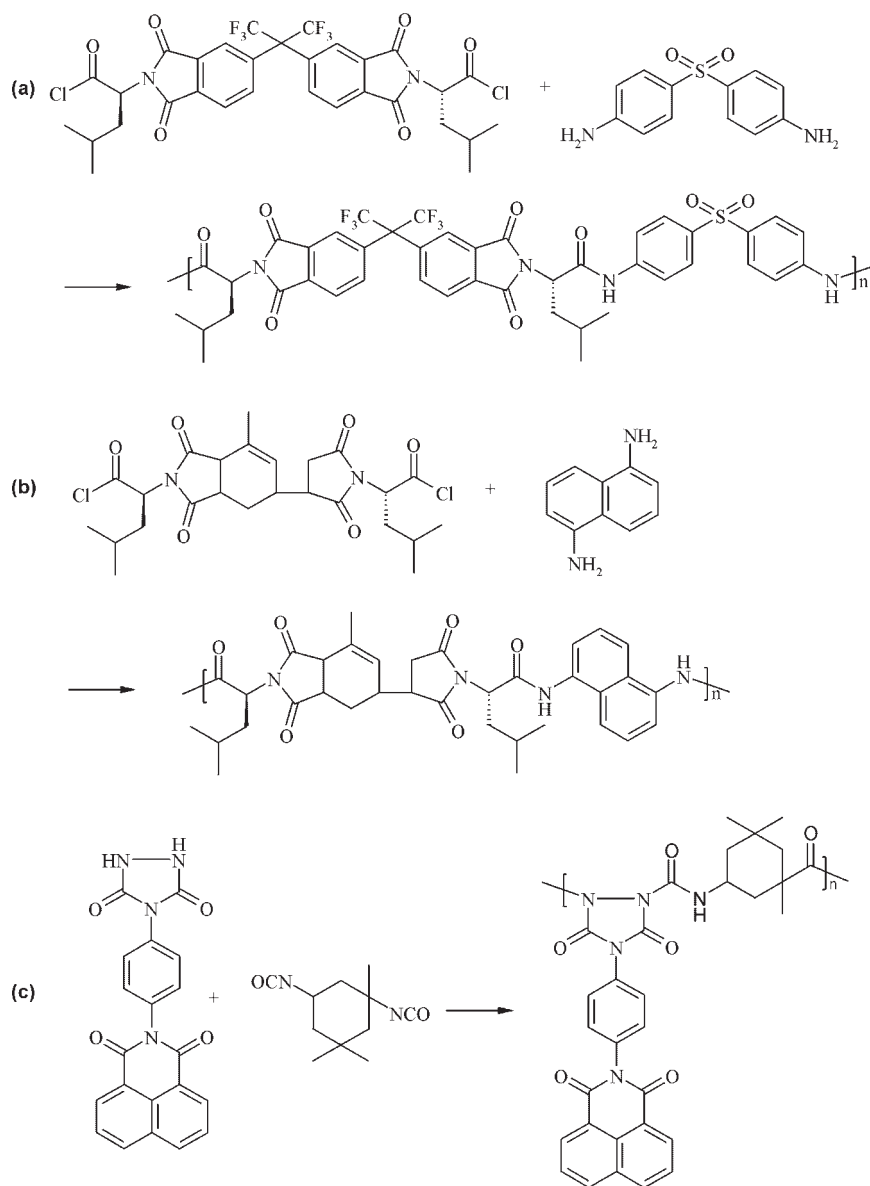
Findings from the above-described series were successfully transferred to the synthesis of polymers from *N,N'*-(4,4'-carbonyldipthaloyl)-bis-L-alanine diacid chloride with bulky derivatives of tetrahydropyrimidone and

tetrahydro-2-thioxopyrimidine (six compounds) (Scheme 3c).<sup>[42]</sup> The monomers were dissolved in *o*-cresol and irradiated for 10 min in a domestic microwave oven to yield, (quasi) quantitatively, polymers with inherent viscosities of 0.25 to 0.45 dL · g<sup>-1</sup>.

A similar group of optically active poly(amide imide)s was prepared by Faghihi et al. from *N,N'*-(4,4'-carbonyldiphthaloyl)-bis-L-alanine diacid chloride and six representative hydantoin and thiohydantoin derivatives.<sup>[43]</sup> Analogously, the polymerizations were carried out in solution in *o*-cresol in a domestic microwave oven to produce polymers within irradiation times of 10 min. Viscosity measurements, however, were not performed. A similar set

of compounds was synthesized by Mallakpour et al. from *N,N'*-(4,4'-hexafluoroisopropylidene)-bis-phthaloyl-L-leucine diacid chloride and a group of ten aromatic diamines (Scheme 4a); the polymers exhibited viscosities of 0.50 to 1.93 dL · g<sup>-1</sup>.<sup>[45]</sup>

The synthesis of optically active poly(amide imide)s containing Epiclone as structural unit additionally emphasized the universality of the concept for the microwave-assisted step-growth polymerization introduced by Mallakpour et al.<sup>[45,46]</sup> The Epiclone-containing diacid chlorides were obtained with conventional heating from reactions involving L-leucine and L-phenylalanine (Scheme 4b). The polymerizations themselves with seven



Scheme 4. Poly(amide imide)s prepared in microwave reactors, Part II: (a) polymers from *N,N'*-(4,4'-hexafluoroisopropylidene)-bisphthaloyl-L-leucine diacid chloride and aromatic diamines; (b) Epiclone-containing polymers; (c) polymers from 4-(4'-*N*-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione and isophorone diisocyanate.

different aromatic diamines were carried out in *N*-methylpyrrolidone solution in a domestic microwave oven. After exposure times of 5 min, poly(amide imide)s with inherent viscosities of 0.12 to 0.22 dL · g<sup>-1</sup> were obtained. For both series, control experiments were carried out to elucidate the microwave's superiority over formerly exercised polymerization techniques: The low-temperature solution polycondensation (in *N*-methylpyrrolidone with trimethylsilyl chloride as promotor), as well as the high-temperature analogon, rendered polymers with comparable properties. However, significantly longer reaction times in the range of hours were employed for these alternatives to microwave-assisted polymerizations.

Similar variations in the polymerization techniques for the synthesis of poly(amide imide)s from *N,N'*-(4,4'-sulfonedipthaloyl)-bis-*L*-phenylalanine diacid chloride and its *L*-leucine congener with seven aromatic diamines showed analogous tendencies.<sup>[47,48]</sup>

The approach to polymers with another type of amide linkages in the main chain, the polyureas, has also been described by Mallakpour et al.<sup>[49-51]</sup> From 4-(4'-acetamidophenyl)-1,2,4-triazolidine-3,5-dione and the 4'-*N*-1,8-naphthalimidophenyl derivative, as well as 4-(4'-*tert*-butylphenyl)-1,2,4-triazolidine-3,5-dione, the three of them prepared under conventional heating, the targeted polymers were obtained by the reaction with three different diisocyanates (hexamethylene diisocyanate, isophorone diisocyanate, and toluene-2,4-diisocyanate) (Scheme 4c). The polymerizations were carried out in a domestic microwave oven in solution in dimethylacetamide<sup>[49,51]</sup> and *N*-methylpyrrolidone<sup>[50]</sup>, with pyridine,<sup>[49,51]</sup> triethylamine,<sup>[50,51]</sup> or dibutyltin dilaurate<sup>[51]</sup> as catalysts. Polyureas with inherent viscosities of 0.06 to 0.20 dL · g<sup>-1</sup> were obtained after 8 min irradiation time. Control experiments were performed comprising steplike heating procedures as well as reflux conditions, both of them performed under conventional heating. Even with a broad variation of the catalysts utilized, it was found that microwave irradiation was superior to the other polymerization techniques, shortening reaction times from up to 24 h down to 8 min.

#### 2.4. Polyethers and Polyesters

Currently, few data on the microwave-assisted preparation of polyethers and polyesters by step-growth polymerizations have been collected (the use of phase-transfer catalysis in the microwave-assisted synthesis of polyethers will be discussed in Section 2.7). The homopolymerization of *D,L*-lactic acid (2-hydroxypropanoic acid) was successfully applied to microwave reactors by Zsuga and co-workers.<sup>[52]</sup> This reaction can be performed as bulk polymerization with conventional as well as with microwave heating because of the high dipole moment of the monomer. Oligomers with molecular weights in the range of 600 to 1000 Dalton were obtained after 24 h with

conventional and within 20 min with microwave heating (domestic microwave oven, 650 W), respectively, exhibiting an acceleration factor of 70 for the transfer to the microwave reactor. Prolonged exposure times to microwave irradiation were found to induce the undesirable formation of cyclic oligomers as shown by matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 6).

The polymerization of a derivative of lactic acid, namely *L*-2-hydroxy-3-phenylpropanoic acid, was studied by Liu et al. (Scheme 5a).<sup>[53]</sup> The polymerizations were carried out with variable time and power in a domestic microwave oven. With maximum power (510 W), polymers with number-average molecular weights of 1 800/3 900/5 400 and PDI values of 1.8/1.0/1.4 (given by the authors) were obtained within 0.5/1.5/2.5 h, respectively. The formation or non-formation of cyclic by-products was not discussed.

Like poly(lactic acid), polyanhydrides also belong to the class of biodegradable polymers and represent potential materials for drug delivery applications. The preparation of polyanhydrides is a two-step process under conventional heating, comprising the synthesis of a polyanhydride pre-polymer, its isolation, purification, and subsequent polymerization. Mallapragada and co-workers showed that the polymerization can be carried out in a single step, admittedly with intermediate removal of unreacted acetic anhydride (Scheme 5b).<sup>[54]</sup> The dicarboxylic acid (like sebacic acid) and excessive acetic anhydride were placed in a high-pressure vial that was capped and irradiated for 2 min in a microwave oven (General Electrics, 1 100 W). Immediately after the reaction, the vial was decapped and the unreacted acetic anhydride was evaporated from the hot reaction solution by an inert gas flow. After eventual addition of a catalyst (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or glass beads), the vial was recapped and heated for 4 to 25 min in order to produce the polyanhydride (Scheme 5b). As a result of the elimination of a complete step of the reaction procedure, reaction times were shortened from four days to a few minutes. Glass beads proved to be the most successful support for that kind of microwave-assisted polymerizations: Polymers with number-average molecular weights of 11 400 Dalton were obtained within 25 min.

The only example of a polyether synthesized in a microwave so far is a poly(phenylene vinylene)-ether (PPV ether) obtained from the polymerization of 1-chloro-4-methoxybenzene in solution in alkaline dimethyl sulfoxide (Scheme 5c).<sup>[55]</sup> Alimi et al. heated the reaction mixture to 200 °C in a domestic microwave oven (that was modified to enable online measurement of the temperature), stopped the exposure as soon as the targeted temperature was reached, and continued stirring at room temperature for six hours. The polymer was obtained in 43% yield; two different oligomer fractions soluble in chloroform and dichloromethane were additionally recovered with yields of 52 and 5%.

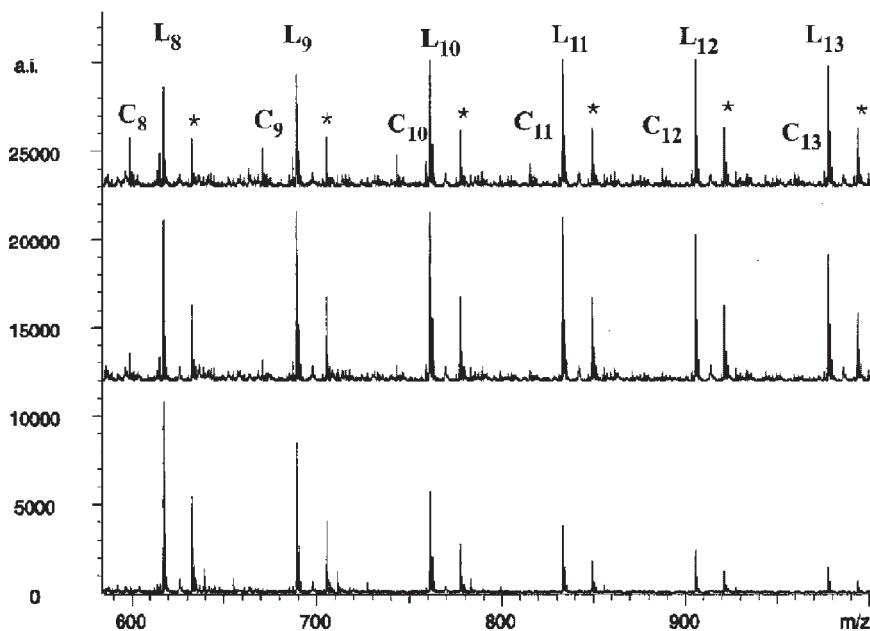


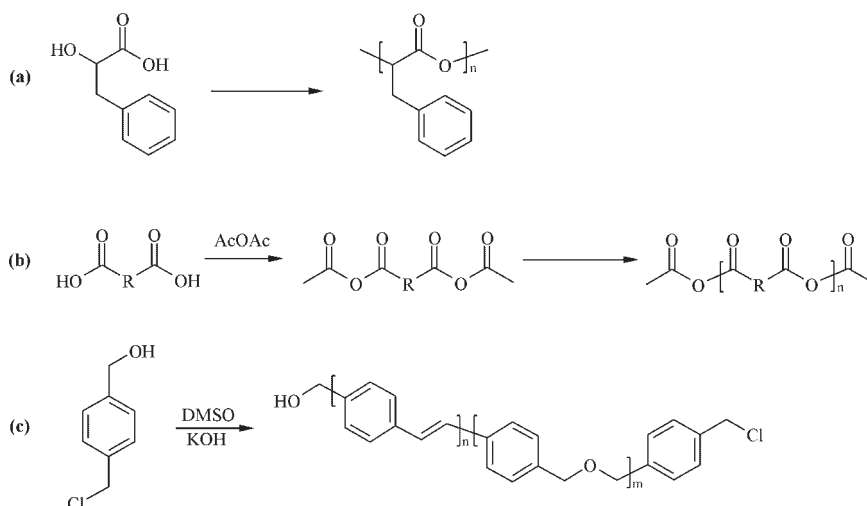
Figure 6. Excerpts from the MALDI-TOF MS spectra of the microwave-assisted bulk polymerizations of D,L-lactic acid after 10 min (bottom), 20 min (middle), and 30 min (top), respectively.  $L_n$  represents the linear polymers composed of  $n$  monomers,  $C_n$  the cyclic analogue. Apparently, the formation of cyclic by-products becomes more likely with prolonged reaction times. Reprinted with permission from reference [52], Copyright John Wiley and Sons.

### 2.5. Poly(ether imide)s and Poly(ester imide)s

Yu and co-workers observed a significant increase in reaction rates for the imidization reaction between poly(tetramethylene oxide)glycol di-*p*-aminobenzoate and benzene-tetracarboxylic acid dianhydride.<sup>[56]</sup> The reaction times were reduced from 12 to 3 h and the reaction temperatures were

decreased from 115 to 60 °C when the reaction was performed in a (domestic) microwave reactor instead of an oil bath. The authors ascribed these advantages to the good absorbance of the microwave irradiation by the water molecules released during the imidization reaction.

Analogously to the synthesis of optically active poly-(amide imide)s, Mallakpour et al. also prepared poly(ester



Scheme 5. Microwave preparation of polyethers and polyesters: (a) homopolymerization of L-2-hydroxy-3-phenylpropanoic acid; (b) polyanhydrides from dicarboxylic acid and acetic anhydride; (c) PPV ether from the homopolymerization of 1-chloromethyl-4-methoxybenzene in alkaline solution in DMSO.

imide)s with chiral carbon atoms in the polymer chain that additionally contained pyromellitoyl units (cf. Section 2.3.).<sup>[57,58]</sup> The compounds *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride and *N,N'*-(pyromellitoyl)-bis-*L*-leucine diacid chloride were synthesized with conventional heating. The step-growth polymerizations involving these diacid chlorides and a series of aromatic diols with rigid scaffolds (like phenolphthalein, bisphenol A, 4,4'-hydroquinone, and others) were performed in a domestic microwave oven. In this way, a basic library of 14 optically active poly(ester imides) was synthesized (cf. Scheme 3). As a result of the low dipole moments and the corresponding low absorbance of the educts, the polymerization reactions were carried out in *o*-cresol, with *o*-cresol acting as solvent and as primary microwave absorber at the same time; 1,4-diazabicyclo[2.2.2]octane was added as catalyst. Within reaction times of 10 min, polymers with inherent viscosities in the range of 0.10 to 0.27 dL · g<sup>-1</sup> were readily obtained. Comparison experiments under solution conditions using triethylammonium chloride as a phase-transfer catalyst only produced oligomers as was concluded from the improved solubility in methanol.

A similar synthetic study resulted in a 14-membered library with optically active carbonyldipthaloyl anhydride derivatives, namely *N,N'*-(4,4'-carbonyldipthaloyl)-bis-*L*-phenylalanine diacid chloride as well as the corresponding *L*-alanine compound, and a set of aromatic diols with rigid scaffolds (cf. Scheme 3).<sup>[59,60]</sup> It was found that the polymerizations involving the *L*-phenylalanine derivative<sup>[59]</sup> could not be performed under microwave irradiation, but only at low temperatures under phase-transfer catalysis. With the *L*-alanine compound,<sup>[60]</sup> on the other hand, a microwave-assisted synthesis was successfully carried out in *o*-cresol without the addition of catalysts. Polymers with inherent viscosities of 0.35 to 0.58 dL · g<sup>-1</sup> were obtained within 12 min in a domestic microwave oven. The difference in reactivity for the two carbonyldipthaloyl anhydride derivatives is not explained by Mallakpour et al.

A similar study focused on the reaction of 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis-(phthaloyl-*L*-leucine) diacid chloride with aromatic diols, all of them with rigid fixation of the hydroxy function (cf. Scheme 4).<sup>[61]</sup> For a systematic investigation, three different solvents (with a bifunctional role as solvent and primary microwave absorber) were tested; *o*-cresol proved to be best suited for those purposes compared with *m*-cresol and 1,2-dichlorobenzene. Reactions in a domestic microwave oven were completed within five minutes and yielded polymers with inherent viscosities of 0.50 to 1.12 dL · g<sup>-1</sup>. Comparison experiments with conventional heating, carried out in 1,2-dichlorobenzene, only yielded polymers with inherent viscosities of 0.09 to 0.18 dL · g<sup>-1</sup>, even after 24 h reaction time. The corresponding polymers derived from *N,N'*-[4,4'-carbonyl-bis-(phthaloylimido)]-bis-*L*-leucine diacid chlor-

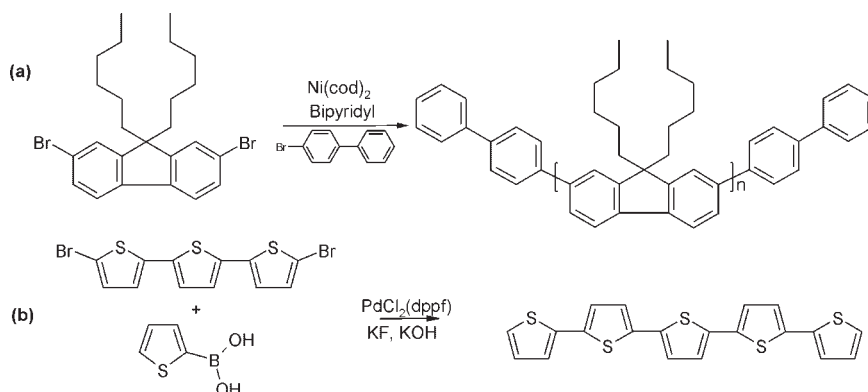
ide, however, were found not to be formed under microwave irradiation, but from low-temperature polycondensation in chloroform with triethylamine as catalyst.<sup>[62]</sup>

## 2.6. Polymerizations Involving C–C Coupling Reactions

Contrary to their well-established use in organic chemistry and the resulting numerous applications in microwave-improved organic synthesis,<sup>[7–14]</sup> microwave-assisted polymerizations by C–C coupling reactions have gained attention only very recently. Apart from the C–C coupling reactions described hereinafter, so far only one metathesis polymerization of phenylacetylene under microwave irradiation has been reported. Utilizing in situ generated [(arene)M(CO)<sub>3</sub>] complexes (M = Cr, Mo, W) as catalysts, the reaction time was reduced from 24 h (under reflux conditions of a solution in 1,2-dichloroethane) to 1 h (in a domestic microwave oven).<sup>[63]</sup> The temperature for the microwave-assisted polymerizations was not measured. It may be concluded, however, that it was higher than conventional reflux conditions as specially designed long-necked round-bottom flasks were utilized in order to perform the reactions under high pressure.

Carter investigated the nickel(o)-mediated coupling polymerization of 2,7-dibromo-9,9-dihexylfluorene in solution in toluene.<sup>[64]</sup> Previous findings for the reaction performed under conventional heating had shown that the polymerization reaction has to be preceded by an activation step for the preparation of the catalyst. The polymerization reaction itself may last up to 24 h and characteristically shows a low reproducibility and a hindered access to high-molecular-weight polymers because of the decreasing solubility of the polymers with an increasing degree of polymerization. Under microwave irradiation, the reaction was carried out in capped vials in a microwave reactor specially designed for chemical synthesis (SmithCreator, PersonalChemistry), resulting in high-temperature and high-pressure synthesis. The polymers were obtained in almost quantitative yield after 10 min at 250 °C. As a result of this tremendous decrease in reaction times, side reactions were kept to a minimum, and the polymerization consequently could be run as a one-step routine with no prior activation of the catalyst in a separate procedure. In addition, polymers with high molecular weights of 100 000 Dalton (or even higher) were formed. The molecular weights could be controlled by the addition of a monofunctional end-capping unit (4-bromobiphenyl) to yield polymers with molecular weights from 5 000 to 40 000 Dalton and PDI values from 1.65 to 2.22, respectively (Scheme 6a).

The preparation of poly(pyrazine-2,5-diyl) from 2,5-dibromopyrazine in a CEM Discover apparatus has been described by Yamamoto et al.<sup>[65]</sup> Using the same nickel(o)-based catalyst system, a similar shortening of reaction times down to 10 min was observed.



Scheme 6. Microwave-assisted C–C coupling reactions: (a) nickel(o)-mediated polymerization of 2,7-dibromo-9,9-dihexylfluorene with 4-bromobiphenyl as end-capping unit; (b) quinquethiophenes from microwave-assisted bulk polymerization, catalyzed by palladium halides. (COD: cycloocta-1,5-diene; DPPF: 1,1'-bis(diphenylphosphino)-ferrocene).

The Suzuki coupling reaction has been transferred to microwave conditions by Barbarella and co-workers for the preparation of thiophene oligomers.<sup>[66]</sup> The synthesis of quinquethiophenes, for example, was achieved from bulk conditions of 2-thiophene boronic acid and dibromo precursors with three thiophene units, catalyzed and promoted by  $[\text{PdCl}_2(\text{dppf})]$ ,  $\text{KF}$ , and  $\text{KOH}$  in a Synthwave 402 apparatus (Prolabo) (Scheme 6b). With a maximum temperature of  $70^\circ\text{C}$ , yields of 74% were obtained after reaction times of 10 min. The synthesis of polymers instead of oligomers, however, was not carried out.

Leadbeater et al. described the successful preparation of biaryl compounds by Suzuki coupling reactions in a microwave reactor.<sup>[67]</sup> First applications of Suzuki and Stille cross-coupling reactions for the preparation of semiconducting polymers were carried out in a monomodal microwave reactor (CEM Discovery) by Scherf and co-workers.<sup>[68]</sup> Reaction times for the preparation of five representative polymers with number-average molecular weights in the range of 11 300 to 15 400 Dalton (and comparably narrow molecular-weight distributions with PDI values around 1.8) were found to decrease from 3 days in the case of conventional heating down to a few minutes under microwave irradiation. The corresponding reaction temperatures, however, were not measured automatically in a straightforward manner. Instead, the applied power was varied and found to require optimization for each specific reaction. The microwave reactor proved its virtues particularly in the case of the Stille cross-coupling polymerization between the electron rich (and consequently less active) 1,5-dioctyloxy-2,6-dibromonaphthalene and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene by yielding polymers with higher molecular weights (13 700 compared with 5 100 Dalton, the latter under conventional heating). In order to determine the reasons for this pronounced microwave effect, results from experiments at identical

temperatures, for both microwave irradiation and conventional heating, will be published in the near future.

### 2.7. Phase-Transfer Catalysis

Only a few examples of microwave-assisted phase-transfer catalyzed polymerizations have been collected so far, all of them aiming at the preparation of polyethers. A first set of investigations, performed by Hurduc et al., focused on polymers from the step-growth polymerization of 3,3-bis(chloromethyl)oxetane and several bisphenols.<sup>[69]</sup> The targeted compounds were prepared both with conventional heating and microwave assistance (domestic microwave oven) from a water/nitrobenzene two-phase system with tetrabutylammonium bromide as phase-transfer catalyst. Compared with conventional heating for 5 h, the same polymer yields could be obtained under microwave irradiation in the temperature range of  $95$  to  $100^\circ\text{C}$  (depending on the bisphenol's chemical structure) within 90 min. The decrease in reaction times is not commented on in detail; the acceleration observed, however, may depend on the enhanced reaction temperatures. The analysis of the thermal behavior of the polymer revealed higher glass temperatures and melting points for the polymers synthesized in the microwave oven, indicative of higher molecular weights. In a more recent publication,<sup>[70]</sup> a similar set of microwave-assisted polymerizations of 3,3-bis(chloromethyl)oxetane and several bisphenols has been performed in a monomodal microwave system (Synthwave 402, Prolabo) and compared with results from conventional heating. The difference in reaction times, 4 to 6 h in the case of conventional heating as opposed to 20 min under microwave irradiation (for the preparation of oligomers with oligomers' degrees of 6 to 8 and comparable yields in the range from 64 to 97%), was found to be very pronounced. However, explanations for the increase in reaction rates

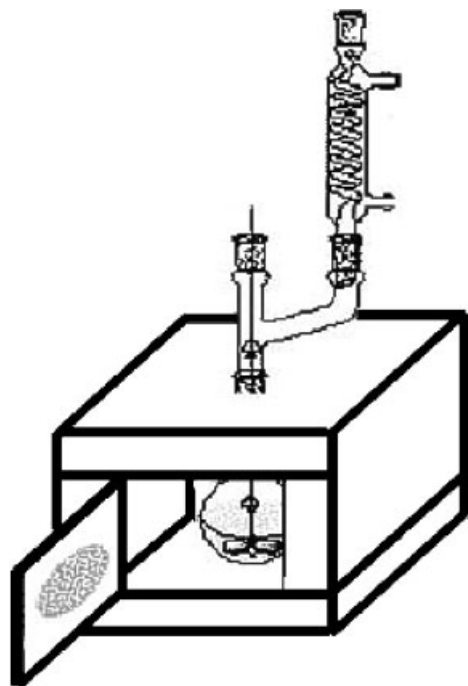


Figure 7. Modification of a domestic microwave reactor for the phase-transfer catalyzed synthesis of poly(ether imide)s. Reprinted with permission from reference [71], Copyright John Wiley and Sons.

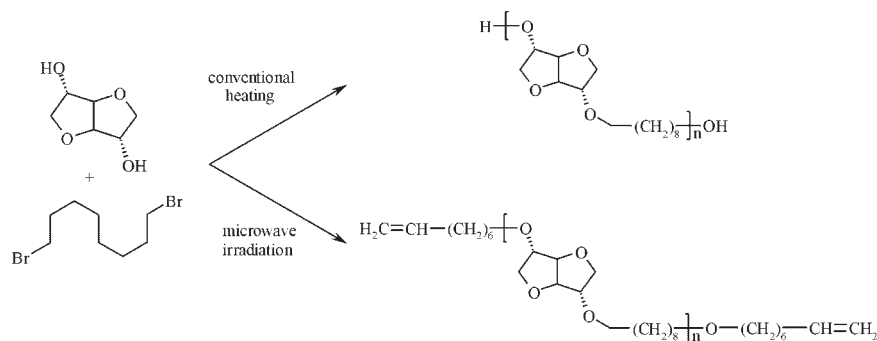
(and the nonimproved oligomers' degrees) are not provided. Zhang and co-workers, on the other hand, ascribed the increase in reaction speed for the phase-transfer catalyzed step-growth polymerization of bisphenol A and bis(chlorophthalimide) in a domestic microwave oven to the selective excitation of the phenol anion and the resulting enhanced reactivity (Figure 7).<sup>[71]</sup>

Loupy and co-workers observed shifts in selectivity (as a consequence of microwave irradiation) for the polyetherification of isosorbide (1,4:3,6-dianhydro-D-sorbitol) or isoidide (1,4:3,6-dianhydro-L-iditol) with 1,8-dibromo and

1,8-dimesyloctane (Scheme 7).<sup>[72,73]</sup> A solution of equimolar amounts of the corresponding educts in toluene was subjected to phase-transfer catalyzed polymerization in the presence of tetrabutylammonium bromide and aqueous potassium hydroxide under microwave irradiation (Synthwave 402, Prolabo) as well as conventional heating. For the isosorbide-containing polymers, it was found that the reaction rates increased under microwave irradiation, providing polymers in yields of around 70% within 30 min. Under conventional heating, reaction times of 24 h were necessary for similar conversions. Furthermore, the polymers synthesized in the microwave reactor showed higher molecular-weight averages according to findings from gel permeation chromatography (GPC) and MALDI-TOF MS analysis. In the case of the isoidide derivative, comparable yields were observed, but also for that congener, a strong tendency to higher polymerization degrees under microwave assistance was observable, as a heavy weight fraction (insoluble in methanol) was formed in relatively higher yield (39–67% compared with 5–12%). Moreover, the two different modes of activation showed specific mechanisms of chain termination: The polyethers prepared under conventional heating had hydroxylated ends, and those synthesized in the microwave reactor exhibited ethylenic group ends (Scheme 7). In a more recent publication, these characteristics were repeatedly recognized for the phase-transfer catalyzed step-growth polymerizations of 1,8-dibromo- and 1,8-dimesyloctane with isosorbide derivatives (two isosorbides linked by alkyl or glycol chains, possessing two equivalent alcohol functions in *exo* positions).<sup>[74]</sup>

### 3. Ring-Opening Polymerizations

Aliphatic polyesters are an important class of biodegradable polymers and are utilized in biomedical and pharmaceutical applications.<sup>[75]</sup> The physical and chemical properties, as well as the degradability, can be easily tuned



Scheme 7. Step-growth polymerization of isoidide with 1,8-dibromooctane and the different mechanisms of chain termination, depending on the activation source.

by the synthesis of copolymers<sup>[76]</sup> or the involvement of more advanced structures like comb-shaped, hyperbranched, or graft (co)polymers.<sup>[77]</sup> In this section, the microwave-assisted polymerization of cyclic lactones (and similar monomers) is described in detail. In addition, the polymerization of other cyclic monomers (e.g.,  $\epsilon$ -caprolactams and 2-oxazolines) will be discussed.

### 3.1. Aliphatic Polyesters

The microwave-assisted ring-opening polymerization of  $\epsilon$ -caprolactone, exploiting a home-built monomodal microwave reactor (Figure 8), was first reported by Albert et al.<sup>[78]</sup> The microwave was equipped with a temperature control and an online viscometry determination. It was demonstrated that  $\epsilon$ -caprolactone could be successfully polymerized with titanium tetrabutylate as catalyst. A comparison of the microwave-assisted polymerization with thermal polymerization did not show a microwave effect since the observed changes were minor and within the experimental error. Ever since, many reports have appeared in the literature dealing with the microwave-assisted ring-opening polymerization of  $\epsilon$ -caprolactone. The contributions are divided according to the catalysts applied and discussed in the following section.

The most commonly used catalyst for the ring-opening polymerization is stannous octoate [ $\text{Sn}(\text{Oct})_2$ ]. Consequently, most microwave-assisted polymerizations were also performed utilizing this catalyst.<sup>[79–85]</sup> Scola and co-workers have shown the possibility of producing poly( $\epsilon$ -caprolactone) under microwave irradiation (multimode with temperature control) at temperatures ranging from 150 to 200 °C with water or butanediol as initiator.<sup>[79,80]</sup> The polymerizations were accelerated from 12 h under thermal heating (110 °C) to 2 h in the microwave (150, 180, and 200 °C), whereby the polymers obtained under microwave irradiation showed thermal and tensile properties similar to those of the conventionally produced materials. Zhuo and co-workers investigated the microwave-assisted ring-open-

ing polymerization of  $\epsilon$ -caprolactone with stannous octoate [ $\text{Sn}(\text{Oct})_2$ ] as catalyst and maleic acid as initiator.<sup>[82]</sup> Up to maximum irradiation times of 135 min (360 W), the molecular weights were found to increase. If the reaction time was elongated further, the molecular weights decreased as may be depicted from Figure 9 (left). This phenomenon was ascribed to the occurrence of transesterification reactions. Irradiation of a mixture of  $\epsilon$ -caprolactone, maleic acid (20:1), and stannous octoate [ $\text{Sn}(\text{Oct})_2$ ] for 25 min with different microwave powers, on the other hand, induced a nearly linear increase of the (weight) average molecular weights of the polymers with microwave power (Figure 9, right). In addition, the microwave-assisted polymerization was performed in the presence of Ibuprofen (Ibuprofen is a nonsteroidal anti-inflammatory drug)<sup>[86]</sup> in order to synthesize a poly( $\epsilon$ -caprolactone)-based system for the controlled release of Ibuprofen. Moreover, the microwave-assisted polymerization was performed in the presence of  $\text{Sn}(\text{Oct})_2$  without additional initiator, whereby a higher polymerization rate was observed (compared with thermal heating).<sup>[81,83,84]</sup> Zhuo and co-workers demonstrated the possibility of using various acids (maleic acid, adipic acid, succinic acid, benzoic acid, and chlorinated acetic acids) as initiators for the microwave-assisted synthesis of poly( $\epsilon$ -caprolactone).<sup>[87–90]</sup> The main advantage of solely using an acid as initiator is the exclusion of metal ions (as catalysts) from the reaction mixture. Those acid-initiated polymerizations also showed an increased reaction speed compared with thermal polymerizations. The maleic acid-initiated polymerizations were also performed in the presence of different amounts of Ibuprofen, yielding a drug release system for which the release rate could be tuned by the amount of incorporated Ibuprofen.<sup>[87,88]</sup> In addition, it was shown that the molecular weights of the synthesized poly( $\epsilon$ -caprolactone)s depend on the strength of the utilized acid initiator: The molecular weights decreased with an increasing acid strength. Those new insights were subsequently applied for the degradation of poly( $\epsilon$ -caprolactone) under microwave irradiation in the presence of a strong

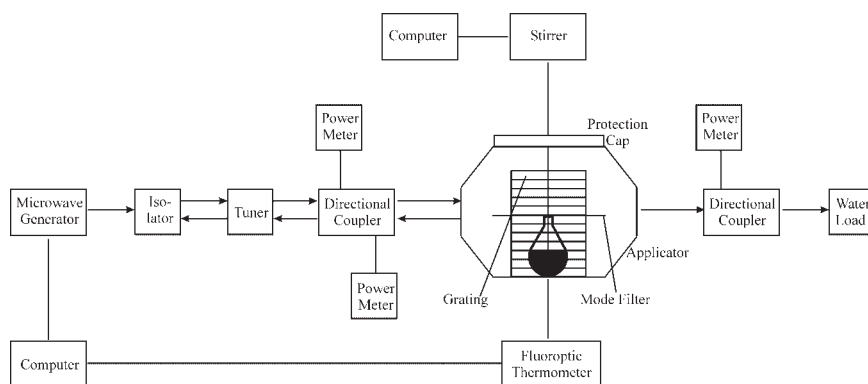


Figure 8. Schematic representation of the home-built monomodal microwave including in situ viscometry determination as employed by Albert et al. (according to reference [78]).

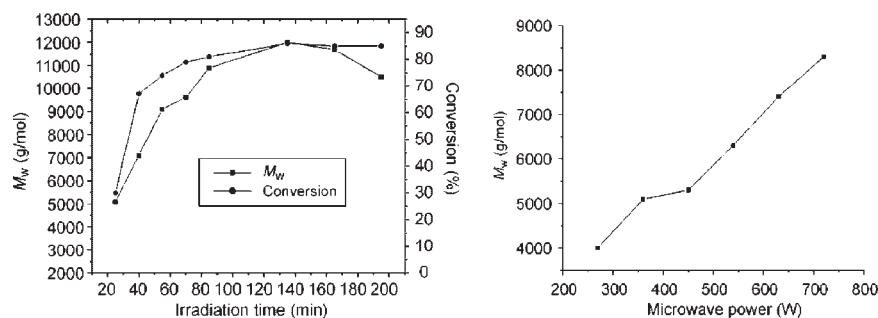


Figure 9. Left: Increase of molecular weight (squares) and conversion (circles) with time for the microwave polymerization of  $\epsilon$ -caprolactone. Right: Increase of molecular weight against applied microwave power. Reprinted with permission from reference [88], Copyright VSP International Science Publishers.

acid.<sup>[89,90]</sup> Increased polymerization rates were also obtained by Koroskenyi and McCarthy who reported kinetic investigations on the microwave-assisted polymerization of  $\epsilon$ -caprolactone.<sup>[85,91]</sup> Furthermore, the optimal conditions were applied for the successful grafting of poly( $\epsilon$ -caprolactone) onto potato starch (for a review on the properties of potato starch, for example, see reference [92]). Zinc-catalyzed polymerizations of  $\epsilon$ -caprolactone were reported by both Zhuo and co-workers<sup>[81]</sup> and by Madras and co-workers.<sup>[93]</sup> The latter used a multimodal microwave oven without controlling devices for temperature or pressure. To prevent overheating, the microwave irradiation was supplied in cycles of 40 or 50 s as it is commonly done with multimodal (domestic) microwaves ovens. Figure 10 shows the heating profile discernible for the polymerization of  $\epsilon$ -caprolactone with heating cycles of 50 s. The nonlinear regression of the temperature could be used as a kinetic parameter. In addition, the activation energy for pulsed microwave-assisted polymerizations ( $5.3 \text{ kcal} \cdot \text{mol}^{-1}$ ) was calculated to be lower than that for polymerizations performed with continuous thermal heating ( $13.4 \text{ kcal} \cdot \text{mol}^{-1}$ ). The activation energy for the microwave polymerizations (with cycled microwave irradiation) was calculated from the molecular weight variation during the polymerization. Therefore, the calculated activation energy for the microwave polymerization might be questioned since it excludes any depolymerization and transesterification reactions that might occur with applied temperatures up to  $200^\circ\text{C}$ . Barbier-Baudry et al. studied the ring-opening polymerization of  $\epsilon$ -caprolactone using lanthanide halides as catalysts.<sup>[94]</sup> The polymerizations performed in a monomodal microwave system yielded polymers with higher molecular weights and lower PDI values compared with polymers synthesized thermally at the same temperature. In addition, it was shown that the PDI of the resulting polymers could be decreased from 3.18 to 1.58 by increasing the microwave power from 200 to 300 W. This effect is assigned to faster heating that suppressed secondary transfer reactions.

To summarize, numerous studies have been performed on the microwave-assisted polymerization of  $\epsilon$ -caprolactone. For a large number of reactions, enhanced polymerization rates were observed (mainly with multimodal microwaves).

Similar to the polymerization of  $\epsilon$ -caprolactone, the polymerization of L-lactide,<sup>[85]</sup> D,L-lactide,<sup>[95]</sup> and trimethylene carbonate<sup>[96]</sup> with stannous octoate were reported to proceed faster under (multimodal) microwave irradiation if compared with thermal polymerizations.

### 3.2. Other Ring-Opening Polymerizations

Besides the ring-opening polymerization of  $\epsilon$ -caprolactone, some other cyclic monomers were also successfully polymerized utilizing microwave synthesizers. Scola and co-workers reported the  $\omega$ -caproic acid-initiated polymerization of  $\epsilon$ -caprolactam resulting in the formation of nylon 6.<sup>[79,80]</sup> The comparison of the microwave-synthesized

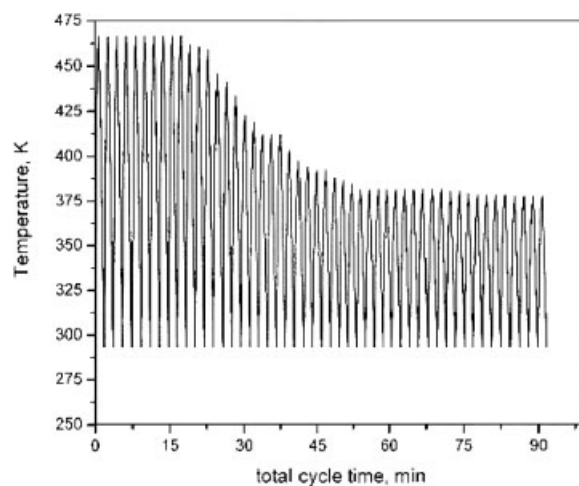


Figure 10. Temperature profile obtained for the pulsed microwave (50 s cycles) irradiated polymerization of  $\epsilon$ -caprolactone. Reprinted with permission from reference [93], Copyright John Wiley and Sons.

polymers with commercial nylon 6 showed that the melting points of the polymers synthesized in a microwave oven were lower because of different crystalline domains. According to the authors, tensile testing exhibited smaller yield strain and strain to break and, in addition, an eight times larger tensile modulus for the microwave-synthesized nylon 6. The polydispersity indices, however, were not determined and, thus, no definite explanation could be given for those phenomena. The same group also described the microwave-assisted copolymerizations of  $\epsilon$ -caprolactone and  $\epsilon$ -caprolactame.<sup>[97]</sup> Compared with thermal polymerization, higher yields and higher amide contents were obtained using microwave irradiation, although similar molecular weights were found. As a result of the higher amide content, the glass-transition temperature of the microwave-synthesized polymers was also higher.

Takeuchi and co-workers described the microwave-assisted copolymerization of ethylene isophthalate cyclic dimer with bis(hydroxyethyl)terephthalate and titanium potassium oxilate.<sup>[98]</sup> The polymerization could be performed successfully in bulk within 60 min.

Very recently, Schubert and co-workers investigated the microwave-assisted living cationic ring-opening polymerization of 2-ethyl-2-oxazoline.<sup>[99]</sup> Performing the polymerization at temperatures of up to 200 °C in acetonitrile, the polymerization was accelerated by a factor of 400, maintaining the living character of the polymerization. Figure 11 shows the conversion (represented by  $\ln\{[M_0]/[M_t]\}$ ) plotted against time for the microwave-assisted polymerization of 2-ethyl-2-oxazoline at several temperatures in the range of 80 to 180 °C, demonstrating the first order kinetics of the monomer consumption. Comparison with thermal polymerizations elucidated that the acceleration resulted only from thermal effects and not from (nonthermal) microwave effects, as the polymerization with thermal heating (well beyond the boiling point of acetonitrile) in a high-pressure NMR tube revealed analogous polymerization rates.

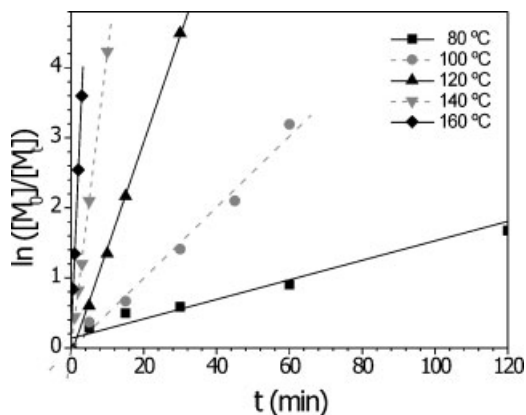


Figure 11. Kinetic results for the microwave-assisted cationic ring-opening polymerization of 2-ethyl-2-oxazoline (according to reference [99]).

## 4. Radical Polymerizations

Free radical polymerization is a widely used technique in industry for the production of numerous bulk materials, for example, polystyrene and poly(methyl methacrylate). The main drawback of the free radical polymerization technique is the poor control of the molecular weights and polydispersity indices. Therefore, controlled free radical techniques have been introduced during the last decades. In this section, investigations on the different radical polymerizations (“classical”, emulsion, and controlled free radical polymerizations) under microwave-irradiation will be discussed.

### 4.1. Free Radical Polymerization

Microwave-assisted free radical polymerizations were initially investigated by Gourdenne et al. in 1979.<sup>[100]</sup> The cross-linking of an unsaturated polyester with styrene was performed under microwave irradiation. In a later contribution, it was shown that hydroxyethyl methacrylate (HEMA) could be polymerized under microwave irradiation without the addition of a radical initiator.<sup>[101]</sup> It was demonstrated that the temperature of the reaction mixture for both, a microwave-irradiated polymerization and a thermal polymerization, gave similar profiles, although the microwave-assisted polymerization was significantly faster. Madras and Karmore reported the accelerated polymerization of methyl methacrylate (MMA) under microwave irradiation.<sup>[102]</sup> According to the authors, an equilibrium between polymerization and depolymerization was reached within 10 min, resulting in equal polymer distributions for different initiator and monomer concentrations as shown in Figure 12. Boey and co-workers described an increase in polymerization rates for the microwave-assisted polymerizations of methyl methacrylate (MMA), styrene (S), and methyl acrylate (MA).<sup>[103,104]</sup> The corresponding polymerizations were performed at three different microwave powers (200, 300, and 500 W). The conversion profiles were shown to be similar for the different microwave powers in terms of radiation energy. Recently, Ritter and co-workers reported the synthesis of (meth)acrylamides and the subsequent polymerization of those monomers in a monomodal microwave synthesizer.<sup>[105]</sup> The (meth)acrylamides could be synthesized from (meth)acrylic acid and the corresponding amines in a single step. The polymerization of these new monomers (using azodiisobutyronitrile (AIBN) as initiator) under microwave irradiation has also proved to be successful. In a final step, it was demonstrated that the microwave-assisted polymerization of acrylic acid (initiated by AIBN) in the presence of hexylamine or benzylamine resulted in the in situ formation of a copolymer of acrylic acid and acrylamide (Scheme 8a). Sitaram and Stoffer described the microwave-assisted polymerization of styrene with different radical initiators.<sup>[106,107]</sup>

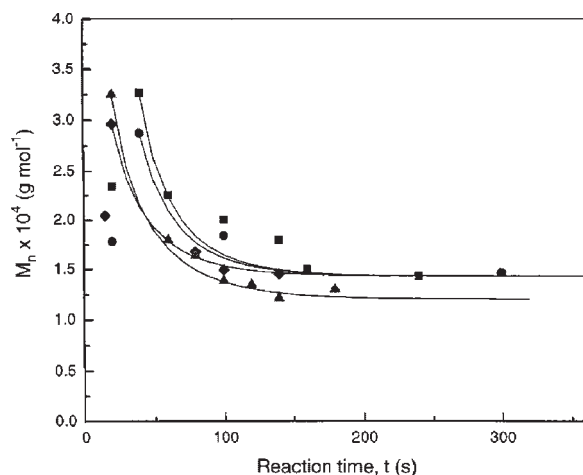
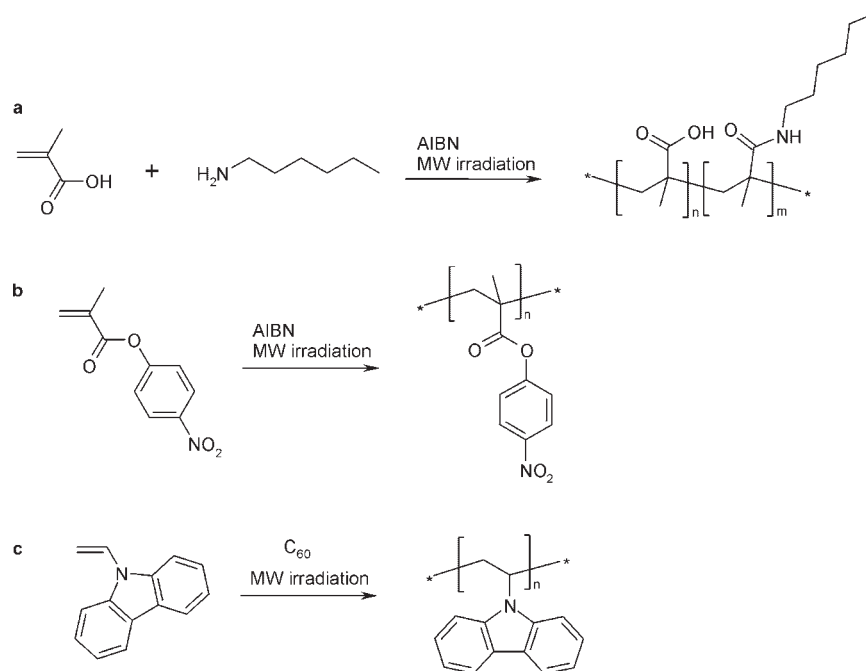


Figure 12. Variation of the molecular weight with time for the polymerization of methyl methacrylate under microwave irradiation with different monomer and initiator concentrations represented by different symbols. Reprinted with permission from reference [102], Copyright Society of Chemical Industry.

Solutions of 5 mol percent initiator in styrene were irradiated for two minutes in a domestic microwave oven at 800 W. Significant polymerization within two minutes only occurred with AIBN, *tert*-butyl peroxybenzoate, and *tert*-amyl peroxybenzoate as initiators. In addition, the microwave-assisted and conventional polymerizations were comparable regarding the conversions and the molecular weights of the polymers obtained. However, the micro-

wave-irradiated polymerizations reached the final temperature faster than the conventionally heated samples. In contrast to those results, Boey and co-workers reported an accelerated polymerization of styrene under microwave irradiation.<sup>[104,108]</sup> Furthermore, a sharp and large auto-acceleration (Trommsdorf effect) was observed under microwave irradiation, whereas only a gradual auto-acceleration effect was present during conventional heating. A clear explanation of this difference between thermal and microwave polymerization was not revealed, but the authors suggest that it might result from an increase in the polymerization rate. This sharp auto-acceleration was also observed for the microwave polymerization of methyl methacrylate but not for methyl acrylate. This absence of a sharp transition for MA could be explained by chain-transfer reactions that occur during the polymerization of MA. Bovin and co-workers investigated the polymerization of 4-nitrophenyl acrylate in a monomodal microwave reactor (Scheme 8b).<sup>[109]</sup> The synthesized poly(nitrophenyl acrylate)s (PNPAs) are interesting precursors for the synthesis of polyacrylamides that can be obtained by the reaction of PNPA with amino-functionalized compounds. Faster polymerizations were observed using microwave irradiation instead of conventional heating. In addition, the polymers from the microwave-supported synthesis had significantly lower PDI values, which implies that the termination of the polymer chains mainly proceeded by disproportionation instead of recombination, which is dominant in the case of thermal heating. Finally, the high



Scheme 8. Free radical polymerization under microwave irradiation: (a) simultaneous polymerization and amidization of acrylamide; (b) polymerization of 4-nitrophenyl acrylate; (c) fullerene-initiated polymerization of *N*-vinylcarbazole.

reproducibility of the microwave-assisted polymerizations and the possibility of up-scaling without a change of the reaction parameters were described.<sup>[109]</sup> Cai and co-workers investigated the fullerene-initiated charge-transfer bulk polymerization of *N*-vinylcarbazole (*N*-VC) under microwave irradiation (Scheme 8c).<sup>[110]</sup> Fullerenes form  $C_{60}^{+\bullet} - N-VC^{-\bullet}$  ion-radical pairs that initiate the polymerization of *N*-VC. Microwave-assisted polymerizations were found to proceed much faster than conventional thermal polymerizations. However, the authors admittedly mentioned that the main reason probably was the higher temperature during the course of the microwave polymerizations. Mattos and co-workers described the possibility of performing the free radical bulk polymerizations of vinyl acetate, styrene, methyl methacrylate, and acrylonitrile utilizing a domestic microwave oven.<sup>[111]</sup> The polymerizations proceeded at least 60 times faster (compared with conventional heating) utilizing azodiisobutyronitrile (AIBN) as initiator. Moreover, the polymerization of the highly absorbing acrylonitrile could also be performed in the absence of AIBN. Elsabee et al. reported the microwave-assisted homopolymerization of *N*-*p*-bromophenylmaleimide (BrPMI) with AIBN.<sup>[112]</sup> The homopolymerization of this solid monomer could not be performed under conventional heating at 135 °C with AIBN as initiator, but occurred readily within 10 min using microwave heating.

Random bulk copolymerizations of hydroxyethyl methacrylate HEMA and methyl methacrylate MMA were investigated by Rodriguez and coworkers.<sup>[113,114]</sup> The microwave-assisted polymerizations were finished within 45 min compared with 125 min using conventional heating as shown in Figure 13. In addition, the polymers synthesized under microwave irradiation showed higher molecular weights and lower PDI values than the thermally synthesized polymers (microwave irradiation: 1.36–2.08, conventional heating: 4.1), although the microstructure and the physical properties of the polymers did not change. Lu et al. described

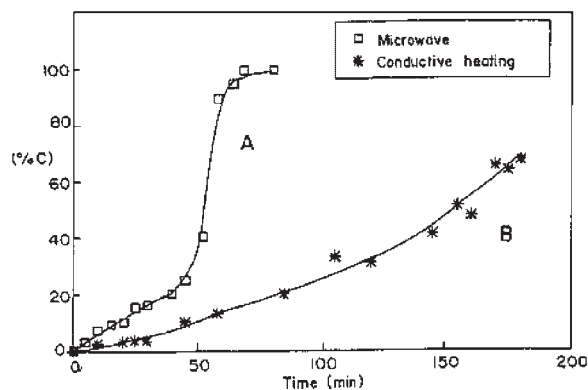
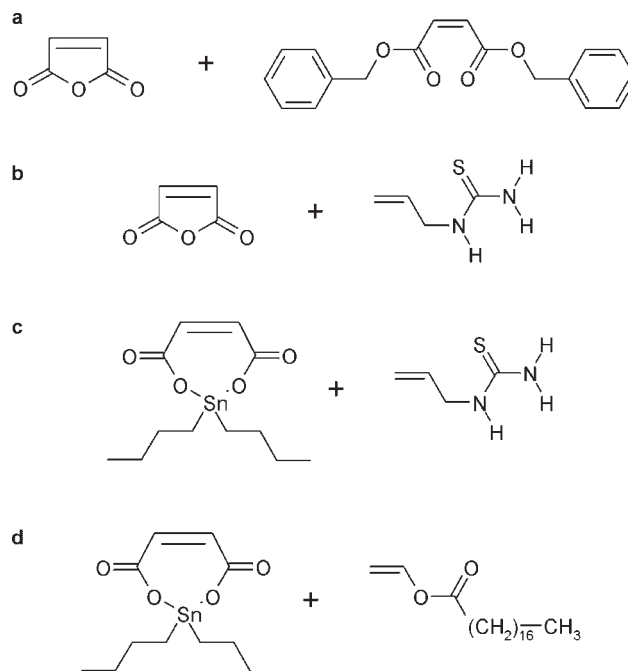


Figure 13. Comparison of the monomer conversion as a function of time for the bulk copolymerization of MMA and HEMA under both microwave irradiation (A) and conventional heating (B). Reprinted with permission from reference [114], Copyright VSP International Science Publishers.



Scheme 9. Solid-phase microwave-assisted copolymerization of (a) maleic anhydride with dibenzyl maleate, (b) maleic anhydride and allylthiourea, (c) dibutyltin maleate and allyl thiourea, and (d) dibutyltin maleate and stearic acid vinyl ester.

a series of solid-state random copolymerizations using various maleate derivatives (Scheme 9).<sup>[115–118]</sup> For the different combinations of monomers, the reactivity ratios were determined. The copolymerization of maleic anhydride with dibenzyl maleate (Scheme 9a) was performed by a 32 s microwave irradiation (power-regulated to obtain 45 °C) of a ground mixture of the monomers.<sup>[115]</sup> Subsequently, the resulting copolymers were used for the preparation of superabsorbent oil resins, obtained by the copolymerization and cross-linking of a variety of acrylates. The copolymerization of ground maleic anhydride and allylthiourea (Scheme 9b) yielded water-soluble polymers with metal ion complexing abilities.<sup>[116]</sup> Both the water solubility and the metal complexing capacities could be influenced by changes in pH. The third investigated system, the copolymerization of dibutyltin maleate and allyl thiourea (Scheme 9c), gave heat-stabilizing organotin polymers.<sup>[117]</sup> The mechanism of the copolymerization was investigated by the addition of a radical scavenger directly after microwave irradiation. An increase in microwave power led to an increase in radical concentration. In addition, it was demonstrated that the polymerization of this monomer combination did not occur in the absence of initiators with conventional heating, whereas the same procedure yielded polymers under microwave irradiation. Furthermore, a drastic increase in reaction speed from several hours down to a few minutes was observed for the solid-phase copolymerization of itaconic acid and acrylamide, sodium acrylate and *N,N*-methylene

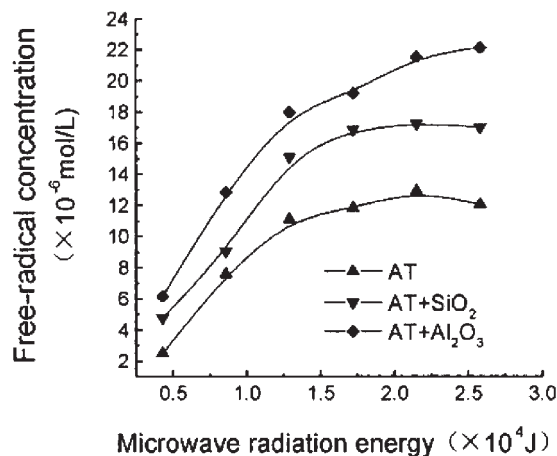


Figure 14. Radical concentration as a function of microwave irradiation energy for the microwave polymerization of allylthiourea (AT) with and without additional carriers. Reprinted with permission from reference [117], Copyright John Wiley and Sons.

biacrylamide, acrylamide and maleic acid anhydride, and also for the copolymerization of dibutyltin maleate and stearic acid vinyl ester (Scheme 9d).<sup>[118]</sup> To further improve the microwave absorption, the effect of carriers was investigated.<sup>[117–120]</sup> It was demonstrated that aluminum oxide enhanced the reaction speed of the copolymerization of dibutyltin maleate and allyl thiourea more than silicon oxide (Figure 14).<sup>[117,118]</sup> A more detailed study revealed that aluminum oxide (an alkaline carrier) was the best carrier for acidic or neutral monomer combinations, and silicon oxide (an acidic carrier) was better for alkaline systems.<sup>[119]</sup> This effect was ascribed to the higher dielectric constant resulting from acid–base interactions. Another study performed by Lu and co-workers revealed that free radical polymerizations (2-ethylhexyl acrylate in solution and solid-phase polymerization of acrylamide) in the presence of silicon oxide or aluminum oxide proceeded by a radical mechanism, whereas in the presence of magnesium oxide the same polymerizations occurred by both radical and anionic mechanisms leading to grafting onto the magnesium oxide surface.<sup>[120]</sup>

## 4.2. Controlled Radical Polymerizations

With a few exceptions only, it is mainly the group of X. Zhu who has transferred controlled radical polymerizations to microwave irradiation. Wisnoski et al., for example, have prepared novel resins in a monomodal microwave reactor (SmithSynthesizer, Biotage).<sup>[121]</sup> A TEMPO-methyl resin (TEMPO: 2,2,6,6-tetramethylpiperidine-*N*-oxyl) was reacted with various functionalized styrenes or 4-vinyl pyridine at 185 °C for 10 min. The resin beads obtained were large (>500  $\mu\text{m}$ ) and exhibited spherical shapes (Figure 15). Hence, the authors strongly assumed a controlled radical mechanism (involving the TEMPO radical) in the course of the polymerization. The high-loading resins (>5.5  $\text{mmol} \cdot \text{g}^{-1}$ ) were prepared in the range of 10 min, which is in fact 150 times faster than with conventional heating. Furthermore, conventional heating (at an identical temperature of 185 °C) failed to yield resins of similar size, loading, or uniform shape. Further investigations aimed at the determination of the reasons for this pronounced microwave effect are in progress.

With these findings in mind, it is interesting to note that Zelentzova et al. observed a re-initiation of the AIBN-initiated (AIBN: 2,2'-azoisobutyronitrile) and TEMPO-mediated radical polymerization of methyl methacrylate under microwave irradiation at 70 °C.<sup>[122]</sup> The radical species were detected by means of electron spin resonance (ESR) spectroscopy. The authors ascribe this observation to the decomposition of the intermediately formed nonradical TEMPO adduct with the 2-cyanopropan-2-yl radical (derived from AIBN).

Zhu and co-workers described the homogeneous atom transfer radical polymerizations (ATRP) as well as the reverse atom transfer radical (solution) polymerizations (RATRP) of methyl methacrylate with the following initiator/catalyst/solvent systems: EBB/CuCl-PMDETA/DMF, PhCH<sub>2</sub>Cl/CuCl-bpy/CCl<sub>4</sub>, *p*TsCl/CuSCN-PMDETA/CCl<sub>4</sub>, AIBN/CuBr<sub>2</sub>-bpy/ACN, AIBN/CuCl-bpy/ACN, AIBN/FeCl<sub>3</sub>-PPh<sub>3</sub>/DMF, AIBN/CuBr<sub>2</sub>-TMEDA/DMF, and *p*TsCl/CuBr-bpy/CCl<sub>4</sub> (EBB: ethyl-2-bromobutyrate; PMDETA: *N,N,N',N',N''*-pentamethyldiethylenetriamine; DMF:

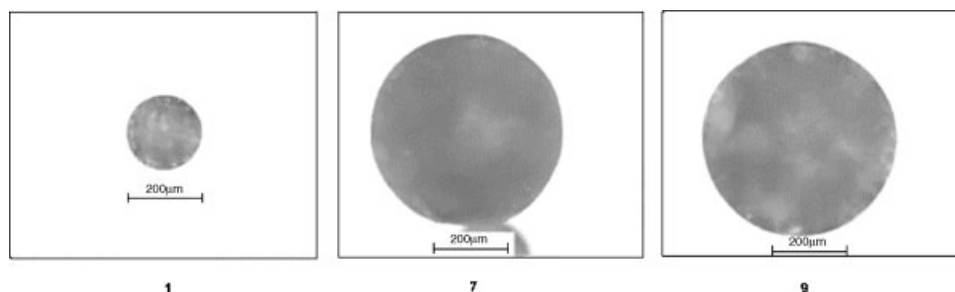


Figure 15. Photographs of the TEMPO-methyl resin before (left) and after loading with *p*-bromostyrene (middle) and a mix of *m*- and *p*-chloromethylstyrene (right). Reprinted with permission from reference [121], Copyright Elsevier Science Ltd.

*N,N*-dimethylformamide; bpy: 2,2'-bipyridine; AIBN: 2,2'-azoisobutyronitrile; ACN: acetonitrile; TMEDA: tetramethylethylenediamine; *p*TsCl: *p*-tosyl chloride).<sup>[123–130]</sup> The temperatures of the reaction mixtures were adjusted, if appropriate, by the boiling points of the solvents in an open reflux system, or by placing the reactors into a thermostat bath. Especially for low concentrations of the corresponding initiators and catalysts, the (modified) domestic microwave reactor proved to be superior to conventional heating in terms of reaction speed, molecular weights, and the narrowness of the molecular weight distributions. Influences of the microwave irradiation on the glass temperatures or stereoregularities of the poly(methyl methacrylate)s, however, were negligible.<sup>[130]</sup> The first-order kinetics for the monomer consumption were illustrated by the linear dependency of the  $\ln\{[M_0]/[M_t]\}$  values on reaction time. An explanation for the fivefold increase in reaction rates, however, was not provided in these references. Corresponding findings were also obtained for the atom transfer radical polymerization (ATRP) of octyl acrylate with the initiator/catalyst/solvent system EBB/CuCl<sub>2</sub>/bpy/CCl<sub>4</sub>.<sup>[131]</sup> In a more recent publication, Zhu and co-workers performed the atom transfer radical polymerization (ATRP) of methyl methacrylate in hexane, with the initiator  $\alpha,\alpha'$ -dichloroxylene and the catalysts CuCl and PMDETA.<sup>[132]</sup> During the course of this polymerization, and by additional investigations that aimed at determining the nature of the increase in reaction rates under microwave irradiation, it was observed that the dissociation of CuCl and consequently the concentration of copper ions in solution were enhanced when the polymerization was performed in a microwave reactor. The authors attributed the increase in reaction speed observable for all the ATRP reactions under microwave assistance to this finding. On this occasion, it should be pointed out that the use of thermostat baths does not necessarily reveal the reaction temperatures in the reaction vial, especially if solid ionic particles are involved in the reaction. These particles optimally absorb microwave irradiation because of its electromagnetic character (cf. Section 1). Consequently, the noncontact heating in the microwave reactors might heat the reaction mixture well beyond the temperature of the thermostat bath. Hence, a direct comparison with findings from reactions performed under conventional heating would be no longer valid.

For the atom transfer radical polymerizations (ATRP) of methyl methacrylate with the initiator/catalyst/solvent systems EBIB/CuCl-NHPMI/*p*-xylene and EBIB/CuCl-NHPMI/DMF, however, Zhang and Schubert observed no acceleration with microwave irradiation [EBIB: ethyl-2-bromo-isobutyrate, NHPMI: *N*-Hexyl-2-pyridylmethanimine].<sup>[133]</sup> To ensure a valid comparison of the experiments, the polymerizations were conducted under conventional heating and in a monomodal microwave reactor (Emrys Liberator, Biotage) at identical temperatures. Furthermore,

it was shown that for reaction temperatures higher than 110 °C, the molecular weight distributions became significantly broader (PDI > 1.4), exhibiting severe deviations from an ideally controlled radical polymerization and thereby limiting the use of microwave reactors for the reaction conditions employed.

### 4.3. Emulsion Polymerizations

Zhu et al. performed the emulsion polymerization of styrene with potassium persulfate as initiator and sodium dodecyl sulfonate as emulsifier under conventional heating as well as under microwave irradiation.<sup>[134]</sup> To ensure a direct comparison of the polymerizations performed under the two different activation modes, the reactions in the modified domestic microwave oven with adjustable mean output power were performed at a constant temperature (around 70 °C) that was held by a thermostat with tetrachloroethylene, which hardly absorbs microwave irradiation (Figure 16). Compared with conventional heating, the polymerization rate was effectively enhanced because of the increase of the decomposition rate of potassium persulfate by a factor of 2.4. Consequently, the amount of particles formed within identical reaction times was higher in the case of microwave activation. Although polymers with higher average molecular weights were formed under microwave irradiation, almost identical glass-transition temperatures and similar atacticity/isotacticity ratios of around 75:25 (determined by <sup>13</sup>C NMR spectroscopy) for the polymers obtained from conventional as well as microwave heating exhibited that their physical properties and microstructures were almost independent of the type of activation source. The corresponding findings were obtained for the emulsion polymerization of methyl methacrylate

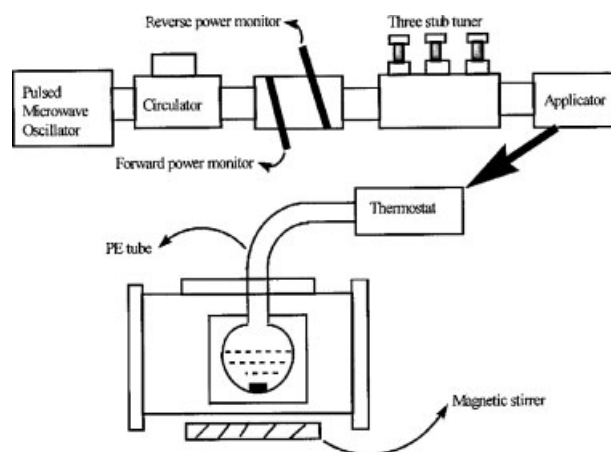


Figure 16. Experimental setup for the emulsion polymerization of styrene in a domestic microwave oven additionally equipped with adjustable mean output power and a thermostatic bath. Reprinted with permission from reference [134], Copyright John Wiley and Sons.

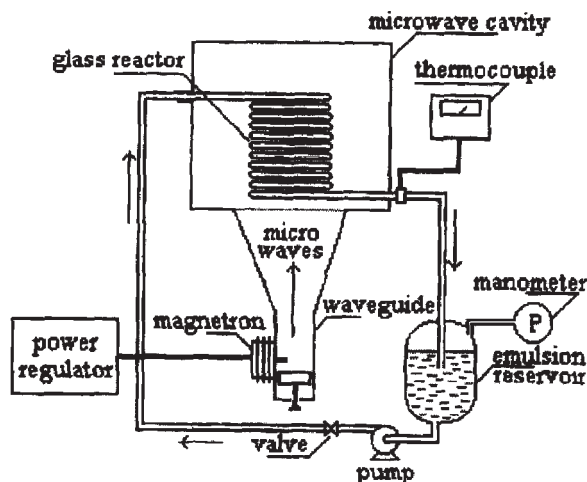


Figure 17. Modification of a domestic microwave reactor in order to conduct batch, semicontinuous, and continuous processes, utilized for the emulsion polymerization of styrene. Reprinted with permission from reference [139], Copyright Elsevier Science Ltd.

under identical conditions (cf. reference [134] and Figure 17).<sup>[135]</sup>

Similar experiments were studied by Palacios and Valverde in order to investigate the characteristics of the two different energy sources.<sup>[136]</sup> In control experiments performed at 50 °C, they found a decrease in reaction times from 6 h to 8.3 min under microwave irradiation. For initiator concentrations lower than  $1.5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ , the polymerization rates were effected by the corresponding concentration, and the ratio of the corresponding  $\ln$  values  $\{\ln(r_p)/\ln[I]\}$  was found to be constant at 0.28. From literature data of the Smith–Ewart theory,<sup>[137,138]</sup> this ratio was known to be at a constant value of 0.4; the authors ascribe this decrease from 0.4 to 0.28 to the facilitated activation of the initiator by the microwave irradiation which renders this step of the mechanism less important. For this and above cited two experiments, it should be stressed that the use of thermostatic baths does not reveal the temperatures in the reaction mixture. Therefore, a direct comparison between microwave and conventional heating is not (necessarily) valid, and the origin of the accelerated reaction rates, selective excitation of the ionic species versus higher reaction temperatures, cannot be deduced reliably.

Correa et al. performed the emulsion polymerization in a specially modified domestic microwave reactor that allowed for batch, semicontinuous, and continuous processes (Figure 17).<sup>[139]</sup> In order to overcome the risk of hazardous explosions associated with prolonged irradiation times, a rectangular pulse function was utilized to heat the reaction emulsion. A decrease in reaction times by a factor of 70 was observed for the emulsion polymerization performed under microwave irradiation. The authors ascribe this advantage

to the good absorption of the irradiation by the water molecules and the resulting higher reaction temperatures.

Wu and co-workers prepared latex particles from styrene and the co-monomers methyl methacrylate, butyl methacrylate, ethyl acrylate, and maleic anhydride by an emulsion polymerization in aqueous acetone with potassium persulfate as initiator in a domestic microwave oven.<sup>[140]</sup> The hydrodynamic radii were determined utilizing a modified commercial laser light scattering spectrometer and found to have a narrow distribution. In fact, the hydrodynamic radii decreased with an increasing acetone content in the reaction mixture because of the corresponding decrease of interfacial tension. The concentration of the comonomer also influenced the hydrodynamic radii. It was mentioned that the preparation of such particles with conventional heating requires longer reaction times and yields particles with a broad distribution; the corresponding values or references, however, are not given.

Polymers that contain rare earth metal ions have been studied extensively because of their applications for luminescence or laser materials. For example, Zhang and co-workers transferred the emulsion polymerization of methyl methacrylate (in the presence as well as the absence of europium cations) to a modified domestic microwave oven.<sup>[141]</sup> Assuming identical temperatures in the control experiments under conventional heating, the reaction was found to proceed faster with microwave assistance, elucidated by the dependency of the particle size on time. After reaction times of 1 h, radii of 165 and 215 nm, respectively, were measured. After prolonged reaction times of 5 h, however, the radii were almost identical at around 215 nm, independent of the heating source. SEM images of those particles (recovered from reaction mixtures without europium ions) consequently were similar to each other (Figure 18a and b). The authors ascribe the higher reaction rates in the case of microwave activation to the good absorbance of the irradiation by the water molecules. In this context, it is worth mentioning that Mülhaupt and co-workers observed no difference in terms of molecular weights, polydispersities, stereoregularities, particle sizes, and particle-size distributions between conventional and microwave heating for the dispersion polymerization of methyl methacrylate in heptane.<sup>[142]</sup> The corresponding experiments were performed in a specially equipped microwave reactor (cf. reference [78] and Figure 8). Zhang and co-workers (cf. herein and above) also recorded SEM images of the PMMA particles obtained from europium containing reaction mixtures. They found a distribution of the europium ions mainly on the surface (Figure 18c), a phenomenon that was explained by the fact that the octonate anion, with a hydrophobic alkyl chain, was used as counterion for the europium ion and prevented the hydrophilic trivalent cation to enter the interior of the particles.

He et al. investigated the persulfate-initiated soapless emulsion polymerization of butyl methacrylate in ethanol

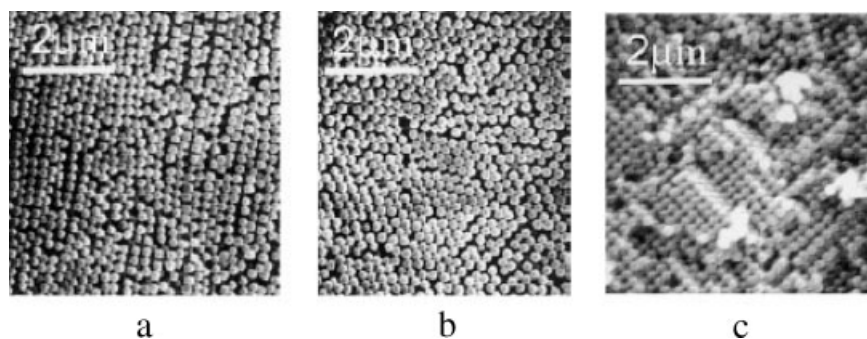


Figure 18. SEM images of PMMA particles obtained from (a) conventional heating, (b) microwave heating, and (c) microwave heating with europium ions present in the reaction mixture. Reprinted with permission from reference [141], Copyright John Wiley and Sons.

under microwave irradiation.<sup>[143]</sup> Control experiments with conventional heating showed a tenfold increase in reaction rates for the polymerization under microwave assistance, originating from the accelerated decomposition of the persulfate anion. The influences of the monomer/initiator amounts and the addition of ethanol on the monomer conversion, the particle sizes, and their distributions were examined and found to be in full agreement with trends observable under conventional heating.

## 5. Conclusion and Outlook

The use of microwave irradiation as a heating source for polymerization reactions is a rapidly growing branch in polymer science as may be determined from the exponential increase in the number of publications originating from that field (Figure 2). With the advent of monomodal microwave reactors (Figure 1) at the beginning of the millennium, the safety uncertainties, like fires or explosions that are likely to accompany organic reactions under microwave irradiation, have been overcome. Controlling the temperature and pressure inside the reaction vials not only shifts the reliability of this type of reactors from hazardous to safe, but also allows for a more detailed insight into the run of the polymerization.

So far, most of the polymerizations performed under microwave irradiation may be entitled as “well-established” polymerization reactions, including the step-growth preparation of polyamides, polyimides, polyethers, and polyesters, the ring-opening polymerizations of (almost exclusively)  $\epsilon$ -caprolactams and  $\epsilon$ -caprolactones, and the free radical polymerizations of some well-investigated monomers like styrene or methyl methacrylate. More advanced techniques among the reactions investigated comprise the phase-transfer catalyzed polymerizations and C–C coupling reactions, as well as controlled radical and emulsion polymerizations.

For the vast majority of reactions, a significant increase in reaction speed becomes discernible under microwave

irradiation (compared with conventional heating). The enhanced reaction rates have been found to originate from thermal effects (higher temperatures) for a large number of these reactions. Concomitant with shorter reaction times, side reactions are reduced to a minimum, and consequently the purity and the polymer properties improve.

For some reactions, however, it seems that these advantages do not result from higher reaction temperatures, but from the selective excitation of one of the educts involved. This might be especially true for ions and (zerovalent) metals that are known to intrinsically absorb microwave irradiation. Pronounced effects of that type are significantly related to the fields of metal catalysis (cf. C–C coupling reactions) and reactions involving ionic species (cf. ring-opening polymerizations). Shifts in selectivity, originating from the specific excitation by the microwave irradiation, have been observed as well (cf. the phase-transfer catalyzed step-growth polymerization of sorbide and 1,8-dibromooctane, for example).

In this respect, some of the findings and the corresponding explanations might be taken into account: With comparably few data on (monomodal) microwave-assisted polymerizations available these days, general conclusions, valid for a whole series of (similar) educts or a specific reaction type, cannot be drawn. Further problems might also arise from the lack of knowledge of the actual reaction conditions, such as temperature or pressure in the case of domestic microwave ovens (resulting from cold and hot spots), especially in the cases where thermostat baths are utilized, disallowing a direct comparison with conventional heating experiments.

With the polymerizations reviewed in this article, however, (monomodal) microwave reactors have been introduced as powerful tools for the synthesis of polymers: Reaction times are greatly shortened, paving the way to higher yields, improved selectivities, and environmentally benign methods (shorter reaction times, low-boiling solvents). Consequently, more data is very likely to be accumulated in the near future, probably focusing on more and more advanced techniques. A direct comparison with

experiments under conventional heating can be made by the accurate measurements of temperature and pressure. In the course of an increasing collection of reliable data, general trends will become discernible and allow for the establishment of general rules for predictions concerning the performance of a specific polymerization under microwave irradiation. This way, reaction times for future polymerizations can be decreased and the way to environmentally benign conditions will be paved.

*Acknowledgements:* This study was generously supported by the Dutch Polymer Institute (DPI), the Nederlandse Wetenschappelijke Organisatie (NWO), and the Fonds der Chemischen Industrie.

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