



## Review

# A concise review on microwave-assisted polycondensation reactions and curing of polycondensation polymers with focus on the effect of process conditions



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## HIGHLIGHTS

- Microwave heating can intensify polycondensation reactions.
- Shorter reaction times, energy savings and better product properties are reported.
- The chosen process conditions determine the magnitude of microwave effect.

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## ABSTRACT

During the past 15 years, increasing application of microwave heating to polycondensation reactions has been witnessed. Experiments have been carried out at laboratory scale using widely different experimental procedures. The use of microwaves has often led to significant benefits compared to conventional heating experiments in terms of multi-fold decrease in reaction times and energy consumption and production of polymers with increased molecular weight and improved mechanical properties. In other cases, microwaves do not appear to produce any significant benefits compared to conventional heating. At present, guidelines to experimentalist as to the process conditions and experimental design that should be applied are missing and experimentation seems to be based on an empirical trial-and-error approach. In view of the very different experimental protocols that have been applied and the contradictory trends that are frequently reported, we aim in this review to shed light on the role of important process parameters, such as the presence and type of solvent, the dielectric properties of the mixture and the individual phases, the use of heterogeneous catalysts, pressure, stirring, reflux conditions, temperature measurement method and microwave absorbing fillers, which all seem to determine the occurrence and magnitude of the benefits enabled by microwaves during polycondensation reactions.

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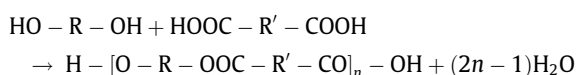
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## 1. Introduction

Polycondensation reactions are a form of step-growth polymerization reactions widely used in the polymer industry to form proteins, polyesters and polyamides and certain resins and silicones. Effective removal of water and volatile by-products from the reaction zone is essential to ensure high reaction rate, conversion and molecular weight of the final product. One example of step-growth polymerization is the formation of polyesters from diols and diacids according to the general scheme



Activation of polycondensation reactions by means of microwave irradiation has been reported to be a fast and facile synthesis method. Previous reviews on the subject were given in books [1,2] and the key review papers [3–10]. Reviews on microwave-assisted polycondensation of polylactic acid, polyesters and polyamides were presented by Hirao and Nakamura [11–13]. Compared to past works, the approach in this review is different. We do not aim at an extensive review of the results from the application of microwaves to different polymer systems and chemistries, but rather, to shed light on the role of important process parameters in microwave-assisted polycondensation processes through selected literature examples; inter alia syntheses of polyamides, polyimides and polyesters. In view of the very different experimental protocols that have been applied and the contradictory trends that are frequently reported, it is important to understand how the choice of process conditions may affect process performance (e.g., process time, energy consumption, conversion and selectivity) and physical and mechanical product properties. Most of the works in which a domestic oven was used without temperature measurement are not included in this review.

In Table 1, a summary of key publications focused on polycondensation reactions arranged in reverse-chronological order is presented. For each reviewed paper, the author's explanation of the observed effect and the experimental conditions are listed, including the type of microwave oven, the temperature measurement technique, the scale of reactor/process, the pressure, the kind of solvent used, and information whether a reference experiment under conventional heating was carried out. In the final section, the effects of various microwave absorbing fillers on the end-properties of polymer composite and hybrid materials prepared under microwave heating are reviewed.

The advantages of microwave heating arise from the specific interactions of particular materials with high frequency electromagnetic waves. Materials such as water, alcohols, ionic liquids, and carbon readily absorb microwave energy, whereas other materials such as plastics, oils and non-polar solvents are effectively transparent. This is determined exclusively by the dielectric properties of the materials [14]. Microwaves can therefore penetrate into the depth of a mixture of components, interacting in different ways with various phases. The materials susceptible to microwave energy will heat selectively and rapidly compared to the non-microwave susceptible materials, quickly generating large temperature gradients [15]. Energy can hence be concentrated selectively within these microwave susceptible components in a mixture, with little or no energy expended on direct heating of the

surrounding. Another important aspect of microwave heating is its volumetric nature, which can help overcome heat transfer limitations often present in processes heated by means of heat conduction or convection through the solid boundaries of the system. Consequently, heating times can potentially be several orders of magnitude shorter with microwave heating than with conventional heating on the basis of equal energy input. This feature has been exploited in the field of chemistry and numerous reports in the literature have shown the potential of microwave energy to accelerate chemical reactions [16]. According to the Arrhenius law, the rate constants vary exponentially with the reciprocal of temperature and hence small changes in temperature can significantly affect the speed of chemistry. However, the inability to accurately probe the temperature excursions in chemical phases inside a reaction medium at microscopic level has generated a lot of controversy regarding the actual wave-material interactions [17]. Nevertheless, it is generally accepted that “local” temperatures in the reaction mixture can be significantly higher than the bulk temperature and this may be the reason of acceleration of microwave-assisted reactions in many cases [18,19].

The principle and mechanisms that underpin microwave heating are well understood and have been extensively discussed in the literature [14,20,21]. In this review, we will provide only a brief description of the mechanisms taking place. Microwave heating in non-magnetic materials takes place via the interaction of the electric field with charged species (free charge, induced dipoles) in a material. This interaction depends upon the polarization of the species. There are mainly two mechanisms associated with the heating of materials at radiofrequency and microwave frequencies. The first one is dipolar reorientation (polarization) and is the dominant mechanism in the GHz region of frequencies. The electric field will interact with the induced dipoles and will force them to rotate until the dipoles are balanced by electrostatic interactions [20]. The molecules' orientation changes but their speed of motion is limited due to dipole-dipole interactions and molecules are unable to completely relax, i.e., they cannot reorient themselves completely. Movement of species creates friction and leads to thermal effect – heat generation. A perturbed system does not return into equilibrium stage before a next portion of energy is delivered because the relaxation times corresponding to rotation of the whole molecule and to rotation of the polar group are longer than the energy transfer time. The second one is due to the presence of ionic species in solid materials, or ionic solutions, and is prominent at lower frequencies. The applied electric field induces motion to cations and anions in opposite directions and further causes a net dipole moment [22]. In heterogeneous systems, a heating mechanism that relates to the interfacial or Maxwell-Wagner polarization could also be observed. It originates from a charge build-up in the contact areas or interfaces between different components. This polarization is due to differences in the conductivity and dielectric properties of the different substances at their interface. As a result, accumulation of charges can occur and lead to field distortions and dielectric heating effects [22].

The extent to which a material heats up when subjected to electromagnetic radiation (e.g., microwave radiation) is mainly determined by its dielectric properties, which can be expressed by the complex permittivity  $\epsilon^*$  that has two components: a real part, the dielectric constant ( $\epsilon'$ ) and an imaginary part, the dielectric loss factor ( $\epsilon''$ ) and is described by the following equation

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