Microwave-Induced Synthesis of Aromatic Polyamides by the Phosphorylation Reaction

Paula Carretero, Ricardo Sandin, Regis Mercier, Angel E. Lozano, Jose G. de la Campa, and Javier de Abajo

A Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006, Madrid, Spain.
B Laboratoire de Matériaux Organiques à Propriétés Spécifiques (CNRS), UMR5041, 69360, Solaize, France.
C Corresponding author. Email: deabajo@ictp.csic.es

This paper reports an optimization of the Yamazaki–Higashi method of direct polyamidation from aromatic diacids and aromatic diamines. As a model reaction, the polycondensation between 4,4′-oxydianiline and isophthalic acid was studied in the presence of a phosphorylation agent and under microwave irradiation. This experimental study revealed that optimal results can be attained by using a great excess of pyridine as catalyst (pyridine-to-monomer ratio of 7), at moderate radiation intensity (200 W), and up to 25% (w/v) monomer concentration. Although the inherent viscosity achieved by microwave and by conventional heating was comparable, an exceptional reaction rate under microwave irradiation yielded a polyamide inherent viscosity of around 1 dL g⁻¹ in only a few minutes.

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Introduction

Microwave (MW) irradiation is a rapid, efficient, and energy saving method to heat molecules directly through the interaction between MW energy and dipole moments of the irradiated materials. The application of MW energy using a commercial domestic MW oven on organic synthesis began in the mid 1980s. Since then, MW-assisted syntheses have been reported for a variety of common organic reactions,[1,2] and polymer synthesis.[3,4] In the field of MW-induced condensation, polymer synthesis was reported some years ago by Park et al.,[5] Imai,[6] and Pourjavadi et al.[7] Thus, it can be stated that nowadays MW irradiation, as a non-conventional energy source, has become a popular and useful technology in organic chemistry as well as in polymer chemistry.[8–12]

In most cases, the use of MWs can accelerate the reaction and can bring about a dramatic reduction of reaction time.

In this work, the preparation of aromatic polyamides has been studied by the Yamazaki–Higashi direct polyamidation reaction. By this method, polyamides of high molecular weight are obtained directly from dicarboxylic acids and aromatic diamines in N-methyl-2-pyrrolidinone (NMP) solutions that contain triphenylphosphite (TPP) as a condensing agent, pyridine (Py) as catalyst, and LiCl to improve the polymer solubility. The mechanism that governs the reaction has been the subject of controversy. Yamazaki and Higashi proposed a mechanism in which pyridine played a key role as it should react with TPP and carboxylic acid to give the corresponding N-phosphonium salt of pyridine.[13] This intermediate would react with primary amines to render the corresponding amide and diphenylphosphite as final products. Some years later, Aharoni et al. proposed another mechanism based on an extensive nuclear magnetic resonance study of the reaction.[14] They concluded that the amidation reaction had two steps. In the first step, diphenoxyminosphosphine is formed, which is then attacked by the available carboxylic acid with the formation of two final products: an amide group and a diphosphite. Either of both mechanisms reasonably explains this reaction.

In the present work, experiments have been carried out to compare the results attained by the MW-assisted polycondensation using the phosphorylation method with those attained by the conventional method. Although there are some antecedents on MW-assisted polyamidation by this method,[5,7] attempts to optimize the reaction conditions have not been made so far. Different factors such as MW power, time of irradiation, monomer concentration, amount of catalyst, and pressure development during the course of the reaction have now been studied and optimized. The reaction of diamine 4,4′-oxydianiline (ODA) and isophthalic acid (IPA) was chosen as a model polymerization reaction (Scheme 1), which may be extended to any diacid/diamine system.

Results and Discussion

A high molecular weight is required for aromatic polyamides to present a high thermal stability and good mechanical properties, characteristics needed for application as high-performance...
materials. The inherent viscosity is an indirect criterion of the molecular weight of experimental polymers, for which there is no viscometric equation, and it is commonly used to compare the molecular weight of polymers of similar composition.

To determine the best polymerization conditions to achieve high-molecular-weight polyamides under MW irradiation, the effect of several factors including the concentration of monomers, amount of catalyst, time of polymerization, power of radiation, and pressure development during reaction were investigated. Initially, a set of primary reaction parameters was selected, and then each parameter was optimized by a ‘one at a time’ method. Two commercial monomers, i.e., ODA and IPA, were chosen, and then each parameter was optimized by a ‘one at a time’ method. Two commercial monomers, i.e., ODA and IPA, were chosen upon consideration of the monomers’ reactivity and market availability.

It is important to point out that the temperature in the MW-induced reactions has a significant influence on the polymerization, but this parameter was not optimized because the temperature was controlled during the reaction using an external temperature sensor, which monitored the flask surface temperature and not the actual temperature inside the reaction vessel. So, the fixed temperature was the external temperature, and the internal temperature might have slightly exceeded this. Previous studies have demonstrated that the use of IR external sensors is, in many cases, not appropriate for MW-heated reactions, and that it can lead to a misinterpretation of results because the true reaction temperature during MW irradiation is not known.[5] Nonetheless, in all cases of this work, reflux and an efficient magnetic stirring during irradiation provided a good homogeneity and stable external temperature (110–115°C when the power applied was 200 W).

First, the influence of monomer concentration was investigated. Fig. 1 shows the plot of the achieved polymer inherent viscosity versus monomer concentration (% w/v). The viscosity values decreased gradually when the monomer concentration decreased, which is a consistent result considering that an increase of the concentration is translated into an increase of effective collisions of reactants in a fixed time interval. So, a larger number of polymeric chains with high molecular mass will be formed by unit of time. In particular, a monomer concentration of 75% (w/v) gave the best results, but the use of concentrations higher than 25–30% was unfavourable in practical terms, and always resulted in a gel-like system. Consequently, the rest of the experiments for the study of experimental conditions were carried out with a 25% monomer concentration.

Next, the amount of pyridine was optimized. Variations in the pyridine concentration indicated that the amount of pyridine present in the reaction played a dramatic role on the polymer inherent viscosity. Thus, the ratio was progressively increased, from the classical pyridine/monomer 1–3/1 ratio until a maximum inherent viscosity was achieved at a ratio pyridine to monomer of about 7, when the polymer achieved a \( \eta_{inh} \) of 1.0 dL g\(^{-1}\). Accordingly, it can be stated that the presence of an excess of base is necessary to achieve a good development of the reaction, what is in agreement with the mechanism proposed by Yamazaki and Higashi. Moreover, it seems that the vigorous reflux caused by the MW irradiation required an excess of pyridine to compensate for evaporation. Table 1 shows the values of inherent viscosity of the polyamides obtained using different amounts of pyridine.

The effect of irradiation time was evaluated at different time intervals that ranged from 2 to 25 min, with the rest of reaction variables fixed. Fig. 2 shows that the maximum viscosity corresponded to a reaction time between 5 and 10 min. At shorter times, the reaction was not complete, whereas at longer times a decrease of inherent viscosity was observed, probably because of thermal degradation produced by prolonged local MW heating.

The microwave power was also optimized. Fig. 3 shows the dependence of the inherent viscosity on the MW intensity. It
seems evident that the increase in power caused a degradation of the polymer, thus decreasing the viscosity. This is a crucial point on applying MW irradiation in the synthesis of organic polymers: the energy of MWs is too low to break covalent bonds, but a high power can lead to a higher internal temperature, which may cause degradation of the polymer chains.

In order to investigate the effect of pressure development during the course of the reaction, the polycondensation was repeated in a closed system. The polyamide obtained under these conditions (again 110–115°C, 200 W, 2.5 equivalents of pyridine, 25% (w/v) concentration, and 15 min reaction) had a viscosity value of 0.86 dL g⁻¹, similar to that obtained under normal pressure and 7 equivalents of pyridine, which indicated that pressure has no significant effect on the course of the reaction. However, the use of a closed system to carry out the polymerization is more convenient because it avoids the evaporation of pyridine.

When the same experiment was conducted by conventional heating under the conditions described in the experimental part (method A), a reaction time of 2 h at 105–110°C (oil bath temperature) was needed to reach an inherent viscosity of 0.90 dL g⁻¹, which is comparable to that obtained in only 2 min under MW irradiation (0.94 dL g⁻¹) at 200 W of power (external temperature 110–115°C). The effect of the reaction time on the inherent viscosity under the two types of heating is depicted in Fig. 4. It is also important to stress that degradation did not occur at longer times with the conventional method.

In this way, although the inherent viscosities obtained by MW irradiation and by thermal heating can become comparable, an exceptional reaction rate was observed under MW irradiation. The exact reasons as to why MW irradiation is able to accelerate chemical processes are still unclear. There are actually experimental studies where the different results in terms of selectivity and yield for the same reaction, using either MW or conventional heating, have led to speculation on the existence of so-called ‘specific’ or ‘non-thermal’ MW effects. Today, it is generally agreed that, in most cases, the observed enhancements in MW-heated reactions are in fact the result of purely thermal/kinetic effects, in other words, are a consequence of fast radiation–matter interactions and subsequent conversion of rotational into thermal energy. Thus, high reaction temperatures can rapidly be attained, in a time shorter than when the reaction is carried out under conventional heating. All these concepts are nevertheless a matter of debate in the scientific community and are beyond the scope of the present work.

In all experiences of this work, a high/medium absorbing solvent was used: NMP is a polar organic medium that acts as a primary MW absorber. In this way, most of the MW energy will in fact be absorbed by the solvent and converted into heat, probably masking any potential non-thermal MW effects as a result of material–wave interactions. This fact, in combination with the high values of heating rate (in only 30 s the external temperature was 60°C, after 1 min the external temperature raised to 90°C, and from 5 to 25 min the external temperature was kept constant at 110–115°C when the power was 200 W), and the high internal local temperatures (hot spots), indicate that the faster polymerization with MWs was most likely a result of thermal effects.

Optimized polymerization conditions outlined from this study are at present being applied to the preparation of different aromatic polyamides, including those derived from low reactive diamines in the Yamazaki–Higashi reaction such as 4,4’-diaminodiphenylsulfone.

Conclusions

The reaction conditions for the preparation of aromatic polyamides using the phosphorylation method of Yamazaki–Higashi could be considerably optimized by means of a conscientious study of the variables, i.e., monomer concentration, pyridine concentration, or heating source, either conventional or by MW irradiation. Taking as a model the polyamide ODA–IPA, polymerization conditions were modulated to obtain high-molecular-weight polyamides derived from diamine ODA and diacid IPA. Pyridine and monomer concentrations were revealed as very important variables to be considered, and a dramatic effect of the heating source on the reaction time was observed. Comparable results of inherent viscosity can be achieved by MW irradiation and by conventional thermal heating, with a remarkable reduction of reaction time in the case of MW irradiation. These results demonstrate that MW irradiation is a very effective, clean, and fast method to synthesize high-molecular-weight aromatic polyamides.

Experimental

Anhydrous NMP and pyridine were used as received. TPP was distilled twice before use. Lithium chloride was dried for 24 h in an oven at 250°C. ODA was purified by sublimation, and commercial IPA was dried at 100°C under vacuum for 1 h just before use. All chemicals were supplied by Aldrich Chemical Co.

The inherent viscosities (ηinh) were measured with an automated Ubbelohde viscometer at 25 ± 0.1°C with NMP as a solvent at 0.5 g dL⁻¹ concentration. The inherent viscosity was calculated according to the equation ηinh = (ln(t/t₀))/c, where t is the time that it took for a given volume of polymer solution of concentration c to flow through the capillary of the viscometer, and t₀ is the corresponding time for the solvent.

The apparatus used for the polycondensation was a multi-mode MW reactor (Ethos Touch Control, Milestone Corporation) without any modification. It is equipped with two magnetrons capable of delivering continuous MW output power from 100 to 1600 W, which provided ‘homogeneous non-regular shape’ electromagnetic waves.

In order to compare the results obtained for the polycondensation by direct MW and by conventional heating, we used in both cases a standard glass flask and similar reaction...
conditions (TPP/monomer ratio: 2.2, 25% (w/v) monomer concentration, 5% (w/v) LiCl, and constant reaction temperature around 110°C). The reaction temperature in the MW-assisted reaction was monitored by an external IR sensor located in the unit, while the temperature during the conventional heating method was controlled by an external thermocouple located in the oil bath.

Polymer Synthesis
A. Classical Method
IPA (10 mmol), 2 mL of pyridine (pyridine/monomer ratio: 2.5), and 1 g of dried LiCl were dissolved in 5 mL of NMP. ODA (10 mmol) dissolved in 10 mL of NMP, and 22 mmol (6 mL) of TPP were then added. The solution was heated at 105–110°C (oil bath temperature) for several hours. The resulting viscous solution was poured into ethanol, and the polymer precipitate was filtered off, washed with distilled water, and then extracted with ethanol for 24 h in a Soxhlet apparatus, and finally vacuum dried over P2O5 at 100°C.

B. Polycondensation of ODA and IPA under MW Irradiation
The same polymerization procedure was carried out under MW irradiation: 10 mmol of ODA and 10 mmol of IPA were dissolved in 15 mL of NMP, and then pyridine (pyridine/monomer ratio: from 2.5 to 7), TPP (6 mL), and LiCl (1 g) were added, and the reaction vessel that contained the reaction mixture was placed in the centre of the cavity in the MW oven. The reaction system was irradiated under normal pressure for a period of time at predetermined values of power and temperature. When the power was 200 W, the temperature was kept constant at 110–115°C (external temperature). After the irradiation was complete, the polymer was isolated and purified as described for method A.

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References

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