

Recent developments in microwave-assisted polymerization with a focus on ring-opening polymerization

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Due to its advantages of direct heating, high temperature homogeneity, reaction rate enhancement, as well as energy savings, microwave-assisted polymerization has become a fast-growing field of polymer research. This paper reviews microwave-assisted polymerization, with an emphasis on the microwave-assisted ring-opening polymerization, covering both homopolymerization and copolymerization of the cyclic monomers. The advantages of microwave-assisted ring-opening polymerization over conventional polymerization are discussed briefly.

Introduction

Microwaves are electromagnetic radiation with frequencies between 300 GHz and 300 MHz (with a wavelength in the range of 1 mm to 1 m). Most commercial microwave ovens produce a microwave wavelength of 12.25 cm, which corresponds to a frequency of 2.45 GHz. Microwaves have been used widely in heating materials for industrial and domestic purposes. As an environmentally benign process, microwave irradiation offers several advantages over conventional heating, such as instantaneous and rapid bulk heating, direct heating, high temperature homogeneity, selective heating (with material that can strongly absorb microwaves in a less polar reaction medium) and energy savings. Over the last decade, microwave irradiation has developed into a highly useful technique and provides an effective alternative energy source for chemical reactions and processes.¹

The unique advantages of microwave-assisted chemistry have triggered an almost exponential increase of publications.² Many chemical reactions undergo an increase/improvement in reaction rate, yield and selectivity under microwave irradiation compared with conventional heating. Microwave irradiation has also been widely used in polymerizations (including polycondensation, free and controlled radical polymerization and ring-opening polymerization) and polymer processing (e.g., polymer modification, curing processes and preparation of dental materials).²

Several review papers² have been published recently on microwave-assisted polymer synthesis and processing; thus, this paper focuses on the new developments in microwave-assisted ring-opening polymerization in recent years. Other types of polymerization, such as step-growth polymerization and free radical polymerization, are briefly discussed.

1. Step-growth polymerization

Extensive research has been conducted in the field of microwave-assisted step-growth polymerization, including

microwave-assisted synthesis of various polyamides, polyimides, poly(amide-imide)s, polyesters and poly(ether-ester)s by means of polycondensation and polyaddition.

Zoldakova and co-workers³ studied microwave-assisted thermal polycondensation of aspartic acid in propylene carbonate solvent. Polysuccinimide, the polycondensation product, was hydrolyzed to obtain linear poly(aspartic acid). A polymeric biocomposite also was synthesized under microwave irradiation by copolymerization of the poly(aspartic acid) with 4-*O*-glucuronoxylan or carboxymethyl-cellulose (CM-cellulose).

Using a mono-mode microwave oven, Loupy and coworkers⁴ synthesized new aromatic polyamides by the microwave-assisted polycondensation of an optically active isosorbide-derived diamine with different diacyl chlorides in the presence of a small amount of *N*-methylpyrrolidinone. Polymers with inherent viscosities between 0.22 and 0.73 dL g⁻¹ were obtained, corresponding to a molecular molar mass (MW) of up to 140 000 g mol⁻¹. Lower MW polymers were obtained with inherent viscosities in the range of 0.04–0.36 dL g⁻¹ by means of interfacial polymerization or the Higashi method. Differential scanning calorimetry measurements clearly demonstrated that polymers with high thermal stability (mp 180–300 °C) were synthesized.

Polyimides have excellent mechanical and heat/chemical resistant properties. Imai *et al.*⁵ studied the solution polycondensation of aliphatic diamines with pyromellitic acid or its diethyl ester in a domestic microwave oven, using various solvents with high boiling points and high dielectric constants. A small amount of polar solvent, such as 1,3-dimethyl-2-imidazolidone, was found to enhance the absorption of microwave irradiation. Recently, Lu *et al.*⁶ investigated the synthesis of polyimide with a p- π conjugated main chain by polycondensation of benzoguanamine (BGA) and pyromellitic dianhydride (PMDA) in a domestic microwave oven. After the polycondensation, the resulting BGA-PMDA polyimide was coordinated with Eu³⁺ in the solid state under microwave irradiation. The effects of microwave irradiation at different power levels and irradiation time were studied.

Mallakpour and co-workers⁷ have synthesized numerous poly(amide-imide)s from various amino acid derivatives and

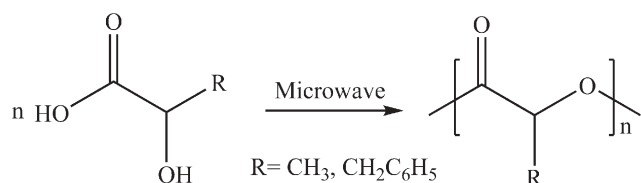
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aromatic diamines in a domestic microwave oven. One of the most interesting works by Mallakpour and co-workers is the combined application of microwave irradiation and ionic liquids in the synthesis of poly(amide-imide)s. Ionic liquids, which are comprised entirely of ions, are non-volatile and non-flammable organic salts. They can be heated rapidly at rates exceeding $10\text{ }^{\circ}\text{C s}^{-1}$ under microwave irradiation by an ionic conduction mechanism. A small amount of ionic liquid has been proved to have a dramatic effect on the heating characteristics of solvents under microwave irradiation. Mallakpour and co-workers reported the microwave-assisted polycondensation of *N,N'*-(4,4'-hexafluoroisopropylidene-diphthaloyl)-bis-L-methionine and various aromatic diamines using 1,3-substituted imidazolium bromide/chloride ionic liquids as a solvent and a catalyst in conjunction with triphenylphosphite. Poly(amide-imide)s with high MWs were synthesized rapidly using this microwave-assisted polycondensation method in the presence of ionic liquids.

Faghihi *et al.*⁸ studied the polycondensation of *N,N'*-(3,3'-diphenylphenylphosphine oxide)-bistrimellitide diacid chloride with hydantoin derivatives or aromatic diamines in a domestic microwave oven. New types of flame-retardant poly(amide-imide)s with high inherent viscosities were synthesized. Compared with the solution polycondensation method under conventional heating, the microwave-assisted polycondensations proceeded rapidly and were completed in approximately 7–12 min.

In contrast with polyamides and polyimides, fewer reports can be found on the microwave-assisted synthesis of polyesters by means of step-growth polymerization. Zsuga *et al.*⁹ studied the polycondensation of D,L-lactic acid in a domestic microwave oven (Scheme 1), and oligomers with number-average molecular molar masses (M_n) ranging from 500 to 2000 g mol^{-1} and yields ranging from 63.2% to 96.2% were prepared in 30 min. In comparison with the reactions conducted in an oil bath at similar conditions, microwave irradiation facilitated the polycondensation of D,L-lactic acid. Interestingly, prolonged microwave irradiation could lead to the formation of cyclic oligomers, which were confirmed by matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS).

The polycondensation of L-2-hydroxy-3-phenyl-propanoic acid, one aromatic group substituted L-lactic acid, was studied under atmospheric pressure by Liu and co-workers¹⁰ using a domestic microwave oven (Scheme 1). Under microwave irradiation power ranging from 340 to 510 W, poly(L-2-hydroxy-3-phenyl-propanoic acid)s were synthesized with weight-average molecular molar masses (M_w) ranging from 1800 to 5300 g mol^{-1} and yields ranging from 9% to 22% in



Scheme 1 Microwave-assisted synthesis of poly(α -hydroxylalkanoate)s by polycondensation

2.5 h; however, it took up to 96 h to obtain similar results using the conventional melting polycondensation method.

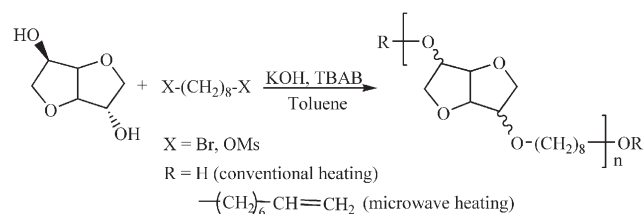
Hurduc *et al.*¹¹ investigated the microwave-assisted synthesis of polyethers. Polyethers were synthesized by polycondensation of 3,3-bis(chloromethyl)oxetane and various bisphenol derivatives, catalyzed by tetrabutylammonium bromide (a phase transfer catalyst), under 60 W microwave irradiation (frequency 2.75 GHz) in a microwave generator. The authors found that microwave irradiation did not have a significant influence on the MW and structure of the polymers except for the shortened reaction time.

Loupy and co-workers¹² recently reported the synthesis of polyesters and poly(ether-ester)s from isosorbide. Polycondensations of aliphatic diols of isosorbide and 1,8-dimesyloctane or other aliphatic dibromo and disulfonated alkylating agents were performed under phase-transfer catalytic conditions in a mono-mode microwave oven (Scheme 2). Reactions were comparatively performed in an oil bath under similar conditions to check the non-thermal microwave effects. The resulting polyethers were characterized by MALDI-TOF MS, and it was found that polymers synthesized under microwave heating had higher MWs and were terminated with ethylenic end groups, while polymers synthesized under conventional heating had lower MWs and were terminated with hydroxyl groups.

2. Radical polymerization

Recent progress in microwave-assisted free radical polymerization, including the classical free radical polymerizations, (mini)emulsion polymerizations, and controlled free radical polymerizations are summarized in this section.

Greiner *et al.*¹³ reported the radical homopolymerizations of styrene (St) and its copolymerizations with methyl methacrylate (MMA) in a CEM Discover mono-mode microwave oven, as well as in a conventional oil bath. The reactions were performed in solvents such as toluene and *N,N'*-dimethylformamide (DMF) using tert-butyl perbenzoate (tBPB), dibenzoyl peroxide (DBPO), di-tert-peroxide (DtBP), dicumylperoxide (DCP), and lauryl peroxide (LP) as the initiators. Compared with the conventional heating, only the homopolymerization of St under microwave irradiation in DMF with DtBP showed significantly enhanced St conversion, whereas other initiators resulted in no increase or only a slight increase of St conversion under microwave irradiation. Since DMF has higher microwave energy absorption than toluene, both the microwave-assisted homopolymerizations and copolymerizations showed increased monomer conversions in



Scheme 2 Efficient microwave synthesis of polyethers from isosorbide.

DMF compared with that under conventional heating. Significantly higher monomer conversions were observed under otherwise comparable conditions in the copolymerization of St with MMA in DMF.

Ritter and co-workers¹⁴ reported the synthesis of N-substituted maleimides, and investigated their free radical polymerization using 2,2'-azoisobutyronitrile (AIBN) as the initiator in a mono-mode microwave oven. Good yields and shortened reaction times were achieved.

Holtze *et al.*¹⁵ studied the microwave-assisted miniemulsion polymerization of St using a pulsed microwave (duration of 9–12 s) at 1000 W. By combining the advantages of the confinement of the polymerization inside nano-reactors during hetero-phase polymerization with the very rapid and efficient microwave heating, short microwave pulses (about 10 s) and longer intervals of cooling (at least 15 min) can be programmed and applied to the reaction. Under optimized conditions, polymer radicals could survive the heating pulse and grow during the cooling period to give polymers with an MW as high as 10^7 g mol⁻¹ and a conversion up to 40% after the first pulse cycle. Besides the ultra-rapid heating by the microwaves, the surviving radical effect is purely thermal in nature and can be explained by the elemental reactions of radical hetero-phase polymerizations.

Zhu *et al.*¹⁶ studied the nitroxide-mediated free-radical miniemulsion polymerization of St in a CEM Discover mono-mode microwave oven at 135 °C; potassium persulfate was used as an initiator in conjunction with 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (OH-TEMPO). The polymerizations proceeded in a controlled manner yielding polymers whose MW increased linearly with increasing conversion. The resulting latexes were colloidally stable. The polymerization behavior under microwave and conventional heating, as well as the MW of the polymers and the Z-average size of the latex particles formed under both heating conditions, were compared. The M_n of polymers obtained under microwave irradiation were close to the theoretical value, while the M_n of polymers obtained under conventional heating were much higher than the theoretical value. The polydispersity indices (PDIs) of latex particles obtained under microwave irradiation were lower than those obtained under conventional heating. Microwave irradiation increased the decomposition rate of the initiator and decreased the particle sizes, resulting in the increase of polymerization rate of St.

Aldana-Garcia¹⁷ studied the microwave-assisted emulsion polymerization of St, and modeled the polymerizations under both microwave and conventional heating using the Predici simulation package of CiT. Microwave activated initiation was modeled as adding a second conventional free-radical chemical initiator, whose concentration is determined by the intensity of microwave irradiation, and its “decomposition” kinetic rate constant is related to the ratio of monomer concentration to the rate of absorbed microwave irradiation. The modeling predictions of conversion and polymer MW for both microwave and conventional heating systems agree well with the experimental data reported in the literature.

Zhu and co-workers¹⁸ have studied various atom transfer radical polymerizations (ATRP) under microwave irradiation. They recently reported the ATRP of St and butylmethacrylate

(BMA) under mono-mode microwave irradiation. Both microwave-assisted ATRPs (*i.e.*, St and BMA) showed increased polymerization rates in comparison with ATRP conducted under similar conventional conditions. Similarly, Schubert *et al.*¹⁹ investigated the controlled polymerizations of both MMA by ATRP and methyl acrylate (MA) by a nitroxide-mediated process under microwave irradiation. Narrower MW distribution was achieved under microwave irradiation. Microwave heating at higher temperatures resulted in a higher probability of chain termination reactions for both types of monomers.

3. Ring-opening polymerization

Ring-opening polymerization (ROP) is a type of polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer cycles than the monomer. As one type of chain polymerization, ROP consists of a sequence of initiation, propagation, and termination.²⁰ ROP plays an important role in academic research and industrial production. A wide variety of cyclic monomers have been successfully polymerized by the ROP, such as cyclic ethers, acetals, amides, esters and siloxanes. Compared with polymerizations of monomers containing a carbon–carbon double bond (such as vinyl), the chain propagation rate constants for ROP are several orders of magnitude lower.²⁰ Completion of the ROP of cyclic monomers is slower than that of the polymerization of monomers containing a carbon–carbon double bond.²⁰ This section presents a detailed review of microwave-assisted ring-opening polymerization (MROP). According to the architectures of polymers obtained from MROP, the content is divided into two general parts in terms of homopolymerization and copolymerization.

3.1 Microwave-assisted ring-opening homopolymerization (MROHP)

The term homopolymerization often is used to distinguish the polymerization of a single monomer from the copolymerization process. In the MROHP, microwave irradiation is used in the living cationic ring-opening homopolymerization (LROHP) of 2-oxazolines and coordination ring-opening homopolymerization (CROHP) of cyclic lactones, lactides, lactam and carbonates.

3.1.1. Microwave-assisted living cationic ring-opening homopolymerization (MLROHP). Over the past decade, living polymerization techniques have attracted much attention for providing simple and robust routes to the synthesis of polymers with predetermined MW, low PDI, specific functionalities and various architectures. According to the reaction mechanism, living polymerization can be classified into two categories: (1) living radical polymerization; and (2) living cationic ring-opening polymerization. Living radical polymerization has been studied intensively under microwave irradiation,²¹ exhibiting advantages such as increased reaction rates and improved polymer properties. MLROHP using 2-oxazolines as monomers was reported recently.²²

Poly(2-oxazolines) have attracted much interest due to the biological activity displayed by many molecules possessing this

core structure, which can provide applications in micelle catalysis, drug delivery and hydrogels. The strong interest generated for this class of molecules has led to the development of numerous synthetic strategies for their preparation. The LROHP of 2-oxazolines is a slow process with a reaction time ranging from hours to days; thus, a reduced reaction time is important to achieve widespread industrial applications. MLROHPs of 2-methyl-2-oxazoline (MeOx), 2-ethyl-2-oxazoline (EtOx), 2-nonyl-2-oxazoline (NonOx), 2-phenyl-2-oxazoline (PhOx) and soy based 2-oxazoline were investigated and the polymerization time had been reduced to only a few minutes (Scheme 3).

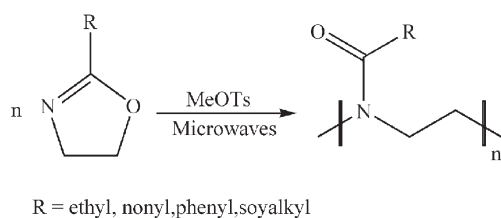
Schubert^{22c} and co-workers reported the methyl tosylate (TsOMe) initiated MLROHP of EtOx, which is the first example in this area. The reaction was carried out in an Emrys Liberator single-mode microwave oven. The kinetic curves on the cationic ring-opening polymerization of EtOx were investigated under both conventional and microwave conditions. For the conventional method, polymerization was carried out at approximately 80 °C in acetonitrile and the reaction took six hours. Under microwave irradiation, the reaction mixtures were heated directly, quickly and homogeneously; cationic ring-opening polymerization of EtOx could be performed either in bulk or with a drastically reduced amount of solvent with minimum side reactions. The temperatures of the polymerizations in bulk under microwave irradiation reached 200 °C without being limited to the boiling point of acetonitrile (82 °C) by conventional heating. The living nature of the microwave-assisted polymerization was observed in the temperature range between 80 and 180 °C, and polymers were obtained with a narrow MW distribution ($PDI < 1.2$). The kinetics of the TsOMe initiated polymerization of EtOx showed that the reaction rate increased with temperature. Consequently, the reaction at 190 °C under microwave irradiation was completed in one minute and was 350 times faster than that by conventional heating at 80 °C. The activation energy for the microwave-assisted polymerization of EtOx was 73.4 kJ mol⁻¹, which was in good agreement with previously reported values (68.7 to 80.0 kJ mol⁻¹) for similar systems by the conventional method.

Since many reactions were improved under microwave irradiation, the mechanisms of the acceleration had been a matter of debate over the existence of the thermal effect and specific/non-thermal effect.²³ The thermal effect, which is related to the fast increase of temperatures when polar groups are irradiated by microwaves, can be estimated easily by temperature measurements. The non-thermal effect was classified as the direct interaction of the electric field with specific

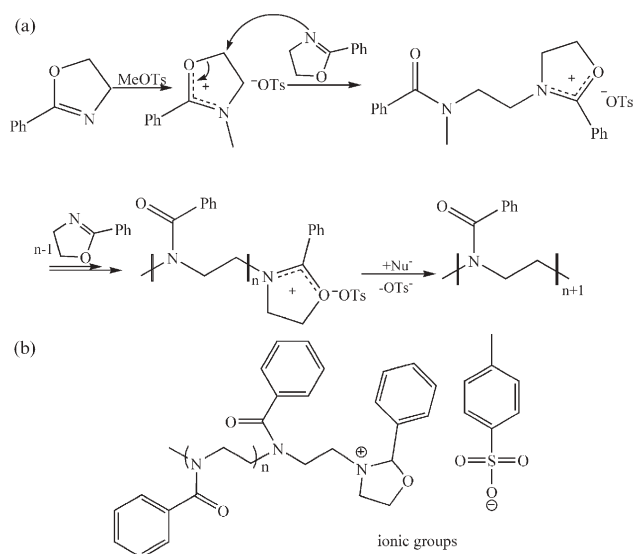
reaction molecules and can be evaluated from the changes in the pre-exponential factor A (representative of the probability of molecular impacts) or the activation energy (entropy term) in the Arrhenius equation.²⁴ It is difficult to make direct comparisons between the microwave method and the conventional method because of the inaccuracy of temperature measurement in the microwave field and the difficulty in reproducing the reaction by the conventional heating method. In the microwave-assisted polymerization of EtOx^{22c} mentioned above, the reaction rate acceleration in the range from 110 to 190 °C was calculated from the Arrhenius equation (rate acceleration factor 54), and complied perfectly with that observed from the reaction (60 min → 1 min, rate acceleration factor 60), suggesting that the improvement of the reaction rate enhancement was caused purely by the thermal effect.

Contradictory arguments about the thermal and non-thermal microwave effects in the MLROHP of PhOx were reported.^{22d,22e} Sinnwell *et al.*^{22d} claimed the existence of the non-thermal effect. The reaction was performed in a CEM-Discover monomode microwave oven under an inert argon atmosphere; a fiber optical sensor was equipped to measure the polymerization temperature. Four systems were used in the LROHP of PhOx: (1) a conventional heating closed system (CCS); (2) a conventional heating open system (COS); (3) a microwave irradiation closed system (MCS); and (4) a microwave irradiation open system (MOS). In the closed system (CS), the monomer and TsOMe were dissolved in acetonitrile and the reaction temperature was approximately 125 °C. In the open system (OS), butyronitrile was used as solvent and the temperature of the reaction medium was approximately 123 °C. In all four systems, the linear plots of $\ln([M_0]/[M_t])$ (where $[M_0]$ is the initial monomer concentration and $[M_t]$ is the concentration of monomer after time, t) against time showed that the reaction rate follows the first-order kinetics. MLROHP showed a great enhancement in reaction rates compared with the thermal LROHP. Both MCS (under a superheated condition) and MOS (under a reflux condition) showed nearly the same enhancement of the reaction rate over CCS and COS, respectively. The same enhancement of the reaction rate was explained by the strong microwave effect that took place mainly in the active growing polymer (Scheme 4a), which was composed of a tosylate counterion of the active oxazolinium end group (Scheme 4b). In the case of the active oxazoline polymer, the microwave radiation was absorbed mainly by the growing, high polar end group. This corresponded to the part of the molecule where the activation energy is required to propagate the polymer chain. To investigate further, the author measured the increase in temperature of the reaction mixtures with various monomer-to-initiator ratios corresponding to a variable ratio of ionic species. The temperature increased with the amount of the initiator, and the final temperature of the pure solvent (80 °C) is considerably lower, which is in accordance with the low dielectric loss of acetonitrile. This interesting behavior indicates that there is a strong microwave effect that mainly takes place at the ionic oxazolinium species.

However, Schubert's group attributed the acceleration of the LROHP of PhOx under microwave irradiation only to the temperature effects.^{22e} In their work, LROHP of PhOx was



Scheme 3 Cationic ring-opening polymerization of 2-oxazolines under microwave irradiation.



Scheme 4 Mechanism of the cationic ring-opening polymerization of 2-phenyl-2-oxazoline using (a) methyl tosylate and (b) active oxazoline polymer.

investigated in three systems: (1) MCS (in butyronitrile); (2) automated CCS (under pressure, in acetonitrile); and (3) automated COS (under reflux, in butyronitrile). Both pressure polymerizations in acetonitrile and reflux polymerization in butyronitrile revealed similar polymerization rates under microwave irradiation and conventional heating. The first-order kinetic plots of the three systems and good correspondence in the gel permeation chromatography (GPC) traces of the polymerization mixtures demonstrated the absence of the non-thermal microwave effects.

Based on the above results, a detailed study on the kinetics and the livingness of the LROHP were performed on a series of linear 2-oxazolines, including MeOx, EtOx, NonOx and PhOx in acetonitrile at high temperatures of up to 200 °C under microwave irradiation.^{22a} The reaction rates of MLROHP were enhanced significantly by factors of up to 400 times of that of the conventional LROHP. The first-order kinetics of the monomer consumption and the livingness of the polymerization were maintained in MLROHP at temperatures ranging from 80–200 °C (Figure 1). The activation energies for the MLROHP of the four 2-oxazolines were determined from the corresponding Arrhenius plots and were found to fall in the range of the values obtained with conventional heating. A comparison of the four activation energies showed that MeOx, EtOx and NonOx had similar activation energies, while that of PhOx is significantly higher because of the +M stabilization effect of the propagating species.

Soy based 2-oxazoline (SoyOx) monomer,²⁵ which is prepared from a sustainable biomass resource—soybean, contains unsaturated groups that can provide cross-links for the resulting polymers. TsOMe initiated LROHP of the SoyOx also was carried out under microwave irradiation in bulk or in acetonitrile (Scheme 5). The polymerization was completed in 15 min when it was heated up to 140 °C in acetonitrile and presented the living characteristics as the other four kinds of 2-oxazoline. These investigations on MLROHP of

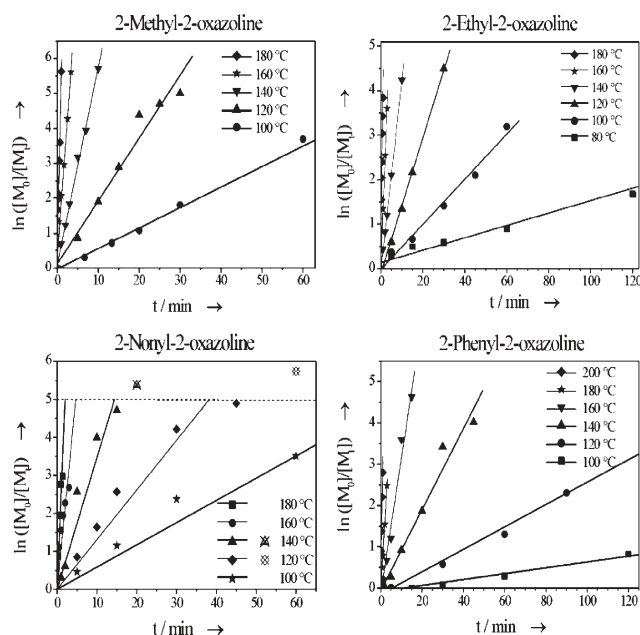
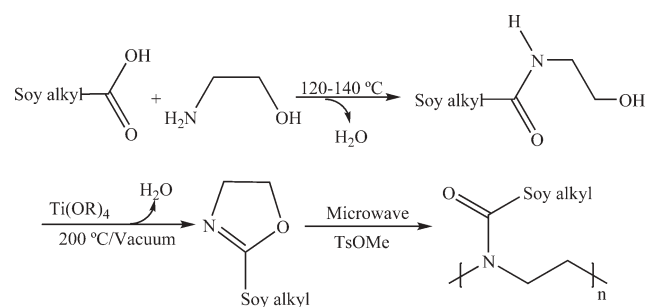


Fig. 1 Kinetics of the different congeners of the 2-oxazolines, plotted against time ($[monomer]/[initiator] = 60$).

2-oxazolines conducted by Schubert and co-workers showed that only temperature effects were responsible for the tremendous increase in 2-oxazoline polymerization rate (*i.e.*, the non-thermal microwave effect was not discernible).

During the polymer synthesis process, various reaction conditions, such as monomers, catalysts, reaction times and temperatures, had to be optimized to obtain well-defined polymers, which is a very time-consuming process. High-throughput methods represent a very promising approach by which different parameters can be screened simultaneously or in a fast serial mode and the results can be compared easily, thereby leading to new structure–property relationships.²⁶ Hoogenboom *et al.*²⁷ reported a microwave-assisted high-throughput method for LROHP of 2-oxazolines. The system included a single-mode microwave synthesizer and high-throughput workflow (high-throughput screening with peripheral characterization equipment) (Figure 2). MLROHP of NonOx at 140 °C was carried out in solvent, and kinetic investigations in dichloromethane revealed a living mechanism. Polymerizations under microwave irradiation proceeded significantly faster than conventionally heated polymerizations (at ambient pressure) because they combined the advantages of



Scheme 5 Synthesis of the soy based 2-oxazoline monomer SoyOx.

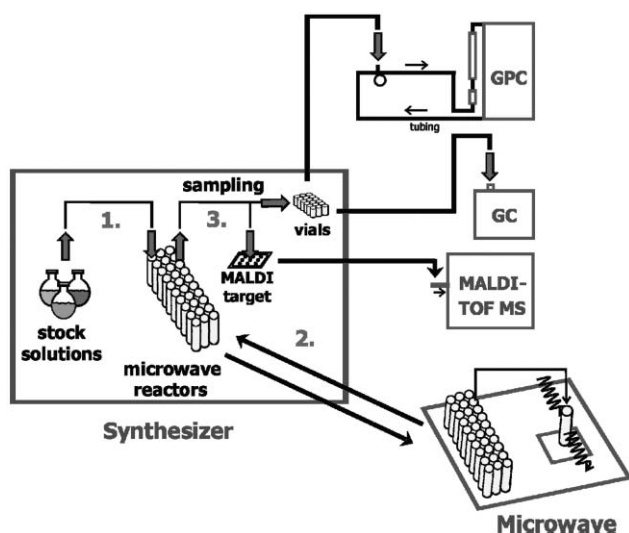


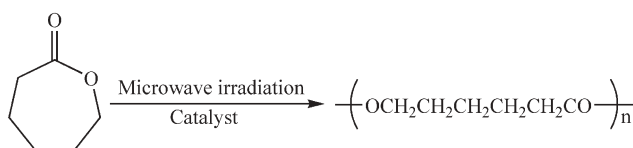
Fig. 2 Microwave high-throughput workflow.

both microwave-assisted polymer synthesis and high-throughput polymer synthesis.

3.1.2. Microwave coordination ring-opening homopolymerization. Aliphatic polyester is one of the most important classes of biodegradable polymers due to its excellent biodegradability and biocompatibility. Aliphatic polyesters are synthesized mainly by ROHP of aliphatic lactones, lactides and cyclic carbonates.

The first microwave coordination ring-opening polymerization (MCROHP) of lactone was reported in 1996,²⁸ when Albert and co-workers first disclosed titanium tetrabutylate catalyzed MCROHP of ϵ -caprolactone (CL) under microwave irradiation. They also compared MCROHP of CL under microwave irradiation and conventional thermal methods in terms of MW, conversion and reaction kinetics. A pulsed microwave was used to control the reaction temperatures. The reactions were carried out at 180 °C with different monomer/catalyst molar ratios. The results showed that the conversion and M_n were similar for both processes and no significant difference was found between the kinetics of the two methods.

Fang and Scola²⁹ applied variable frequency (2.4–7.0 GHz) microwave irradiation in the CROHP of CL to gain optimum processing control (Scheme 6). CL can absorb microwave energy effectively; therefore, the polymerization mixture can be heated easily to induce chemical reaction during the microwave processing. Under 70–100 W of microwave irradiation, the temperatures of the reaction mixtures could reach 150–200 °C, and poly(ϵ -caprolactone) (PCL) with a M_w of 9900–86 000 g mol⁻¹ was obtained after 2 h of irradiation.



Scheme 6 Polymerization of ϵ -caprolactone under microwave irradiation.

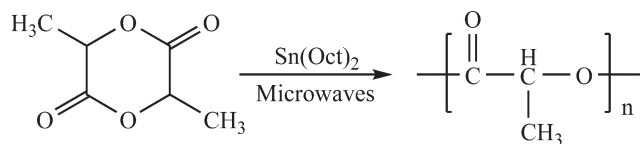
Compared with commercial products produced by the conventional heating process, microwave-produced PCL had equivalent glass transition temperature (T_g), melting temperature (T_m) and thermal stability. The characterization results revealed that high quality PCL could be prepared by microwave irradiation within 2 h, *versus* more than 12 h by the commercial thermal process.

Liu and Liao³⁰ reported the CROHP of CL that was conducted in a domestic microwave oven at a frequency of 2.45 GHz. The CROHP of CL was carried out effectively with constant microwave powers of 170, 340, 510, and 680 W. The temperatures of the polymerization ranged from 80 to 210 °C. PCL with a M_w of 124 000 g mol⁻¹ and a yield of 90% was obtained at 680 W for 30 min using 0.1% (mol/mol) stannous octanoate ($\text{Sn}(\text{Oct})_2$) as a catalyst. When the polymerization was catalyzed by 1% (wt/wt) zinc powder, the M_w of PCL was 92 300 g mol⁻¹ after the reaction mixture was irradiated at 680 W for 270 min.

Heating characteristics of the CROHP of CL under microwave irradiation also were studied.^{30d} Liu and Liao found that the reaction temperature of CL was self-regulated to an equilibrium temperature under microwave irradiation. For example, at 680 W of microwave irradiation, the temperature of CL (10 g) increased rapidly from 20 to 355 °C during the first 10 min and then fluctuated slightly around 360 °C during the next 20 min. An exothermic peak was observed from the thermogram of MCROHP of CL with $\text{Sn}(\text{Oct})_2$ as a catalyst. When a mixture of 10 g of CL with 0.1% (mol/mol) $\text{Sn}(\text{Oct})_2$ was irradiated at 680 W, an exothermic peak appeared between 2 min and 5 min with a maximum temperature of 343 °C at 3 min. During this period of time (2–5 min), the MCROHP of CL was very fast, resulting in PCL with an M_w of 123 000 g mol⁻¹ and yield of 95%. The author concluded that the thermal effect of microwave energy on the CL monomer and the reaction mixture was dependent on the power levels of microwaves and the mass scale of materials.

Sivalingam and Madras³¹ studied the kinetics of MCROHP of CL in bulk at 350 W with different cycle-heating periods (30–50 s). They set up two models for both thermal and microwave heating processes. The MW distributions, which were measured by GPC, were determined as a function of reaction time. Because the temperature of the system continuously varied with the reaction time, a model was proposed based on continuous distribution kinetics with time/temperature-dependent rate coefficients. Experiments were conducted under thermal heating to quantify the effect of the microwave on polymerization. The polymerization also was investigated with thermal and microwave heating in the presence of a zinc catalyst. The activation energies determined from temperature-dependent rate coefficients for pure thermal heating, thermally aided catalytic polymerization, and microwave-aided catalytic polymerization were 24.3, 13.4, and 5.7 kcal mol⁻¹, respectively. This indicates that microwaves increase the polymerization rate by lowering the activation energy.

Sinnwell and co-workers³² studied the direct synthesis of methacrylate PCL macromonomers. The MCROHP of CL in the presence of methacrylic acid or acrylic acid yields radical polymerizable polyester macromonomers. Studies showed fast



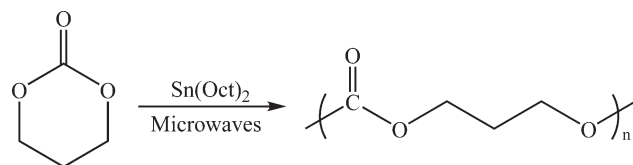
Scheme 7 Microwave-assisted ring-opening polymerization of lactide.

access to defined unsaturated macromonomers from unpurified educts. The process has the advantages of requiring only one step and providing high functionality. Investigation of the thermal properties shows that the melting point of the macromonomers was adjustable between 46 and 51 °C.

Poly(lactide/poly(lactic acid) (PLA) is one of the most important biodegradable polyesters because it can be derived from naturally renewable biomass such as corn. As a biobased, biodegradable polyester, the synthesis of PLA has attracted much more interest. Most of the commercial PLA is produced by CROHP of lactide (LA), which is a time-consuming process. Liu and co-workers³³ first reported the MCROHP of D,L-lactide (D,L-LA) (Scheme 7). Poly(D,L-lactide) (PDLA) with a M_w of 4×10^5 g mol⁻¹ and a yield over 90% was produced in 10 min by the CROHP of D,L-LA under 255 W microwave irradiation. Degradation of PDLA was also induced by microwaves with a power level over 340 W. The MW of PDLA was dependent upon the competition between the polymerization of D,L-LA and the degradation of the resulting polymer. Wang and co-workers³⁴ investigated the MCROHP of D,L-LA under atmospheric conditions with carborundum as a heating assistant material. The effects of the heating medium, monomer purity, catalyst concentration, microwave irradiation time and vacuum level were discussed. PDLA with a viscosity-average molar mass (M_η) over 250 000 g mol⁻¹ and a yield over 85% was obtained.

Several groups also studied MCROHP of L-lactide (L-LA). McCarthy and co-workers³⁵ presented some preliminary results of MCROHP of L-LA. Liu and Zhang³⁶ conducted a more detailed study on the MCROHP of L-LA. The heating characteristics of L-LA, Poly(L-lactide) (PLLA) and L-LA/Sn(Oct)₂ mixture under 2.45 GHz microwave irradiation were investigated. It was observed that the temperatures of the three systems increased rapidly and were self-regulated to an equilibrated temperature. As expected, the microwave power level had a significant influence on the equilibrium temperatures—a higher level of microwave power induced a higher equilibrium temperature. Exothermal peaks in the temperature–time curves were observed for L-LA/Sn(Oct)₂ mixtures when the irradiation power was above 170 W. The CROHP of L-LA proceeded quickly under microwave irradiation, with a simultaneous degradation of the resulting PLLA. The MW of PLLA depended on the competition between the polymerization of L-LA and the degradation of the resulting polymer, which was greatly influenced by the microwave power level. PLLA with a MW of 10^5 g mol⁻¹ was obtained when the MCROHP of L-LA was carried out under 170 W microwave irradiation for 10 min.

Besides CL and LA, Liu and co-workers³⁷ also investigated the CROHP of an aliphatic cyclic carbonate monomer, trimethylene carbonate (TMC), under microwave irradiation



Scheme 8 Microwave-assisted ring-opening polymerization of trimethylene carbonate.

(Scheme 8). High MW poly(trimethylene carbonate) (PTMC) ($M_w = 10^5$ g mol⁻¹) was obtained when the MCROHP of TMC was carried out with microwave forward energy at 255 W for 20 min. Compared with CROHP in an oil bath at the same temperature, MCROHP of TMC showed a slower reaction rate but a higher MW, indicating more serious degradation under the conventional heating method.

3.1.3 Other types of ring-opening homopolymerization. The application of biodegradable polyesters in the biomedical field requires the material to be highly safe for the living body. PCL usually is synthesized by CROHP of CL with Sn(Oct)₂ as a catalyst, which has been approved by FDA as a food additive. However, Sn(Oct)₂ contains the organic tin element, which leads to potential toxicity problems for biomedical applications.³⁸ Therefore, there is an increased interest in using a non-toxic or non-metallic catalyst/initiator during the polymerization. Liu and co-workers³⁹ reported carboxylic acid catalyzed MCROHP of CL. Benzoic acid and chlorinated acetic acids were studied in the metal-free reaction. The product was characterized as PCL by proton nuclear magnetic resonance spectroscopy, Fourier transform infra-red spectroscopy, ultra-violet spectroscopy, and GPC. For a mixture of CL and benzoic acid with a molar ratio of 25/1, the M_w and PDI of the PCL synthesized by microwave irradiation at 680 W for 4 h were 44 800 g mol⁻¹ and 1.6, respectively. Starting from the same mixtures, the M_w and PDI of the PCL synthesized by conventional heating at 210 °C for 4 h were 12 100 g mol⁻¹ and 4.2, respectively. Clearly, the polymerization improved significantly under microwave irradiation both in terms of MW and PDI. Degradation of the resultant PCL was observed during microwave polymerization processes in the presence of chlorinated acetic acids, which caused a reduction in MW of PCL.

The effect of microwave energy on the chain propagation of benzoic acid-initiated MCROHP of CL also was investigated.⁴⁰ The molar ratios of CL to benzoic acid used were 5, 15 and 25. The mixtures of CL–benzoic acid were heated under microwave irradiation, and the temperature was self-regulated to an equilibrated temperature between 204 and 240 °C, with microwave power ranging from 340 to 680 W. The polymer chain propagated rapidly between 160 and 230 °C, and the rate of propagation increased with higher temperatures within this temperature range. Degradation of the resultant PCL occurred when the temperature was above 230 °C. The results suggested that under microwave irradiation, the propagation of PCL chains was enhanced significantly but the formation of growing centers at the beginning stage of the polymerization was greatly inhibited (Table 1). With this metal-free method, PCL with a MW over 4×10^4 g mol⁻¹ was prepared.

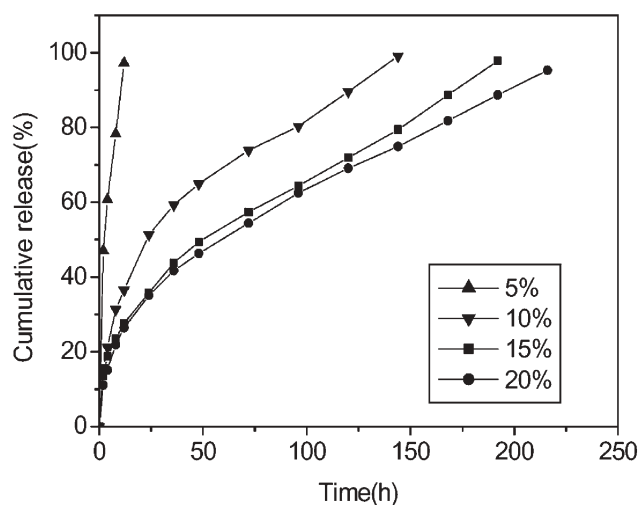
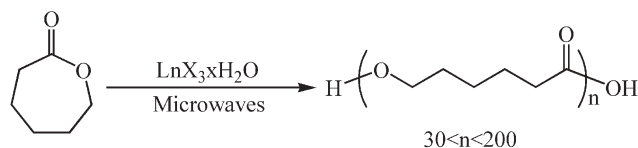
Table 1 Results of ring-opening polymerization of ϵ -caprolactone ($M/I = 5$)

Experiment ^a	Time/ min	$M_n/g\ mol^{-1}$	Monomer conversion (%)	N_t/N_m	$M_{n(m)}/M_{n(t)}$
1 ^t	30	1500	92.1	19.0	6.6
2 ^m		9900	32.0		
3 ^t	60	1700	99.0	6.8	6.5
4 ^m		11 100	95.0		
5 ^t	100	2300	99.0	6.7	6.4
6 ^m		14700	94.9		

^a t: Thermal polymerization at 210 °C, m: microwave-assisted polymerization at 680 W.

Liu and co-workers⁴¹ studied acid-initiated MCROHP of CL and its application in the preparation of a drug controlled-release system. The effects of microwave power, irradiation time, CL/acid molar ratio, and acidity of acid on the polymerization were investigated. Both the polymerization rate and the MW of polymers obtained were enhanced in comparison with the conventional thermal method. PCL with an M_w higher than 12 000 $g\ mol^{-1}$ and a PDI below 1.6 was synthesized in the presence of maleic acid, succinic acid and adipic acid. MCROHP also was carried out when the CL monomer was mixed with a certain amount of ibuprofen (IBU), from which the IBU-PCL controlled-release system was prepared directly. Neither ibuprofen particles nor microphase separation were observed from the surface of the ibuprofen-PCL controlled-release system by scanning electron microscopy. The sustained release of IBU from the system was observed from 12 h to 9 days with an increasing IBU loading level from 5 to 20 wt% (Figure 3). This appeared to be a promising method to prepare drug controlled-release systems.

Since lanthanide compounds are efficient catalysts for ROP of cyclic esters and also lack toxicity,⁴² MCROHP of CL using early lanthanide halides as catalysts was investigated.⁴³ Two types of microwave ovens, a monomodal reactor (Synthwave S402, Prolabo) and a multimode microwave oven, were used for MCROHP of CL. Hydrated lanthanide halide catalyzed MCROHP of CL is a very easy and efficient method to obtain

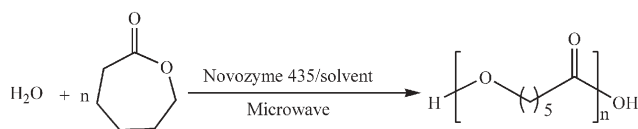
**Fig. 3** *In vitro* release of ibuprofen from PCL-ibuprofen system prepared by microwave irradiation.**Scheme 9** Microwave ring-opening polymerization of ϵ -caprolactone using lanthanide halides as catalyst.

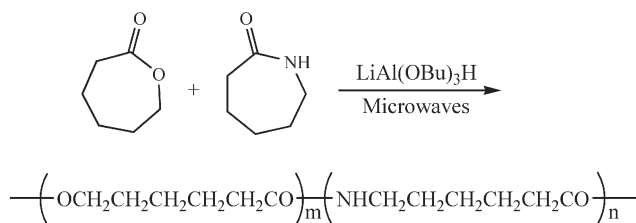
macro-monomers with controlled MWs in the range of 3000–5000 $g\ mol^{-1}$, which can be used as starting materials for functionalization and copolymerization reactions (Scheme 9). Differential scanning calorimetry and thermal gravity analyses were performed to study the thermal properties of the polymers produced by MCROHP and conventional CROHP. The results revealed no significant difference between the polymers.

Ritter and co-workers⁴⁴ reported the microwave-assisted Novozyme 435-catalyzed CROHP of CL in organic solvents. (Scheme 10). Since the Novozyme 435-catalyzed ROP strongly depends on the temperature and the polarity of the medium, five solvents with varying polarity and boiling points, tetrahydrofuran, dioxane, toluene, benzene and diethyl ether, were chosen for this study. No polymerization was observed using the two polar solvents tetrahydrofuran and dioxane. Using less polar solvents such as toluene, benzene and diethyl ether could lead to the enzymatic polymerization of CL, although the M_w is only up to several thousands (5800 $g\ mol^{-1}$, in diethyl ether). The authors discovered the unexpected accelerating and decelerating effects of the microwave upon the ROP in different solvents. They found that in boiling benzene and toluene, the polymerization rate under microwave irradiation was significantly lower than that conducted in a conventional oil bath, but monomer conversion accelerated when using boiling diethyl ether as solvent. It was concluded that the enzyme-catalyzed CROHP of CL was influenced significantly by the microwave irradiation.

Schubert *et al.*^{22g} have studied the microwave-assisted cationic ring-opening polymerization of EtOx in different ionic liquids as reaction media and the polymerization was completed in one minute. Based on the solubility difference between polymer and ionic liquid, polymer can be isolated by simple water extraction, which is considered a convenient and “environmentally friendly” process, while the ionic liquid can be efficiently recovered from water, thereby completely avoiding the use of volatile organic compounds during the purification step.

More recently, Liao and Gong *et al.*⁴⁵ investigated the microwave-assisted ring-opening polymerization of CL in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. Using zinc oxide as the catalyst, PCL with a M_w

**Scheme 10** Reactivity of the microwave-assisted ring-opening polymerization of ϵ -caprolactone compared with conventional thermal heating in different solvents.



Scheme 11 Microwave-assisted ring-opening copolymerization of ϵ -caprolactone and ϵ -caprolactam.

of $28\,500\text{ g mol}^{-1}$ could be obtained in 30 min in a domestic microwave oven (85 W) by adding 30 wt% ionic liquid to the reaction mixture. Temperature profiles of the reaction mixtures revealed that the addition of ionic liquid drastically changed the temperature of the reaction.

3.2. Microwave-assisted ring-opening copolymerization

Copolymerization is the simultaneous polymerization of two or more types of monomers and it is a useful method to obtain polymers with adjustable properties. In ring-opening copolymerizations (ROCP), microwaves have been introduced to prepare random copolymers and block copolymers. The following section of this paper discusses two kinds of copolymers (copolymers based on lactones and 2-oxazolines, respectively) synthesized by microwave-assisted ring-opening copolymerization (MROCP).

3.2.1. Microwave-assisted ring-opening copolymerization of lactones/lactides. While PCL is one of the most widely used biodegradable polyesters, copolymers of PCL have attracted much attention due to their adjustable properties. Anionic-catalyzed ring-opening copolymerization (AROCP) of ϵ -caprolactam and CL was conducted using a Lambda LT502XB variable frequency microwave furnace (Scheme 11).⁴⁶ The microwave frequency used in the reactions is 4.69 GHz with a bandwidth of 1.0 GHz and a sweep rate of 0.5 s. The reaction was programmed to a set temperature, which was controlled by a pulsed power on/off system. Dielectric properties of ϵ -caprolactam and CL measured in the microwave region ranging from 0.4 to 3.0 GHz showed that both monomers exhibited effective absorption of microwave energy. After a 30 min reaction, poly(amide ester) with a yield of 70% and M_w of $22\,000\text{ g mol}^{-1}$ was obtained.

Compared with conventional AROCP, microwave-assisted anionic ring-opening copolymerization was more effective for the preparation of a higher yield, higher amide content, and

higher T_g poly(amide-ester) with an equivalent MW (Table 2). The higher yield under microwave irradiation suggested that microwave energy provides a more efficient synthetic route as a consequence of the direct interaction between microwaves and the molecular dipole moments of the reactants; however, it is difficult to measure accurately the temperature in the bulk of the reaction mixture. A higher amide/ester ratio in MROCP synthesized copolymers was obtained. This phenomenon suggested that microwave energy was more efficiently absorbed by caprolactam than CL, thus providing greater reactivity of caprolactam during MROCP. As a result of the higher amide/ester ratio, MROCP produced copolymers exhibited a higher T_g .

Liu⁴⁷ and co-workers reported the microwave-assisted graft ring-opening copolymerization (MGROP) of CL onto chitosan. The MGROP was carried out by a protection-graft-deprotection procedure, with phthaloylchitosan as the precursor, and $\text{Sn}(\text{Oct})_2$ as the catalyst (Scheme 12). After being irradiated at 450 W for 15 min, a high grafting percentage of 232% was achieved. The graft of CL onto chitosan was greatly accelerated and enhanced under microwave irradiation.

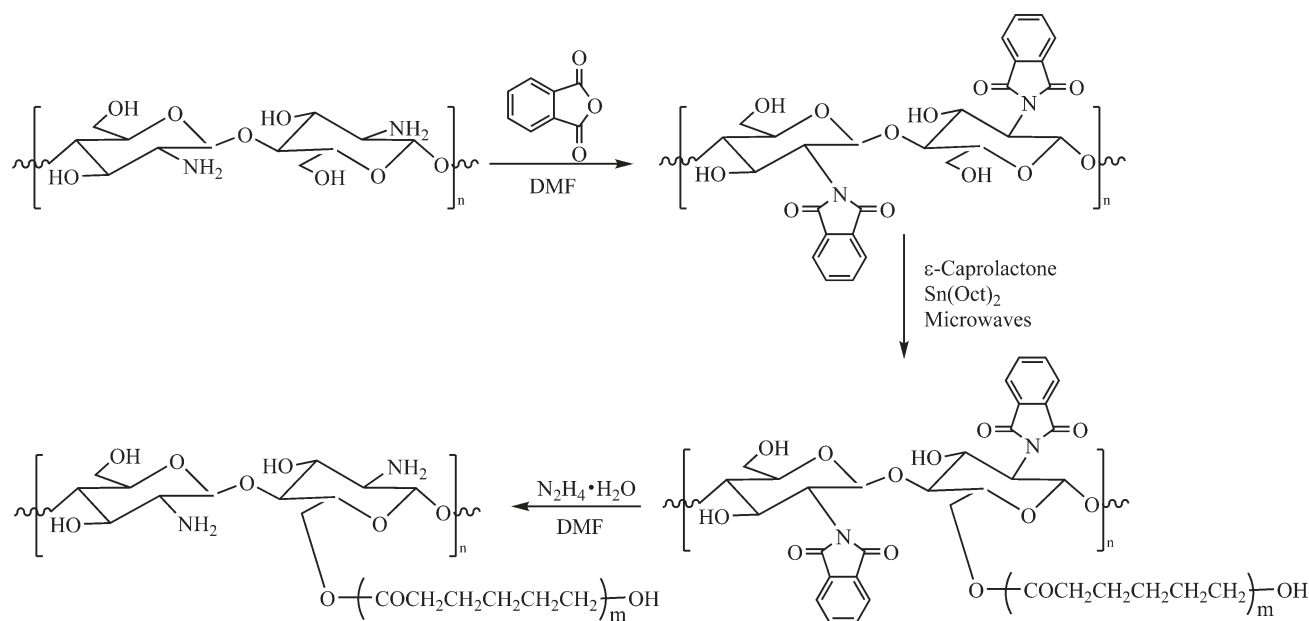
Block copolymers with hydrophilic and hydrophobic segments can aggregate into micelles in an aqueous solution, giving them a wide range of applications in micellar catalysts, drug delivery vehicles and tissue engineering scaffolds. The microwave method also has proved useful for the preparation of amphiphilic ABA triblock copolymers containing PCL and poly(ethylene glycol) (PEG) segments. Poly(ϵ -caprolactone-co-PEG-co- ϵ -caprolactone) (PCL-PEG-PCL) with an M_n over $20\,000\text{ g mol}^{-1}$ was synthesized by PEG initiated MROCP of CL in a domestic microwave oven.⁴⁸ The M_n and composition of the resulting triblock copolymers can be controlled by varying the amount and the length of the PEG segment. Another ABA block copolymer has also been synthesized using either PEG or water-soluble N-terminal functionalized CL as the central hydrophilic portion and peptide sequences of non-polar residues as the flanking hydrophobic segments.⁴⁹

Gong *et al.*⁵⁰ recently reported the microwave-assisted synthesis of triblock copolymers of L-lactide with PEG (PLLA-PEG-PLLA) in a CEM Discover mono-mode microwave oven. Poly(L-lactide)-co-poly(ethylene glycol)-co-poly(L-lactide) triblock copolymer with a M_n of $28\,230\text{ g mol}^{-1}$ and an L-lactide conversion of 92.4% could be synthesized after the L-lactide-PEG2000 reaction mixture was irradiated for 3 min at $100\text{ }^\circ\text{C}$. Compared with the polymerizations conducted under similar conventional conditions, the microwave-assisted synthesis of PLLA-PEG-PLLA triblock copolymers was much faster and resulted in higher MW products.

Table 2 Comparison of microwave energy and thermal energy in copolymerization reactions ($160\text{ }^\circ\text{C}$, 0.5 h)^a

Sample	TH-PAE 1%	TH-PAE 2%	TH-PAE 3%	MW-PAE 1%	MW-PAE 2%	MW-PAE 3%
Ester/amide feed ratio	1 : 2	1 : 2	1 : 2	1 : 2	1 : 2	1 : 2
Ester/amide found ratio	1 : 0.61	1 : 1.19	1 : 1.29	1 : 1.08	1 : 1.36	1 : 2.00
Yield (%)	51.2	52.7	57	61.9	70.1	78.2
T_g (meas.)	-25.0	-18.5	-14.5	-14	-7.5	6.0
$M_w/\text{g mol}^{-1}$	25 400	19 800	17 100	22 000	21 300	16 200
M_w/M_n	1.4	1.5	1.6	2.1	2.0	1.5

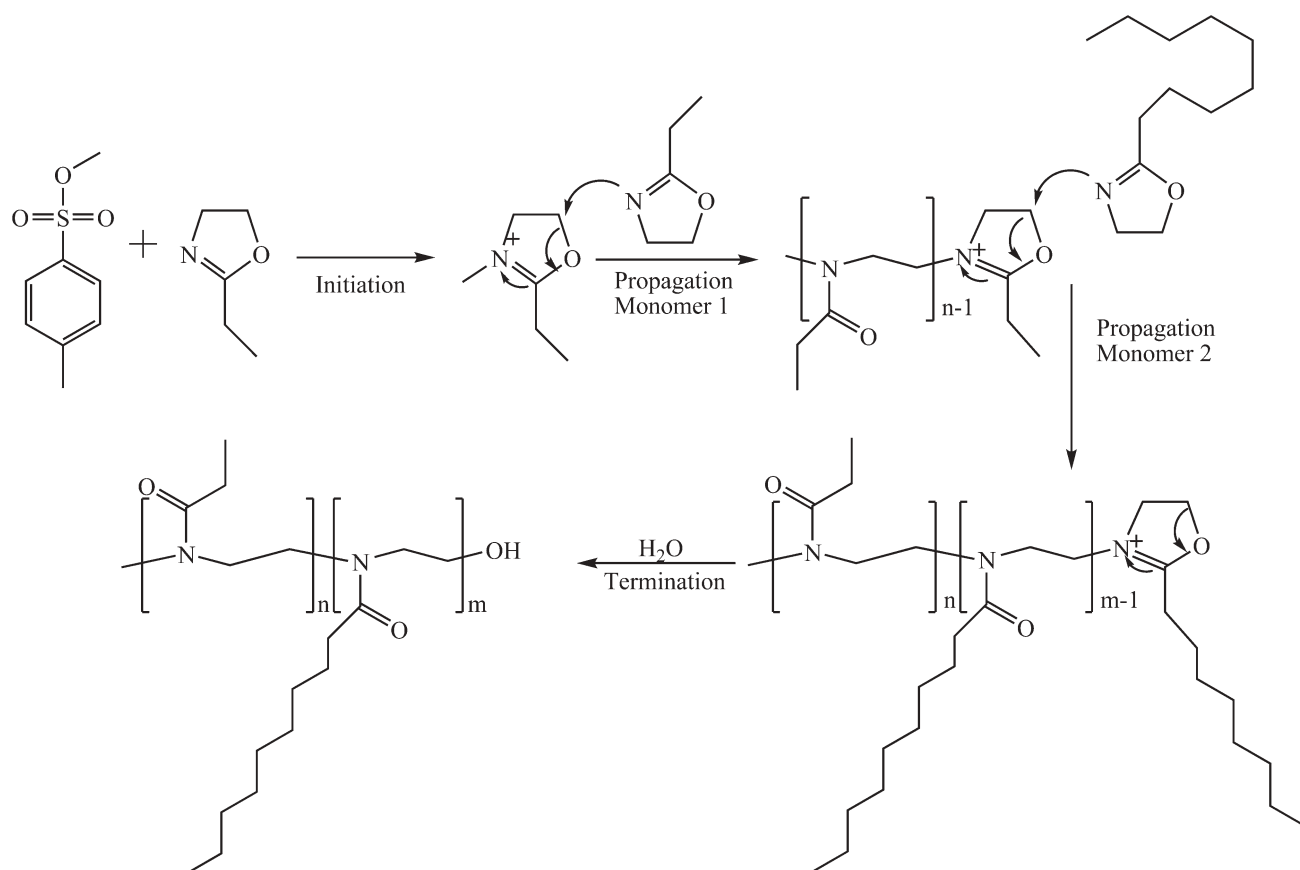
^a PAE-poly(ϵ -caprolactam-co- ϵ -caprolactone); TH-thermal process; MW-microwave process; 1%, 2%, 3%-catalyst level.



Scheme 12 Microwave graft copolymerization of ϵ -caprolactone and chitosan.

3.2.2. Microwave-assisted ring-opening copolymerization of 2-oxazolines. Tunable properties of poly(2-oxazoline) copolymers, which have become the focus of many investigations, can be achieved by selecting an appropriately substituted

monomer. For example, amphiphilic block co-poly(2-oxazoline)s can be obtained by a combination of a hydrophilic block poly(2-ethyl-2-oxazoline) and a hydrophobic block poly(2-nonyl-2-oxazoline). Similar to their LROHP, the living



Scheme 13 Mechanism for the stepwise preparation of the et50-non50 block copolymer from the cationic ring-opening polymerization of 2-ethyl- and 2-nonyl-2-oxazoline, initiated by methyl tosylate.

ring-opening copolymerization (LROCP) of 2-oxazolines also took hours or days to be completed. Schubert *et al.*⁵¹ expanded the LROHP of 2-oxazolines to the LROCP in preparation of block co-poly(2-oxazolines), using four monomers: MeOx, EtOx, NonOx and PhOx (Scheme 13).

This LROCP was initiated by TsOMe and performed in acetonitrile at 140 °C in a single-mode microwave reactor.^{51b} A total number of 100 (50 + 50) monomer units were incorporated into the polymer chains, resulting in a library of four chain-extended homo- and 12 diblock co-poly(2-oxazoline)s with narrow distributions (PDI < 1.30). The polymerization kinetics of LROCP of 2-oxazolines in acetonitrile was investigated under different pressures. In addition, a series of block copolymers was synthesized in an automated parallel synthesis robot by this pressure polymerization method. These studies indicated that the microwave copolymerization of 2-oxazolines was an efficient method for preparing copolymers in batch.

Besides the copolymers containing CL or 2-oxazolines, MROCP of ethylene isophthalate cyclic dimer (EI c-2mer) and bis(2-hydroxyethyl) terephthalate (BHET) in bulk was also reported.⁵² Poly(ethylene terephthalate-co-isophthalate) with $M_w > 20\,000\text{ g mol}^{-1}$ was obtained, and the polymerization mechanisms were investigated by the MALDI-TOF MS. The results showed that the reaction involved three stages. In the first stage, the homopolymerization of BHET proceeded with the copolymerization simultaneously; in the second stage, reactive end-groups of poly(ethylene terephthalate) or BHET attacked the EI c-2mer and gradually produced an EI-terminated copolymer; in the third stage, the propagation reactions composed of three types of elementary reaction routes took place.

In summary, microwave irradiation is a fast and effective method for copolymer synthesis. Compared with the conventional method, the microwave can not only reduce the reaction time, it also can yield copolymers with improved properties.

Concluding remarks of microwave-assisted ring-opening polymerization

During the past decade, significant progress has been made in the field of microwave-assisted polymer synthesis, including step-growth polymerization, free radical polymerization and microwave-assisted ring-opening polymerization. However, there are still many issues that are far from being elucidated, such as the so-called non-thermal effect. Many researchers now believe that there is no general non-thermal effect, and attribute the so-called non-thermal effect to inaccurate temperature measurement.^{1a,53} More studies in this challenging field are required to further understand the mechanism and kinetics of microwave-assisted polymerization.

Despite the conflicts about the non-thermal effects, interest in microwave-assisted polymerization is increasing quickly because of its unique advantage of rate enhancement over the conventional heating method. For the ring-opening polymerization of cyclic monomers under microwave irradiation, the enhancement of reaction rate and product yield, as well as polymer property improvement, have become the most promising features of this technology.

References

- (a) D. Adam, *Nature*, 2003, **421**, 571–572; (b) C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, **43**, 6250–6284.
- (a) D. Bogdal, P. Penczek, J. Pielichowski and A. Prociak, *Adv. Polym. Sci.*, 2003, **163**, 193–263; (b) F. Wiesbrock, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 1739–1764; (c) L. Zong, S. Zhou, N. Sgriccia, M. C. Hawley and L. C. Kempel, *J. Microwave Power and Electromagnetic Energy*, 2003, **38**, 49–74.
- A. Zoldakova, V. Tomanova, K. Pielichowski, J. Polaczek and J. Pielichowski, *Modern Polymeric Materials for Environmental Applications, 2nd International Seminar*, Krakow, Poland, March 23–25, 2006, 205.
- A. A. Caouthar, A. Loupy, M. Bortolussi, J.-C. Blais, L. Dubreucq and A. Meddour, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**(24), 6480–6491.
- (a) S. Watanabe, K. Hayama and Y. Imai, *Makromol. Chem., Rapid Commun.*, 1993, **14**, 481–184; (b) Y. Imai, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1995, **36**, 735–736; (c) Y. Imai, N. Hisashi, S. Watanabe and K. Masaki, *Polym. J. (Tokyo)*, 1996, **28**, 256–260.
- Y. Xue, W. Dai and J. Lu, *Chem. J. Internet*, 2005, **7**(5), 38, <http://www.chemistrymag.org/cji/2005/075038pe.htm>.
- (a) S. Mallakpour and E. Kowsari, *J. Appl. Polym. Sci.*, 2006, **99**(3), 1038–1044; (b) S. Mallakpour and E. Kowsari, *Polym. Eng. Sci.*, 2006, **46**(4), 558–565; (c) S. Mallakpour and E. Kowsari, *Polym. Adv. Technol.*, 2005, **16**(10), 732–737; (d) S. Mallakpour and E. Kowsari, *Polym. Adv. Technol.*, 2005, **16**(6), 466–472; (e) S. Mallakpour and E. Kowsari, *J. Appl. Polym. Sci.*, 2005, **96**(2), 435–442; (f) S. Mallakpour and E. Kowsari, *Polym. Bull. (Heidelberg, Ger.)*, 2005, **53**(3), 169–180.
- (a) K. Faghihi, *J. Appl. Polym. Sci.*, 2006, **102**(5), 5062–5071; (b) K. Faghihi and K. Zamani, *J. Appl. Polym. Sci.*, 2006, **101**(6), 4263–4269.
- S. Keki, I. Bodnar, J. Borda, G. Deak and M. Zsuga, *Macromol. Rapid Commun.*, 2001, **22**(13), 1063–1065.
- L. Liu, L. Liao, C. Zhang, F. He and R. Zhuo, *Chin. Chem. Lett.*, 2001, **12**(9), 761–762.
- N. Hurdac, D. Abdelyah, J.-M. Buisine and P. Decock, *Eur. Polym. J.*, 1997, **33**, 187–190.
- (a) S. Chatti, M. Bortolussi, A. Loupy, J. C. Blais and D. Bogdal, *Eur. Polym. J.*, 2002, **38**, 1851–1861; (b) S. Chatti, M. Bortolussi, D. Bogdal, J. C. Blais and A. Loupy, *Eur. Polym. J.*, 2006, **42**, 410–424.
- H. Stange, M. Ishaque, N. Niessner, M. Pepers and A. Greiner, *Macromol. Rapid Commun.*, 2006, **27**(2), 156–161.
- (a) E. Bezdushna and H. Ritter, *Macromol. Rapid Commun.*, 2005, **26**(13), 1087–1092; (b) P. Eckstein and H. Ritter, *Des. Monomers Polym.*, 2005, **8**(6), 601–607.
- C. Holtze, M. Antonietti and K. Tauer, *Macromolecules*, 2006, **39**(17), 5720–5728.
- J. Li, X. Zhu, J. Zhu and Z. Cheng, *Radiat. Phys. Chem.*, 2007, **76**(1), 23–26.
- M. Aldana-Garcia, J. Palacios and E. Vivaldo-Lima, *J. Macromol. Sci., Pure Appl. Chem.*, 2005, **A42**(9), 1207–1225.
- (a) W. Xu, N. Zhou, X. Zhu and Z. Cheng, *Huaxue Yanjiu Yu Yingyong*, 2005, **17**(2), 223–225; (b) Z. Cheng, X. Zhu, N. Zhou, J. Zhu and Z. Zhang, *Radiat. Phys. Chem.*, 2005, **72**(6), 695–701.
- R. Hoogenboom, F. Wiesbrock, M. A. M. Leenen, H. Zhang and U. S. Schubert, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2005, **46**(2), 293–294.
- G. Odian, *Principles of Polymerization*, John Wiley & Sons, Inc., 4th edn, 2004, p. 544.
- (a) D. D. Wisnoski, W. H. Leister, K. A. Strauss, Z. Zhao and C. W. Lindsley, *Tetrahedron Lett.*, 2003, **44**(23), 4321–4325; (b) G. Chen, X. Zhu, Z. Cheng, J. Lu and J. Chen, *Polym. Int.*, 2004, **53**(4), 357–363; (c) H. Zhang and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**(13), 1225–1230; (d) W. Xu, X. Zhu, Z. Cheng, G. Chen and J. Lu, *Eur. Polym. J.*, 2003, **39**(7), 1349–1353.
- (a) F. Wiesbrock, R. Hoogenboom, M. A. M. Leenen, M. A. R. Meier and U. S. Schubert, *Macromolecules*, 2005, **38**(12), 5025–5034; (b) R. Hoogenboom, M. W. M. Fijten, H. M. L. Thijs, B. M. Van Lankvelt and U. S. Schubert, *Desgn. Monom. and Polym.*, 2005, **8**(6), 659–671; (c) F. Wiesbrock, R. Hoogenboom, C. H. Abeln and U. S. Schubert, *Macromol. Rapid Commun.*, 2004,

- 25(22), 1895–1899; (d) S. Sinnwell and H. Ritter, *Macromol. Rapid Commun.*, 2005, **26**(3), 160–163; (e) R. Hoogenboom, M. A. M. Leenen, F. Wiesbrock and U. S. Schubert, *Macromol. Rapid Commun.*, 2005, **26**(22), 1773–1778; (f) C. Guerrero-Sanchez, R. Hoogenboom and U. S. Schubert, *Abstr. Pap.*, 231st ACS National Meeting, Atlanta, GA, USA, March 26–30, 2006, IEC-123; (g) C. Guerrero-Sanchez, R. Hoogenboom and U. S. Schubert, *Chem. Commun.*, 2006, **36**, 3797; (h) M. Nuchter, U. Muller, B. Ondruschka, A. Tied and W. Lautenschlager, *Chem. Eng. Technol.*, 2003, **26**, 1207–1216.
- 23 (a) N. Kuhnert, *Angew. Chem., Int. Ed.*, 2002, **41**, 1863–1866; (b) C. R. Strauss, *Angew. Chem., Int. Ed.*, 2002, **41**(19), 3589–3590.
- 24 L. Perreux and A. Loupy, *Tetrahedron*, 2001, **57**, 9199–9223.
- 25 (a) R. Hoogenboom, F. Wiesbrock and U. S. Schubert, *Abstracts of Papers, 230th ACS National Meeting*, Washington, DC, United States, Aug. 28–Sept. 1, 2005, PMSE-516; (b) R. Hoogenboom, F. Wiesbrock and U. S. Schubert, *PMSE Prepr.*, 2005, **93**, 894–895.
- 26 (a) S. Schmatloch, H. Bach, R. A. T. M. van Benthem and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 95–107; (b) S. Schmatloch and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 69–76; (c) N. Adams and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 48–58; (d) M. A. R. Meier, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 21–23; (e) H. Zhang, R. Hoogenboom, M. A. R. Meier and U. S. Schubert, *Meas. Sci. Technol.*, 2005, **16**, 203–211; (f) M. A. R. Meier and U. S. Schubert, *Rev. Sci. Instrum.*, 2005, **76**, 062211; (g) R. Hoogenboom and U. S. Schubert, *Rev. Sci. Instrum.*, 2005, **76**, 062202; (h) R. Hoogenboom, *Expanding the Polymer Science Toolbox: High-throughput Experimentation, Microwave Irradiation and Grid-like Metal Complexes*, Technische Universiteit, Eindhoven, 2005, p. 3.
- 27 R. Hoogenboom, F. Wiesbrock, M. A. M. Leenen, M. A. R. Meier and U. S. Schubert, *J. Comb. Chem.*, 2005, **7**(1), 10–13.
- 28 P. Albert, H. Warth, H. Muehlhaupt and R. Janda, *Macromol. Chem. Phys.*, 1996, **197**(5), 1633–1641.
- 29 (a) X. M. Fang, S. J. Huang and D. A. Scola, *Polym. Mater. Sci. Eng.*, 1998, **79**, 518–519; (b) X. M. Fang, S. J. Huang and D. A. Scola, *Book of Abstracts, 216th ACS National Meeting*, 1998, PMSE-279; (c) X. M. Fang, C. D. Simone, E. Vaccaro, S. J. Huang and D. A. Scola, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**(14), 2264–2275.
- 30 (a) L. Q. Liao, L. J. Liu, C. Zhang, F. He, R. X. Zhuo and K. Wan, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**(11), 1749–1755; (b) L. Q. Liao, L. J. Liu, C. Zhang and R. X. Zhuo, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2003, **44**(1), 864–865; (c) L. Q. Liao, L. J. Liu, C. Zhang and R. X. Zhuo, *Abstr. Pap.*, 225th ACS National Meeting, New Orleans, LA, United States, March 23–27, 2003, POLY-220; (d) L. Q. Liao, L. J. Liu, C. Zhang, F. He and R. X. Zhuo, *J. Appl. Polym. Sci.*, 2003, **90**(10), 2657–2664.
- 31 G. Sivalingam, N. Agarwal and G. Madras, *J. Appl. Polym. Sci.*, 2004, **91**(3), 1450–1456.
- 32 S. Sinnwell, A. M. Schmidt and H. Ritter, *J. Macromol. Sci., Pure and Appl. Chem.*, 2006, **43**(3), 469–476.
- 33 (a) L. J. Liu, C. Zhang, L. Q. Liao, X. L. Wang and R. X. Zhuo, *Chin. Chem. Lett.*, 2001, **12**(8), 663–664; (b) C. Zhang, L. J. Liu and L. Q. Liao, *Macromol. Rapid Commun.*, 2004, **25**(15), 1402–1405.
- 34 K. Zhang, P. Wang, W. K. Li and J. Shu, *Gaofenzi Cailiao Kexue Yu Gongcheng*, 2004, **20**(3), 46–48.
- 35 (a) B. Koroskenyi and S. P. McCarthy, *J. Polym. Environ.*, 2002, **10**(3), 93; (b) S. P. McCarthy and B. Koroskenyi, *PMSE Prepr.*, 2002, **86**, 350–351.
- 36 (a) C. Zhang, *MSc Thesis*, Wuhan University, 2002; (b) C. Zhang, L. Q. Liao and L. J. Liu, 39th IUPAC World Polymer Congress (Macro2002), July 7–12, 2002, Beijing, China, 9e-1P-19, 64; (c) C. Zhang, L. Q. Liao and L. J. Liu, 2003, *National Conference on Polymers (Polymer 2003)*, October 9–14, 2003, Hangzhou, China, E5-6; (d) C. Zhang, *PhD Thesis*, Wuhan University, 2005.
- 37 C. Zhang, L. J. Liu, L. Q. Liao and R. X. Zhuo, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2003, **44**(1), 874–875.
- 38 (a) H. R. Kricheldorf, I. Kreiser-Saunders and D.-O. Damrau, *Macromol. Symp.*, 2000, **159**, 247–258; (b) M. C. Tanzi, P. Verderio, M. G. Lampugnani, M. Resnati, E. Dejana and E. Sturani, *J. Mater. Sci.: Mater. Med.*, 1994, **5**(6–7), 393–396.
- 39 (a) Z. J. Yu, L. J. Liu and R. X. Zhuo, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**(1), 13–21; (b) Z. J. Yu, L. J. Liu, Y. Song and R. X. Zhuo, *Abstr. Pap.*, 225th ACS National Meeting, New Orleans, LA, USA, March 23–27, 2003, POLY-222; (c) Z. J. Yu, L. J. Liu, Y. Song and R. X. Zhuo, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2003, **44**(1), 868–869.
- 40 Z. J. Yu and L. J. Liu, *Eur. Polym. J.*, 2004, **40**(9), 2213–2220.
- 41 (a) Y. Song, L. J. Weng, X. C. Liu and R. X. Zhuo, *J. Biomater. Sci., Polym. Ed.*, 2003, **14**(3), 241–253; (b) Y. Song, L. J. Liu, Z. J. Yu, X. C. Weng and R. X. Zhuo, *Abstr. Pap.*, 225th ACS National Meeting, New Orleans, LA, USA, March 23–27, 2003, POLY-259; (c) Y. Song, L. J. Liu, Z. J. Yu, X. C. Weng and R. X. Zhuo, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2003, **44**(1), 936–937; (d) Y. Song, L. J. Liu and R. X. Zhuo, *Chin. Chem. Lett.*, 2003, **14**(1), 32–34.
- 42 (a) S. Aime, M. Botta, M. Fasano and E. Terreno, *Chem. Soc. Rev.*, 1998, **27**, 19–29; (b) K. H. Thompson and C. Orvig, *Science*, 2003, **300**, 936–939.
- 43 D. Barbier-Baudry, C. H. Brachais, A. Cretu, A. Loupy and D. Stuerge, *Macromol. Rapid Commun.*, 2002, **23**(3), 200–204.
- 44 P. Kerep and H. Ritter, *Macromol. Rapid Commun.*, 2006, **27**, 707–710.
- 45 L. Liao, L. Liu, C. Zhang and S. Gong, *Macromol. Rapid Commun.*, 2006, **27**, 2060.
- 46 X. M. Fang, R. Hutcheon and D. A. Scola, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**(8), 1379–1390.
- 47 L. Liu, Y. Li, Y. Fang and L. X. Chen, *Carbohydr. Polym.*, 2005, **60**(3), 351–356.
- 48 Yu Zhaoju and Liu Lijian, *J. Biomater. Sci., Polym. Ed.*, 2005, **16**(8), 957–971.
- 49 M. B. Anzovino, K. E. Rutledge, M. A. Baron and S. L. Goh, *Abstr. Pap.*, 231st ACS National Meeting, Atlanta, GA, United States, March 26–30, 2006, POLY-202.
- 50 C. Zhang, L. Liao and S. Gong, *Macromol. Rapid Commun.*, DOI: 10.1002/marc.200600709.
- 51 (a) R. Hoogenboom, F. Wiesbrock, M. A. M. Leenen and U. S. Schubert, *PMSE Prepr.*, 2005, **93**, 814–815; (b) F. Wiesbrock, R. Hoogenboom, M. Leenen, S. F. G. M. Van Nispen, M. Van der Loop, C. H. Abeln, A. M. J. Van den Berg and U. S. Schubert, *Macromolecules*, 2005, **38**(19), 7957–7966; (c) R. Hoogenboom, M. W. M. Fijten, R. M. Paulus, H. M. L. Thijs, S. Hoeppener, G. Kickelbick and U. S. Schubert, *Polymer*, 2006, **47**(1), 75–84.
- 52 R. Nagahata, J. Sugiyama, S. Velmathi, Y. Nakao, M. Goto and K. Takeuchi, *Polym. J. (Tokyo)*, 2004, **36**(6), 483–488.
- 53 Committee on microwave processing of materials: an emerging industrial technology, National Materials Advisory Board, *Microwave Processing of Materials*, National Academy Press, Washington D. C., 1994.