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PERSPECTIVE

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Microwave-Assisted Polymerizations: Recent Status and Future Perspectives

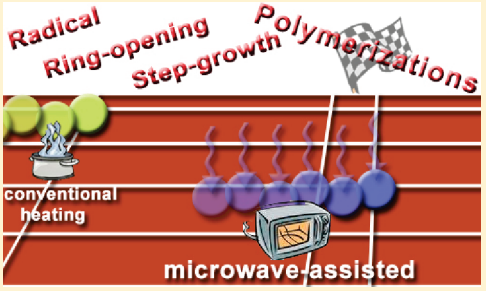
Kristian Kempe,[†,‡] C. Remzi Becer,[*,†,§] and Ulrich S. Schubert[*,†,‡,§]

[†]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany

[‡]Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany

[§]Dutch Polymer Institute (DPI), John F. Kennedylaan 2, 5612 AB Eindhoven, The Netherlands

ABSTRACT: Microwave heating is frequently used in the synthesis of polymers owing to the precise temperature and pressure control when using monomodal microwave synthesizer. The ever since growing interest in this sort of heating source is expressed by a near-exponential increasing number of publications in this research field every year. This Perspective encompasses the progress of microwave-assisted polymerizations in the past four years with a special focus on controlled and living polymerizations. Furthermore, polymer syntheses under microwave irradiation in ionic liquids as well as the upscaling of microwave-assisted polymerizations are discussed with regard to an energy-saving green process and a potential expansion to industrial applications, respectively.



1. INTRODUCTION

Microwave heating has developed into a powerful tool for a broad variety of chemical reactions. Known to be an alternative heating source not only for the heating of meals and drinks but also for reactions in the laboratory, microwave-assisted reactions gained an enormous attention in the past decades. Nowadays, microwave synthesizers belong to the standard equipment kit in almost every organic and pharmaceutical chemistry laboratory.[1−3] In contrast to the common domestic microwave ovens, microwave synthesizers were developed for special laboratory needs. These are typically monomodal microwave systems that offer several advantages, such as precise temperature and pressure control, which improve the safety and reproducibility of the reactions.[4]

Domestic microwave ovens (Figure 1a) were frequently used for reactions of highly microwave radiation absorbing materials at high temperatures and short reaction periods. Modern microwave synthesizers have a protected cavity against explosions and also for an improved heat transfer. A robotic arm can move the vials in and out the cavity to perform several reactions sequentially in an automated manner (Figure 1b). Other microwave synthesizers offer a flexible platform which can easily be modified according to the actual needs, such as a continuous flow coil, large batch vial with a magnetic stirrer, or a round-bottom flask with a reflux condenser on top (Figure 1c). Recently, unattended automated microwave synthesizers were introduced which can not only perform microwave-assisted reactions but also prepare the vials to be reacted from stock solutions or samples from vials following the reactions (Figure 1d).

These technical improvements have given rise to a wide range of new application areas, such as in polymer science, as summarized in a number of review articles.[5−9] In general, processes performed under microwave heating offer several advantages compared to conventional heating, such as shorter reaction times, increased yields as well as reduced side reactions, and, thus, cleaner products. Microwave-assisted syntheses are based on the ability of microwave radiation to excite polar molecules due to their dipolar character (dipolar polarization) or to conduct charged particles. The oscillating electromagnetic field force the dipole and ion fields to (re)align with the electric field whereby heat is generated caused by rotation, friction, and the collision of molecules. As a result of the direct interaction of the electromagnetic irradiation (microwave energy) with the molecules, a rapid internal heating of the reaction mixture takes place. It was shown that in case of low absorbing reaction components a tremendous acceleration can be observed simply by the addition of polar additives, such as ionic liquids. In fact, polar components, in particular solvents or monomers, play an important role as to the comparison of classical and nonclassical heating. While the temperatures of reactions under reflux conditions are limited by the boiling point of the solvent, applied microwave heating in conjunction with sealed vessels/reactors allows for the employment of much higher temperatures when using the same solvent. Nowadays, this thermal/kinetic effect is recognized as the main reason for the enhancement in microwave-heated processes. Taking into consideration the Arrhenius law [$k = A \exp(-E_a/RT)$], the frequently observed accelerations can be simply attributed to the higher temperature attainable in a sealed vessel in the microwave reactor. Nevertheless, rate enhancements caused by the dielectric character of microwave heating have to be considered as well. As a consequence, "specific

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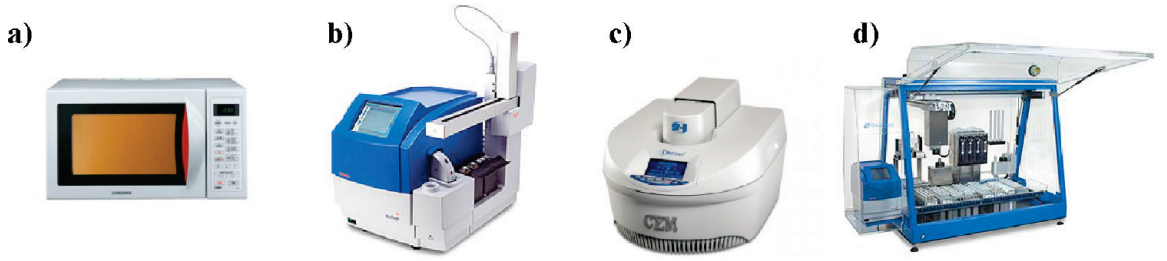

Figure 1. Selected examples for microwave reactors used for chemical reactions: a domestic microwave oven (a), Initiator Eight (Biotage, Sweden) (b), CEM Discover (CEM) (c), and Chemspeed Swave automated microwave synthesizer (Chemspeed, Switzerland) (d).

microwave effects" or "nonthermal microwave effects" are also frequently discussed in the literature. The former comprising factors such as superheating, selective heating of components, and the minimization of wall effects, which cannot be achieved in syntheses using classical reflux conditions, are essentially still thermal effects. A more controversial discussion has arisen on the existence of truly "nonthermal microwave effects" ever since microwave irradiation was applied as alternative heating source. In this respect, several studies were accomplished dealing with the rationalization of such microwave effects.

In this Perspective, we aim to provide an overview of the recent literature on microwave-assisted polymerizations with a special focus on controlled and living polymerizations. For this purpose, representative examples are listed in tables, and the reaction conditions as well as special notes were included for their easy and quick comparison. The tables were divided in different sections covering reversible "addition−fragmentation" chain transfer (RAFT) polymerizations, nitroxide-mediated polymerizations (NMP), atom transfer radical polymerizations (ATRP), free radical polymerizations (FRP), ring-opening polymerizations (ROP), step-growth polymerizations, microwave-assisted reactions in ionic liquids, and examples on upscaling approaches.

2. CONTROLLED RADICAL POLYMERIZATIONS

Controlled/"living" radical polymerization (CRP) techniques have attracted significant attention in the past two decades. The first reports on CRP techniques were published in the early 1990s, and they were based on chain transfer mechanisms to gain control over the chain growth. The most widely applied techniques are the RAFT polymerization, NMP, and ATRP. These techniques allow moderate to good control over the polymer chain growth processes. Besides, the preparation of telechelic polymers and block copolymers became relatively easy using these techniques. Each technique has advantages and disadvantages over others, and the polymerization conditions require optimization steps depending on the monomer, initiator, catalyst, and solvent used in these reactions. Reaction time and temperature are other important parameters that need to be taken into consideration carefully. For this purpose, not only conventional heating sources but also microwave reactors have been utilized to explore and improve the polymerization conditions. In recent years, RAFT polymerization was extensively studied, whereas up to now just a few reports are published on ATRP and NMP using microwave irradiation. As summarized in Table 1 (entries 01−10), various monomers and conditions were investigated in case of the microwave-assisted RAFT polymerization.

Perrier and co-workers studied the polymerization of styrene (St), methyl acrylate (MA), and methyl methacrylate (MMA) in a monomodal microwave synthesizer.[10] The bulk polymerizations were performed with two RAFT agents, namely ethylthiosulfanylcarbonylpropionic acid ethyl ester (ETSPE) and cyanoisopropyl dithiobenzoate (CPDB) at 50 and 60 °C, respectively, yielding well-defined polymers without loss of control. As to the polymerization rates, a difference was observed between the polar and nonpolar monomers. MMA and MA as rather polar monomers showed an acceleration of the reaction rates, whereas the nonpolar styrene was polymerized with similar rates as under conventional heating. These observations attributed the authors to an actual dielectric heating enhancement. In contrast, accelerated RAFT polymerizations of St in a modified domestic microwave oven were reported by Zhu et al.[11] Schubert and co-workers reported contrary findings for the RAFT polymerization of MMA under microwave irradiation.[12] Comparative studies of microwave and conventional heating revealed quasi-identical polymerization rates under similar conditions indicating the absence of nonthermal microwave effects. In addition, high-temperature polymerizations (120−180 °C) of MMA were accomplished using CPDB as RAFT agent in the absence of AIBN. Microwave-assisted polymerizations of MA, vinyl acetate (VA), and St were further investigated at maximum power without temperature control by Perrier, Rannard, and co-workers.[13] In this case ultrafast polymerizations were observed for both polar and nonpolar monomers, which are characterized by a maintained control over molar mass and molar mass distributions. Furthermore, the polymerization of styrene using RAFT polymerization conditions was investigated from a theoretical point of view, yielding a kinetic model for the polymerization rates and molar mass development.[14] Eight different systems were analyzed in this study encompassing the RAFT polymerization of styrene (RAFT agent: 2-cyanoprop-2-yl 1-dithionaphthalate) with and without initiator under microwave irradiation as well as conventional heating resulting in a good quantitative agreement of the presented model with the obtained experimental data. More recently, Zetterlund and Perrier reported the comparison of data obtained by simulations performed using the software PREDICI and reported experimental data based on the RAFT polymerization of St with CPDB as model system.[15] According to the best fitting model, the increase in polymerization rate under microwave irradiation is related to an increase in the propagation (k_p) as well as addition to the RAFT moiety (k_{add} and k_{add1}) constant of about 1 order of magnitude. Nanogel particles and double hydrophilic block copolymers were prepared by Hawker and co-workers using hydrophilic as

Table 1. Radical Polymerizations Performed under Microwave Irradiation[a]

entry	monomer (copolymer)	microwave reactor type	conditions: temperature	conditions: time	conditions: solvent	M_n [kDa], PDI	ref
			Reversible Addition−Fragmentation Chain Transfer (RAFT)				
01	MA, MMA, St	CEM discover BenchMate	50 °C (MA, MMA); 60 °C (St)	0−4 h (MA, MMA); 0−20 h (St)	bulk	20−40, <1.2 (MMA); 15−35, 1.05−1.3 (MA)	10
02	St	domestic MW oven	72, 98 °C	<10 h	bulk	<50, 1.1−1.2	11
03	MMA	Initiator Sixty (Biotage)	70, 120, 150, 180 °C	<6 h, <9 h	tol, bulk	<10, 1.2−1.4 (70 °C); <12.5, 1.2−2.4 (high temp)	12
04	MA, VA, St	CEM discover BenchMate	70 °C (VA); 50 °C (MA); 60 °C (St)	<15 min (VA); <20 min (MA); 7 h (St)	bulk	<40, <1.2 (MA); 1−5, <1.1(VA); <40, <1.1 (St)	13
05	St	theoret model					14
06	St	theoret. model					15
07	DMA, NiPAm (PDMA-*b*-PNiPAm)	Initiator Eight (Biotage)	70 °C	10−30 min (gels)	water (pH 2.5)	10−50, 1.1−1.3	16
08	DMA, NiPAm (diverse blocks)	CEM discover Labmate	60 °C (NiPAm); 70 °C (DMA)	10−50 min (NiPAm) 5 min (DMA)	C_6H_6	7−20, 1.1−1.2 (DMA); 6−13,1.15−1.2 (NiPAm)	17
09	diallyldimethylammonium chloride	CEM discover	60 °C	15−240 min	water	10−30, 1.05−1.2	18
10	vinyl cyclic silazane (PVS-*b*-PS)	MARS-5 CEM	120 °C	3−4 h	tol	1−7, 1.07−1.16; 10−13.5, 1.2−1.24 (blocks)	19
			Nitroxide-Mediated Polymerization (NMP)				
11	St	CEM discover	125 °C; (115−135 °C)	0−5 min (100 W), 0−2 min (200 W)	bulk	2.5−15, 1.14−1.41	20
12	St	CEM discover	135 °C	0−7 h	water	10−35, 1.1−1.15	21
13	MA, tBA	Emrys Liberator (Biotage)	120 °C	<3 h	dioxane	1.5−3, <1.3 (MA); 1−5, 1.2−1.4 (tBA)	22
14	acrylamide	CEM discover	80, 90, 97, 105 °C	30−300 min	water	5−65, 1.05−1.4	23
15	St	theoret model					24
			Atom Transfer Radical Polymerization (ATRP)				
16	AN	domestic MW oven	77 °C (CCl_4 bath)	0−100 min	bulk	<13, <1.24	25
17	MMA	Emrys Liberator (Biotage)	90, 110, 130, 150 °C	<8 h	xylene	<30, <1.4 (<110 °C), <1.8 (>110 °C)	26
18	MMA	CEM-discover	85−160 °C	0−3 h	tol	8−30, 1.2−1.75	27
19	St (PEG-*b*-PSt)	XH-100A(Beijing XianHu Science)	75 °C	1 h	water	n.a.	28
			Free Radical Polymerization (FRP)				
20	St, MMA (PS-*co*-MMA)	CEM discover	100 °C	60 min	tol, DMF	13−200, ∼2	29
21	St, MMA	CEM discover	100 °C (diff power levels)	45 min	tol, DMF	7−40, 1.7−2.4	30

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Table 1. Continued

entry	monomer (copolymer)	microwave reactor type	conditions			M_n [kDa], PDI	ref
			temperature	time	solvent		
22	CH_3CN	domestic MW oven	<100 °C	diff times	water		31
23	acrylamide	domestic MW oven	<100 °C (fixed power)	25−125 s	bulk	40−130, n.a.	32
24	diisopropyl fumarate	domestic MW oven	140, 210, 240 W	2−20 min	bulk	20−40, 1.6−2.0	33
25	*N*-benzenesulfonamide maleimide	CEM discover	max 100 °C (80 W)	2 h	DMF	<5, 1.3	34
26	2-ethylhexyl MA, vinylbenzyl chloride, fluoroalkyl MA	MARS (CEM)	70 °C	4−5 h	NFEE	n.a.	35
27	*N*-acryloyl-L-phenylalanine, MMA	CEM discover	80 °C (250 W)	30 min	dioxane	108, 1.3	36

[a] St = styrene, MA = methacrylate, MMA = methyl methacrylate, VA = vinyl acetate, NiPAm = *N*-isopropylacrylamide, AN = acrylonitrile, tBA = *tert*-butyl acrylate, DMF = *N*,*N*′-dimethylformamide, tol = toluene, C_6H_6 = benzene, NFEE = nonafluorobutyl ethyl ether.

well as amphiphilic poly(dimethylacrylamide) chain transfer agents (CTA) in RAFT precipitation polymerization.[16] The polymerization of *N*-isopropylacrylamide (NiPAm) in water at 70 °C was dependent on the progress of the polymerization and the choice of the macro-CTA due to the lower critical solution behavior of the corresponding polymer. For the preparation of permanent fully hydrophilic nanoparticles a cross-linker (*N*,*N*′-methylenebisacrylamide, BIS) was applied. The absence of BIS yielded double hydrophilic block copolymers after cooling to room temperature (Figure 2). Thus, nanogels were prepared using the macro-CTAs and a positively charged initiator (2,2′-azobis(2-methylpropionamidine)-dihydrochloride; V-50) in aqueous solution (pH value 2.5). The core-shell nanostructures obtained were subsequently used for the preparation of bioconjugates. Sumerlin and co-workers demonstrated the homopolymerization of NiPAm and dimethylacrylamide (DMA) and their potential to be used as macro-CTA for the preparation of block copolymers (NiPAm, DMA, MA, *n*-butyl acrylate) under microwave irradiation (Figure 3).[17] The polymerizations were performed in a relatively short period of time using microwave heating while maintaining the control over the molar masses combined with low polydispersity index (PDI) values and a high end-group fidelity. Attempts by the authors in mimicking the microwave conditions for the conventional heating process failed and resulted in rather slow reactions and a loss of the control of the molar mass.

Moreover, polymerizations of more complex monomers are described. Agarwal and co-workers studied the microwave-assisted RAFT polymerization of diallyldimethylammonium chloride (DADMAC) in water.[18] Under the formation of five-membered rings high molar mass polymers with low PDI values were obtained with up to 520% acceleration of the polymerization rate compared to conventional heating. The authors propose that the homogeneous heating accompanied by the existence of polar molecules is responsible for the acceleration observed. Nguyen et al. investigated the homopolymerization of vinylcyclicsilazanes as well as their ability to be used in block copolymerizations with St.[19] The usage of microwave heating allowed the synthesis of higher molar mass polyvinylsilazanes (H-PVSZ) with an excellent control over the polymerization compared to conventional heating, which was attributed to the superior dielectric properties of the PVSZ mixture obtained by microwave irradiation. As a result, the rates of propagation and chain transfer were accelerated by the high energy generated by microwave irradiation.

The nitroxide-mediated polymerization of styrene was investigated by Zhu and co-workers.[20] The bulk polymerizations turned out to be controlled as demonstrated by linear kinetic plots, a linear increase of the molar mass with conversion as well as low PDI values (about 1.3), which was supported by chain extension experiments. Similar results were obtained by the same group for the nitroxide-mediated miniemulsion polymerization of St which yielded stable PS latexes.[21] In contrast, Schubert and co-workers reported the NMP of MMA and *tert*-butyl methacrylate in a monomodal microwave reactor.[22] Both polymerizations feature a perfect control over the polymerization but do not show an acceleration compared to conventional heating. Grassl and co-workers polymerized acrylamide under microwave-assisted conditions in water using a water-soluble radical initiator and a β-phosphonylated nitroxide. Two different microwave modes were studied: pulsed and dynamic (high

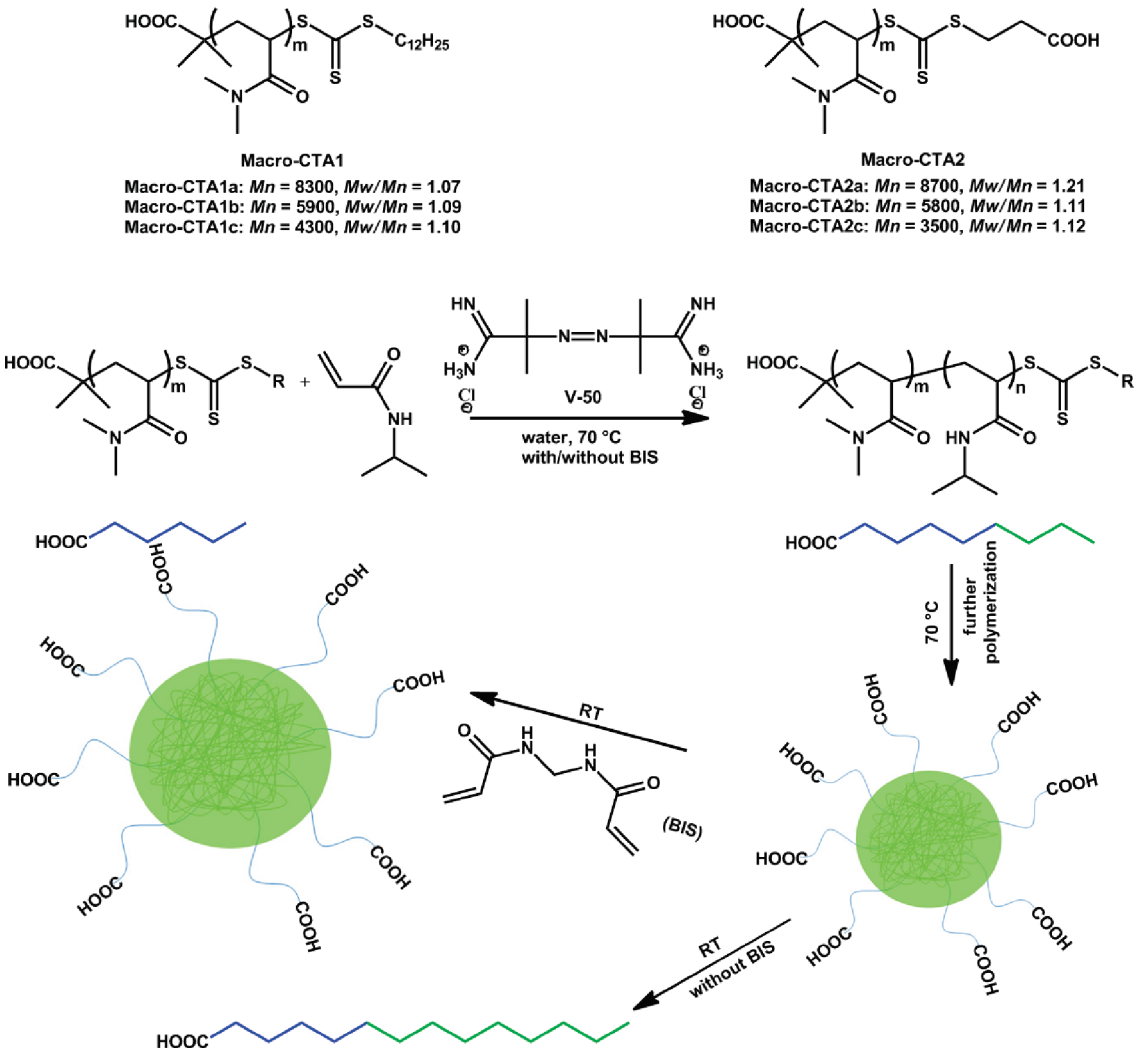

Figure 2. RAFT precipitation polymerization of NiPAm in water using two different poly(dimethylacrylamide) chain transfer agents toward the synthesis of double hydrophilic block copolymers and fully hydrophilic nanoparticles when using a water-soluble cross-linker (*N,N′*-methylenebisacrylamide, BIS) [adapted from ref 16].

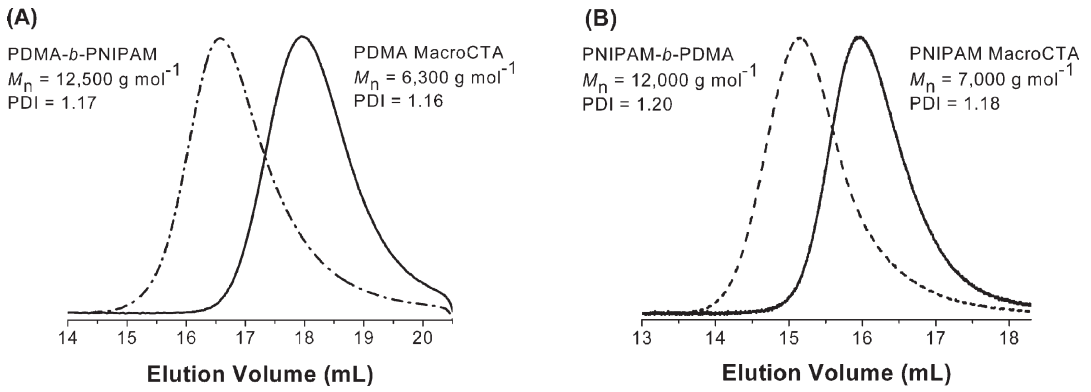

Figure 3. SEC traces for macro-chain-transfer agents (macroCTA) and block copolymers. (A) PDMA macroCTA and PDMA-*b*-PNIPAm block copolymer. (B) PNIPAm macroCTA and PNIPAm-*b*-PDMA block copolymer Reprinted with permission from ref 17.

initial power) mode. Whereas the pulsed mode resulted in a 50 times enhancement of the polymerization without the loss of the living/controlled behavior, the dynamic mode had no effect.[23] A theoretical model for the NMP under microwave irradiation with the assumption of a production of free radicals by monomer decomposition ("microwave-initiation" step) was developed by

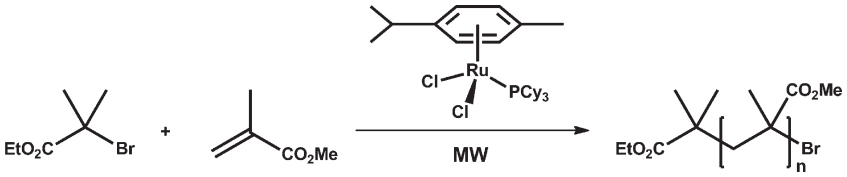

Figure 4. Schematic representation of the ATRP of methyl methacrylate catalyzed by [$RuCl_2$(*p*-cymene)(PCy_3)] and a summary of the apparent rate constants, k_{app}, obtained under microwave heating and under conventional heating [adapted from ref 27].

Vivaldo-Lima and co-workers.[24] Using slow NMP controllers (e.g., OH-TEMPO), the authors concluded that the polymerization rate of the NMP can be increased.

The ATRP of acrylonitrile under microwave irradiation was described by Hou and co-workers.[25] The polymerizations were performed in a domestic microwave oven with a $FeBr_2$/isophthalic acid catalyst system and 2-bromopropionitrile as initiator. The good control of the polymerization with a catalyst-to-initiator ratio of 1:2 was demonstrated by a chain-extension reaction. The microwave-assisted polymerization of MMA in a monomode microwave synthesizer was reported by Zhang et al.[26] The results obtained were almost the same as in conventional heating experiments, which is contrary to the studies of Zhu and co-workers. They used modified domestic microwave ovens for a series of ATRP studies and attributed the existence of accelerated reactions to a "microwave effect". Furthermore, the ATRP of methyl methacrylate in the presence of a Ru complex as catalyst was reported by Demonceau and co-workers.[27] Two different methods were applied: conventional microwave synthesis (CMS) and enhanced microwave synthesis (EMS), operating with and without simultaneous cooling, respectively, which showed different results in terms of the living/controlled character of the polymerization. Whereas polymerizations performed by the EMS showed a loss of control, the CMS was characterized by a retained control in the temperature range from 85 to 120 °C but losing control at 130 °C. The acceleration of the polymerization accompanied by a loss of control in case of the EMS and at higher temperatures for CMS was attributed to a high concentration of radicals which enhanced the propagation but also termination, in particular the disproportionation rates. Compared to conventional heating, the CMS revealed the same polymerization rate at 85 °C and increased to be 3 times higher at 120 °C, which is summarized in Figure 4. Xu et al. prepared poly(ethylene glycol)-*b*-polystyrene nanoparticles starting from a poly(ethylene glycol) macroinitiator in water via the atom transfer radical emulsion polymerization process.[28] The size of the particles and their distribution was manipulated by the ratio of the catalyst (CuCl/bpy) and styrene as well as the ratio of catalyst and macroinitiator, respectively. It was stated that particles obtained under microwave irradiation are smaller in size (<50 nm) and exhibit lower PDI values than the ones prepared at conventional heating, which was described by the authors as a consequence of the higher initiator efficiency and, thus, the formation of larger amounts of active species resulting in more stable primary particles in a shorter time.

To sum up, reports on microwave-assisted CRP are rather sparse even though publications on rate-enhanced microwave CRP polymerizations have been increased in recent years. Among the CRP techniques, RAFT polymerizations are the best studied so far. Moreover, still several discrepancies on the influence of microwave radiation on the polymerization rates appeared in the literature. Most of the differences seem to be ascribable to the application of different equipment. In several cases rate enhancements were observed when using domestic microwave ovens, whereas the differences were smaller or negligible, respectively, for polymerizations in mono- or single-mode microwave synthesizers. In our opinion, these differences might be due to a nonexact control and measurement of the temperature and inhomogeneous electric fields in a domestic microwave oven. As a result, more detailed studies will be necessary in the future to elucidate the power and potential new effects of microwave heating in the field of CRP.

Furthermore, in the past years a variety of monomers were polymerized under microwave-assisted free radical polymerization conditions, such as St and MMA,[29,30] acrylonitrile,[31] acrylamide,[32] dissopropyl fumarate,[33] *N*-benzenesulfonamide maleimide,[34] 2-ethylhexyl methacrylate,[35] and *N*-acryloyl-L-phenylalanine,[36] as summarized in Table 1 (entries 20−27).

3. RING-OPENING POLYMERIZATIONS

Cyclic monomers are able to undergo a polymerization by a ring-opening mechanism, which is characterized by an initiation step, the ring-opening of the monomer, caused by either ions (cationic and anionic, respectively) or metal catalysts and the subsequent chain-growth of the polymer. Ring-opening polymerization (ROP) technique encompasses a variety of prominent polymer classes, such as poly(lactic acid) (PLLA), poly(caprolactone) (PCL), poly(ethylene glycol) (PEG), and the poly(2-oxazoline)s (POx), which are widely discussed as materials for biomedical research. The ROP was found to benefit significantly from microwave-assisted heating allowing a good control over the polymerizations combined with a tremendous acceleration of the polymerization rates. However, the potential of microwave heating for the ROP, e.g. of CL, was discussed controversial as indicated by reports on thermal as well non-thermal effects.[37,38] These facts motivated researchers to deepen the work in the area of microwave-assisted ROP in recent years. A summary of the microwave-assisted ROP is given in Table 2.

3.1. Microwave-Assisted Polymerization of Lactone, Lactide, Carbonate, and Other Monomers. The usage of ε-caprolactone (CL) and L-lactide (LLA) as monomers for the preparation of diverse (block or graft) copolymers was investigated thoroughly. The enzymatic polymerization of CL under microwave irradiation was described by Kerep and Ritter.[39,40] The polymerization showed a strong dependency on the temperature and polarity of the medium/solvent referred to the activity of the enzyme. While an increase of the polymerization rate was observed for the polymerizations under reflux conditions in diethyl ether, the rates in boiling toluene or benzene decreased. Moreover, in polar solvents, e.g., THF and dioxane, no polymerization occurred. The differences in case of the nonpolar solvents originate in view of the authors from the

Table 2. Microwave-Assisted ROP under Microwave Irradiation[a]

			conditions				
entry	monomer (copolymer)	microwave reactor type	temperature	time	solvent	M_n [kDa], PDI	ref
			ε-Caprolactone (CL)				
01	CL	CEM discover	reflux	90 min	DEE; tol/C_6H_6	3−6, 1.5−2.2	39
02	CL (PS-*b*-PCL)	CEM discover	reflux (const 200 W)	90 min	DEE	5−12.5, 1.4−4.1	40
03	CL; 2-phenyl-5,5-bis(oxymethyl)-TMC (PCL-*co*-PTMC)	CEM discover	fixed power mode (50 W); dynamic mode (180 °C)	15−60 min	tol	14.7−23.3, 1.13−1.26	41
04	CL (PVA-graft-PCL)	Whirlpool-VIP275	various powers (340, 510, 680 W) and temperatures	3 h ([CL]/ [OH] = 8)	bulk	80, 723, 1033	42
05	CL (PCL-*b*-PEG-*b*-PCL)	Emrys Optimizer EXP (Biotage)	140 °C	30 min	bulk	0.193−1.258, 1.04−1.24	43
06	CL, LLA(PCL-*b*-mPEG; PLLA-*b*-mPEG)	Milestone S.r.1 MicroSYNTH	100 °C	5−60 min	bulk	2.1−5.3, 1.1−1.2	44
07	CL (PCL-*b*-PLLA)	CEM discover	120 °C	about 20 min	bulk	23−60, 1.1−1.25	45
			L-Lactide (LLA)				
08	LLA	CEM discover	max 200 W	20−80 min	bulk	5.6−13.6, 0.4−1.5	46
09	LLA (PLLA-*b*-PEG)	CEM discover	100 °C	10−30 min	bulk	7−70, 1.3−1.8	47
10	LLA (PLLA-*b*-PEG-*b*-PLLA)	CEM discover	100 °C	3−30 min	bulk	18−50, 1.3−1.9	48
11	LLA, GA(PLLA-*co*-PGA)	MAS-II	120 °C (300 W)	3−9 min	bulk	43−77, 1.9−2.4	49
			Trimethylene Carbonate (TMC)				
12	TMC	CEM discover	various powers (5, 10, 20, 30 W)	2.5−60 min	bulk	1.4−15.6, 1.06−1.66	50
13	TMC PTMC-*b*-PEG-*b*-PTMC)	CEM discover	80, 100, 120, 140 °C	30 min, 60 min	bulk	3.8−16.6, 0.5−1.6	51
14	TMC	CEM discover	120 °C	30 min	bulk	4.2−75, 1.4−2.3	52
			Diverse Monomers				
15	*p*-dioxanone	MAS-I (Shanghai Sineo)	80, 100 °C	30 min, 60 min	bulk	11−197	53
16	[2.2]paracyclo-phanedienes	CEM discover, CEM explorer	80 °C	60 min	1,2-dichloroethane	11−90, 1.18−1.34	54
17	PO (PEO-*b*-PPO)	Initiator Eight (Biotage)	130−175 °C	20−180 min	bulk; dioxane C_6H_6, tol, CH		55

[a] CL = ε-caprolactone, VA = vinyl alcohol, LLA = L-lactide, TMC = trimethylene carbonate, GA = glycolic acid, CH = cyclohexane, DEE = diethyl ether, tol = toluene, C_6H_6 = benzene.

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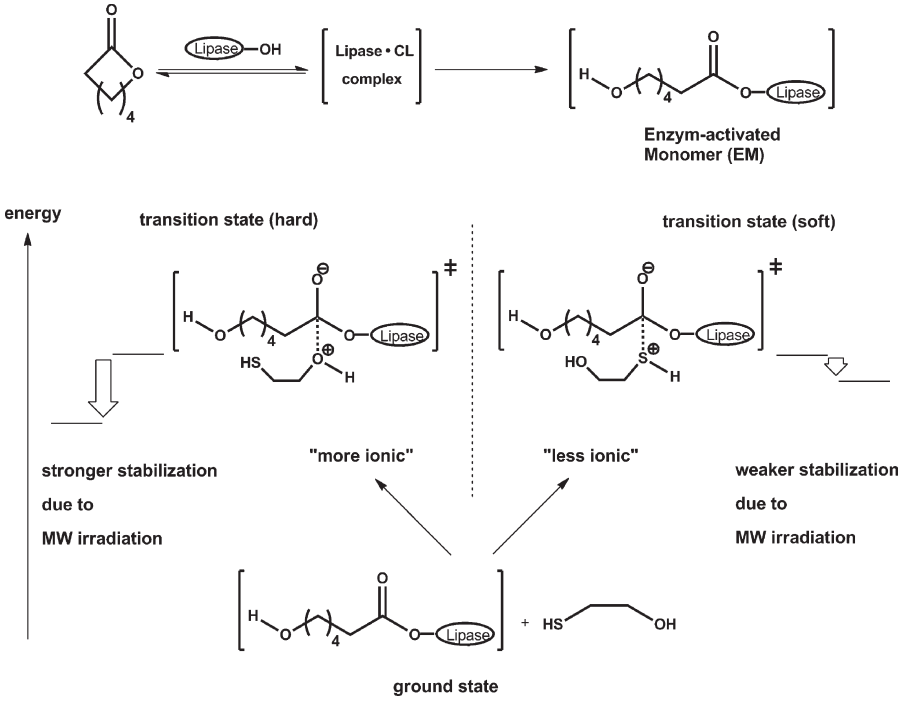
Scheme 1. Schematic Representation of the Potential Stabilization of the Different Transition States of the Enzymatically Catalyzed Ring-Opening Polymerization of ε-Caprolactone Using 2-Mercaptoethanol as Initiator in the Microwave Field [According to Ref 40]



milder conditions (lower polymerization temperature) when using diethyl ether, yielding a better spatial fit between the active center of the enzyme and the ester substrate. The same group reported the polymerization of CL initiated with 2-mercaptoethanol, performed under reflux in diethyl ether for 90 min. The polymer obtained showed a high chemoselectively, as it was concluded from the smaller formation of side products and the higher yields under microwave irradiation. Thus, the terminal SH group could be subsequently used as chain transfer agent for the synthesis of PCL-*b*-PS. The favored formation of the thiol end group of the PCL was ascribed to a "microwave effect" caused by the stronger stabilization of a "more ionic" transition state occurring during the microwave-assisted heating as schematically depicted in Scheme 1.

Lu et al. synthesized a series of copolymers consisting of CL and 2-phenyl-5,5-bis(oxymethyl)trimethylene carbonate (PTC).[41] The polymerizations were performed either using the fixed power mode (50 W) or the dynamic mode (180 °C) in order to study the molar mass dependency from the microwave power, the reaction time, and the temperature. Poly(vinyl alcohol) (PVA) was used as initiator for the preparation of PVA-*graft*-PCL by Yu and Liu.[42] The degree of polymerization (DP) of the PCL side chains as well as the degree of substitution (DS) was controlled by the microwave power applied: the DP and DS increased proportionally by the increase of power. Moreover, an increase in the irradiation time yielded higher DP values and conversions, whereas the DS increased first and subsequently reached a plateau. The higher conversion, DP and DS values with increasing microwave power were explained by the authors with higher temperatures obtained by the higher microwave power. The preparation of PCL-*b*-PEG-PCL triblock copolymers initiated by difunctional PEG was

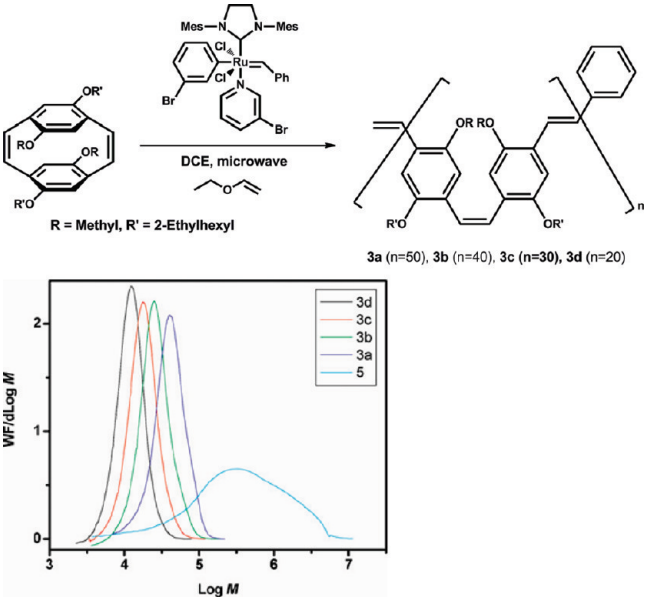


Figure 5. Schematic representation of the synthesis of MEH-PPV by microwave-assisted ROMP (top) and the molar mass distributions obtained (**3a**−**3d**) in comparison to a polymer prepared by the conventional Gilch route (**5**) using Mark−Houwink parameters (bottom) Adapted and reprinted with permission from ref 54. DCE = 1,2-dichlorethane.

reported by Trathnigg and co-workers.[43] In a bulk polymerization at 140 °C two different triblock copolymers with varying ratio PEG/PCL were synthesized by microwave heating exhibiting a higher content of triblock structures than observed in commercial

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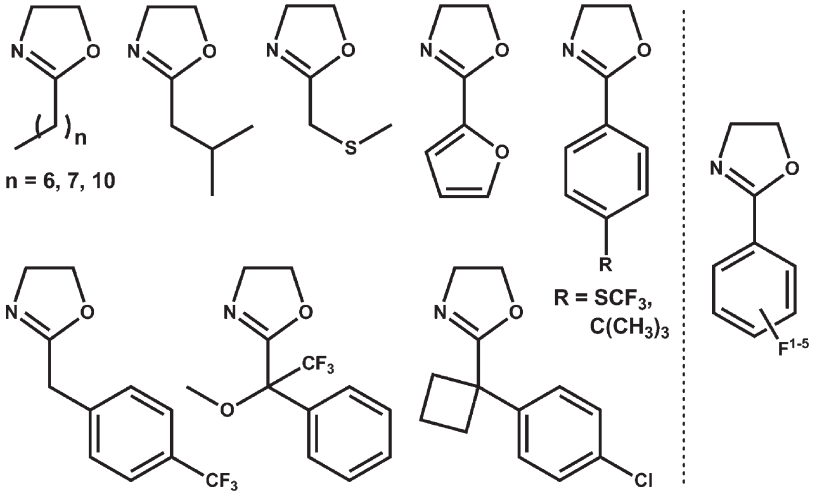
Scheme 2. Schematic Representation of a Set of Diverse Substituted 2-Oxazoline Monomers [According to Ref 70] and a Schematic Structure of Fluorinated 2-Phenyl-2-oxazolines [According to Ref 71] Polymerized under Microwave-Assisted Cationic Ring-Opening Polymerization Conditions



products. Karagoz and Dincer described the synthesis of PCL-*b*-mPEG as well as PLLA-*b*-mPEG under microwave conditions.[44] The authors concluded that these block copolymers can be obtained in a short reaction time with narrow molar mass distribution and similar monomer conversions compared to conventional heating. Starting from dipentaerythritol as initiator, star-shaped PCL-*b*-PLLA copolymers were obtained by Ren and co-workers.[45] Another report by Frediani and co-workers described the usage of cone-25,27-dipropyloxy-26,28-dioxo-calix[4]arene titanium(IV) chloride as catalyst for the ROP of LLA.[46] Even if the polymerization could be accelerated using microwave-assisted heating, the control over the molar mass and PDI values could not be maintained. The synthesis of PLLA-*b*-PEG diblock copolymers and PLLA-*b*-PEG-*b*-PLLA triblock copolymers was reported by Gong and co-workers.[47,48] In both cases the microwave-assisted polymerizations occurred much faster than the ones under conventional heating; no potential explanation was provided by the authors. The copolymerization of LLA with glycolic acid (GA) was described by Xiong and co-workers.[49] Polymerization solutions with different feed ratios of both monomers were prepared and polymerized for 5 min at 120 °C, which was optimized for a 50/50 feed ratio prior to the polymerization of the remaining feed ratios. Gong and co-workers investigated the microwave-assisted (co)polymerization of trimethylene carbonate (TMC).[50,51] Using ethylene glycol and difunctional PEGs as initiators in the absence of a metal catalyst yielded the corresponding homopolymers and ABA triblock copolymers, respectively. The molar masses as well as conversions obtained by microwave-assisted heating were higher than in the case of conventional heating; this observation was not further elucidated. Zhang et al. described the initiation of the microwave-accelerated polymerization of TMC with zinc lactate.[52] They observed a degradation of the polymer after prolonged reaction times and found that anhydrous zinc lactate is more effective for the synthesis of high molar mass polymers.

Furthermore, the microwave-assisted polymerization of *p*-dioxanone was reported by Zhang and co-workers.[53] In the presence of $AlEt_3$ or tin powder as catalyst the polymerization could be accelerated under microwave-assisted heating (no potential explanation was provided). In particular, $AlEt_3$ yielded polymers with a high molar mass and a high conversion in a short time. The ring-opening metathesis polymerization (ROMP) of [2.2]paracyclophane dienes for the synthesis of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) polymers was described by Turner and co-workers.[54] This approach yielded MEH-PPV with controllable polymer length and low PDI values (Figure 5). As an example for the anionic ring-opening polymerization, the polymerization of propylene oxide using deprotonated PEG macroinitiators was studied by Trathnigg and co-workers.[55] The investigation of different parameters, such as monomer concentration, hydroxyl content in the feed, polarity of the medium, and the used temperature, revealed an acceleration of the polymerization up to a factor of 5 compared to conventional heating at similar conditions. The authors attribute this behavior to enormous differences in the heating and cooling profiles. In case of the microwave-assisted heating the polymerization temperature was reached more than 20 times faster than in case of the conventional heating experiment. Furthermore, this approach was expanded by the same group for the synthesis of higher alkylene oxides.[56]

In summary, the biomedical relevance of some of the presented polymers obtained by ROP, such as the biodegradable aliphatic poly(ester)s PGA, PLA, and PCL, is the key factor for the constant search for new biomaterials based on these polymers. As such, the acceleration using microwave-assisted polymerization pocesses allows for the rapid screening and improvement of diverse copolymers and will be therefore under continuous investigation.

3.2. Microwave-Assisted Polymerization of 2-Oxazolines. Another class of cyclic monomers which can undergo a ring-opening polymerization are the 2-oxazolines. Because of the ease in substitution of these five-membered cyclic imino ethers, a variety of functionalized polymers are imaginable. Not only this fact but also the biocompatibility of the poly(2-oxazoline)s,[57] namely of poly(2-methyl-2-oxazoline) (PMeOx) and poly(2-ethyl-2-oxazoline) (PEtOx) and their copolymers, makes them an emerging class of polymers.[58] The properties of the poly(2-oxazoline)s can be fine-tuned by the choice of the substituent, in particular in the 2-position influencing the water solubility and crystallinity as well

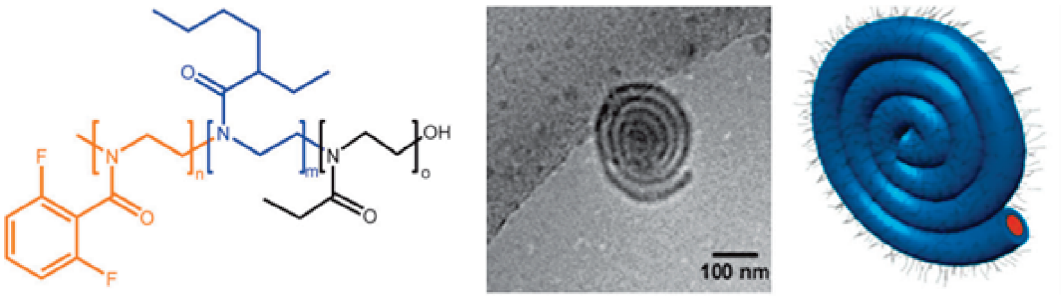


Figure 6. Left: schematic representation of the triblock terpoly(2-oxazoline) consisting of 2-ethyl-2-oxazoline (EtOx), 2-(1-ethylpentyl)-2-oxazoline (EPOx), and 2-(2,6-difluorophenyl)-2-oxazoline (ODFOx). Right: spiral-like micellar aggregate of the triblock copolymer in water, cryo-TEM image as well as schematic representation (EtOx in black, EPOx in blue, and ODFOx in orange). Reprinted with permission from ref 76. Copyright 2010 Royal Society of Chemistry.

as the postmodification ability of the resulting polymer.[59] This gives raise to and opens up plenty of potential applications, another reason why this class of polymers has attracted the interest of a large number of researchers.[60] Until the beginning of the 21st century, the cationic ring-opening polymerization (CROP) of 2-oxazolines was known to suffer from their rather long reaction times (from days to weeks). This drawback was overcome by the introduction of microwave synthesizers into polymer science allowing the synthesis under pressurized conditions. As the group of Schubert and co-workers could elucidate, the CROP of the commercial available 2-oxazolines (MeOx, EtOx, NonOx, and PhOx) could be performed under microwave-assisted heating maintaining the living character of the polymerization. Investigations of the polymerizations with focus on a detailed kinetic study revealed an acceleration of the polymerizations up to a factor of 400 at elevated temperatures.[61−63] The rate enhancements observed were ascribed to solely temperature effects as it was shown that the Arrhenius parameters for both microwave-assisted and conventional heating were in the same range. A similar acceleration in case of the microwave-assisted polymerization of PhOx in open and closed vessels was obtained by Sinnwell and Ritter.[64] Contrary to the studies of Schubert and co-workers, conventional heating experiments in the same temperature range revealed lower polymerization rates. This observation was attributed to nonthermal effects caused by a specific absorption of intermediately formed cationic species during the polymerization. In the following Schubert and co-workers used the power of microwave heating to establish the fast and controlled microwave-assisted synthesis of POx, which resulted in the preparation of di-, tri-, and tetrablock copolymers[65,66] as well as statistical, gradient, and quasi-block copoly(2-oxazoline)s.[67−69]

The knowledge obtained during a detailed screening of commercial available 2-oxazolines was further transferred to the polymerization of more sophisticated monomers (Scheme 2). In the past four years, a variety of new monomers were polymerized benefitting from a combinatorial approach by implementing microwave-assisted reaction conditions. Thus, the synthesis as well as the polymerization of a set of new 2-oxazolines was described by Schubert and co-workers. By means of an automated parallel synthesizer, the ASW 2000 from Chemspeed, the feasibility of preparing novel 2-substituted-2-oxazoline monomers was investigated, and the gained results were validated by performing larger scale syntheses.[72] The subsequent microwave-assisted polymerizations of 2-substituted-2-oxazolines containing thioether bonds, trifluoromethyl groups, and alkyl and aryl groups revealed a living character of the majority of the polymerizations as indicated by linear pseudo-first-order kinetics, a linear increase of molar mass with conversion, and a relatively narrow molar mass distribution.[70] The microwave-assisted polymerization rates obtained for the 2-oxazolines tremendously depended on the actual structure of the 2-oxazoline; i.e., an electron-rich aromatic system in the 2-position accelerated the polymerization, whereas a lower polymerization rate was observed for bulky substituents. Two different initiators were used for the polymerization of 2-((methylthio)-methyl)-2-oxazoline, resulting in a linear relationship in the first-order kinetics using methyl triflate. The obtained PDI values were reasonable but indicative for side reactions due to the nucleophilic character of the thioether group as it was confirmed recently by Grayson and co-workers for the polymerization of diverse thiol ether containing 2-oxazolines.[73] Lobert et al. described the synthesis of a complete set of fluorinated 2-phenyl-2-oxazolines including the fastest polymerizable 2-oxazoline monomer under microwave-assisted conditions up to date.[71,74] The microwave-assisted polymerizations were performed in nitromethane at 140 °C, demonstrating the living character of mono to full fluorine substituted 2-phenyl-2-oxazolines. The enormous acceleration in the polymerization of the 2-(2,6-difluorophenyl)-2-oxazolines (ODFOx) was attributed to an interaction of the cationic reaction center N^+ with the ortho-fluorine substituent and a nonplanarity of the oxazoline ring and the phenyl ring. These findings were subsequently used for the preparation of triblock copolymers consisting of EtOx, a branched alkyl 2-oxazoline, and ODFOx self-assembling in vesicular and aggregated cylindrical micellar structures in aqueous solution (Figure 6).[75,76]

Besides the branched 2-oxazoline used for this synthesis, another one, the 2-(3-ethylheptyl)-2-oxazoline, was prepared revealing the poly(2-oxazoline) with the lowest T_g (−6 °C) up to date.[77] A detailed kinetic study under microwave-assisted conditions was performed including the homopolymerization, the copolymerization with EtOx, and the determination of the reactivity ratios showing the existence of truly random copolymers. As it was demonstrated in all the examples mentioned above, the living character of the CROP of 2-oxazolines was maintained, allowing the systematic end-group functionalization of the resulting polymers by the initiator and/or termination method. Therefore, different initiators were tested for the polymerization of EtOx. In order to prepare clickable poly(2-oxazoline)s, two functional tosylate initiators, namely propargyl and 3-butynyl toluene-4-sulfonate, were employed.[78] The former one was tested as initiator for four different monomers and found to yield well-defined polymers in a living manner under microwave irradiation. The application of a respective PEtOx homopolymer in click reactions was demonstrated

Table 3. Selected Microwave-Assisted Polycondensation Reactions

			conditions				
entry	monomer (copolymer)	microwave reactor type	temperature	time	solvent	M_n [kDa], PDI	ref
01	click condensation dialkyne-ester + diazide alkyne	MWO-1000S EYELA/Japan	0−50 W, 153 °C	15−30 min	DMF	1.3−59.3, 1.4−5.8	97
02	HOAsp- (COOH)-OH	Biotage Initiator	<200 W, 120 °C	20 min	bulk; DMF	1.5−2.1, 1.05−1.18	98
03	lactic acid	CEM discover	30 mmHg/200 °C	30 min	bulk	0.6−4.6, 3.2−3.7	99
04	5-(4-methylthio-2-phthalimidybutanoylamino) isophthalic acid + diamines	domestic microwave oven	630 W (900 W)	3 × 60 s	bulk	n.a, n.a.	100
05	acrylamide	EYELA Wave Magic WMO-1000S	78−130 °C (100 W)	100−180 s	DMF	n.a., n.a.	101

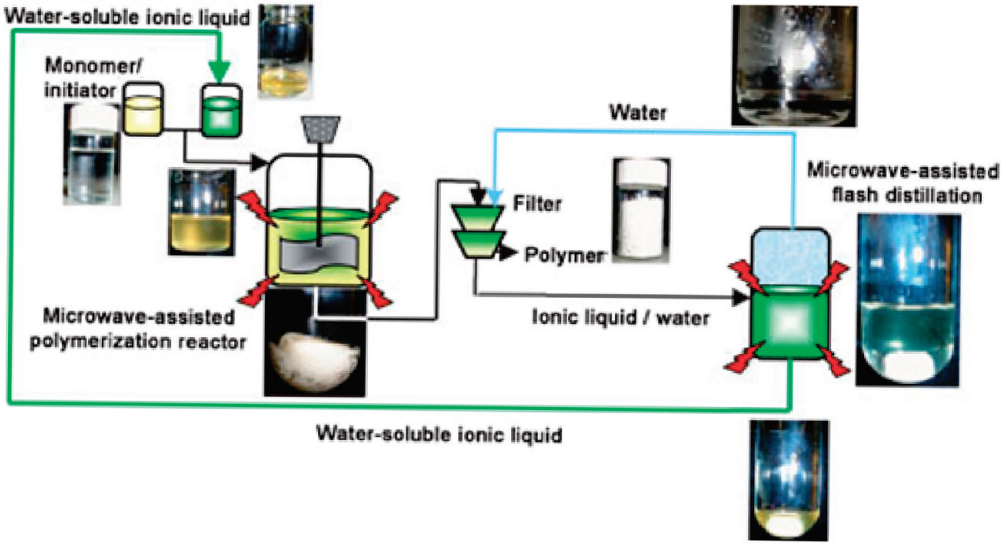


Figure 7. Conceptual green process for the continuous microwave-assisted synthesis of hydrophobic polymers in water-soluble ILs which allows for the depletion of emissions of volatile organic compounds into the environment. Reprinted with permission from ref 104. Copyright 2007 Wiley-VCH.

using 9-azidomethylanthracene, benzyl 2-azidoethyl ether, and a heptakis-azido-β-dextrin for the preparation of star polymers. Besides triflates and tosylates, acetyl halids are suitable initiators for the CROP of 2-oxazolines. Kinetic studies of acetyl chloride, acetyl bromide, and acetyl iodide in a microwave oven revealed living polymerizations with low PDI values in a temperature range from 80 to 220 °C.[79] The polymerization rate was influenced by the basicity of the halides, leading to the lowest rate for the acetyl chloride and the highest for the acetyl iodide. Based on these results, a dual initiator which exhibits two reaction sites, an acetyl bromide as initiator for the CROP and a tertiary bromide function as an initiator for the CRP, was investigated, resulting in the formation of well-defined PS-*b*-PEtOx block copolymers.[80] After the evaluation of the initiator to be used for the CROP of EtOx a macroinitiator was prepared and used for the synthesis of the corresponding block copolymers with styrene. In addition, the living character that is confirmed under microwave irradiation allowed the direct termination of the cationic reaction center with diverse nucleophils, such as water, amines, and carboxylic acids. Thus, this fact offers another route to functional poly(2-oxazoline)s, as it was shown for the synthesis of PEtOxMA macromonomers[81−83] as well as labeled copolymers.[84] In the latter publication by Schubert and co-workers, the homopolymerization of 2-dec(-9-enyl)-2-oxazoline (DecEnOx) as well as the copolymerization of EtOx and DecEnOx in a single-mode microwave oven is described. The living manner of the (co)polymerization enabled the defined synthesis of labeled copolymers which were used for the preparation of functional nanoparticles[84] as well as glycopolymers, which were obtained by postpolymerization modifications via thiol−ene photoaddition reactions.[85,86] The same system was investigated in view of its application in bulk (co)polymerizations.[87] Linear first-order kinetics and a linear increase of the molar mass with conversion proved the living character of the homopolymerization of DecEnOx under bulk conditions. Furthermore, copolymers with EtOx in bulk were obtained with low PDI values, and thiol−ene reactions in green solvents could be performed. Similar to DecEnOx, the "soy-based" 2-oxazoline monomer SoyOx can be regarded as a natural feedstock monomer.[88] Both monomers were polymerized in bulk, yielding polymers with terminal and internal double bonds in the side chain, respectively.[89,90] Thus, the corresponding polymers can be postmodified either by thiol photoaddition or by cross-linking reactions.[91] 2-Oxazolines can be substituted not only in the 2-position but also in 4- and/or 5-position. The polymerization of enantiopure 4-/5-substituted-2-oxazolines yield chiral main-chain poly(2-oxazoline)s. Recently, the microwave-assisted polymerization of (*R*-2-butyl-4-ethyl)-2-oxazoline

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as well as (*S*-2-butyl-4-ethyl)-2-oxazoline and their self-assembly behavior was described in detail.[92−95]

Because of the straightforward tuning of the materials properties in conjunction with their biocompatibility, this class of polymers attracted attention ever since its discovery. The establishment of microwave irradiation as optimal heating source further increased the interest of a large number of researchers owing to the reduction of polymerization time from hours or days to several minutes. With regard to the enormous potential of these polymers for a wide range of applications, microwave-assisted polymerization will represent an essential tool to further broaden the scope of this polymer class in the future.

4. STEP-GROWTH POLYMERIZATIONS

Polymers such as polyamides, polyimides, polyesters, polyureas, polyethers, poly(amide imide)s, and their derivatives have a great importance as commercial products. On the basis of this economic importance, it is highly interesting to optimize or improve their polymerization conditions. For this purpose, several researchers investigated step-growth polymerization using microwave-assisted techniques. Application of microwave-assisted reactions in step-growth polymerizations have recently been reviewed in detail by Mallakpour and Rafiee.[96] Here, we will discuss a few representative examples in this field as listed in Table 3.

Takasu et al. have described the Cu(I)-catalyzed click condensation reaction of diynes and diazides to produce polyesters of relative high molar mass (10 000−70 000 g/mol).[97] Organic azides and inorganic azides are known to be explosive materials under pressure or shock. Therefore, the authors produced the diazides of short alkyne chains (C4−C7) *in situ* and reacted them under microwave irradiation to accelerate the polymerization. Triazole-containing polyesters were prepared in DMF at relatively short reaction times (15−30 min). This safe and efficient procedure might also be applicable in industry. Kolitz et al. reported the preparation of biodegradable polyesters that are derived from amino acids using a straightforward, reliable, and inexpensive chemical method of diazotization.[98] In their comparison of conventional and microwave-assisted polymerizations, the authors were able to synthesize polymers with higher molar mass (3300−3800 g/mol) using microwave irradiation. The reactions were performed using a Biotage microwave synthesizer in DMF or neat (120 °C, for 20 min). Takeuchi et al. reported a facile method for the synthesis of poly(lactic acid) with a molar mass higher than 10 000 g/mol.[99] The authors investigated the effect of various catalysts and obtained the best results using a binary catalyst system of $SnCl_2$/*p*-TsOH. The reactions were performed at 200 °C for 30 min under reduced pressure (30 mmHg). The obtained polymers showed enough strength to produce pellets and films that can be applied as a raw material of biodegradable plastics. Mallakpour et al. prepared an optically active diacid containing phthalimide and L-methionine moieties for polymerization with several aromatic diamines.[100] The authors compared the conventional heating versus microwave-assisted heating; a drastic decrease in the reaction time from 5 h to 3 min under microwave-assisted heating could be observed. It should be noted that overirradiation caused degradation of the products which caused a decrease in the viscosity.

Iwamura et al. reported an efficient anionic polymerization of acrylamide and hydrolysis of the obtained polymers by microwave irradiation.[101] The authors have used the acrylamide monomer for polymerization assuming that it will have a very high dielectric constant because polar solvents such as 1-methyl-2-pyrrolidone (ε = 32.3), dimethyl sulfoxide (ε = 46.7), and *N*,*N*-dimethylformamide (ε = 36.7) have relatively high dielectric constants. They have performed the anionic polymerization in DMF (30 mL), using acrylamide (73.3 mmol), a radical inhibitor, and potassium *tert*-butoxide as an initiator. The reaction was irradiated for 100−180 s using 100 W microwave power. The obtained polymer was purified by a Soxhlet extractor for 48 h in boiling acetone. The reaction time was shortened by 1/30 using microwave irradiation in comparison to conventional heating. Furthermore, the hydrolysis of poly(β-alanine) was performed under both acidic and basic conditions. Under basic conditions, there was no difference in the hydrolysis rate between microwave and conventional heating. However, microwave-irradiated reactions were much more efficient under acidic reaction conditions.

It should be noted that step-growth reactions generally require higher temperatures and longer reaction times to reach high conversions under conventional heating conditions. Therefore, in several cases a significant acceleration in the reaction rate has been reported when a polar solvent or monomer was used.

5. MICROWAVE-ASSISTED POLYMERIZATIONS IN IONIC LIQUIDS

Ionic liquids (ILs) attracted a lot of attention as alternative solvents in organic reactions in recent years. Because of their ionic character and the associated exceptional heating efficiency, they emerged to be perfectly suited for microwave-assisted reactions.[102] Furthermore, the excellent solubility behavior and the existence of hydrophilic as well as hydrophobic ILs enable the systematic usage for respective applications even in polymer science. Thus, for instance, more hydrophobic ILs can be used for polymerizations of water-soluble polymers, allowing the simple isolation of the polymer and the recovery of the IL after the polymerization. This approach was used by Schubert and co-workers for the CROP of EtOx.[103] Microwave-assisted polymerizations were performed at different temperatures and ILs, ranging from hydrophilic to hydrophobic. Linear pseudo-first-order kinetics, a linear increase of the molar mass with conversion, and additional chain-extension experiments proved the living character in pure ILs as well as in a mixtures of IL and acetonitrile (50/50 wt%). By means of extensive kinetic investigations the acceleration of the CROP of EtOx in both, in IL and the mixture with acetonitrile, was revealed as demonstrated by higher k_p values and lower activation energies for the microwave-assisted polymerizations in ILs. This study mainly focused on a hydrophobic IL composed of $[PF_6]^-$ anions, allowing the ease of isolation of the polymer product after finalizing the polymerization just by washing with water, due to the better solubility of the polymer in the water phase. The same strategy but vice versa was applied for the FRP of MMA and the CROP of PhOx and F_2Ox in water-soluble ILs.[104] Homogeneous polymerizations were performed due to the solubility of all the monomers and even of the majority of the polymers in this ILs. Furthermore, a "green" process for the continuous microwave-assisted synthesis of hydrophobic polymers in water-soluble ILs is described which includes the polymerization of the monomers, the recovery of the IL, its flash distillation, and its reusage in the polymerization process, as depicted in Figure 7. Schmidt-Naake and co-workers investigated the FRP of MMA and St as well as the copolymerization of styrene/acrylonitrile and MMA/NPI in

Table 4. Microwave-Assisted Polymerizations Using Ionic Liquids (ILs) as Solvent[a]

			conditions				
entry	monomer (copolymer)	microwave reactor type	temperature	time	ionic liquid	M_n [kDa], PDI	ref
01	EtOx	Biotage Emrys Liberator	different temperatures	different times	[EMIM]Tos; trihexyl(tetradecyl)phosphonium chloride; [BMIM]BF_4; [BMIM]CF_3SO_3; [BMIM]PF_6	1.0−6.0, 1.1−1.3	103
02	MMA, PhOx, F_2Ox	Biotage Emrys Liberator	100 °C (MMA), 140 °C (PhOx, F_2Ox)	20 min (MMA), 10−30 min (PhOx, F_2Ox)	[BMIM]CF_3SO_3; [BMIM]BF_4	2.5−26.4, 1.1−3.8	104
03	MMA, St, acrylonitrile	microPREP 1500 (MLS GmbH)	60 °C (AIBN); 80 °C (BPO)	0−90 min (60 °C); 0−50 min (80 °C)	[EMIM]$EtSO_4$, [BMIM]BF_4; (DMF, MeOH)	5.0−30.0, n.a.	105
04	CL	domestic MW oven	different power levels	30 min	[BMIM]BF_4	2.3−11.1, 1.3−2.5	106
05	TMC	CEM discover	5 W	10−60 min	[BMIM]BF_4	1.1−36.4, 1.1−1.8	107
06	3-methyl-2-(1,8-naphthalimidyl)butanoic acid; diverse diisocyanates	domestic MW oven	different power levels (900 W; 70−100%)	30−180 s	various symmetrical ILs	n.a., n.a.	108
07	*N*,*N*′-(4,4′-hexafluoroisopropylidenediphthaloyl)-bis-L-methionine; diverse diamines	domestic MW oven	different power levels (900 W; 60−100%)	20−60 s; (50 + 30) s	various symmetrical ILs	n.a., n.a.	109
08	5-(3-methyl-2-phthalimidylpentanoylamino) isophthalic acid; diverse diisocyanates	domestic MW oven	900 W	3 min + 1 min	tetrabutylammonium bromide	n.a., n.a.	110
09	5-(4-methyl-2-phthalimidylpentanoylamino) isophthalic acid; diverse diisocyanates	domestic MW oven	900 W	3 min	tetrabutylammonium bromide	n.a., n.a.	111
10	5-(4-methylthio-2-phthalimidy-butanoylamino)-isophthalic acid; diverse diamines	domestic MW oven	630 W	4 × 30 s	[1,3-(pr)$_2$IM]Br	n.a., n.a.	112
11	(2*S*)-4-[(4-methyl-2-phthalimidylpentanoylamino)-benzoylamino] isophthalic acid; diverse diamines	domestic MW oven	630 W	60 s	various symmetrical ILs	n.a., n.a.	113
12	4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione; diverse diisocyanates	domestic MW oven	different power levels (900 W; 60−100%)	60 s + 30 s + 30 s	various symmetrical ILs; tetrabutylammonium bromide	n.a., n.a.	114

[a] IL = ionic liquid, EtOx = 2-ethyl-2-oxazoline; MMA = methyl methacrylate, PhOx = 2-phenyl-2-oxazoline, F_2Ox = 2-(*m*-difluorophenyl)-2-oxazoline, St = styrene, CL = ε-caprolactone, TMC = trimethylene carbonate.

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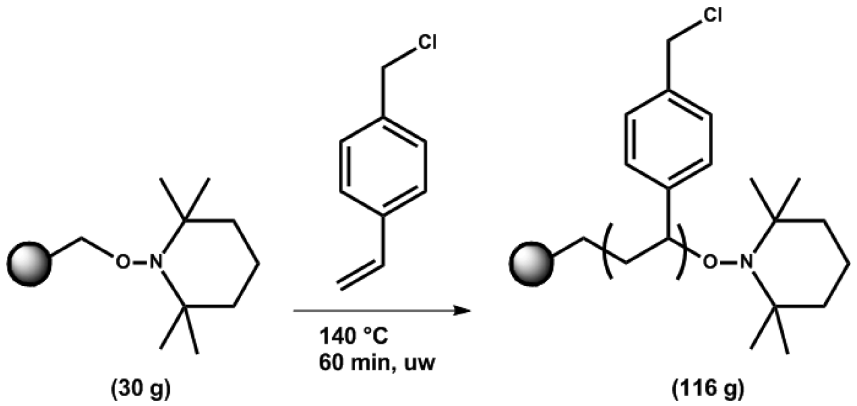
Table 5. Summary of Large Batch Microwave-Assisted Polymerizations as Well as Continuous Flow Reactions[a]

			conditions				
entry	monomer (copolymer)	microwave reactor type	temperature	time	solvent	M_n [kDa], PDI	ref
01	NiPAm		90 °C	max 60 min	1,4-dioxane	13.4−21.5, 1.1−1.3	116
02	EtOx	CEM voyager; Milestone FlowSYNTH	140 °C	1000 s	acetonitrile	6.2−8.8, 1.1−1.5	117
03	EtOx	CEM discover; Biotage Advancer	140 °C	900 s; 1000 s	acetonitrile	9.2−9.7, 1.1	118
04	St	Biotage Advancer	160 °C	30 min (5−15 min)	NMP	n.a., n.a.	119
05	St	Synthos 300 (Anton Paar), Emrys Liberator (Biotage)	150−280 °C (water), 150 °C (ethanol)	10 min (water), 1 h (EtOH)	water, ethanol	6−46, 1.3−1.9	120
06	lactic acid	SMW-087, SMW-101, SMW-114 (Shikoku Instrumen-tation)	different temperature programs	different times	bulk	3.6−18.3, 1.7−2.1	121

[a] NiPAm = *N*-isopropylacrylamide, EtOx = 2-ethyl-2-oxazoline, St = styrene, NMP = *N*-methylpyrrolidone.

Scheme 3. Large-Scale Run of the Microwave-Assisted Free Radical Polymerization of Functionalized Styrenyl Monomers on High-Loading TEMPO-Methyl Resin (Rasta Resin) [Adapted from Ref 119]



view of their acceleration under microwave irradiation compared to conventional heating.[105] While the polymerization rates for MMA and St/AN in IL were higher under microwave irradiation, similar rate values were determined for St and MMA/NPI. The authors ascribed these findings to a disturbance of the polar interactions between the IL and the monomer molecules and polymer radicals, respectively.

Another report by Gong and co-workers describe the microwave-assisted ROP of CL in IL.[106] Prior to the polymerizations with ZnO as initiator, the heating characteristics of CL in the presence of the IL was studied for precaution reasons: power levels of 170 and 225 W; using 10−20 wt % IL led to the formation of polymers within 30 min at temperatures higher than 200 °C. Without the IL no polymer was obtained, which was observed even in the presence of ZnO at 85 W. An increase of the IL weight percentage yielded PCL with molar masses in the range of 14 800−28 500 g mol^{-1} and PDI values from 1.6 to 2.4 in the same time frame. The microwave-assisted ROP of TMC in the presence of ILs was described by the same group.[107] An improvement of the polymerization in view of conversion and molar mass was observed in contrast to bulk microwave reactions and oil bath reactions as well; however, no potential explanation for this observation was provided by the authors. The addition of 5 wt % IL showed increasing values over the complete time range, whereas ≥ 10 wt% IL resulted in an acceleration of the polymerization combined with higher molar masses up to 20 min followed by a decrease of the molar mass owing to a degradation of the polymer due to the high temperatures caused by the high amount of IL. Furthermore, IL found also access to polycondensation and polyaddition reactions as demonstrated by Mallakpour and co-workers in several publications describing the synthesis of a variety of optically active polyamides[108−113] and poly(urea−urethane)s (Table 4, entries 06−12).[114]

To date, the superiority of ionic liquids as ideal solvents under microwave conditions has been exploited only by a limited number of researchers. The ongoing synthesis of new ionic liquids and their exploration as alternative ("green") solvent for materials that are insoluble in other organic solvents will certainly further increase their applications in microwave-assisted polymerizations.

6. UPSCALING OF MICROWAVE-ASSISTED POLYMERIZATIONS: BATCH AND CONTINUOUS FLOW MODE

Even if microwave-assisted reactions offer a lot of advantages over conventional heating, their use for upscaling reactions and,

thus, for industrial applications is rather limited. The problem which arises from larger batch reactions is the insufficient penetration depth of the microwaves causing rather a heating by convection than by direct dielectric heating. Depending on the dielectric properties of the medium, the penetration depth is just in the order of a few centimeters (operating frequency: 2.45 GHz). An alternative approach to overcome this issue uses continuous flow (CF) processes.[115] However, both the batch (BM) and the CF mode have been used recently to study the ability of polymerizations to be scaled up as summarized in Table 5. In view of CF external heating can be applied either by a heated oil bath or microwave irradiation. The former was demonstrated very recently by Seeberger and co-workers, who reported on accelerated RAFT polymerization of NiPAm under continuous flow conditions.[116] Kinetics obtained in the CF mode under conventional heating were similar to the ones determined by microwave heating while the controlled character of the polymerization could be maintained. In contrast, Schubert et al. described the combination of CF with microwave irradiation using CF microwave synthesizer.[117] Depending on the type of reactor, namely tube, Teflon coil, glass coil, and continuous stirred tank reactor (CSTR), poly(2-ethyl-2-oxazoline)s with rather broad molar mass distributions were obtained. Polymerizations performed in the coils yielded monomodal molar mass distributions with sharp peak maxima, whereas broad maxima were achieved with the Teflon reactor and the CSTR. These findings were traced back to the different flow profiles in the different types of reactors. Furthermore, the scaling of the CROP of EtOx using the batch mode was reported by the same group.[118] In a comparative study the polymerization was investigated in view of the molar mass and polydispersity of the resulting polymers in microwave synthesizers with different reaction volumes ranging from 1 to 250 mL. Even if different heating profiles were observed, the polymers obtained were highly comparable and well-defined. Thus, the living character of the CROP of EtOx was maintained even at higher reaction volumes. Pawluczyl and co-workers investigated the influence of large batch polymerizations on the free radical polymerization of styrene using high-loading TEMPO-methyl resins (Scheme 3).[119] After an optimization step, large batches (100 g scale) with loading levels higher than 3.8 mmol g^{-1} and diameters of more than 375 μm could be obtained.

Another free radical polymerization approach dealing with the autopolymerization of styrene was reported by Schubert and co-workers.[120] This intermediate scale polymerizations with about 30 mL reaction volume represents a combination of the advantages of the thermally initiated FRP of styrene with a precipitation polymerization. The polymerizations were performed at 250−350 °C in near-critical water, yielding PS with similar molar masses even if different styrene concentrations were applied. Thus, it was concluded that the monomer as well the polymer was not soluble in water even not at high temperature. More recently, the large-scale polycondensation of lactic acid in batch mode was investigated by Takeuchi and co-workers.[121] Polymerizations up to 20 L were performed within 5 h, yielding poly(lactic acid)s with molar masses about 10 000 g mol^{-1}. The authors demonstrated that the total incident microwave power necessary per mole can be decreased using the large batch reactors making this mode environmentally friendly in terms of power savings.

The scalability and, thus, the industrial applicability of microwave-assisted polymerizations and reactions in general is one of the main critical issues in this research field. However, due to the numerous advantages of this heating source, we believe that microwave ovens will become an essential tool in every polymer research laboratory. Recently, the first commercial plant using microwave heating has been opened by the National Institute of Advanced Industrial Science and Technology of Japan (AIST). It is noteworthy that in particular in view of energy efficiency the production in kilogram or ton scale is more promising, which could be an argument for the upscaling to production quantities in the future.

7. CONCLUSION

Microwave-assisted reactions have become an exciting and vibrant field for researchers since the mid-1980s. The first reactions utilized domestic microwaves under poorly controlled conditions. Although this is not a critical problem for free radical polymerizations or polycondensation reactions, it is very important to accurately control the temperature, pressure, and atmospheric conditions for more advanced synthesis techniques. Controlled radical polymerizations require an oxygen free atmosphere, whereas ionic polymerizations require water free media. These requirements can easily be met using modern microwave synthesizers. There are several leading companies that provide microwave synthesizer platforms with extra functionalities. For instance, continuous flow systems that can perform at relatively high viscosities and temperatures, automated pipetting systems to prepare the reactors in a parallel manner, or systems equipped with cameras that allows the visual monitoring of the reaction are only a few examples that allows researchers to accelerate their research and to collect more information regarding their experiments.

Very clearly and as different from conventional heating microwave irradiation provides a homogeneous heating profile for the reaction. This may be an important parameter in particular for living polymerization techniques that provides polymers with narrow molar mass distributions. Depending on the polarity of the solvent or monomer and the type of catalyst used in some reactions differences in the reaction rates may be created. Furthermore, the acceleration of a variety of microwave-assisted polymerizations was attributed to the higher temperatures applied and superheating conditions under pressurized conditions, which allow for the increase of the polymerization temperatures above their actual boiling points, respectively. As it is demonstrated in this Perspective, the effect of microwave radiation as acceleration source for polymerizations is still controversially discussed as it has been shown by numerous divisive studies as well as reports which do not provide any explanation to the observed or speculated acceleration. Therefore, extensive research is still ongoing using microwave irradiation in organic reactions and polymerizations. In particular, the usage of ionic liquids as perfect "microwave solvents" has opened up a new research area among microwave-assisted polymerizations. Furthermore, the knowledge obtained and collected over the past years for small-scale polymerizations could be transferred to a more industrially suitable scale as demonstrated by first dedicated reports. We believe the interest of using microwave synthesizers for polymerizations will grow further due to their advantages highlighted in this Perspective.

AUTHOR INFORMATION

Corresponding Author
*Fax +49 3641 948 202; e-mail ulrich.schubert@uni-jena.de (U.S.S.), c.r.becer@warwick.ac.uk (C.R.B.).

BIOGRAPHIES

Kristian Kempe was born in 1983 in Borna (Germany) and studied chemistry at the Friedrich-Schiller-University Jena (Germany) and the Eindhoven University of Technology (The Netherlands). In 2007, he obtained his MSc degree in Chemistry. Since 2007, he is performing his PhD studies in Jena under the supervision of Prof. Ulrich S. Schubert. In 2010, he spent 5 months at the University of California, Santa Barbara (UCSB), where he worked under the supervision of Prof. Craig J. Hawker. His research focuses on the combination of the microwave-assisted preparation of novel (co)poly-(2-oxazoline)s and their postmodification using efficient ("click") reactions.

C. Remzi Becer has received his BSc degree in 2003 at the Chemistry Department of the Istanbul Technical University (ITU). In 2005, he received his MSc degree in Polymer Science and Technology at the ITU. He completed his PhD study titled as "Controlling Polymer Architectures" in 2009 under the supervision of Prof. Ulrich S. Schubert at the Eindhoven University of Technology (Netherlands) and the Friedrich-Schiller-University Jena (Germany). Since late 2009, he has been a Marie Curie Research Fellow in the group of Prof. David M. Haddleton in the University of Warwick (United Kingdom). Recently, he received a Science City Interdisciplinary Research Fellowship to conduct research in the area of magnetic nanomedicines at the University of Warwick.

Ulrich S. Schubert was born in Tübingen (Germany) in 1969. He studied chemistry in Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His PhD studies were performed at the Universities of Bayreuth and South Florida/Tampa. After postdoctoral training with J.-M. Lehn at the University in Strasbourg (France), he moved to the TU München (Germany) and obtained his Habilitation in 1999. In 1999−2000 he was Professor at the Center for NanoScience, University of Munich (Germany), and in 2000−2007 he was Full-Professor at TU Eindhoven. Currently he holds a chair at the Friedrich-Schiller-University Jena (Germany). His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG, the Dozenten-Stipendium of the Fonds der Chemischen Industrie, the VICI award of the NWO, the Piet-Lemstra innovation award of the DPI and the BPG biannual international award.

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