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Application of Microwave-assisted Reactions in Step-growth Polymerization: A Review

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A B S T R A C T

n modern synthetic organic chemistry laboratories protocols for convenient and rapid transformations are highly desired. Microwave activation has received considerable attention in recent years and it is a subject of intense debate in the scientific community. This technique as an alternative to conventional energy sources for introduction of energy into reactions has become a very well-known and practical method in various fields of chemistry. Microwave-assisted organic synthesis is known for the spectacular accelerations produced in many reactions as a consequence of the heating rate, a phenomenon that cannot be easily reproduced by classical heating methods. As a result, higher yields, milder reaction conditions, and shorter reaction times can often be attained. Microwave is now extensively accepted as an efficient and non-ionized electromagnetic energy source in several different fields of polymerization reactions such as step-growth, ring-opening and radical polymerizations. Its specific heating method attracts extensive interest because of rapid volumetric heating, suppressed side reactions, energy saving, direct heating, decreased environmental pollutions, and safe operations. This review introduces the application of microwave irradiation in step-growth polymerization in details up to 2008. In order to demonstrate the effectiveness of microwave-assisted reactions, some comparisons are made with the classical heated polycondensations.

Key Words:

microwave irradiation; polycondensation reactions; green chemistry.

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INTRODUCTION

Microwaves (i.e., short waves or high frequency radio waves) are electromagnetic waves with wavelengths ranging from 1 mm to 1 m, or frequencies between 300 MHz to 300 GHz, displaying the medial location of these waves between infrared and radio waves. When molecules with enduring dipoles are located in an electric field, they align with this field. Thus, if electric field oscillates, the orientation of the molecules will also change in reply to each oscillation therefore, energy is lost in the form of heat through molecular frictions and dielectric loss. The most domestic and commercial microwave ovens used for chemical synthesis operate at a frequency of 2.45 GHz (corresponding to a wavelength of 12.24 cm) to avoid the interferences with telecommunication and cell phone frequencies. Electromagnetic waves in the range of microwave make the polar molecules absorb a great quantity of energy which dissipates in the form of heat from internal resistance to the rotation of the molecular dipoles. Non-polar molecules such as diethyl ether, carbon tetrachloride, benzene, and toluene are microwave-inactive, while polar molecules such as N,N-dimethylformamide, acetonitrile, CH₂Cl₂, ethanol, and H₂O are microwave-active. Microwave heating is a fast technique of heating materials for domestic, industrial, and medical uses. It is an alternative to conventional conductive heating methods for introducing energy into reactions. Gedye et al. [1] and Giguere et al. [2] used microwave heating to accelerate organic chemical transformations in 1986. Under microwave irradiation, superheating to temperatures above the conventional boiling point of a solvent can be reached and therefore, decrease in reaction time is not astonishing. This technique has become a very recognized and useful technology in organic chemistry as well as in macromolecular chemistry. Microwave heating uses the ability of some compounds (liquids or solids) to transform electromagnetic energy into heat and thereby drive chemical reactions. In recent years researchers have witnessed extensive use of microwaves energy in organic syntheses reported in several outstanding reviews [3-13] and technical books [14,15]. The number of research works using microwave heating is increased to more than 3000

publications by the middle of 2008, and we believe that this trend will continue to increase in the near future. The recently emerged use of microwave energy as an environmentally friendly method offers many discrete benefits over conventional synthetic methods, such as volumetric, fast, directly selective, instantaneous, controllable heating, energy economy, low cost, decreased environmental pollutions, and safe operations, therefore, it has the potential of being used in large-scale commercial production. It presents a clean, cheap, and convenient method of heating, which often results in higher yields, shorter reaction times, higher pure products due to less unwanted side reactions, and better reliability and reproducibility.

Microwave heating take places on molecular levels as opposed to relying on convection currents and thermal conductivity when using conventional heating methods. This offers an explanation to why microwave-assisted reactions are much faster. With microwave irradiation, since the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be, for short times, much greater than the overall recorded temperature of the bulk reaction mixture. In essence, there will be sites of instantaneous localized super-heating where reactions will take place much faster than in the bulk. This localized superheating can be especially marked when the reaction mixture contains highly polar reagents or metal salts.

Microwave energy is transferred by dielectric loss, and therefore the dielectric loss factor (ε ") and the dielectric constant (ε ') of a material are two determinants of the efficiency of heat transfer to the sample. The quotient (ε "/ ε ') namely the dissipation factor (tan δ) with a high value shows ready susceptibility to microwave energy. Tan δ factor is proportional to the polarizability and the electrical conductivity of the reaction medium where polar and ionically conducting solvents are preferable for microwave-assisted reactions. The rate of temperature increase is a function of tan δ , the specific heat capacity, the emissivity, the geometry and the volume of the reaction mixture, and the strength of the applied field.

Two different kinds of reactors exist for microwave-assisted organic synthesis: a multimode reactor and a monomode reactor. The most general apparatus used in the multimode reactor is identified

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as the commercial kitchen microwave oven. In the multimode reactors, the radiation created by the magnetron is directed through a waveguide and a mechanical field distributor in a rather large volume (microwave cavity). In the cavity, radiation is homogeneously distributed thus, avoiding the formation of standing waves. In the much smaller monomode cavities, the electromagnetic irradiation is directed through an accurately designed rectangular or circular wave guide onto the reaction vessel mounted at a fixed distance from the radiation source thus, creating a standing wave. The main difference between the two types of reactor systems is that while in multimode cavities several reaction vessels can be irradiated simultaneously in a multi-vessel rotor, however, in monomode systems there is only one vessel which can be irradiated at one time. In the latter case high throughput can be achieved by integrated robotics that moves individual reaction vessel in or out of the microwave cavity. However, recently commercial microwave ovens for synthesis have been introduced equipped with multi-vessel rotors.

Significant studies have been performed on the synthesis of valuable processes using microwave dielectric heating effects. These include the preparation of samples for organic chemistry [16-20], extraction of natural products from plants [21,22], ballast water treatment [23], synthesis of nanoparticles [24,25], polymer technology [26-30], drug release targeting [31], ceramics [32], and modifying the coal physicochemical property [33]. In addition, in the field of polymer synthesis, microwave energy has been widely used for polycondensation, free and controlled radical polymerizations, and ring-opening polymerization as well as the curing of epoxy and polyurethane resins. Several review papers have been published recently on microwave-assisted polymer synthesis and processing (e.g., processing of thermoplastics, polymer modification, and curing processes and preparation of dental materials) [34-42].

Since 1986, when the first articles were published on microwave assisted syntheses in household microwave ovens [1,2] there has been a progressively increasing attention in this research field. There have been several reviews and books dealing with various aspects of medium effects and mechanistic considerations of microwaves in organic syntheses [3-13]. These reviews have covered microwave-assisted technique in performing high-speed organic reactions. In addition, it is possible to conduct very clean and selective reactions with low energy inputs. These review works indicate that the microwave strategy provides broad scope in the future development of clean and sustainable organic chemistry. Some of these reviews demonstrate the potential of microwave technology in revolutionizing the combinatorial chemistry industry [4]. The application of microwave irradiation to the synthesis of natural products, heterocyclic systems, and fullerene derivatives shows that the effect of microwaves on the yield is particularly important for compounds of low reactivity as well as for highly sensitive reagents and products, due to the fact that mild reaction conditions, shorter reaction times, and/or lower temperatures can be used [7]. Another review discusses the use of microwave irradiation as a tool for the preparation of biological samples for subsequent mass spectrometric characterization and reduction in overall experimental time observed when microwave assistance is applied [11].

Step-growth polymerization is among the first polymerizations to be studied by using microwave heating technology and numerous examples have been summarized in previous mentioned review articles and books [33-36]. Conventional polycondensation reactions involve, in many cases, the use of harsh conditions such as high temperatures and long reaction times, but they can be performed with great success with the assistance of microwave energy. Some more recent review articles show an overview on the potentials of microwave-assisted reactions for synthesis of polymers.

Gong et al. reviewed microwave-assisted polymerization, with an emphasis on the microwave-assisted ring-opening polymerization, covering both homopolymerization and copolymerization of the cyclic monomers in which the advantages of microwave-assisted ring-opening polymerization over conventional polymerization are also discussed [33]. Microwave-assisted polymer synthesis, including step-growth, free and controlled radical, as well as ring-opening polymerizations have been reviewed by Schubert et al. [34]. Most microwave assisted polymerizations are performed in domestic ovens. The domestic microwave reactor has shown to be superior

to conventional heating in terms of reaction rate, inherent viscosity, and yield. The same group has also reviewed microwave-assisted polymer synthesis with the main focus on step-growth polymerizations, ringopening polymerization, and (controlled) radical polymerizations [35]. One of the most common uses of the microwave irradiation is in the polycondensation reactions therefore, in this review, we focus on the new publications in microwave assisted stepgrowth polymerization in recent years up to 2008. However, in all examples reviewed above, microwave heating reduced the reaction time of polycondensation reactions from hours to minutes/seconds. These reaction time reductions are speculated to arise from the rapid "in-core" heating of polar solvents and reagents.

Several review papers have been also published on microwave-assisted polymer processing [37,39-41]. Microwave activation presents many advantages in material processing over conventional heating methods e.g., greater flexibility, greater speed and energy savings, improved product quality and properties, and the synthesis of new materials that cannot be produced by other heating methods.

In this review we wish to report in details the application of microwave energy for the formation of non-vinyl polymers such as polyamides, polyimides, polyesters, polyureas, polyethers, poly(amideimide)s, poly(amide-ester)s, poly(ester-imide)s, poly(ether-imide)s, poly(ether-ester)s, poly(amideimide-urethane)s and poly(amide-ether-urethane)s via polycondensation reactions.

STEP-GROWTH POLYMERIZATION

The development of efficient and mild methods for

the synthesis of condensation polymers is a significant aspect of polymer chemistry. Microwave irradiation has received increasing applications in step-growth polymerization.

Polyamides

The approach to aliphatic polymers with amide linkages has been described by Imai et al. [43] from polycondensation of amino acids and nylon salts. The polymerization reactions are carried out in a domestic microwave oven in the presence of polar organic solvents and polyamides with inherent viscosities around 0.50 dL/g which have been reached after 5 min of irradiation time. These workers have investigated the temperature of various solvents under microwave irradiation and the effect of each solvent on the polymerization temperature and inherent viscosity of the polyamides formed by the polycondensation of 12aminododecanoic acid as a function of microwave irradiation time. It has been reported that highly polar solvents such as water, 1,3-dimethyl-2-imidazolidone and tetramethylene sulphone (sulpholane) produce heat quickly under microwave irradiation. The above authors have prepared polyamides having inherent viscosities in the range of 0.20-0.50 dL/g from nylon salts in high boiling solvents after 3-5 min of irradiation time, with inherent viscosity of polymers is found to be independent of the kind of the solvents.

Pourjavadi et al. [44] studied the polymerization reactions of linear aliphatic dicarboxylic acids (the length of the dicarboxylic acids chain were 2, 4, 6, and 8 -CH₂- moieties) with aromatic diamines such as *p*-phenylenediamine or 2,5-bis(4-aminophenyl)-3,4diphenylthiophene by the Yamazaki phosphorylation reaction (Scheme I). The polymerization was carried out in the presence of *N*-methylpyrrolidinone (NMP)



Scheme I. Microwave-assisted polymerizations of linear aliphatic dicarboxylic acids with aromatic diamines by the Yamazaki phosphorylation reaction.



Scheme II. Polycondensation reactions of 4,4'-azodibenzoyl chloride with different derivatives of 5,5-disubstituted hydantoin.

as a solvent and in a vessel of polyethylene screwcapped cylinder. The polymers were obtained after short reaction times (30 or 40 s) with medium to high yields (60-100%) and intrinsic viscosities in the range of 0.10-0.80 dL/g.

Faghihi et al. [45] reported the synthesis of polyamides by polycondensation reactions of 4,4'azodibenzoyl chloride [4,4'-azobenzenedicarboxylic acid chloride] and eight different derivatives of 5,5disubstituted hydantoin in the presence of a small amount of a polar organic medium such as o-cresol under microwave irradiation in domestic microwave oven (Scheme II). Polyamides with high yields and inherent viscosities between 0.35 and 0.60 dL/g were obtained within 7-12 min. A comparison of microwave-assisted polymerization with bulk polycondensation and the classical solution polycondensation showed that polymers obtained under microwave irradiation had higher viscosities and yields.

Loupy et al. [46] synthesized aromatic polyamides from an optically active isosorbide-derived diamine and diverse diacyl chlorides in the presence of a small amount of NMP in a monomodal microwave reactor (Scheme III). The molecular weight (MW) of polymers under microwave and interfacial polymerization or the Higashi process was compared. Thus, it was found that the MW of polymers obtained under microwave heating was much higher than the conventional conditions. The polymers were obtained with inherent viscosities between 0.22 and 0.73 dL/g, cor-



Scheme III. Synthesis of polyamides from optically active isosorbide-derived diamine and various diacyl chlorides.

responding to MWs up to 140,000 g/mol, while with interfacial polymerization or the Higashi method, lower MW polymers were acquired with inherent viscosities in the range of 0.04-0.36 dL/g.

Caouthar et al. [47] report the formation of optically active polyamides from reaction of an optically active isosorbide-derived diacyl chloride with two aromatic diamines, diphenylamino-isosorbide (DAI) and 4,4'-diaminodiphenylsulphone (DDS) in NMP under microwave irradiation and interfacial polymerization from an isosorbide-derived diamine with different diacyl chlorides. The polymers were obtained in 52% and 70% yields with inherent viscosities of 0.11 and 0.92 dL/g after 30 and 6 min of reaction time for diamines of DAI and DDS, respectively, while the polymerization reaction using interfacial technique has not been unsuccessful.

More recently, Mallakpour et al. [48] observed a higher reaction speed in microwave-assisted direct synthesis of photoactive polyamides by the stepgrowth polymerization of 5-(3-acetoxynaphthoylamino)isophthalic acid with a variety of aromatic diamines such as 1,5-naphthalenediamine, 4,4'diaminodiphenylmethane, benzidine, 4,4'-diaminodiphenylether, 2,5-diaminotoluene, 1,3-phenylenediamine and 1,4-phenylenediamine (Scheme IV). The polymerization was carried out in a domestic microwave oven by means of triphenyl phosphite and pyridine (Py) in the presence of calcium chloride and NMP. The polymerization reactions were optimized based on microwave power and time of reaction to obtain polymers with high yields and inherent viscosities. Polyamides with inherent viscosities of 0.27 to 0.56 dL/g were obtained after 2 min of irradiation time. Compared with conventional heating for 5 h under reflux conditions of the used solvents (NMP), higher yields and inherent viscosities were obtained using microwave irradiation, which also uses smaller amounts of Py and NMP. The solubility of these polymers improved due to the presence of bulky side group acetoxynaphthalamide while their thermal stability was preserved.

Mallakpour et al. [49,50] have also studied the reactions of chiral 5-(3-methyl-2-phthalimidylpen-



Scheme IV. Polyamidation reactions of 5-(3-acetoxynaphthoylamino)isophthalic acid with different aromatic diamines.



Scheme V. Polycondensation reactions of 5-(3-methyl-2-phthalimidylpentanoylamino)isophthalic acid and 5-(4-methyl-2-phthalimidyl-pentanoylamino)isophthalic acid with several aromatic and aliphatic diisocyanates.

tanoylamino) isophthalic acid and 5-(4-methyl-2phthalimidyl-pentanoylamino)isophthalic acid with several aromatic and aliphatic diisocyanates like 4,4'methylenebis (phenyl isocyanate), toluylene-2,4diisocyanate, isophorone diisocyanate and hexamethylene diisocyanate under microwave irradiation as well as conventional technique via direct polycondensation (Scheme V). The reactions were carried out in the presence of a small amount of NMP, dibutyltin dilaurate, Py or triethylamine as catalysts and/or under no catalyst conditions. The use of such an organic medium was necessary to induce effective homogeneous heating of the monomers. The polymerization occurred rapidly under microwave radiation and produced a series of optically active and thermally stable polyamides containing pendant phthalimide and L-leucine or L-isoleucine groups, with good yields and moderate inherent viscosities. They obtained comparable results from the point of yield and inherent viscosity of the polymers with lower reaction time by several orders of magnitude under microwave conditions and straightforward procedure.

Polyimides

Imai et al. [51] synthesized aliphatic polypyromellitimides from the reaction of the salt monomers composed of aliphatic diamines (the length of the diamines chain were 6-12 -CH2- moieties) and pyromellitic acid or its diethyl ester. The polymerization reactions were carried out in a domestic microwave oven in high boiling point and polar organic media such as NMP, N-cyclohexyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidone and tetramethylene sulphone. The best polymerization medium for this polycondensation was 1,3-dimethyl-2-imidazolidone and polymers were obtained with inherent viscosities of about 0.70 dL/g or above in only 2 min. When pyromellitic acid diethyl ester was used, microwave-assisted polycondensation rapidly provided a series of polyimides with higher viscosity values between 0.80 and 1.60 dL/g.

Lu et al. [52] prepared polyimides, having thirdorder non-linear optical properties, from sodium tetrazodiphenyl naphthionate and pyromellitic dianhydride under microwave irradiation as well as oil-bath heating in *N*,*N*-dimethylformamide (DMF) as a sol-



Scheme VI. Synthesis of polyimides by the reaction of sodium tetrazodiphenyl naphthionate and pyromellitic dianhydride.

vent by a two-step method (Scheme VI). Using microwave heating, the imidization time was reduced from hours to minutes and due to the fast heating rate the imidization degree was noticeably increased.

Lu et al. [53] also introduced polyimides containing the pyromellitoyl unit via two steps pathway, in the first step, from reaction of benzoguanamine and 2,4-tolylenediisocyanate generated polyurea, then polyimidation of the resulting polyurea and pyromellitic dianhydride in solid phase gave polyimide (Scheme VII). They found that the degree of imidization under microwave irradiation reached a maximum value in 8 min while by conventional heating it reached its highest value in 5 h.

Yi et al. [54] reported the copolycondensation of 3,3',4,4'-benzophenonetetra-carboxylic dianhydride, 4,4'-diaminodiphenylmethane and 4,4'-oxydianiline in DMF by the direct polycondensation under microwave irradiation as well as conventional solution polycondensation via a two-step procedure (Scheme VIII). In the first step, a certain amount of 4,4'-diaminodiphenylmethane and 4,4'-oxydianiline was dissolved in DMF. The reaction vessel, containing a mixture of a reactant and a solvent, was placed on the centre of the turntable in the microwave oven,

and then nitrogen gas was introduced from the top of the reaction vessel through a thin Teflon tube to minimize the danger of fire in the reaction system. Then, a certain amount of 3,3',4,4'-benzophenonetetracarboxylic dianhydride was dropped into the reaction vessel. The reaction system was irradiated with microwaves for a prescribed time at a low temperature. The polymerizations were carried out at different microwave irradiation times for which 2 h was found best for the preparation of poly(amic acid) with highest yield and inherent viscosity. The polyimidation was provided into the reactor under N₂ for 1 h and dehydrated under continuous microwave radiation. Compared with the conventional solution method, results showed that the polymers obtained via microwave-assisted polymerization had superior inherent viscosities and yields in a much shorter reaction time.

More recently, Xu et al. [55] have used a microwave-assisted polycondensation method for the synthesis of poly(amic acid) (PAA) and polyimide using pyromellitic dianhydride and 3,3', 4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-oxydianiline under microwave irradiation in DMF as a solvent. The polymerization under



Scheme VII. Synthesis of polyimide containing the pyromellitoyl unit.



Scheme VIII. Copolycondensation of 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-diaminodiphenylmethane and 4,4'-oxydianiline under microwave irradiation.



Scheme IX. Polycondensation of D,L-lactic acid.

microwave irradiation resulted in enhancement of the reaction rate as well as higher yield and inherent viscosity.

Polyesters

Using a single-mode microwave synthesizer (2.45 GHz frequency and 300 W maximum power), Takeuchi et al. [56] studied microwave-assisted direct polycondensation of lactic acid by use of a binary catalyst of SnCl₂/p-TsOH. They reported that microwave irradiation successfully accelerated the reaction and produced poly(lactic acid) (PLA) with a molecular weight higher than 10,000 g/mol. The reactions were performed with different catalysts like SnCl₂, Sn(Oct)₂, Bu₂SnCl₂, DCTB, SnCl₂/p-TsOH, p-TsOH, phosphoric acid and sulphuric acid. Under optimized conditions, the SnCl₂/p-TsOH binary catalyst gave white polymer with a molecular weight of 16,000 g/mol within 30 min of microwave irradiation at 200°C and the reaction time can be reduced significantly compared to conventional polycondensation at the same temperature. An oligomer of lactic acid with a weight-average molecular weight of 1800 g/mol in 53.5% isolated yield under normal pressure was obtained after 30 min of microwave irradiation. In contrast, no polymer was obtained upon the conventional heating system under the same conditions. PLA with molecular weights 6400 and 15,000 g/mol was resulted after 60 and 300 min of microwave irradiation, respectively. While, polymers with molecular weights 2300 and 8600 g/mol were produced at the same reaction times under conventional heating, respectively.

Recently, Nagahata et al. [57] studied direct polyesterification of succinic acid and butane-1,4-diol in the presence of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane as a catalyst. Under optimum conditions, within reaction time of 20 min, poly(butylene succinate) with a weight-average molecular weight of 2.35×10^4 g/mol was obtained. In comparison with the reactions conducted via conventional heating (5 h), microwave irradiation showed a ten-fold increase in the rate of polymerization.

Zsuga et al. [58] investigated the polycondensation of D,L-lactic acid under microwave conditions and conventional heating (Scheme IX). The oligomers were obtained after 20 min of irradiation with nearly the same molecular mass as those created under conventional heating at 100°C for 24 h. Compared with conventional heating the reaction proceeds with much higher rate and the molecular mass of the linear poly(lactic acid) obtained was within the range of 500 g/mol to 2000 g/mol as determined by means of matrix-assisted laser desorption ionization time-offlight mass spectrometry (MALDI-MS). Overheating of the reaction mixture led to decreased yield of polycondensation product probably due to the loss of oligomers with lower molecular mass during polycondensation reaction.

Sivalingam et al. [59] have studied the kinetics of zinc catalyzed polymerization of ε -caprolactone in bulk under microwave activation and thermal heating (under both catalytic and non-catalytic conditions). 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, respectively. This indicates that microwave irradiation increases the catalytic polymerization rate compared to the thermally aided processes by lowering the activation energy.

Polyureas

The synthesis of high-molecular-weigh polyureas and polythioureas via the reaction of aromatic and aliphatic amines with urea and thioureas in the presence of a catalytic amount of *p*-toluenesulphonic acid are reported by Banihashemi et al. [60] using a microwave oven (for duration of 12 min) at 400 W (Scheme X). The reactions are being performed in different solvents such as dimethyl sulphoxide, *N*,*N*dimethylacetamide (DMAc), chlorobenzene, dioxane,



Scheme X. Polycondensation reactions of aromatic and aliphatic diamines with urea and thiourea.

and toluylene. DMAc was chosen as the most appropriate solvent owing to the greater solubility of the substrates, the higher rate of the reactions, and the excellent energy-transfer properties. In comparison with the conventional thermal method, the microwave irradiation reduces the reaction time and simplifies the workup processes. Owing to partial degradation of the aliphatic polymers, increasing the reaction time up to 15 min led to polymers with lower viscosities.

Mallakpour et al. [61-63] reported solution poly-

condensation reactions of 4-(4'-N-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione, 4-(4'-acetamidophenyl)-1,2,4-triazolidine-3,5-dione and 4-(4'-*t*butylphenyl)-1,2,4-triazolidine-3,5-dione with hexamethylene diisocyanate, isophorone diisocyanate and toluene-2,4-diisocyanate in DMAc or NMP solution in the presence of pyridine, triethylamine or dibutyltin dilaurate as a catalyst under microwave activation (Scheme XI). After irradiation times of 8-18 min, polyureas with inherent viscosities of 0.06 to 0.30 dL/g were obtained.



Scheme XI. The polycondensation reactions of different urazole derivatives with various diisocyanates.



Scheme XII. Preparation of PPV-ether.

Polyethers

Hurduc et al. [64] studied tetrabutylammonium bromide catalyzed polycondensation of 3,3bis(chloromethyl)oxetane and various bisphenol derivatives under microwave irradiation. They found that microwave irradiation did not have a considerable influence on the molecular weights of polymers, but reduced reaction times.

Alimi et al. [65] investigated microwave-assisted homopolycondensation of 1-chloro-4-methoxylbenzene in solution in alkaline dimethyl sulphoxide for producing poly(phenylene vinylene)-ether (PPVether) (Scheme XII). The mixture was exposed to 600 W microwaves for a few minutes until a temperature of 470 K was achieved and then continued stirring at room temperature for 6 h. This raw mixture was composed of three fractions: a yellow fraction of PPV-ether insoluble in all common organic solvents with 43% yield, a white fraction soluble in CHCl₃ with 52% yield and a yellow-green fraction soluble in the CH₂Cl₂ with 5% yield.

Loupy et al. [66,67] reported microwave-assisted polycondensation of isosorbide or isoiodide with 1,8dibromo- or 1,8-dimesyl-octane in the presence of a small amount of toluene under phase-transfer catalytic (PTC) conditions within 30 min. In the case of isosorbide, microwave-assisted polymerization showed increased total yields (68-76% against only 28-30%) compared with conventional heating. Furthermore, under microwave irradiation, polyethers with higher molecular weights in the presence of ethylenic groups as chain terminations were prepared while under conventional heating shorter hydroxylated compounds were obtained.

Poly(amide-imide)s

Polymers with optically active properties have found interesting applications, including chiral phases for enantiomeric separations in chromatography methods, chiral media for asymmetric synthesis, polymeric chiral catalysts, etc.

Given the extensive experience in the field of thermally stable and optically active polymers based on α -amino acids, the polycondensation of 4,4'-carbonyl-bis(phthaloyl-*L*-alanine) diacid chloride with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds were investigated by Mallakpour et al. [68] in the presence of a small amount of *o*-cresol (Scheme XIII). Under microwave irradiation power of 900 W, a series of optically active and thermally stable poly(amideimide)s were produced within 10 min with inherent viscosities of about 0.25-0.45 dL/g in high yields. The resulting polymers have potential to be used in a proper column chromatography technique for the separation of enantiomeric mixtures.

Mallakpour et al. [69-71] developed another category of optically active poly(amide-imide)s via reaction of N,N'-(4,4'-carbonyldiphthaloyl)-bis-L-phenylalanine diacid chloride (or compounds containing other amino acids such as L-alanine or L-leucine) with several aromatic diamines in o-cresol (Scheme XIV). The polymers were obtained with high yields and inherent viscosities of 0.22-0.85 dL/g within 7-10 min. The microwave-assisted polycondensation reactions were carried out in a Teflon dish as well as in a porcelain dish. The resulting poly(amide-imide)s in a porcelain dish had higher yields and inherent viscosities during the shorter period of irradiation than the one produced in the Teflon dish.

As part of their continuing attempts in developing novel optically active polymers under microwave technique, Mallakpour et al. [72-75] reported the syntheses of optically active poly(amide-imide)s derived from diacid chloride containing epiclon and several amino acids such as *L*-phenylalanine, *L*-isoleucine, *L*methionine or *L*-Leucine with aromatic diamines in the presence of a small amount of a polar organic



Scheme XIII. Microwave assisted polycondensation reactions of 4,4'-carbonyl-bis(phthaloyl-*L*-alanine) diacid chloride with different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds.



Scheme XIV. Polycondensation reactions of *N*,*N*'-(4,4'-carbonyldiphthaloyl)-bis-*L*-phenylalanine diacid chloride (or compounds containing other amino acids such as *L*-alanine or *L*-leucine) with different aromatic diamines.



Scheme XV. Synthesis of optically active poly(amide-imide)s derived from diacid chloride containing epiclon and several amino acids such as *L*-phenylalanine, *L*-isoleucine, *L*-methionine or *L*-Leucine with aromatic diamines.

medium such as NMP (Scheme XV). To compare microwave irradiation polymerization with solution polymerization methods, poly(amide-imide)s were also synthesized by both low temperature and hightemperature classical solution polycondensation. The results of these methods were comparable with the microwave method. But the microwave heating is a more efficient method (shorter reaction time and high efficiency of energy) for these polycondensation reactions.

Mallakpour et al. **[76**,77] have also investigated preparation of poly(amide-imide)s containing the pyromellitoyl unit in polymer chains under microwave heating in a porcelain dish (Scheme XVI). Microwave-assisted polycondensation reactions proceeded rapidly compared to conventional solution polycondensation and it was almost completed within a short period of time.

They also studied microwave-promoted polycondensation of N,N'-(4,4'-oxydiphthaloyl)-bis-*L*-methionine diacid chloride or diacid chlorides contain amino acids of (s)-valine or *L*-leucine with several aromatic diamines (Scheme XVII) [78-80]. The microwaveassisted polymerization reactions were performed for only 4-6 min and yielded polymers with inherent viscosities of 0.25-0.52 dL/g. In comparison with the reactions conducted via conventional solution polycondensation, microwave irradiation accelerated the rate of polymerization drastically.

Faghihi et al. [81] synthesized optically active poly(amide-imide)s from the polycondensation reactions of 4,4'-carbonyl-bis(phthaloyl-*L*-alanine) diacid chloride with six different derivatives of hydantoin and thiohydantoin compounds in *o*-cresol solvent. Polymers were obtained with inherent viscosities about 0.25-0.45 dL/g and yields ranging from 90% to 95% in 10 min.

Mallakpour et al. [82] reported the direct polycondensation reactions of *N*-trimellitylimido-S-valine with aliphatic and aromatic diisocyanates under



Scheme XVI. Synthesis of poly(amide-imide)s containing the pyromellitoyl and amino acid units under microwave heating.



Scheme XVII. Polycondensation reactions of *N*,*N*'-(4,4'-oxydiphthaloyl)-bis-*L*-methionine diacid chloride or diacid chlorides containing also other amino acids such as S-valine or *L*-leucine with several aromatic diamines.



Scheme XVIII. Polycondensation reactions of trimellitylimido-S-valine with different aliphatic and aromatic diisocyanates.

microwave irradiation as well as conventional heating techniques in presence of different catalysts and also without catalyst via diisocyanate route (Scheme XVIII). The reaction mixture was irradiated in a microwave oven for 5 min at 100% of its power and gave poly(amide-imide)s with good yields and inherent viscosities in the range of 0.18-0.36 dL/g.

A series of optically active poly(amide-imide)s by the reactions of chiral diacid chlorides containing 3,3',4,4'-diphenylsulphonetetracarboxylic dianhydride and S-valine (or other amino acids such as *L*- phenylalanine, *L*-leucine or *L*-isoleucine) moieties with several aromatic diamines such as 4,4'-sulphonyldianiline, 4,4'-diaminodiphenyl methane, 4,4'diaminodiphenylether, *p*-phenylenediamine, *m*phenylenediamine, 2,4-diaminotoluene, and 1,5diaminonaphthalene were synthesized by Mallakpour et al. (Scheme XIX) [83-86]. The polymerization reactions were carried out in the presence of a small amount of *o*-cresol and polymers with high yields and moderate inherent viscosities were obtained within 6 min with 100% of radiation power. At high powers



Scheme XIX. Synthesis of optically active poly(amide-imide)s containing 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride and S-valine (or other amino acids like *L*-phenylalanine, *L*-leucine or *L*-isoleucine) moieties.



we set set as	many my myring
b: R1=R2=CH3	e: R1=R2= -(CH2)4-
c: R1=CH3, R2=C2H5	f: R ₁ =R ₂ = -(CH ₂)s-

Scheme XX. Polycondensation reactions of N,N'-(3,3'-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride with different derivatives of diamines.



Scheme XXI. Synthesis of optically active poly(amide-imide)s by the polycondensation reactions of 4,4'-(hexafluo-roisopropylidene)-*N*,*N*'-bis-(phthaloyl-*L*-methionine) diacid chloride (or *L*-leucine compound) with several diamines.

dark products were obtained and at low radiation times or power reactions low yields were obtained.

Faghihi et al. [87] described formation of poly(amide-imide)s under microwave irradiation through the polycondensation reactions of N,N'-(4,4'- diphenylether) bistrimellitimide diacid chloride with six different derivatives of 5,5-disubstituted hydantoin in *o*-cresol solvent. The reaction mixture was irradiated for 7-10 min to afford polymers in 84-94% yield.

A number of flame-retardant poly(amide-imide)s containing phosphine oxide and hydantoin moieties in main chain was also successfully prepared by Faghihi et al. (Scheme XX) [88,89]. Irradiation of the reaction mixtures in a microwave oven led to the desired poly(amide-imide)s within a short time (7-12 min) while classical thermal polycondensation required 1 day for performing polymerization reactions.

Mallakpour et al. have also investigated microwave-assisted polycondensation of 4,4'-(hexa-fluoroisopropylidene)-*N*,*N*'-bis-(phthaloyl-*L*-methionine) diacid chloride (or *L*-leucine compound) with aromatic diamines in the presence of *o*-cresol (Scheme XXI) [90,91]. Compared to conventional heating, microwave-assisted polymerizations led to faster polymerization reactions and provided poly(amide-imide)s with higher inherent viscosities.

Mallakpour et al. [92] investigated step-growth polymerization reactions of monomer bis(*p*-ami-

dobenzoic acid)-*N*-trimellitylimido-*L*-leucine with different diisocyanates via direct polycondensation under microwave irradiation, solution polymerization under gradual heating and reflux conditions in the presence of pyridine, dibutyltin dilaurate, and triethylamine as a catalyst and without a catalyst (Scheme XXII). The optically active poly(amide-imide)s were obtained after a short time of 3 min in good yields (53-95%) and inherent viscosities in the range of 0.17 to 0.61 dL/g.

Khoee et al. [93,94] investigated the synthesis of photoactive poly(amide-imide)s containing anthracenic or naphthalenic pendent groups with fluorescent property in a domestic microwave (Scheme XXIII). The reactions were performed in *o*-cresol solvent and yielded photoactive polymers in high yields. Compared with the solution polycondensation method under conventional heating, the microwave-assisted polycondensation reactions proceeded rapidly and were completed within 8-10 min.

More recently, Mallakpour et al. have developed for the first time a facile and benign environmentally methodology to synthesize polyamides and poly(amide-imide)s using combination of ionic liquids and microwave irradiation [95,96].

Poly(amide-ester)s, Poly(ester-imide)s, Poly(etherimide)s, and Poly(ether-ester)s

Borriello et al. [97] investigated the synthesis of



Scheme XXII. Polycondensation reactions of bis(p-amidobenzoic acid)-N-trimellitylimido-L-leucine with different diisocyanates.



Scheme XXIII. Synthesis of photoactive poly(amide-imide)s containing naphthalenic pendent group.

poly(amide-ester)s by polycondensation of sebacic acids and ω -amino alcohols in the presence of stannous 2-ethyl hexanoate Sn(Oct)₂ as a catalyst under microwave irradiation (Scheme XXIV). Polymerization reactions were also comparatively performed using conventional melt polycondensation; it was found that under microwave conditions polymers with higher molecular weights and equivalents or higher yields were achieved in one third of the time required for a thermal process.

Mallakpour et al. [98-101] reported facile and rapid polycondensation reactions of *N*,*N*'-(pyromellitoyl)-bis-*L*-leucine diacid chloride, *N*,*N*'-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride, 4,4'-carbonyl-bis(phthaloyl-*L*-alanine) diacid chloride or 4,4'-(hexafluoroisopropylidene)-*N*,*N*'-bis(phthaloyl-*L*leucine) diacid chloride with several aromatic diols such as phenol phthalein, bisphenol-A, 4,4'-hydroquinone, 1,8-dihydroxyanthraquinone, 1,5-dihydroxy naphthalene, 4,4-dihydroxy biphenyl and 2,4-dihydroxyacetophenone by using a domestic microwave oven in the presence of a small amount of a polar organic solvent such as o-cresol (Scheme XXV). The polymerization reactions proceeded rapidly and are completed within 10-20 min, producing a series of optically active poly(ester-imide)s with good yields and moderate inherent viscosities.

Zhang et al. [102] studied the polycondensation reaction of disodium bisphenol A with bis(chloroph-thalimide)s with a domestic microwave oven in *o*-dichlorobenzene by phase-transfer catalysis (PTC) (Scheme XXVI). Poly(ether imide)s with inherent viscosities between 0.55 and 0.92 dL/g were obtained within 25 min.

Chatti et al. [103] described the synthesis of poly(ether-ester)s based on diol-ether of isosorbide and adipoyl chloride or terephthaloyl chloride (Scheme XXVII). The polymerizations were carried

Scheme XXIV. Synthesis of poly(amide-ester)s by reaction of sebacic acids and ω-amino alcohols.



Scheme XXV. The polycondensation reactions of *N*,*N*'-(pyromellitoyl)-bis-*L*-leucine diacid chloride and *N*,*N*'-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride with different diols.



Scheme XXVI. Polycondensation reaction of disodium bisphenol A with bis(chlorophthalimide)s by phase-transfer catalysis.



Scheme XXVII. Synthesis of poly(ether-ester)s based on diol-ether of isosorbide and adipoyl chloride or terephthaloyl chloride.



Scheme XXVIII. Copolymerization reaction of 4,4'-methylene-bis(4-phenylisocyanate) with: (a) poly(ethylene glycol diol) polyol and chain extension of an NCO-terminated polyol by a diacid monomer (two-step method I) and (b) diacid bis(*p*-amidobenzoic acid)-*N*-trimellitylimido-*L*-leucine and chain extension of an NCO-terminated oligoamide by poly(ethylene glycol diol) polyether polyol (two-step method II).

out in a monomode system with focused waves operating at 2.45 GHz. The polymerizations proceeded at least 5 times faster (compared with conventional heating) thus, the reactions being almost completed (yields up to approximately 95%) within 5 min. The comparison of the microwave-synthesized polymers with those synthesized via conventional heating using adipoyl chloride showed that yield of 86% was achieved after 5 min at 150°C with weight average molecular weights of 4200 g/mol while under



Scheme XXIX. Synthesis of poly(amide-ether-urethane)s by: (a) the one-step synthesis of poly(amide-ether-urethane)s via the reaction of 4,4'-azodibenzenedicarboxylic acid, PEG-400 and different diisocyanates and (b) a two-step reaction. Step 1: reaction of 4,4'-azodibenzenedicarboxylic acid with different diisocyanates and preparation of NCO-terminated oligoamide. Step 2: chain extension reaction of NCO-terminated oligoamide with PEG-400 polyether polyol.

conventional heating, the polymer was obtained in 19% yield with weight average molecular weight of 4050 g/mol.

Poly(amide-imide-urethane)s and Poly(amideether-urethane)s

Mallakpour et al. [104] have synthesized new class of optically active poly(amide-imide-urethane)s via a two-step diisocyanate route under microwave irradiation (Schemes XXVIIIa and XXVIIIb). The polymerization reactions were examined by the type of solvent, irradiation intensity and time. The use of NMP as a solvent and 4-5 min of irradiation time at 100% intensity were recognized as preferable conditions, providing the best viscosities and yields.

Mallakpour et al. [105] have also reported four series of new self-coloured segmented polymeric dyes via the reaction of an azo-based diacid, different diisocyanates and polyethylene glycol with molecular mass of 400 (PEG-400), under microwave irradiation via diisocyanate route in NMP or NMP containing 4% w/w CaCl₂ as a solvent in the presence of different catalysts (such as dibutyltin dilaurate or Py) or without catalyst by one-step as well as two-step methods (Schemes XXIXa and XXIXb). They investigated the effects of different reaction conditions such as irradiation time, reaction catalysts, polymerization methods (one step vs. two steps), reaction solvent and changes in the structure of diisocyanates on the polymer chain growth as well as their properties.

CONCLUSION

Since its inception in 1986, microwave-assisted organic chemistry has become an exciting and vibrant field for research and development. In this review, we have presented an overview on microwave-assisted technique for performing successful high-speed homogeneous polycondensation reactions. This method has advantages over conventional technology, because it is very convenient to utilize it in polymer synthesis which mainly leads to higher yield products. In this method reaction times are reduced from days/hours to minutes/seconds. Thus, there can be significant time saving in polymerization reactions, in contrast to the conventional heating which needs very longer reaction times. Besides, we have shown that it is possible to conduct very clean reactions with the use of less toxic reagents than conventional heating. The overall process in which direct "in-core" heating of the medium takes place is more energy efficient than classical oil-bath heating. Some advantages and disadvantages of using microwave irradiation both in laboratory and industry may be counted as follows:

Advantages:

- Dramatically enhanced rate of polymerization
- Direct heating
- Energy savings
- High temperature homogeneity
- Improved isolated yields of polymers
- Polymer property enhancement
- Cleaner polymerization reactions
- Using less amount of solvents
- Performing reaction under solvent free conditions
- Environmentally friendly process under green chemistry
- Rapidly achieved high reaction temperatures
- Solvent selection for polycondensation reactions which is not imposed by its boiling point but rather by the dielectric properties of reaction medium

Disadvantages:

- Equipment cost of monomode reactors
- Insufficient temperature control in the multimode reactors

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