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Microwave-Assisted Polyester and Polyamide Synthesis

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Abstract: Microwave-assisted polymerizations such as radical polymerization, polycondensation, and cation polymerization have been numerously reported. Recently, researches on condensed polymers by microwave heating have been energetically conducted about not only basic synthesis research but also scale-up for a commercial process. This mini review focuses on microwave-assisted polyester and polyamide syntheses and describes our works to develop a 30 kg scale microwave reactor in anticipation of a commercial process.

Keywords: Microwave-assisted, polyester, polyamide, polycondensation, ring-opening polymerization, scale-up.

INTRODUCTION

Polymerization is a reaction process during which monomer molecules form polymer chains. Polymerization is mainly categorized as chain-growth or step-growth polymerization according to reaction type. In chain-growth polymerization, individual monomer molecules add on a growing polymer chain sequentially. In step-growth polymerization, bifunctional or multifunctional monomers react to form dimers, trimers, then longer oligomers, and eventually long-chain polymers.

Classified as a chain-growth polymerization, radical polymerization [1] is initiated with free radicals formed using initiators like azobisisobutyronitrile, benzoyl peroxide, and azo compounds (initiation step). Then, the formed radicals continuously react with monomers in the propagation step. Finally, propagation reaction is interrupted by coupling where two radical species react with each other to form a single molecule. Radical polymerization progresses under mild condition due to high reactivity of radical species. Polyethylene, polypropylene, and polyvinyl alcohol are generic polymers synthesized by radical polymerization.

Classified as step-growth polymerization, polycondensation continuously combines monomers to form polymers while eliminating small molecules such as water, methanol, and ethanol [2]. The reaction is accelerated upon efficient removal of the small molecules, requiring prolonged heating at high temperature and under low pressure. Polycondensation is, therefore, a type of reaction that consumes considerable energy. Polyesters and polyamides are polycondensed polymers used in plastic bottles, textiles, and engineered plastics [3-7].

Polycondensations of polyesters and polyamides are shown in Schemes **1** and **2**, respectively.

Taking the polymerization of polyesters as an example, the simplest method for polyester synthesis is to directly condense hydroxycarboxylic acids or a mixture of diols and dicarboxylic acids at temperatures where esterification leads to the formation of polyester and water by-product. The first option has been widely used for poly(lactic acid) and poly(glycolic acid), while the second option has been applied to poly(ethylene terephthalate) and poly(butylene succinate).

Direct polycondensation is acceptable, because the water by-product formed is not an environmental load. However, the water causes depolymerization to the resulting polyester and is more difficult to remove from the reaction mixture than methanol and ethanol. Hence, the degree of polymerization is hard to increase. To overcome this problem, dialkyl diesters are used as monomers because they form alcohols as a by-product. Acyl chloride is also used as a monomer because of its high reactivity.

Ring-opening polymerization using cyclic anhydride or condensate as reagents has been conducted for polymerization without by-product elimination. Multistep reactions are available to generate these reagents and energy has been consumed because of demand for prolong heating and high temperatures. Reaction schemes for the synthesis of poly(lactic acid) (PLA) through direct polycondensation and lactide methods are compared in Scheme **3**.

Direct polycondensation, which forms water as a by-product, is a shortcut and a less energy-consuming method for PLA synthesis compared to the lactide method, which is a production process involving polycondensation, depolymerization, and ring-opening polymerization at high temperatures and for long reaction times. Thus, if PLA synthesis enables to innovate direct polycondensation, energy and time to synthesize PLA may be decreased through the total process. For this innovation, microwave heating is a candidate (described later).

Microwaves are a band of electromagnetic waves within the 300 MHz–300 GHz frequency range. 2.45 GHz microwaves have been determined as an industrial, science, and medical radio band available for heating and communication purposes. They have widely been used to dry wood, cure rubber, and heat food since the 1960s [8, 9].

In microwave heating, microwaves directly interact with polar molecules and subsequently generate heat from inside of matter [9]. On the other hand, conventional methods using oil bath and heating mantle heat matter from outside. Heat transfers toward the inside of matter by conduction and convection. Heating modes used in microwave and conventional methods are, therefore, different. This difference leads to advantages in microwave-assisted chemical synthesis such as shorter reaction times, increased yields, and high selectivity. Microwave heating has been applied to organic chemistry since 1989. Gedye *et al.* [10] and Giguere *et al.* [11] reported microwave-assisted esterification and Diels-Alder synthesis, respectively. Numerous chemical reactions using microwave heating have been carried out and summarized in review articles [12, 13] and books [14, 15].

Microwaves have been used to cure polymers since the early 1960s. Regarding polymer synthesis applications, Yanagawa *et al.* [16] have reported the synthesis of polyamino acids by microwave irradiation of glycine, alanine, valine, and asparagines in water to investigate the “beginning of life.” However, the purpose of their report was not a microwave-assisted polymer synthesis. Since the late 1990s, microwave heating has focused on polymer synthesis. Radical polymerization, polycondensation, anion polymerization, and cation polymerization have been reported under optimized reaction conditions such as reaction time, temperature, and catalyst type. Numerous results concerning microwave-assisted polymer synthesis have been also summarized in several review articles [17-20] and a book [21].

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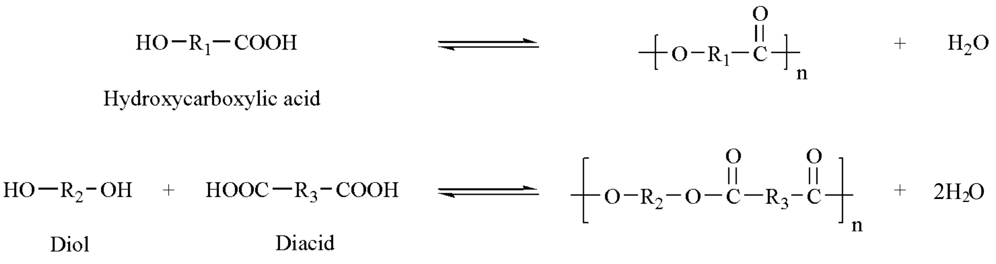
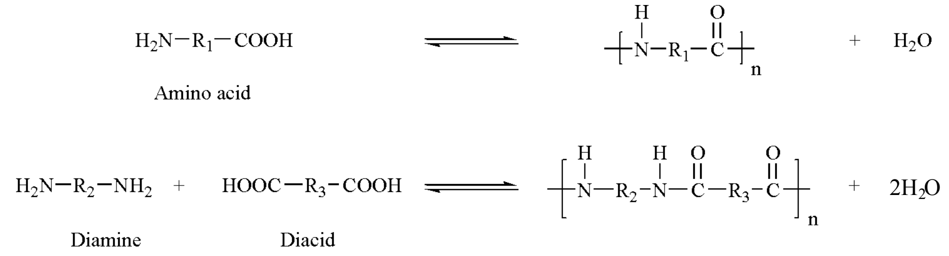
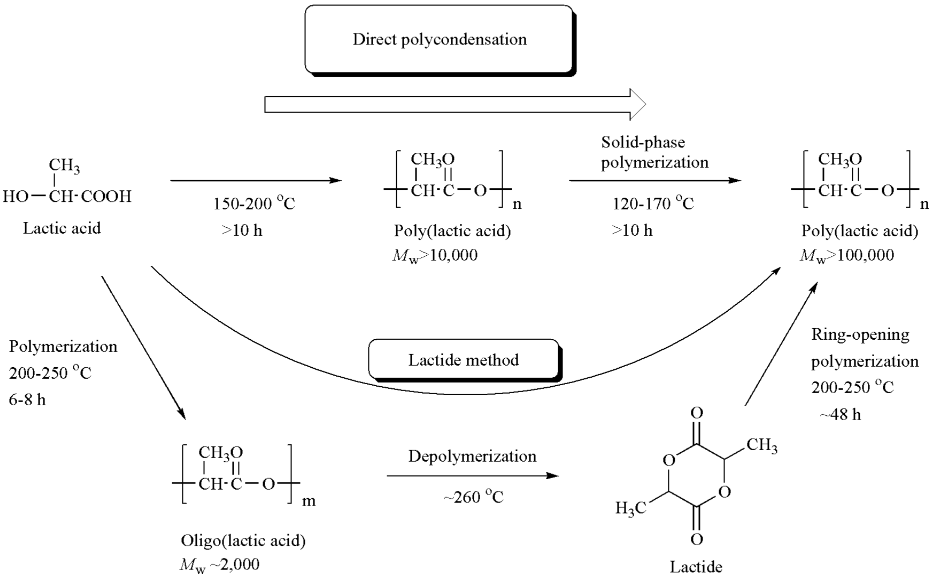


Scheme 1. Polyesterification.



Scheme 2. Polyamidation.



Scheme 3. Flow diagram of the PLA synthesis process.

As mentioned above, microwave heating differs from conventional heating. Matter exposed to microwaves generates heat. In the case of a dielectric material, the efficiency of heat generation depends on the dielectric properties of irradiated matter. The complex dielectric constant is a dielectric property expressed as [8, 9].

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

where ε' is the dielectric constant, and ε'' is the dielectric loss. The dielectric constant corresponds to the degree of storage of electromagnetic energy. The dielectric loss defines the lag in alternating applied electric field. The microwave generated heat is expressed using the dielectric property as

$$P = \omega\varepsilon_0\varepsilon'' E^2 V \quad (2)$$

where ω is the angular frequency, ε_0 is the vacuum permittivity, E is the electric field strength, and V is the volume. ε'' is necessary to evaluate the heating efficiency of a chemical reaction system during microwave-assisted chemical synthesis.

Microwave energy penetrates matter at an appropriate depth for heat generation. This depth is defined as the half-power penetration depth. It has to be estimated because it provides a direction for applicator design, reactor construction, and microwave irradiation method. This depth is estimated as

$$D = \lambda / (2\pi\sqrt{\varepsilon'}\tan\delta) \quad (3)$$

where λ is the wavelength, and tan δ = ε''/ε'. Two physical quantities related to microwave heating are determined by measuring dielectric constant and loss.

Dielectric constants and losses of representative small molecules are listed in Table **1** [22]. Polar molecules with hydrogen bonding groups have higher dielectric losses, suggesting that they are efficiently heated by microwave irradiation. Polar molecules without hydrogen bonding groups have intermediate dielectric losses. Nonpolar molecules have low dielectric losses.

As mentioned above, water and ethanol are polycondensation by-products, which efficiently absorb microwave energy and are readily activated. In contrast, the resulting polymer absorbs little microwave energy because of its low dielectric loss (Table **2** and **3**) [21, 23]. This variation on dielectric losses of compounds may

Table 1. Dielectric Properties of Chemical Compounds at 2.45 GHz at Room Temperature [22]

Solvent	Dielectric Loss (ε″)	Dielectric constant (ε′)
Ethylene glycol	49.95	37.0
Ethanol	22.866	24.3
Methanol	21.483	32.6
Water	9.889	80.4
1-Butanol	9.764	17.1
Acetonitrile	2.304	37.5
Acetone	1.118	20.7
Chloroform	0.437	4.8
Ethyl acetate	0.354	6.0
Toluene	0.096	2.4
Hexane	0.038	1.9

Table 2. Dielectric Properties of Representative Polymers at Room Temperature [21]

Polymer	Dielectric Loss (ε″)		Dielectric constant (ε′)	
	1×10^9 Hz[a]	3×10^9 Hz	1×10^9 Hz	3×10^9 Hz
Polychloroprene	–	0.136	–	2.84
Poly(methylmetacrylate)	–	0.018	–	2.57
Poly(ethyleneterephthalate)	0.008	–	2.80	–
Nylon-6	0.062	–	3.10	–
Poly(vinylidene fluoride)	0.300	–	2.90	–
Polypropylene	0.005	–	1.20	–
Butyl rubber[b]	–	0.002	–	2.40
Butadiene-styrene[c]	–	0.011	–	2.45
Hevea rubber[d]	–	0.006	–	2.15

a) Measurement frequency. b) Isobutene-isoprene copolymer (99:1–98:2). c) Butadiene-styrene copolymer (75:25 wt/wt). d) Purified, natural rubber (pale crepe): >98% cis-1,4-polyisoprene.

Table 3. Dielectric Properties of Polyamides at 1 ×10^9 Hz at Various Temperatures [23]

Polyamide	Temperature / °C	Dielectric Loss (ε″)	Dielectric constant (ε′)
6	-30	0.0018	3.0
	0	0.0033	3.0
	30	0.0065	3.1
	60	0.0081	3.2
	90	0.016	3.4
66	-30	0.0016	3.0
	0	0.0027	3.0
	30	0.0045	3.0
	60	0.0077	3.1
	90	0.014	3.2
610	-30	0.0018	3.0
	0	0.0033	3.0
	30	0.0043	3.0
	60	0.0083	3.0
	90	0.011	3.1

cause accelerated reaction. Microwaves activate polar reactant and by-product molecules in the reaction system, allowing polycondensation to proceed. On the other hand, the resulting polymers are activated to a lesser extent than the reactants and by-products because of their low dielectric properties. Product decomposition is, therefore, inhibited, and polycondensation may be accelerated by microwave irradiation. For polyester and polyamide synthesis by polycondensation which is a reversible reaction, this selective interaction by microwaves has an advantage. Ring-opening polymerization may be also accelerated because of differences in dielectric properties between reactant and product.

Namely, reactants and by-products having high dielectric loss may be activated by microwaves. In contrast, property of low dielectric loss inhibits resulting polymer from reverse reaction. Consequently, polycondensation is accelerated. In a case of ring-opening polymerization, reaction may be accelerated because of difference of dielectric property between reactant and resultant.

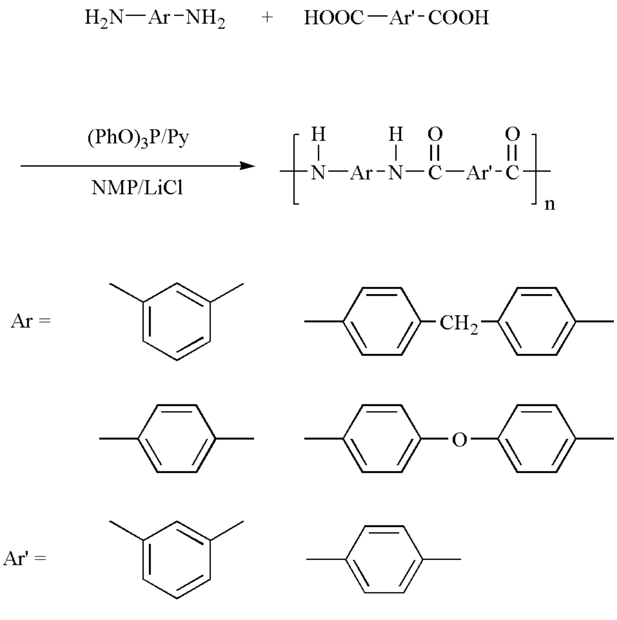
This mini review focuses on polyester and polyamide syntheses by polycondensation and ring-opening polymerization with time series. The end of the review describes an approach to scale-up microwave-assisted direct polycondensation with a view to a commercial process.

Microwave-assisted Polyamide Synthesis

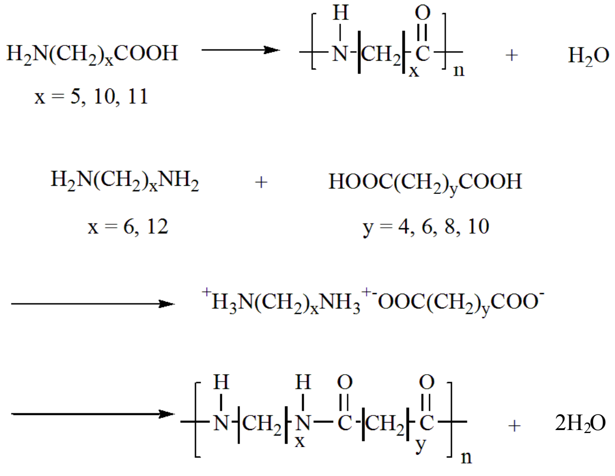
Several microwave-assisted polycondensations have been reported by Imai *et al.* since 1993 [24]. Aromatic diamines were polymerized by microwave heating in the presence of aromatic dicarboxylic acids, showing that microwave heating accelerated the direct polycondensation to a greater extent as compared to conventional heating (Scheme **4**). Using a domestic microwave oven, mixtures of aromatic diamine with aromatic dicarboxylic acid were heated at 500 W for 30-50 s. The reaction temperature was over 250 °C as indicated by thermocouple measurements. The resulting polymers exhibited intrinsic viscosities of 0.29-0.92 dL/g. Comparing to conventional heating, microwave heating achieved shorter reaction time and reaction acceleration in cases of various combinations of monomers.

Imai *et al.* have also reported the microwave-assisted direct polycondensation of ω-amino acid and aliphatic polyamide (Scheme **5**) [25]. Nylon with an intrinsic viscosity of 0.5 dL/g was obtained by microwave heating after a 5 min irradiation. They optimized the polycondensation solvent by choosing among water, dimethylsulfoxide, dimethylacetamide, nitrobenzene, ethanediol, *m*-cresol, and *o*-chlorophenol. Using *m*-cresol and *o*-chlorophenol as solvents, nylon was polycondensed in higher molecular weights compared to other solvents. The microwave-induced acceleration was monitored by measuring the degree of polymerization as a function of time and comparing microwave and oil bath heating (Fig. **1**).

Later works by Imai have reported the microwave-assisted rapid synthesis of polyamides at frequent intervals. Mallakpour *et al.* have used microwave heating to synthesize polyamide [20, 26-30]. They have recently energetically worked on synthesizing optically active polyamides using microwave heating [28]. Aromatic polyamides having optically active 4-(2-phthalimidiylpropanoylamino)benzoylamino groups have been synthesized by microwave heating using a domestic microwave oven (Scheme **6**). A mixture of modified isophthalic acid and diamine in *N*-methylpyrrolidone (NMP) was placed in a porcelain dish and irradiated with microwaves at 900 W for 2 min without temperature measurement. Polyamides with inherent viscosities of 0.50-0.79 dL/g were obtained. The advantage of microwave heating was confirmed by comparison with conventional heating under reflux temperature of NMP.



Scheme 4. Direct polycondensation for synthesis aromatic polyamides.



Scheme 5. Direct polycondensation for synthesis aliphatic polyamides.

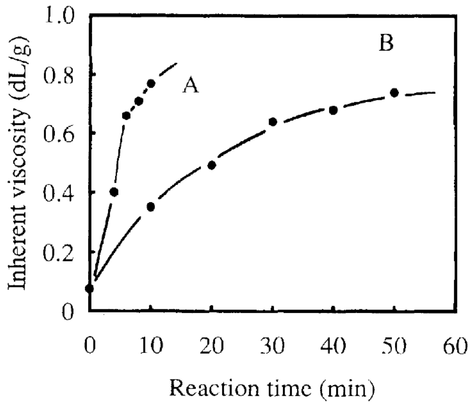
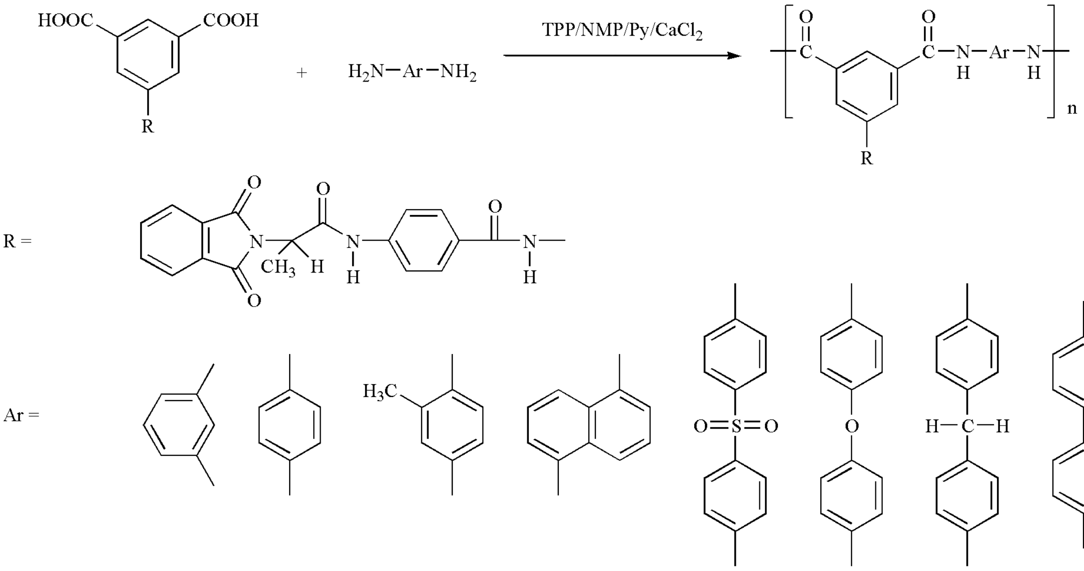


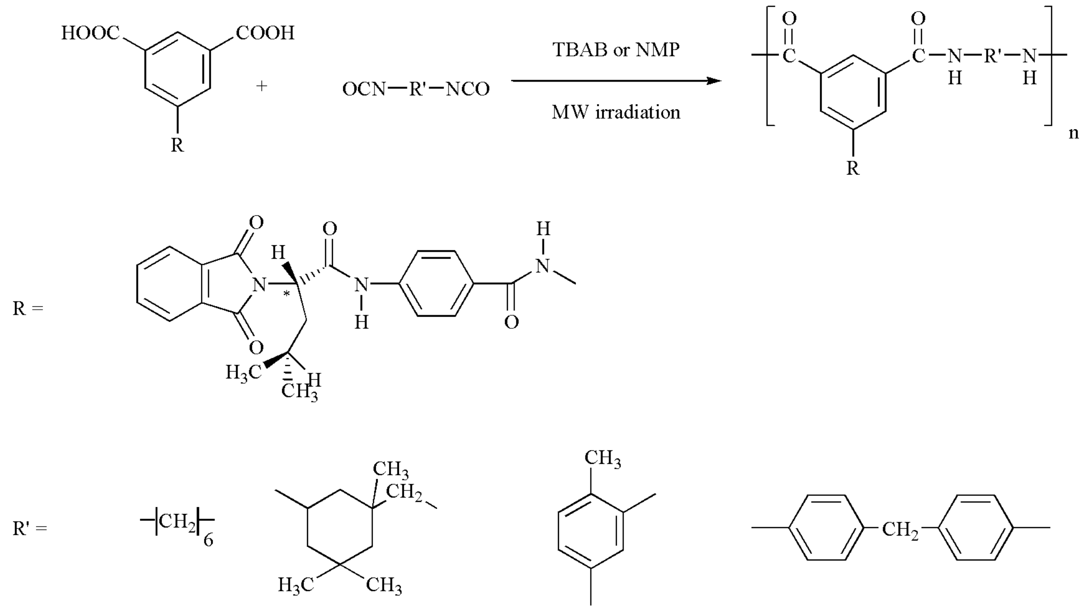
Fig. (1). Time dependence of inherent viscosity of the polyamide formed by the polycondensation of 12-aminododecanoic acid (2 g): (A) the microwave-assisted polycondensation in *m*-cresol, and (B) the melt polycondensation at 210 ºC Reproduced from ref. 25 with permission. Copyright 1996 by The Society of Polymer Science, Japan.

Ionic liquid solvents are prime candidates to optimize microwave effects [31-35]. They are high microwave absorber compounds. Rapid heating was achieved using ionic liquids and the organic reaction was accelerated. Mallakpour *et al.* [30] reported that the microwave-assisted polycondensation was accelerated upon ionic liquid addition to the reaction mixture (Scheme **7**). Diacid, diisocyanate, and dibutyltin dilaurate catalyst (DBTDL) were ground in the presence of the tetrabutylammonium bromide (TBAB) ionic liquid and heated by microwave irradiation. Polymers with inherent viscosities of 0.36-0.91 dL/g were synthesized at 900 W for 4 min. With NMP as a solvent, polymers with inherent viscosities of 0.36-0.68 dL/g were obtained. Hence, polyamidation by microwave heating combined with ionic liquid was accelerated to a greater extent as compared to that without combining ionic liquid.

Microwave heating not only accelerated the reaction but also improved the physical properties of the resulting polymers. Lu *et al.* [36-38] have reported the synthesis of polyimides exhibiting optical nonlinearity. Their property was improved using microwave heating. Benzoguanamine (BGA) was reacted with pyromellitic dianhydride (PMDA) in dimethylformamide (DMF) using microwave



Scheme 6. Synthesis of optically active polyamides.



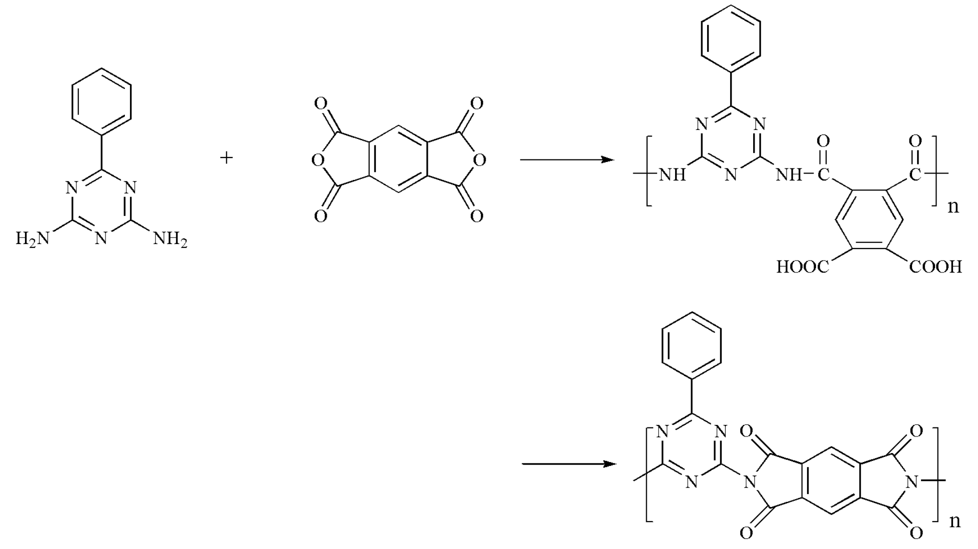
Scheme 7. Synthesis of optically active polyamides.

heating to give polyamic acid (PAA) (Scheme **8**) [36]. PAA was precipitated and the solid-phase polymerization was carried out for 10 min under microwave heating. The imidization degree of the polyimide obtained by microwave heating was 1.5 times as large as that for the polymer synthesized in 5 h by conventional heating. The third-order nonlinear optical coefficients were improved two times upon increasing the degree of imidization.

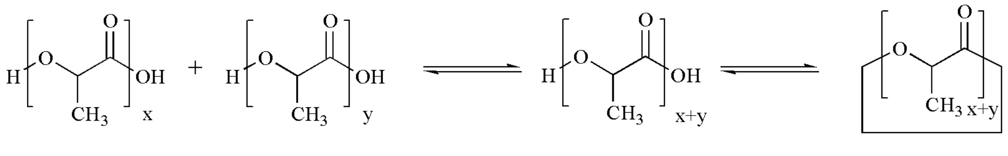
Microwave-assisted Polyester Synthesis

Several microwave-assisted polyester syntheses have been reported since 2001. Zsuga *et al.* synthesized oligo(D, L-lactic acid) (ODLLA) by microwave and conventional heating (Scheme **9**) [39]. Microwave heating was carried out by using a domestic microwave oven without temperature measurement. The average molecular weight of ODLLA synthesized using microwaves for 20 min was the same as that synthesized by conventional heating at 100 °C for 24 h. MALDI MS measurements showed that the structure of ODLLA prepared by microwave heating had unique advantage over conventional heating. Linear ODLLA was synthesized more selectively than cyclic ODLLA (Fig. **2**). Selective synthesis of linear oligo(lactic acid) (OLA) by microwave heating have been also described by Takeuchi *et al.* [40].

For microwave-assisted polyester synthesis, microwaves have been frequently applied to a ring-opening polymerization than polycondensation and verified accelerating reaction. Microwaves have been applied to polyester synthesis through ring-opening polymerization. Liu *et al.* [41, 42] have reported the microwave-assisted ring-opening polymerization of ε-caprolactone (CL). A mixture of ε-CL (10 g) and $Sn(Oct)_2$ (0.1 mol% catalyst concentration) was heated above 300 °C using a domestic microwave for 30 min (Scheme **10**). The average molecular weight (M_w) of the resulting polymer amounted to 123,000. In addition, the product was colorless, a unique advantage of microwave heating.



Scheme 8. Polyamidation and imidation for synthesis of a nonlinear optical polymer.



Scheme 9. Polycondensation of oligo (lactic acid).

Liu *et al.* have also reported the microwave-assisted ring-opening polymerization of D,L-lactide (Scheme **11**) [43]. Under optimized reaction conditions, a mixture of D,L-lactide with $Sn(Oct)_2$ (0.1 mol% catalyst concentration) was heated using a domestic microwave oven at 225 W for 10 min. An M_w value of 400,000 was obtained for the resulting polymer.

To clarify the microwave acceleration, Silvalingam *et al.* have described microwave effects in a ring-opening reaction of ε-CL through kinetics studies [44]. Three conditions involving microwave heating with catalyst, conventional heating with catalyst and conventional heating without catalyst, were compared. The corresponding activation energies were 5.7, 13.4, and 24.3 kcal/mol, respectively, estimated by using temperature-dependent rate coefficients. The ring-opening polymerization was significantly accelerated upon microwave heating.

Ritter *et al.* have described the unique effect of microwave heating on reaction selectivity (Scheme **12**) [45]. A ring-opening reaction was conducted using lipase as a catalyst and 2-mercaptoethanol as an initiator. A mixture of ε-CL, 2-mercaptoethanol, and Novozyme 435 in diethyl ether was heated under reflux for 90 min in a single-mode microwave reactor (Discover, CEM). An -SH terminated oligo(ε-caprolactone) (OCL) with an M_w value of 3,600 was obtained in 29% yield. An OCL with approximately equivalent average molecular weight was obtained in 18% yield under the same reaction conditions using conventional heating. This polyester had a terminal -OH or -SH moiety. Terminal -SH groups were, therefore, selectively formed using microwave heating.

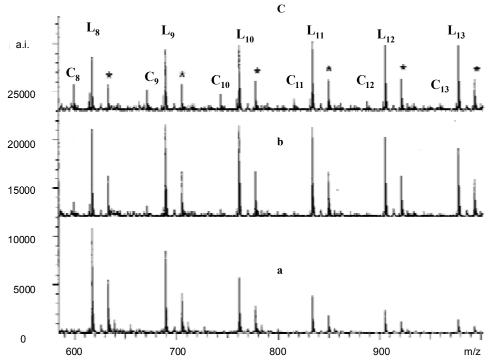
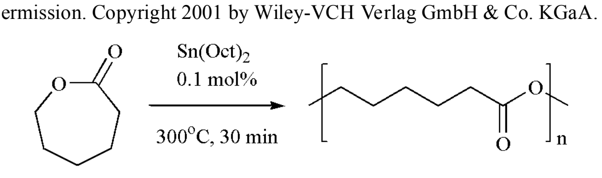
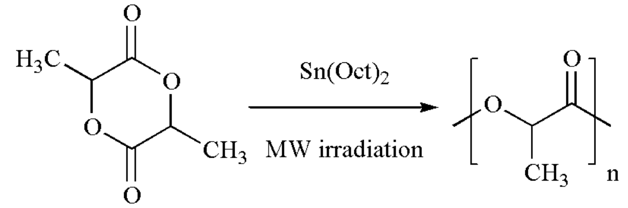


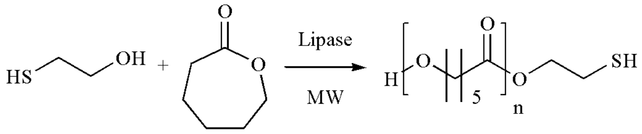
Fig. (2). MALDI MS spectrum of the products of the melt polycondensation of lactic acid performed under microwave irradiation for 10 min (a), 20 min (b), and 30 min (c) (load: 5.0 g). "L" represents the linear, "C" the cyclic oligomers. Subscripts denote the corresponding degree of polymerization, and asterisks the potassium-cationized peaks. Reproduced from ref. 39 with permission. Copyright 2001 by Wiley-VCH Verlag GmbH & Co. KGaA.



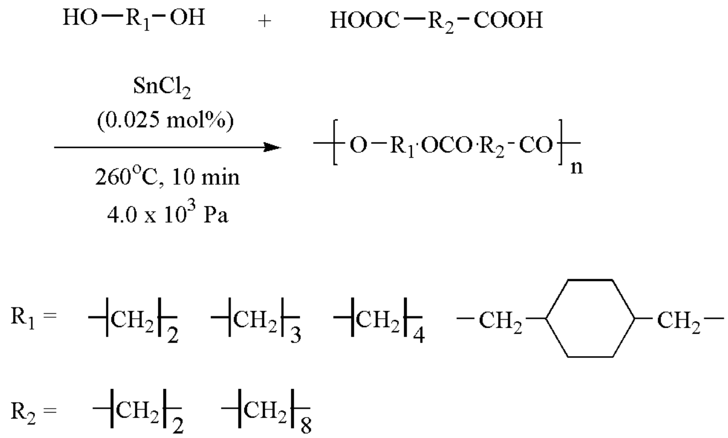
Scheme 10. Ring-opening polymerization of ε-caprolactone.



Scheme 11. Ring-opening polymerization of lactide.



Scheme 12. Ring-opening polymerization of ε-caprolactone by using chemoenzymatic catalyst.

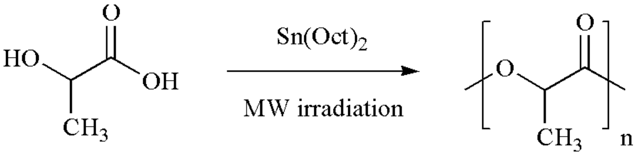


Scheme 13. Synthesis of aliphatic polyesters by direct polycondensation.

Nagahata *et al.* have reported the microwave-assisted direct polycondensation of aliphatic polyesters in a single-mode microwave reactor (Discover, CEM) (Scheme **13**) [46, 47]. Catalysts were optimized by selecting among $HfCl_4{\cdot}2THF$, $Sc(Otf)_3$, $ZrCl_4$, $Ti(OiPr)_4$, $SnCl_2(C_4H_9)_2$, $SnCl_2$, and p-$TsOH{\cdot}H_2O$. Reaction conditions such as temperature, time, and catalyst concentration were also optimized [46]. Poly(butylene succinate) with an M_w value of 29,000 was obtained using $SnCl_2$ as catalyst (0.025 mol% catalyst concentration) at 260 °C for 10 min under 4,000 Pa. In comparison with conventional heating for 5 h, microwave irradiation showed a ten-fold increase in the polycondensation rate. Under the same reaction conditions, poly(ethylene succinate), poly(propylene succinate), poly(1,4-cyclohexanedimethylene succinate), poly(ethylene sebacate), poly(propylene sebacate), poly(butylene sebacate), and poly(1,4-cyclohexanedimethylene sebacate) with average molecular weights ranging within 5,100-36,000 were synthesized.

Takeuchi *et al.* have reported the microwave-assisted direct polycondensation of L-LA using a single-mode microwave reactor (Discover, CEM) [40]. PLA with an M_w value greater than 10,000 was obtained using microwave heating with $SnCl_2/p$-TsOH as catalyst (Scheme **14**). The optimal catalyst was found among $SnCl_2$, $Sn(Oct)_2$, $SnCl_2(C_4H_9)_2$, p-$TsOH{\cdot}H_2O$, $SnCl_2/p$-TsOH, phosphoric acid, and sulphuric acid. PLA with an M_w value of 16,000 was synthesized using $SnCl_2/p$-TsOH (0.6 mol% catalyst concentration) at 200 °C for 30 min under 4,000 Pa. The microwave-induced acceleration of the polycondensation was compared with conventional heating under the same reaction conditions. For direct polycondensation, it is necessary to operation under vacuum for obtaining high-molecular weight polymers. However, microwave discharge occurred under 4,000 Pa of pressure in a microwave field. The authors inhibited the discharge by controlling the electromagnetic field in the microwave cavity.

Takeuchi *et al.* have tried to develop 300 g and 30 kg batch-scale multimode microwave reactors having prevention of microwave discharge under vacuum in anticipation of a commercial process. These microwave instruments operated under vacuum ($P < 1{,}000$ Pa) [48]. PLAs with M_w values of 9,600 and 13,200 were obtained after 5 h at reaction scales of 200 g (Fig. **3**) and 20 kg (Fig. **4**), respectively, using $SnCl_2/p$-TsOH (0.6 mol% catalyst concentration) at 180 °C. In addition, the authors have noticed energy efficiency for polycondensation of L-LA. The consumed energy was estimated from the accumulated microwave power at each reaction scale. The energy per mol consumed by the PLA synthesis was reduced by 94% during the hundred-fold scale-up.



Scheme 14. Synthesis of poly(lactic acid) by direct polycondensation.

Based on this development, a 30 kg scale microwave reactor has been released in a commercial plant to synthesize OLA without catalyst. Compared to the previous process, which involved multiple small-scale production lines and electrothermal heaters, this reaction process using microwave heating required one third of the original total reaction time. Furthermore, the energy consumption of the microwave was compared to the previous process. The microwave process reduced CO_2 emission by 70% [49].

To construct the large-scale microwave reactor, the authors also measured the dielectric properties during the polycondensation of LA [50]. Dielectric properties of LA solution, dehydrated LA ($M_w = 620$), and OLA ($M_w = 2{,}240$) were measured as a function of temperature using a vector network analyzer, allowing the half-

Fig. (3). 300 g scale multimode microwave reactor.

Fig. (4). 30 kg scale multimode microwave reactor.

power penetration depths to be calculated. The dielectric properties decreased with progressing polycondensation. Microwaves deeply penetrated into LA with progressing polycondensation because of decreasing dielectric properties. At 120 °C, microwaves penetrated OLA at a depth that was 6 times as that in LA solution (Fig. **5**).

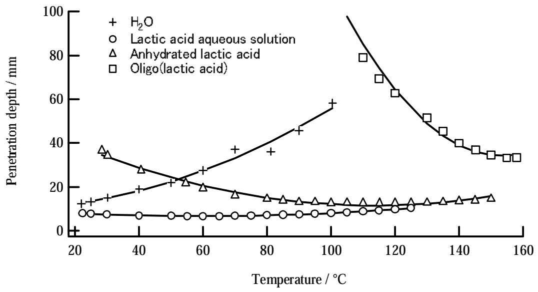


Fig. (5). Calculated penetration depths of samples as a function of temperature. Weight-average molecular weights of anhydrated lactic acid and oligo(lactic acid) were 622 and 2240, respectively. Reproduced from ref. 50 with permission. Copyright 2010 by Elsevier.

CONCLUSIONS

This mini review focused on the microwave-assisted direct polycondensation and ring-opening polymerization to synthesize polyesters and polyamides. Since the report by Imai *et al.*, many reactions have been carried out and remarkable accelerations of reactions have been observed. In the future, microwave heating may be applied to more reactions to synthesize polyesters, polyamides, and their copolymers than ever before. However, microwave techniques must be applied for the development of bench- and plant-scale reactors. Knowledge of reactant and resulting polymer dielectric properties concerning progressing reaction and temperature dependence is important when constructing large-scale reactors. Microwave synthesis and measurement of physical properties will be widely reported in future.

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REFERENCES

[1] Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science Ltd.: Oxford, **1995**.

[2] Flory, P. J. Fundamental principles of condensation polymerization. *Chem. Rev.,* **1946**, *39*, 137-197.

[3] Karayannidis, G. P.; Achilias, D. S. Chemical recycling of poly(ethylene terephthalate). *Macromol. Mater. Eng.*, **2007**, *292*, 128-146.

[4] Nikles, D. E.; Farahat, M. S. New motivation for the depolymerization products derived from poly(ethylene terephthalate) (PET) waste: A review. *Macromol. Mater. Eng.,* **2005**, *290*, 13-30.

[5] Satyanarayana, K. G.; Arizaga, G. G. C.; Wypych, F. Biodegradable composites based on lignocellulosic fibers-An overview. *Prog. Polym. Sci.,* **2009**, *34*, 982-1021.

[6] Weil, E. D.; Levchik, S. V. Flame retardants in commercial use or development for textiles. *J. Fire Sci.,* **2008**, *26*, 243-281.

[7] Perepelkin, K. E. Principles and methods of modification of fibres and fibre materials. A review. *Fibre Chem.,* **2005**, *37*, 123-140.

[8] Von Hippel, A. R. *Dielectric Materials and Applications*; Artech House: Boston, **1995**.

[9] Metaxas, A. C.; Meredith, R. J. *Industrial Microwave Heating*; Peter Peregrinus Ltd.: London, **1983**.

[10] Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. The use of microwave-ovens for rapid organic-synthesis. *Tetrahedron Lett.,* **1986**, *27*, 279-282.

[11] Giguere, R. J.; Bray, T. L.; Duncan, S. M.; Majetich, G. Application of commercial microwave-ovens to organic-synthesis. *Tetrahedron Lett.,* **1986**, *27*, 4945-4948.

[12] Kappe, C. O. Microwave dielectric heating in synthetic organic chemistry. *Chem. Soc. Rev.,* **2008**, *37*, 1127-1139.

[13] Kappe, C. O. Controlled microwave heating in modern organic synthesis. *Angew. Chem., Int. Ed.,* **2004**, *43*, 6250-6284.

[14] Kappe, C. O.; Stadler, A. *Microwaves in Organic and Medicinal Chemistry*; Wiley-VCH: Weinheim, **2005**.

[15] Loupy, A. *Microwaves in Organic Synthesis*; 2nd ed.; Wiley-VCH Verlag: Weinheim, **2006**.

[16] Yanagawa, H.; Kojima, K.; Ito, M.; Handa, N. Synthesis of Polypeptides by Microwave-Heating .1. Formation of polypeptides during repeated Hydration-Dehydration cycles and their characterization. *J. Mol. Evol.,* **1990**, *31*, 180-186.

[17] Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. Microwave assisted synthesis, crosslinking, and processing of polymeric materials. *Adv. Polym. Sci.,* **2003**, *163*, 193-263.

[18] Wiesbrock, F.; Hoogenboom, R.; Schubert, U. S. Microwave-assisted polymer synthesis: State-of-the-art and future perspectives. *Macromol. Rapid Commun.,* **2004**, *25*, 1739-1764.

[19] Hoogenboom, R.; Schubert, U. S. Microwave-assisted polymer synthesis: Recent developments in a rapidly expanding field of research. *Macromol. Rapid Commun.,* **2007**, *28*, 368-386.

[20] Mallakpour, S.; Rafiee, Z. Application of microwave-assisted reactions in step-growth polymerization: A review. *Iran. Polym. J.,* **2008**, *17*, 907-935.

[21] Bogdal, D.; Prociak, A. *Microwave-Enhanced Polymer Chemistry and Technology* Blackwell Publishing: Iowa, **2007**.

[22] Hayes, B. L. *Microwave Synthesis - Chemistry at the Speed of Light*; CEM Publishing: Matthews, **2002**.

[23] Brandrup, J.; Immergut, E. H. In *Polymer Handbook*; 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, **1989.**

[24] Park, K. H.; Watanabe, S.; Kakimoto, M.; Imai, Y. Rapid synthesis of aromatic polyamides by microwave-assisted directed polycondensation of aromatic diamines with aromatic dicarboxilic acids. *Polym. J.,* **1993**, *25*, 209-213.

[25] Imai, Y.; Nemoto, H.; Watanabe, S.; Kakimoto, M. A new facile and rapid synthesis of aliphatic polyamides by microwave-assisted polycondensation of omega-amino acids and nylon salts. *Polym. J.,* **1996**, *28*, 256-260.

[26] Mallakpour, S. E.; Hajipour, A. R.; Faghihi, K. Synthesis of novel optically active poly(esterimide)s with benzophenone linkages by microwave-assisted polycondensation. *Polym. Int.,* **2000**, *49*, 1383-1388.

[27] Mallakpour, S.; Sepehri, S. Preparation of new optically active polyamides containing a L-Phenylalanine, Phthalimide side-chain *via* the Diisocyanate Route by microwave energy: comparison with conventional heating. *Des. Monomers Polym.* **2008**, *11*, 535-546.

[28] Mallakpour, S.; Rafiee, Z. Microwave-induced synthesis of new optically active and soluble polyamides containing pendent 4-(2-phthalimidiyl-propanoylamino)benzoylamino-groups. *Amino Acids* **2009**, *37*, 665-672.

[29] Mallakpour, S.; Seyedjamali, H. Fast synthesis of optically active polyamides containing l-methionine linkages in ionic liquid *via* a microwave-assisted process. *Colloid Polym. Sci.* **2009**, *287*, 1111-1116.

[30] Mallakpour, S.; Zadehnazari, A. Fast synthesis, using microwave induction heating in ionic liquid and characterization of optically active aromatic polyamides. *J. Macromol. Sci. Part A-Pure Appl. Chem.* **2009**, *46*, 783-789.

[31] Kubisa, P. Ionic liquids as solvents for polymerization processes-progress and challenges. *Prog. Polym. Sci.* **2009**, *34*, 1333-1347.

[32] Strauss, C. R. A strategic, 'green' approach to organic chemistry with microwave assistance and predictive yield optimization as core, enabling technologies. *Aust. J. Chem.* **2009**, *62*, 3-15.

[33] Sun, N.; Rahman, M.; Qin, Y.; Maxim, M. L.; Rodríguez, H.; Rogers, R. D. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chem.* **2009**, *11*, 646-655.

[34] Hoffmann, J.; Nüchter, M.; Ondruschka, B.; Wasserscheid, P. Ionic liquids and their heating behavior during microwave irradiation – A state of the art report and challenge to assessment. *Green Chem.* **2003**, *5*, 296-299.

[35] Nguyen, H. P.; Matondo, H.; Baboulene, M. Ionic liquids as catalytic "green" reactants and solvents for nucleophilic conversion of fatty alcohols to alkyl halides. *Green Chem.* **2003**, *5*, 303-305.

[36] Lu, J. M.; Chen, N. Y.; Ji, S. J.; Sun, Z. R.; Ding, M. X.; Zhu, X. L. Polymerization of benzoguanamine and pyromellitic dianhydride under microwave radiation and its third-order optical nonlinearities. *J. Appl. Polym. Sci.* **2001**, *82*, 1356-1363.

[37] Lu, J. M.; Ji, S. J.; Chen, N. Y.; Sun, Z. R.; Zhu, X. L.; Shi, W. P.; Wang, Z. G. Third-order nonlinear optical properties of polyureas and polyimide synthesized by microwave irradiation. *J. Appl. Polym. Sci.* **2003**, *89*, 2611-2617.

[38] Tang, X. B.; Lu, J. M.; Zhang, Z. B.; Zhu, X. L.; Wang, L. H.; Li, N. J.; Sun, Z. R. Polycondensation of sodium tetrazodiphenyl naphthionate and pyromellitic dianhydride under microwave irradiation and the performance of the third-order nonlinear optics. *J. Appl. Polym. Sci.* **2003**, *88*, 1121-1128.

[39] Kéki, S.; Bodnár, I.; Borda, J.; Deák, G.; Zsuga, M. Fast microwave-mediated bulk polycondensation of D,L-lactic acid. *Macromol. Rapid Commun.* **2001**, *22*, 1063-1065.

[40] Nagahata, R.; Sano, D.; Suzuki, H.; Takeuchi, K. Microwave-assisted single-step synthesis of poly(lactic acid) by direct polycondensation of lactic acid. *Macromol. Rapid Commun.* **2007**, *28*, 437-442.

[41] Liao, L. Q.; Liu, L. J.; Zhang, C.; He, F.; Zhuo, R. X. Heating characteristics and polymerization of epsilon-caprolactone under microwave irradiation. *J. Appl. Polym. Sci.* **2003**, *90*, 2657-2664.

[42] Liao, L. Q.; Liu, L. J.; Zhang, C.; He, F.; Zhuo, R. X.; Wan, K. Microwave-assisted ring-opening polymerization of epsilon-caprolactone. *J. Polym. Sci. Pol. Chem.* **2002**, *40*, 1749-1755.

[43] Zhang, C.; Liao, L. Q.; Liu, L. J. Rapid ring-opening polymerization of D,L-lactide by microwaves. *Macromol. Rapid Commun.* **2004**, *25*, 1402-1405.

[44] Sivalingam, G.; Agarwal, N.; Madras, G. Kinetics of microwave-assisted polymerization of epsilon-caprolactone. *J. Appl. Polym. Sci.* **2004**, *91*, 1450-1456.

[45] Kerep, P.; Ritter, H. Chemoenzymatic synthesis of polycaprolactone-block-polystyrene *via* macromolecular chain transfer reagents. *Macromol. Rapid Commun.* **2007**, *28*, 759-766.

[46] Velmathi, S.; Nagahata, R.; Takeuchi, K. Extremely rapid synthesis of aliphatic polyesters by direct polycondensation of 1 : 1 mixtures of dicarboxylic acids and diols using microwaves. *Polym. J.* **2007**, *39*, 841-844.

[47] Velmathi, S.; Nagahata, R.; Sugiyama, J.; Takeuchi, K. A rapid eco-friendly synthesis of poly(butylene succinate) by a direct polyesterification under microwave irradiation. *Macromol. Rapid Commun.* **2005**, *26*, 1163-1167.

[48] Nakamura, T.; Nagahata, R.; Kunii, K.; Soga, H.; Sugimoto, S.; Takeuch, K. Large-Scale Polycondensation of Lactic Acid using microwave batch reactors. *Org. Process Res. Dev.* **2010**, *14*, 781-786.

[49] Takeuchi, K.; Nagahata, R. AIST home page. http://www.aist.go.jp/aist_e/latest_research/2009/20091216/20091216.html (accessed January 2010).

[50] Nakamura, T.; Nagahata, R.; Suemitsu, S.; Takeuchi, K. *In-situ* measurement of microwave absorption properties at 2.45 GHz for the polycondensation of lactic acid. *Polymer* **2010**, *51*, 329-333.

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