JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 11, November 2007, p. 3463 - 3465

Microwave imidation of itaconic acid and N-hexyl amine

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The microwave synthesis represents a very convenient method of obtaining chemical compounds not very easy to synthesize by the means of organic chemistry. The high energy electromagnetic radiation can easily induce polymerization, dehydration, etc. In this study, the reaction of itaconic acid (IA) and N-hexyl amine was studied. The microwave synthesis leads to a mixture of imide and diamides while the oil bath reaction leads to mono and diamides. By simply adding an initiator a high purity polymer was obtained. This technique is particularly useful when working with low reactivity compounds, allowing a much shorter reaction time and high conversions. The possibility to control the power gives a good chance to maintain the temperature at low values.

(Received March 23, 2007; accepted November 1, 2007)

Keywords: Microwave synthesis, Itaconimide, Green polymers

1. Introduction

Since the discovery of microwaves, there has been mentioned a lot of domains with possible application for these electromagnetic radiation, from the well known radar, to macromolecular chemistry. Microwaves are electromagnetic waves, with a frequency range between 3 and 30 GHz, and able to deliver energy of 0.66×10^{-5} to 0.12×10^{-3} eV. The possibility of using microwaves in organic and macromolecular chemistry attracted many scientists [1]. The main advantages of using microwaves in chemistry are the rapid heating of the probe, depending on the dipole moment of its molecules, short induction times, short reaction times, high conversion rates and the user friendly instruments. Solventless reactions without the use of supporting reagents are particularly interesting – as environmental friendly procedures [2].

Monoamides, diamides and imide of itaconic acid and N hexyl amine were synthesized in the lab, using a CEM Discover® LabMate™ system.

The products were characterized using an IR spectrometer, NMR, GC/MS.

2. Materials and methods

For this study, itaconic acid (IA) was chosen, as it is a green product. The itaconic acid is produced by fermentation of carbohydrates, a renewable resource. Itaconic acid (IA) (CAS #: 97-65-4) methylenebutane dioic acid) is an α-substituted acrylic acid that is used in the manufacture of synthetic resins, coatings, and other industrial products. It is produced commercially by the fungal fermentation of carbohydrates [3, 4].

Itaconic acid (IA) and its derivatives, both monoester (or hemiester) and diesters have been extensively studied with regard to their polymerization kinetics, role of bulky substituents, chain stiffness, glass-transition temperatures, etc. [5, 6].

The synthesis of amides and imide was carried in a long neck round bottom flask, fitted with a water condenser, as the temperature during the reaction was 140 ˚C, well above the boiling temperature of the itaconic acid:N-hexyl amine mixture. A monomodal microwave CEM Discover® LabMate™ equipped with an infrared pyrometer with maximum operation power of 300 W was used [7].

The reactants were purchased from Fluka and used as purchased.

Two modalities to perform the microwave synthesis were studied. In a first approach, (15 mmol) IA and (15 mmol) of N-hexyl amine were placed into a pressure resistant test tube and the microwave synthesis was carried at a pressure below 20 atm. The temperature was kept around 140 °C.

In order to compare the results obtained in the microwaves experiments with those obtained in the oil bath experiments, the most part of the microwave assisted synthesis were performed in open systems. A water condenser was used. The temperature was also maintained at 140 °C.

An equimolar mixture of itaconic acid and N hexyl amine (38,46 mmol) was added into a long neck round bottom flask. The flask was placed into the circular cavity of the Discover® LabMate™ and irradiated for 30 minutes at a power of 100W and the temperature was kept to 140˚ C through the use of compressed air. After the reaction was completed, the compound was allowed to cool down,

and then IR was performed. GC/MS of the crude compound was performed as well.

The IR spectrum shows the presence of the two amidic bands. Also NMR was performed for the crude compound. The GC/MS shows the formation of 3 compounds, with molecular weights of 214, 297 and 196. These values were attributed to monoamide (214), diamide (297) and to imide (196).

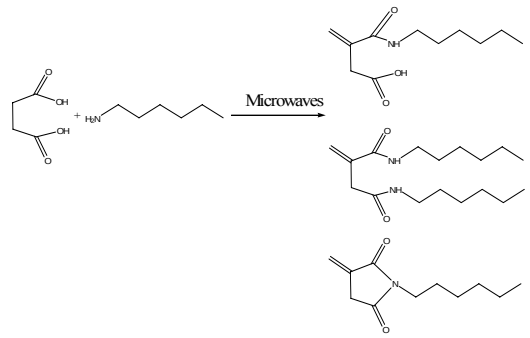

Fig. 1. The mixture of products obtained by microwave reaction of itaconic acid and N-hexyl amine.

In another set of experiments, a mixture of itaconic acid (5g), N-hexyl amine (2,13g) and benzoyl peroxide BP (1% molar) was used. The product was a polymer as proven by NMR.

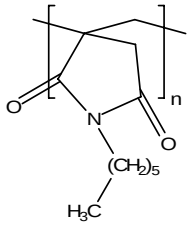

Fig. 2. The structure of the polymer obtained by adding BP to reaction mixture.

Depending on the ratio between the itaconic acid and the N-hexyl amine, it is possible to obtain a poly(itaconic acid) grafted with N-hexyl amine units. It was found that changing the degree of grafting it's a very easy task, simply by changing the ratio between the two reagents.

In the experiments where a radicalic initiator (benzoyl peroxide) was added to the reaction mixture, the final compound was a macromolecular one, as proved by the absence of double bond from the IR and NMR spectra.

By adding IA (76.9 mmol) and N-hexyl amine (170.7 mmol) to a round bottom flask and performing the microwave reaction, diitaconamide was obtained. The conversion was 99% after only 3 minutes reaction time.

The crude compound was washed with a 0.1 M HCl solution in order to eliminate the amine excess.

In order to determine the kinetic of the reaction, parallel experiments were performed, both on oil bath and under microwave conditions. In both cases, samples were collected for different reaction times, and submitted to GC/MS in order to determine the conversion in imide and monoamide.

The final crude compound was dissolved in dichloromethane and washed with 0.1 M HCl solution, then washed with a 0.1 M NaOH solution in order to remove any residual acid or amine. The resulted solution was dried with $MgSO_4$ in order to remove traces of water.

The same experiment was performed in the absence of microwaves, on oil bath, at the same temperature. Both experiments were performed at atmospheric conditions.

3. Results and discussion

The amides and imide of itaconic acid were synthesized via microwave and also in oil bath, in order to be able to compare the kinetic for both methods.

The yield in amide was very high in both cases. In the microwave condition, after the first minute, it is not possible to determine any of the reactants in the reaction mixture. After four minutes, the conversion in imide reaches 20%, while the conversion in amide is 80%.

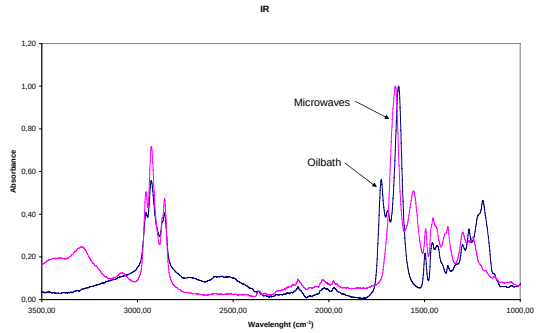

Fig. 3. IR spectra of crude compound obtained by microwaves/oil bath reaction of IA and N-hexyl amine.

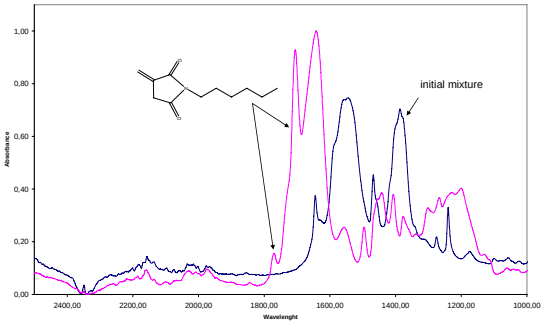

Fig. 4. IR spectra of The crude compound, obtained from an initial 1:1 mixture of IA and N-hexyl amine.

After 20 minutes the imide:amide ratio starts to change again, the final compound containing only 10% imide and 90% amide. Trying the same reaction in oil bath led to a compound that contains almost only amide – 98.9%. But the content of imide never reached a value bigger than 5%. The temperature was the same as in the microwave conditions, so the only difference between the two reactions is the presence/absence of microwaves.

When starting with a 1:1 mixture, under microwaves, only a very small percent of diitaconamide is obtained

(less than 2%). The conversion in itaconimide is about 20%, (15 times bigger than oil bath conversion). As pointed by many authors [7, 8] microwaves provide a very convenient non-contact heating as well as an activating agent.

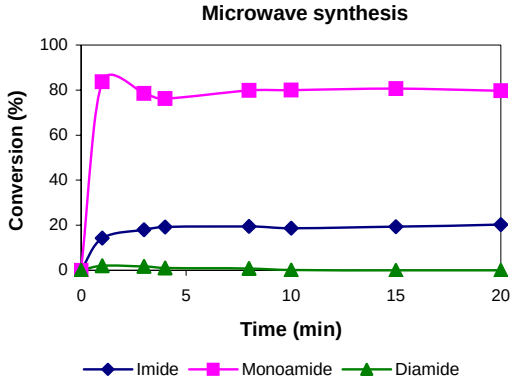

Fig. 5. Itaconic acid and N-hexyl amine microwave reaction.

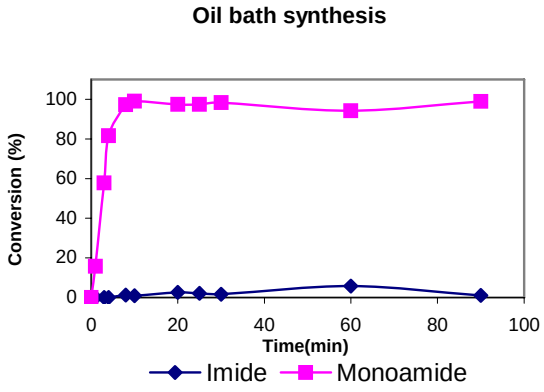

Fig. 6. Conversions in imide and amide for the oil bath reaction. The conversion was determined by GC/MS.

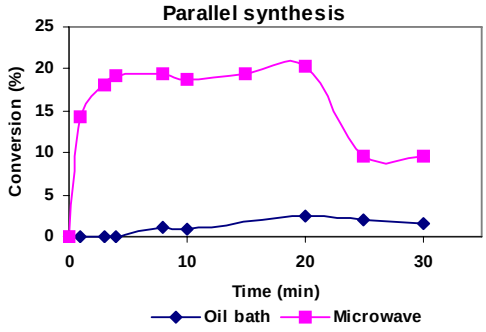

Fig. 7. Comparison between the microwave imidation and the oil bath imidation (in the absence of any supporting agents).

4. Conclusion

Some of the very well known reactions from the organic chemistry are very sensible to the influence of microwaves. For the high dipole molecules, the presence of microwaves significantly increases the kinetic and the yield.

For the very specific combination: itaconic acid and N-hexyl amine, the presence of microwaves lead to an imide (in the absence of any dehydrating agent), almost impossible by classical means. The parallel experiments performed in order to reveal the difference between the two processes, show a 15 times better yield when microwaves are implied.

In the presence of BP, the final product is a polymer of high purity.

The microwaves allow the one pot synthesis of many optical active polymers, being a helpful aid for the chemists.

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