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Short communication

Synthesis and modification of oxetane based oligomers with 3-ethoxypropylamine by focused microwave irradiation

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Abstract

Synthesis of oligomers was achieved via condensation of several bisphenol sodium salts in water with 3,3′-bis(chloromethyl)oxetane in nitrobenzene under phase transfer catalysis with tetrabutyl ammonium bromide. All proceedings were developed both by classical and under focused microwave irradiation with complete experimental parameters control. The rigid oxetane chain was then opened partially with 3-ethoxypropylamine in order to generate some specific properties. Higher substitution was obtained by microwave activation in the presence of the zinc chloride which is well known to react as microwave absorber. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oligomers; Phase transfer catalysis; Microwave irradiation; NMR spectroscopy

1. Introduction

Phase transfer catalysis (PTC) has been frequently used due to its simplicity and low working temperature [1]. In an effort to devise a strategy for the synthesis of oxetane oligomers, we were prompted to investigate the possibility of coupling this technique with microwave irradiation which is now well established in providing a wide variety of organic reactions [2]. We have previously reported some results concerning the oligomerisation of polyethers on a multimode cavity without temperature enslavement [3].

The aim of this new study was to resynthesise oligoethers based on 3,3′-bis(chloromethyl)oxetane (BCMO) and various bisphenols by a combination of PTC and microwave irradiation with temperature enslavement during all the procedures and to extend this work on other new oligoethers.

Then, the modification of these compounds with 3-ethoxypropylamine was studied in order to partially open the oxetane rings and to ensure some specific properties [4,5]. Microwave and thermal treatment of the reactive epoxy mixture was performed in the presence of $ZnCl_2$. This latter material is well known as Lewis acid catalyst but it is often used on solvent free reactions on microwave. The functionalisation of the oxetane ring was performed by combining these two effect.

2. Experimental

The BCMO was synthesised as described by Moorodian and Farthing [6,7]. The bisphenols, solvents and catalyst were purchased from Aldrich and were used without further purification. Irradiation of reaction mixtures was performed using a monomode reactor Synthewave 402 (power 300 W) from Prolabo. Chemical shifts are expressed in ppm downfield from Me_4Si as an internal standard and recorded with a Brucker AC-250 spectrometer operating in the FT mode.

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2.1. Synthesis of oligomers

In a 100 ml dedicated reactor, 4,4′-dihydroxybiphenyl **1**, 4,4′-thiodiphenol **2**, 4,4′-cyclohexylidenebisphenol **3**, 4,4′-ethylidenebisphenol **4** or bisphenol A **5** (4.5 mmol) and the BCMO (4.5 mmol without excess or 6.5 mmol with excess) were mixed together at room temperature with 25 ml of 40% aqueous hydroxide sodium solution. 1 mmol of tetrabutyl ammonium bromide and 25 ml of nitrobenzene were then added. The mixture was submitted to focused microwave or classical heating for the specified time (Table 1). After cooling, the reaction mixture was precipitated in methanol and collected by filtration. The respective final oligomers (**6** to **10**) was washed successively with water and methanol and placed at 60 °C in a drying oven.

All NMR spectra were consistent with assumed formulae for all the oligomers synthesised by microwave heating or classical one. The corresponding chemical shifts were precisely described for **10** in Table 2. For the oligomers **8** and **9**, the additional signals confirmed the presence of an alkyl substituent between the two aromatic structures.

2.1.1. Procedure for the ring opening of the oxetanic groups

A mixture of 0.25 mmol of **6** and 75 mmol of 3-ethoxypropylamine in DMF (50 ml) was allowed to react for 20 min at 120 °C under microwave irradiation. After cooling, the reaction mixture was precipitated in methanol. The crude product was filtered, washed with water and methanol, and dried at 60 °C. The oxetanic ring opening was confirmed by the presence of a signal at $\delta = 2.8$ corresponding to the methylene aminic group. The substitution degree was calculated by the integration ratio between this latter signal and the aromatic protons at $\delta = 7.00$ and $\delta = 7.45$ of the main chain of **6**.

3. Results and discussion

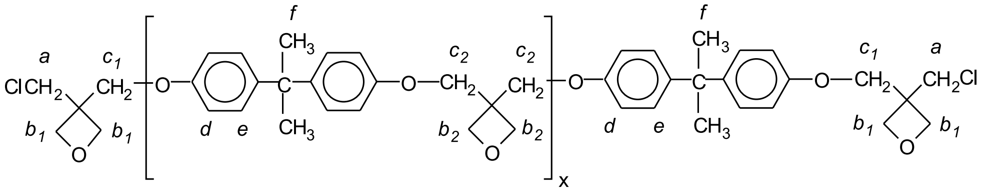
The oligomers were obtained by PTC O-alkylation between the bisphenol salts and BCMO as described in Scheme 1.

All the experiments were carried out by both the classical method (reflux) and by focused microwave ir-

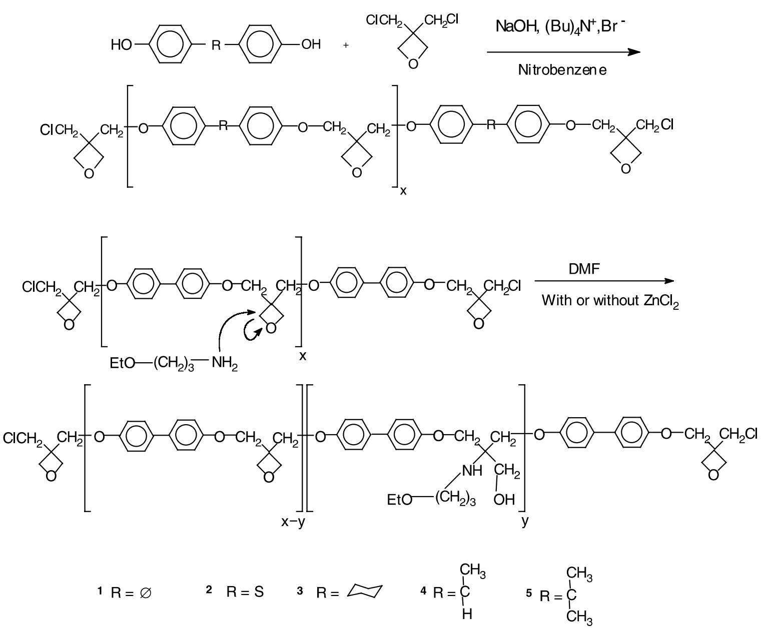
Table 1
Oligomerisation degree and yield at comparative time and temperature on microwave and thermal activation for each monomers

Starting materials	Oligomers	Activation	Temperature (°C)	Reaction time	DPn	Yield (%)
1	**6**	*Δ*	100	6 h	6	64
1	**6**	MW	100	20 min	7	70
2	**7**	*Δ*	100	4 h	8	81
2	**7**	MW	100	20 min	7	86
3	**8**	*Δ*	100	6 h	8	55
3	**8**	MW	100	20 min	8	60
4	**9**	*Δ*	100	6 h	7	78
4	**9**	MW	100	20 min	6	83
5	**10**	*Δ*	100	5 h	8	75
5	**10**	MW	100	20 min	7	97

Table 2
NMR assignments for monomer **5** and corresponding oligomer **10**



	a	b_1	b_2	c_1	c_2	d	e	f
$x = 0$	3.98	4.60	–	4.23	–	6.82	7.16	1.63
$x = 1$	3.98	4.61	–	4.25	–	6.82	7.13	1.62
$x = 7$	3.98	4.63	3.80	4.24	4.11	6.81	7.12	1.63



Scheme 1.

radiation for the specified time and were worked up and purified in the same way. Examination of the results, resumed in Table 1, shows that yields of oligomers were good and the derivatives were obtained with dramatical reduced time on microwave irradiation.

Each product's data performed in these dedicated experiments were consistent with assumed formulae and, for example, the assignment for oligomer **10** was reported in Table 2. All the chemical shifts were assigned by comparison with the monomer spectra. The final choloromethyl and aromatics protons, present in the monomer and oligomer structures, were assigned at 3.98 and 6.80–7.10. The new signal at $\delta = 3.80$ was attributed to the protons of the oxetanic ring of the main chain. The oligomers' degree (DPn) is deduced by integration as the ratio between the final CH_2Cl groups and the aromatics protons.

Interestingly enough is the comparison of the reaction time for the same oligomerisation degree. This work confirms a specific radiation effect because all the experiments were performed with the same stirring at the temperature.

This is probably due to better transfer of the catalytic complex ($Bu_4N^+ \, {}^-O–Z–O^- \, {}^+NBu_4$) from the aqueous to the organic phase. Moreover, accurate conditions like efficient stirring is essential in both methods. The present procedure appears to be very simple and efficient and represents a straightforward alternative for the synthesis of low molecular weight oligoethers.

These latter compounds constitute a rigid rod chain with regular cyclic unit. In the second part of this study, the oxetanic ring was opened to ensure some specific properties. For example, the oligomer **6** (DPn $= 7$) was reacted with 3-ethoxypropylamine to obtain the isolated product as is illustrated in Scheme 1.

The reaction was performed by nucleophilic attack of the target amine on the oxetanic ring under classical or non-conventional heating. As expected, a microwave effect was observed. A dramatic diminution in the reaction time was obtained for the same substitution degree, determined by spectral data, under the same experimental conditions.

More interesting is the study of the influence of $ZnCl_2$ as catalyst for the substitution reaction. The presence of this Lewis acid appeared to be very efficient: an increase of 15% of the oxetanic ring opening is observed with $ZnCl_2$. Therefore, one could presume that it also reacts as a polar inorganic medium which acts as a primary microwave absorber.

4. Conclusion

In conclusion, we have extended the efficient route for the preparation and characterisation of several oligoethers with oxetanic rings. The most important aspect of this approach is the possibility to work under efficient stirring and precise temperature with focused single mode microwave oven which is well adapted for PTC conditions. Focused microwave heating provides a large reduction time on same experimental conditions. The functionalisation of the oxetane ring was performed by introducing some quantities of acid catalyst which is also a primary microwave absorber. The coupling of these two properties extended the rate of the reaction.

The extension of these reactions to other bisphenol derivatives is presently under progress. Further studies concerning the thermal behaviour of the oligomers are currently engaged.

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