ELSEVIER

European Polymer Journal 38 (2002) 1851–1861

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Efficient synthesis of polyethers from isosorbide by microwave-assisted phase transfer catalysis

S. Chatti [a], M. Bortolussi [a], A. Loupy [a,*], J.C. Blais [b], D. Bogdal [c], M. Majdoub [d]

[a] *Laboratoire des Réactions Sélectives sur Supports, ICMO, UMR 8615, Université Paris-Sud, Bâtiment 410, 91405 Orsay cedex, France*
[b] *Laboratoire de Chimie Structurale Organique et Biologique, Université Pierre et Marie Curie, CNRS, UMR 7613, 4 Place Jussieu, F 75252 Paris cedex 5, France*
[c] *Institute of Polymer Chemistry, Politechnika Krakowska, ul. Warszawaska 24, 31-155 Krakow, Poland*
[d] *Laboratoire des Polymères et Membranes, Faculté des Sciences, Monastir, Tunisie*

Received 30 July 2001; received in revised form 28 January 2002; accepted 7 February 2002

Abstract

Polyetherification of isosorbide with 1,8-dibromo or dimesyl octane was realized under phase transfer catalysis with increased efficiency when performed under microwave activation. In addition to rate increase in the reaction, microwave effects on polymer structures (as determined by MALDI-TOFMS) were observed. Polymers with higher molecular weights with the presence of ethylenic groups as chain terminations were thus obtained, unlike to conventional heating where shorter hydroxylated compounds were achieved. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Isosorbide; Polyethers; Phase transfer catalysis; Microwave activation; MALDI-TOFMS

---

1. Introduction

Phase transfer catalysis (PTC) has became a widely applied technique in various fields of chemistry [1]. It is of special interest in polycondensation procedures (access to polyethers [2], polyesters, polycarbonates [3] or polythiocarbonates [4]) as well as for chemical modifications of polymers [5] involving nucleophilic substitutions.

This method leads to noticeable improvements over classical methods in solution [6] as avoiding the use of polar aprotic solvents (often expensive and even toxic). It can offer too the possibility of carrying out reactions in liquid organic phase or under solvent-free PTC [2–5] with liquid reagent acting both as electrophile and liquid organic phase for the reaction.

In other respects, it was recently shown that microwave (MW) activation for polymers synthesis [7] allows enhancements in reactivity and selectivity. When these two techniques are associated, it often results a large decrease in reaction time, improvement in yields and purity of products. We are thus concerned with efficient, economical, safe clean procedure in the so-called "green chemistry" [8].

Within the frame of non-alimentary valorization of biomass derivatives [9,10], we have synthesized polyethers derived from isosorbide (1,4:3,6-dianhydrosorbitol) with 1,8-dibromo (dimesyl) octane using PTC conditions under MW irradiation. For sake of comparison, the reactions were also performed under conventional heating (Δ) with identical reaction medium, temperature, pressure, reaction times with even same profiles of raise in temperature with both type of activation (MW or Δ). To this purpose, a monomode reactor (Prolabo, Synthewave 402) with accurate measurement and monitoring of temperature by infrared detection during the reaction course was used.

---

[*] Corresponding author. Tel.: +33-1-69-15-76-50; fax: +33-1-69-15-46-79.

E-mail address: aloupy@icmo.u-psud.fr (A. Loupy).

PII: S0014-3057(02)00071-X

2. Experimental part

2.1. Reactant and equipment

The different starting materials involved were purchased from Aldrich or Acros, and were used without any purification. Isosorbide (from Roquette-Frères) was previously crystallized from acetone.

The microwave reactor was a monomode system (Synthewave 402 from Société Prolabo) with focused waves operating at 2.45 GHz. The temperature was controlled all along the reaction and evaluated by an infrared detector which indicated the surface temperature (the IR detector was calibrated by tuning the emissivity factor using an optical fiber introduced into the reaction mixture). Temperature was maintained constant at a chosen value by modulation of emitted power. Mechanical stirring all along the irradiation provided a good homogeneity (power and temperature) and a data treatment which was followed by a computer. All reactions were performed in cylindrical Pyrex open vessels. There is no need to use an upright condenser as only small amounts of solvent are involved and as the vessel walls remain at ambient temperature.

In order to compare microwave irradiation with conventional heating, the reactions were performed under similar sets of experimental conditions (weight of reactants, reaction time and temperature). When using a thermostated oil bath, the temperature was measured with a Quick digital thermometer introduced into the reaction mixture. The rate of temperature rise was adjusted to be similar to that measured under microwave irradiation.

^{1}H and ^{13}C NMR spectra were recorded at 250 and 62.91 MHz (Bruker WP 250). Chemical shifts are given in ppm downfield from internal standard tetramethylsilane ($\delta = 0.00$ ppm). IR spectra were recorded on a FT-IR (Perkin–Elmer).

2.2. Preparation of *n*-octyl 1,8-methanesulphonate [15]

A solution of CH_2Cl_2 (240 ml), 1,8-octanol (7.3 g, 50 mmol), and triethylamine (10.1 g, 120 mmol) was stirred in an ice bath, and methanesulfonyl chloride (15.6 g, 120 mmol) was added via a syringe at a rate of 0.25 ml/min. The reaction was allowed to stir for 1 h at this temperature and then quenched with 250 ml of ice-water. The mixture was washed successively with 1.5 M HCl (200 ml) and 10% $NaHCO_3$ (200 ml). The organic layer was dried over Na_2SO_4 and concentrated under vacuum and the raw product was recrystallized from absolute ethanol.

Yield: 13.2 g (87%), white solid, m.p.: 78 °C (lit. [15] m.p. 78–79 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (*t*, 3H, $J = 6.8$ Hz), 1.08–1.82 (*m*, 12 H), 2.97 (*s*, 3H), 4.16 (*t*, 2H, $J = 6.5$ Hz).

2.3. General procedure for the synthesis of polyethers

Syntheses of polyethers derived from isosorbide were performed under microwave irradiation or conventional heating. In a Pyrex cylindrical open reactor adapted to the Synthewave reactor, 5 mmol (0.73 g) of isosorbide were mixed with 5 mmol of *n*-octyl 1,8-dibromide (1.36 g) or *n*-octyl 1,8-methanedisulphonate (1.51 g), 0.00125 mmol (0.403 g) of TBAB, 12.5 mmol of powdered KOH (0.813 g) (containing roughly 15% of water) and 1 ml of toluene. The mixture was submitted to microwave irradiation under mechanical stirring. The resulting mixture was cooled down to room temperature and diluted with 5 ml of chloroform.

The solution was precipitated in methanol to obtain polymers. The precipitate was dried overnight under vacuum to give a yellow syrup ($T_g = -48$ °C (X = Br)).

^{1}H NMR (250 MHz, $CDCl_3$): δ 1.26 (m, 4 CH_2, H-9 and H-10), 1.53 (m, 2 CH_2, H-8), 3.50–3.38 (m, 2H, H-6), 3.61 (m, 1H, H-1b), 4.10–3.80 (m, 7H, H-la, H-2, H-5, H-7), 4.45 (d, 1H, $J_{3,4} = 4.1$, H-3), 4.60 (dd, 1H, $J_{3,4} = J_{4,5} = 4.1$ Hz, H-4); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 25.91 (CH_2, C-10), 29.23 (CH_2, C-9), 29.61 (CH_2, C-8), 69.73 (CH_2, C-7), 70.81 (C-1), 73.35 (C-6), 80.03 (C-2), 80.27 (C-5), 84.31 (C-4), 86.25 (C-3); FT-IR: ν (cm^{-1}) = 3440, 2932, 2858, 1096, 1017, 776.

$(C_{14}H_{24}O_4)_n$	Calc.	C 64.60	H 9.23	O 24.61
MW = *n*.260	Found	C 65.21	H 9.47	O 25.16

2.4. Size exclusion chromatography (SEC)

SEC was performed using a Knauer apparatus working at room temperature with tetrahydrofuran (THF) as eluent at a flow rate of 1 ml min^{-1} and equipped with a set of 5–10 μm PLgel columns (8 × 250 mm). 100 μl of polymer solution in THF (concentration: 1%) were injected. A differential refractive index detector was used and molecular weights were derived from a calibration curve based on MALDI-TOFMS molar mass determination [11] of isomolecular fractions (0.5 μl) collected every 30 s.

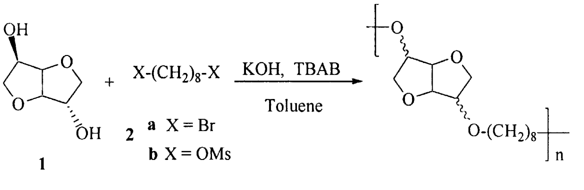
2.5. MALDI-TOF mass spectrometry

MALDI mass spectra were recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA, USA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflexion modes. The mass spectra shown represent an average over 256 consecutive laser shots (3 Hz repetition rate). Peptides and porphyrin derivatives were used to calibrate the mass scale using the two points calibration software 3.07.1 from PerSeptive Biosystems.

The polymer solutions were prepared in THF at a concentration of 2 gl^{-1}. SEC fractions were evaporated to dryness and diluted with 50 ml of THF. The matrix (2,5-dihydroxybenzoic acid) was from Sigma (France) and used without further purification. It was also dissolved in THF (10 gl^{-1}). Five microliters of polymer solution were mixed with 50 μl of matrix solution. Five microliters of sodium iodide solution (5 gl^{-1} in THF) were added in some experiments to induce cationization. One microliter of the final solution was deposited onto the sample stage and allowed to dry in air.

3. Results and discussion

Reactions were carried out using equivalent quantities of isosorbide **1** and dialkylating agent, **2a** and **2b**, in the presence of potassium hydroxide (2.5 eq. i.e. 1.25 eq./hydroxyl function) and 10% of tetra *n*-butylammonium bromide (TBAB) with small amount of toluene (1 ml for roughly 5 g of reagents) (Eq. (1)). The role of solvent is twofold: to insure a good temperature control under microwave exposition and to allow a decrease in the viscosity of reaction medium.



(1)

At the end of the reaction, the mixture was dissolved in the minimum amount of chloroform (roughly 5 ml). The solution is poured into 100 ml of methanol, leading thus to a part of insoluble polyethers (the heaviest ones). The lightest ones (oligomers) remained soluble in methanol which is subsequently removed; they are treated next with *n*-hexane where they are precipitated. The most significant results are given in Table 1 for reactions performed at 110 °C within 30 min, carried out under identical conditions for both type of activation (MW or Δ) including similar profiles of raise in temperature (Fig. 1).

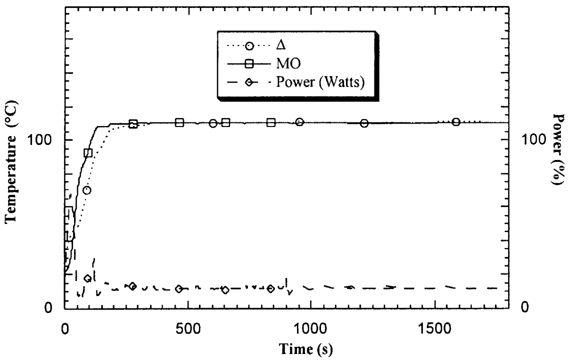


Fig. 1. Profiles of raise in temperature for the reaction of **1** with **2a** under both type of activation (MW or Δ).

It is obvious that the heaviest polymers (FP MeOH) were only obtained under MW irradiation whereas lightest ones (FP Hex) were formed under both conditions. Conversions are nearly quantitative (>95%) and total yields are much more higher under MW when compared to Δ (68–76% against only 28–30%). *Clearly, reactivity as well as selectivity are affected by the activation mode.*

4. Molecular weight and structures of methanol-insoluble polymers (FP MeOH)

The weight and number average molecular weights (M_p, M_n) and the polydispersity index (I_p) of the polyethers were estimated by size exclusion chromatography (SEC) using low mass polystyrene standards. The values have been subsequently revisited after calibration by matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOFMS) [11] (Table 2).

Table 1
Fraction of polyethers precipitated from methanol (FP MeOH) and from *n*-hexane (FP Hex) for the reaction of **1** with **2** at 110 °C for 30 min

2	FP MeOH (%)		FP Hex (%)		Total yields (%)	
	MW[a]	Δ[b]	MW[a]	Δ[b]	MW[a]	Δ[b]
X = Br	24	0	44	28	68	28
X = OMs	31	0	45	30	76	30

Completion to 100% is constituted of starting materials (conversion >95%).

[a] Microwave activation.

[b] Classical heating in thermostated oil bath.

Table 2
Distribution parameters of FP MeOH estimated by SEC using a MALDI-TOFMS calibration

	Calibration polyether		
2	M_n	M_p	I_p[a]
X = Br	3300	4300	1.30
X = OMs	3650	5100	1.39

[a] Polydispersity index $I_p = M_p/M_n$.

Analysis of Tables 1 and 2 indicates that isosorbide polycondensation with 1,8-dibromooctane (**2a**) led to slightly lower yields than with 1,8-dimesyloctane (**2b**) (24% versus 31% respectively) and to lower molecular weights. However, the homogeneity is higher with **2a** when compared to **2b** ($I_p = 1.30$ and 1.39 respectively).

^1H and ^{13}C NMR analysis of these fractions indicate clearly the presence of a terminal ethylenic double bond (^1H NMR: signals at 4.95 and 5.75 ppm — cf. Fig. 2; ^{13}C NMR: peaks at 114 and 151 ppm — cf. Fig. 3).

These polyethers were further analyzed by MALDI-TOFMS which allows characterization of the individual constituents of the polymer.

The mass spectra of this methanol-insoluble fraction (Fig. 4) clearly shows the presence of two main series of peaks (repeating unit: 256.17 u) which can be attributed to sodium cationized (Na^+ is provided by the sodium iodide added to the matrix) structures $\mathbf{A}_1$ and $\mathbf{B}_1$. One can also characterize the presence of other minor structures which differ from the previous ones by 18 u: $\mathbf{A}_2$ and $\mathbf{B}_2$ respectively. In both structures $\mathbf{A}_i$ and $\mathbf{B}_i$ ($i = 1$ or 2) the chain terminations are constituted by double bonds, in good agreement with NMR results.

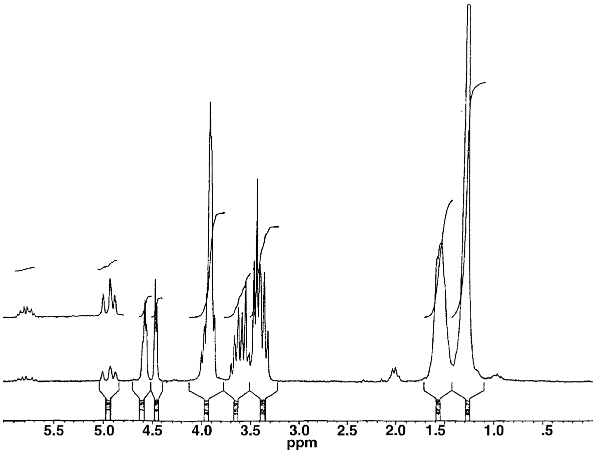


Fig. 2. ^1H NMR spectrum of FP MeOH obtained for the reaction of **1** with **2a**.

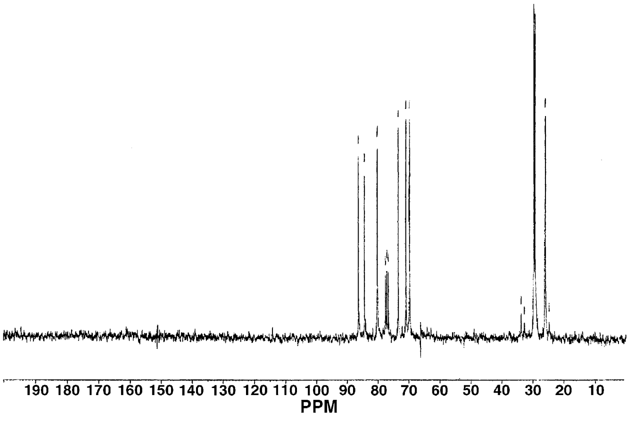


Fig. 3. ^{13}C NMR spectrum of FP MeOH obtained for the reaction of **1** with **2a**.

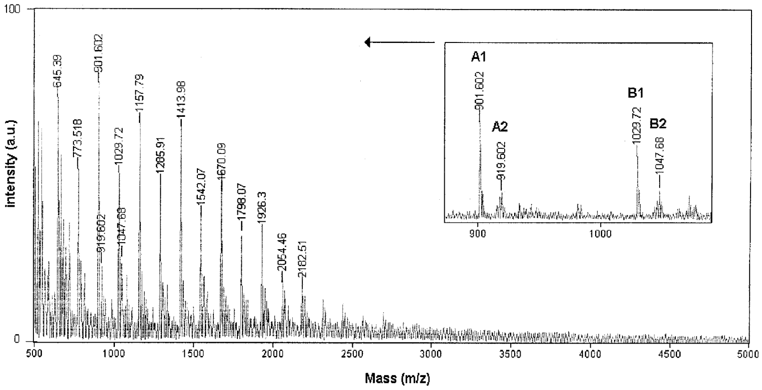
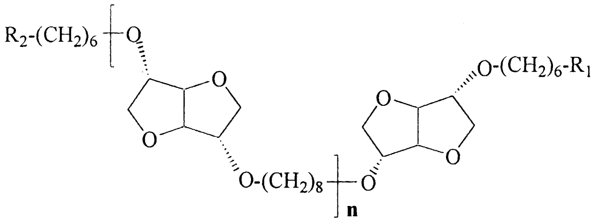


Fig. 4. MALDI-TOF spectrum of FP MeOH obtained for the reaction of **1** with **2a** under MW (yield = 24%).

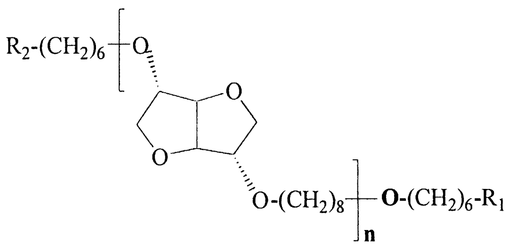
n		1	2	3	4	5	6	7
A_1	Calc.	645.44	901.61	1157.77	1413.94	1670.11	1926.27	–
	Meas.	645.39	901.60	1157.79	1413.98	1670.09	1926.30	–
A_2	Calc.	663.45	919.62	1175.78	1431.95	1688.12	1944.28	–
	Meas.	663.38	919.60	1175.50	1431.63	1687.74	1943.77	–
B_1	Calc.	–	773.53	1029.70	1285.86	1542.03	1798.20	2054.36
	Meas.	–	773.52	1029.72	1285.91	1542.07	1798.07	2054.46
B_2	Calc.	–	791.55	1047.71	1303.87	1559.71	1815.21	2071.81
	Meas.	–	791.60	1047.68	1303.58	1559.65	1815.36	2071.89



1 $R_1 = R_2$ $-CH=CH_2$

2 $R_1 =$ $-CH=CH_2$, $R_2 =$ $-CH_2-CH_2-OH$

Structure A_i



1 $R_1 = R_2$ $-CH=CH_2$

2 $R_1 =$ $-CH=CH_2$, $R_2 =$ $-CH_2-CH_2-OH$

Structure B_i

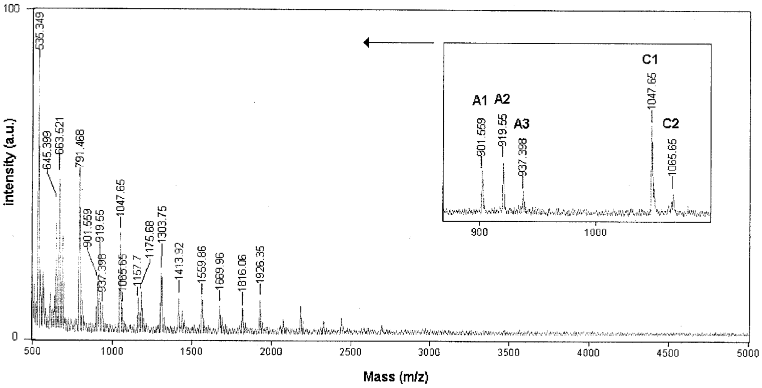


Fig. 5. MALDI-TOF mass spectrum of FP Hex obtained for the reaction of **1** with **2a** under MW (yield = 44%).

4.1. Structures of hexane-insoluble polymers (FP Hex)

4.1.1. Microwave activation

^{1}H NMR spectrum clearly indicates a mixture of several products, involving a lot of terminal double bonds, the number of which is increased in the hexane-soluble fraction. A typical MALDI-TOF mass spectrum of the hexane-insoluble polyethers obtained under MW-assisted reaction of isosorbide and **2a** (X = Br) is given in Fig. 5.

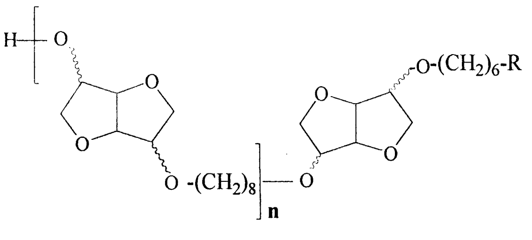
The mass spectrum reveals the presence of two main series of peaks (repeating unit: 256.17 u): one corresponds to the already described structures $\mathbf{A}_1$, $\mathbf{A}_2$ and new one $\mathbf{A}_3$ (which is constituted by two OH functional end groups) and the other one can be attributed to sodium-cationized structures $\mathbf{C}_1$ and $\mathbf{C}_2$.

The presence of a functional OH end group indicates that this reaction could be extended whereas structures $\mathbf{A}_2$, $\mathbf{A}_3$, $\mathbf{B}_2$, $\mathbf{C}_1$ and $\mathbf{C}_2$ constitute extensible ones (functional end groups are available for further reactions).

4.2. Conventional heating

The results obtained by MALDI-TOFMS analysis are noticeably different from those resulting from MW activation (Fig. 6). Two major series of peaks (repeating unit: 256.17 u) attributed to sodium-cationized structures $\mathbf{C}_i$ and **D** are observed.

n		2	3	4	5	6	7
$\mathbf{C}_1$	Calc.	535.37	791.54	1047.71	1303.87	1560.04	1816.21
	Meas.	535.35	791.47	1047.65	1303.75	1559.86	1816.06
$\mathbf{C}_2$	Calc.	553.41	809.58	1065.75	1321.92	1578.10	1834.26
	Meas.	553.43	809.61	1065.65	1321.81	1578.09	1834.18



1 R = CH=CH$_2$ (major)

2 R = CH$_2$-CH$_2$-OH (minor)

Structure C$_\mathbf{i}$

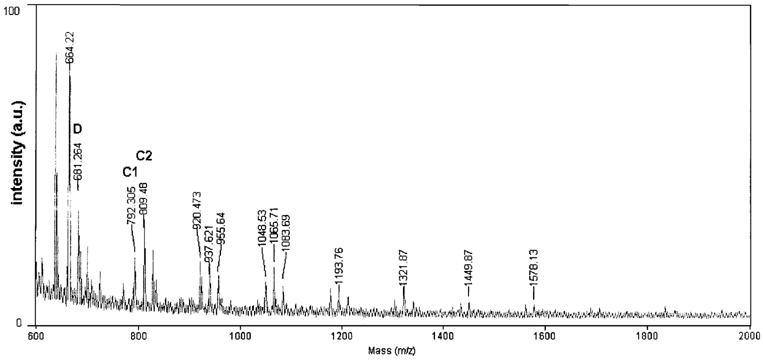
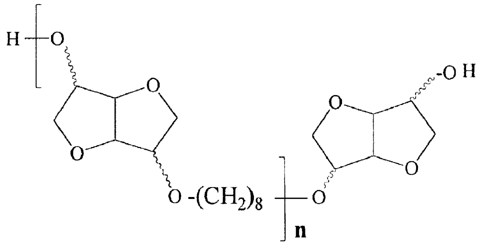


Fig. 6. MALDI-TOF mass spectrum of FP Hex obtained for the reaction of **1** with **2a** under conventional heating (yield = 28%).

n	2	3	4	5
$(M+Na)^+_{calc.}$	681.46	937.63	1193.79	1449.96
$(M+Na)^+_{meas}$	681.26	937.62	1193.76	1449.87



Structure D

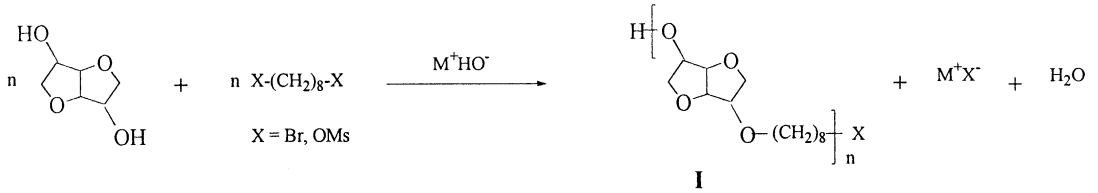
As it clearly appears, due to the presence of OH functional end groups, these polymers are under growth phase. The reaction can thus be extended for longer reaction times. The main results are given in Table 3.

Under conventional heating, yields are improved by extending reaction time up to 1 day, then remain unchanged with further prolongation up to 7 days. The reaction seems to be stopped even if analysis revealed the presence of functional OH end groups.

4.3. Mechanisms of polycondensation

All the structures of polymers we have identified are resulting from multistep procedures that we could describe here in terms of chain polymerization mechanism:

Initial step. It consists in successive nucleophilic substitutions (n times) leading to the precursor polymer **I** with repetitive unit (256.17 u).



(2)

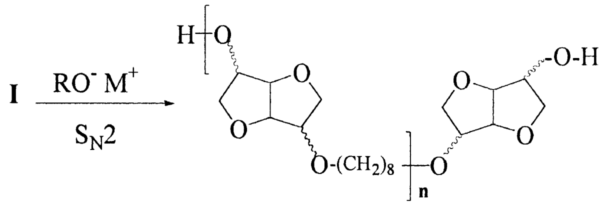
Table 3
Effects of reaction time on the yields in FP MeOH and FP Hex for the reaction of **1** with **2b**

Time	Mode of activation	FP MeOH (%)	FP Hex (%)
30 min	MW	31	45
30 min	Δ	0	30
1 day	Δ	19	64
7 days	Δ	18	67

Growing phase. One can expect two different pathways:

(i) *a normal propagation*, which consists in three steps from precursor **I**:

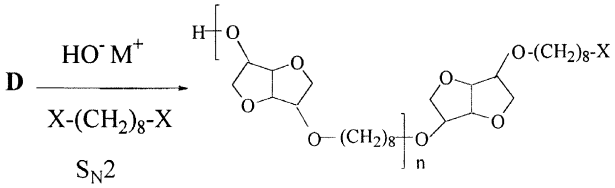
- a S_N2 reaction with isosorbide alkoxide (RO^-)



D

(3)

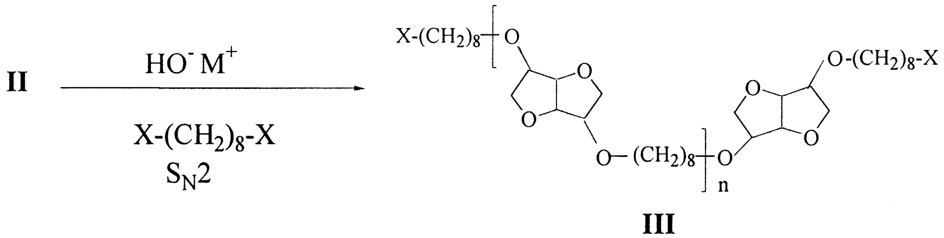
- a subsequent alkylation on **D** leading to the intermediate **II**



II

(4)

- a S_N2 reaction on **II** with RO^- leading to the intermediate **III**

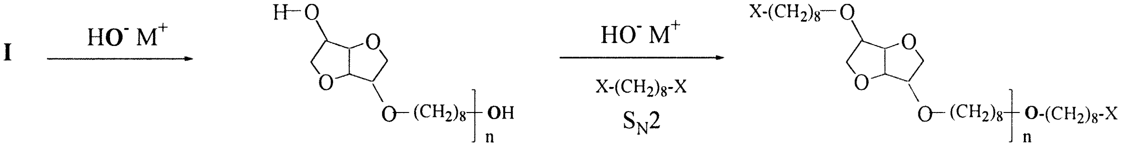


III

(5)

(ii) a propagation with introduction of complementary oxygen atom

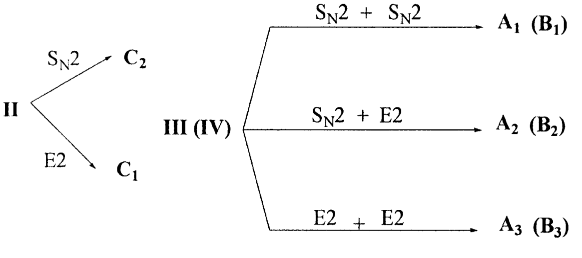
A competitive pathway consists in the hydrolysis of **I** (S_N2 by HO^-M^+) followed by double alkylation leading to a new intermediate **IV**.



IV

(6)

Termination phase. Each one of the intermediates **II**, **III** and **IV** can be subjected to either S_N2 reaction by the base HO^-M^+ (hydrolysis) or β-elimination (E2) by RO^-M^+ or HO^-M^+.

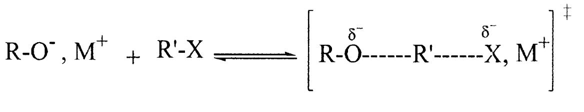


(7)

4.4. Comparison of the two techniques

Noticeably different results are obtained when polymerization is performed under MW instead of classical heating:

(i) Reactions times are largely decreased, as already advocated for such type of alkylation. This effect can be attributed to an increase in system polarity from the ground state of the reaction, which consists in tight ion pairs (involving hard alkoxide anions), toward the transition state where ion pairing is much more loose due to negative charge delocalization. It results in an enhancement in polarity during the reaction progress and, consequently, to an increase of MW-materials interactions magnitude responsible for the observed acceleration [13].



$$R\text{-}O^-, M^+ + R'\text{-}X \rightleftharpoons \left[R\text{-}\overset{\delta^-}{O}\text{------}R'\text{------}\overset{\delta^-}{X}, M^+ \right]^{\ddagger}$$

Ground state
(tighter ion pair)

Transition state
(looser ion pair)

(ii) Higher molecular weights polymers are obtained with a better homogeneity. This effect could originate from some dipole orientation influence in the presence of an electromagnetic field that could induce some mutual special orientation of reagents. Such a conclusion was already drawn from some studies in the literature [12].

(iii) The structure of polymers are quite different with essentially large discrepancies in the chain terminations as shown by the MALDI-TOF mass spectra.

In fact, under MW irradiation, ethylenic end groups are formed rather rapidly and set up an hindrance to further growth of polymers. Reciprocally, under conventional heating, terminations are essentially constituted by hydroxyl functions that nevertheless did not allow further polymerization.

Evidently, ethylenic formation appeared as favoured under MW when compared to Δ. This could be considered as an example of MW effect on selectivity, the competitive β-elimination being enhanced towards nucleophilic substitution, when the reaction is performed under electromagnetic field. This observation is consistent with an enhanced MW stabilization by dipole–dipole interaction of the more polar transition state (TS). In elimination TS, due to a greater delocalization of negative charge when compared to substitution TS, polarity is enhanced in connection with a looser ion pair (Fig. 7, Scheme 1) [13].

5. Conclusion

We have developed a new facile method for the rapid synthesis of linear polyethers from isosorbide by using microwave irradiation under solid–liquid phase-transfer catalytic conditions in the presence of a small amount of toluene. The use of a small amount of solvent was crucial to insure a good temperature control and decrease in the viscosity of the reaction medium.

The interest of microwave irradiation is at least threefold:

- It was demonstrated that the microwave-assisted synthesis proceeded more rapidly, compared with conventional heating, and was reduced to 30 min with

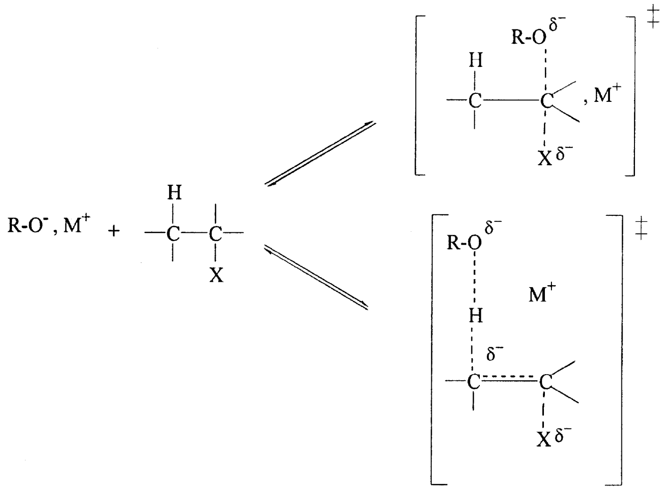
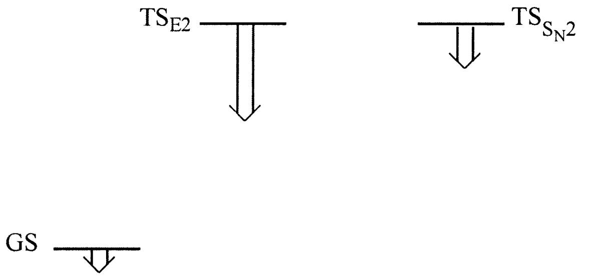


Fig. 7. Competitive E2-S_N2 reaction mechanisms.



Scheme 1. Relative stabilizations of ground state (GS) and transition states (TS) for E2 and S_N2 reactions due to dipole–dipole interactions with MW.

yields approximately 68–76%. Under conventional conditions, the polyethers were afforded with 28–30% yields within 30 min, and similar yields in the polyethers were obtained while the reaction time was extended to 1 day. They remained practically unchanged even though the synthesis was carried out for up to 7 days.

- The analysis of the properties of synthesized polyethers revealed that the structures of the products depended on the activation mode. The polyethers were characterized by higher molecular weights with a better homogeneity under microwave conditions.
- Moreover, it was found that the mechanism of chain termination is different under microwave and conventional conditions. The polyethers prepared under conventional heating possessed shorter chains with hydroxylated ends, whereas under microwave irradiation the polymer chains were longer with ethylenic group ends.

Polymers and oligomers mixtures were investigated by means of matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) as well as by NMR and SEC techniques.

Very recently [14], rather similar conclusions were drawn during a study of the microwave-mediated bulk polycondensation of D-L-lactic acid in comparison with conventional heating using the same means of analysis.

Acknowledgements

We are grateful to Société Roquette-Frères (Lestrem, France) for a kind gift of isosorbide and to Higher Education Ministry of Tunisia for financial support (Saber Chatti).

References

[1] Sasson Y, Neumann R. Handbook of phase transfer catalysis. London: Blackie Academic & Professional Ed., Chapman & Hall; 1997.

[2] (a) Keller P. Polyethers based on 4,4′-dihydroxyazoxybenzene: a new class of liquid crystalline main chain polymers. Makromol Chem Rapid Commun 1985;6:255–9;
(b) Percec V, Schaffer TD. Functional polymers and sequential copolymers by phase transfer catalysis. XXVI. Synthesis and characterization of thermotropic liquid crystalline polypodants. J Polym Sci, Polym Lett Ed 1987;25(3):2755–79;
(c) Schaffer TD, Antolin K, Percec V. Synthesis of aromatic-aliphatic polyformals by polyetherification of 1,4-bis(chloromethoxy)butane with 4,4′-isopropylidenediphenol. Makromol Chem 1987;188:1033–46.

[3] (a) Ueda M, Sato K, Kondo S. Polymers synthesis by solid–liquid two-phase polycondensation of ethyl cyanoacetate with α,α'-dichloro-*p*-xylene in the presence of potassium carbonate and crown ether. Makromol Chem, Rapid Commun 1983;4:613–5;

(b) Kanno T. Synthesis of polycarbonate by interfacial polycondensation of bis(2,4,6-trichlorophenyl) carbonate with 4,4′-isopropylidenediphenol. Makromol Chem, Rapid Commun 1990;11:181–3;
(c) Iyer VS, Sehra JC, Sivaram S. Phase transfer catalyzed interfacial polycondensation of activated diaryl carbonates with 4,4′-isopropylidenediphenol: a remarkable rate acceleration. Makromol Chem, Rapid Commun 1993;14:173–7;
(d) Tagle LH. In: Phase transfer catalysis in polymer synthesis. Handbook of phase transfer catalysis. London: Blackie Academic & Professional Ed., Chapman & Hall; 1997. p. 200–43 [Chapter 6].

[4] Bandiera M, Berti C, Manaresi P. Sulfur-containing polymers. New polythiocarbonates and polydithiocarbonates based on 4,4′-isopropylidenedibenzene-thiol. Makromol Chem 1993;194:2453–61.

[5] (a) Lewis J, Naqvi MK, Park GS. The replacement of chloride by acetoxy groups in PVC using a crown ether complex. Makromol Chem, Rapid Commun 1980;1:119–23;
(b) Leung LM, Chik LG. Phase transfer catalyzed synthesis of disubstitued poly(phenylene vinylene). Polymer 1993;34(24):5174–9;
(c) Nishikubo T. Chemical modification of polymers via phase transfer catalysis. In: Handbook of phase transfer catalysis. London: Blackie Academic & Professional Ed., Chapman & Hall; 1997. p. 480–509 [Chapter 15].

[6] Majdoub M, Loupy A, Fléche G. Nouveaux polyéthers et polyesters á base d'isosorbide: synthése et caractérisation. Eur Polym J 1994;30(12):1431–7.

[7] (a) Imai Y, Nemoto H, Watanabe S, Kakimoto M. A new facile and rapid synthesis of aliphatic polyamides by microwave-assisted polycondensation of ω-amino acids and nylon salts. Polym J 1995;28(3):256–60;
(b) Hurduc N, Abdellah D, Buisine JM, Decock P, Surpateanu G. Microwave effects in the synthesis of polyethers by phase transfer catalysis. Eur Polym J 1997;33(2):187–90;
(c) Liu YL, Sun XD, Scola DA. Kinetics of the crosslinking reaction of a bisamide model compound in thermal and microwave cure processes. J Polym Sci, Polym Chem 1998;36:2653–65;
(d) Mallakpour SE, Hajipour AR, Khoee S. Microwave-assisted polycondensation of 4-4′(hexafluoroisopropylidene)-*N*-*N*′-bis(phthaloyl-L-leucine) diacid chlorid with aromatic diols. J Appl Polym, Polym Sci 2000;77:3003–9.

[8] (a) Loupy A, Petit A, Hamelin J, Texier-Boullet F, Jacquault P, Mathé D. New solvent-free organic synthesis using focused microwaves. Synthesis 1998:1213–34;
(b) Varma RS. Solvent-free organic synthesis using supported reagents and microwave irradiation. Green Chem 1999;1:43–55;
(c) Deshayes S, Liagre M, Loupy A, Luche JL, Petit A. Microwave activation in phase transfer catalysis. Tetrahedron 1999;55:10851–70.

[9] (a) Thiem J, Bachmann F. Synthesis and properties of polyamides derived from anhydro and dianhydroalditols. Makromol Chem 1991;192:2163–82;
(b) Stross P, Hemmer R. 1,4:3,6-Dianhydrohexitols. Adv Carbohydr Chem Biochem 1991;49:93–141;
(c) Storbeck R, Rehahn M, Ballauff M. Synthesis and properties of polyesters based on 2,5-furandicarboxylic acid and l,4:3,6-dianhydrohexitols. Makromol Chem 1993;194:53–62;
(d) Kricheldorf HR, Sun ST. Photoreactive cholesteric polycarbonates based on isosorbide, 4,4′-dihydroxy-chalcone and 4,4′-dihydroxybiphenyl. Makromol Chem Phys 1997;198:2197–210;
(e) Bachmann F, Reimer J, Ruppenstein M, Thieme J. Synthesis of a novel starch-derived AB-type polyurethane. Macromol Rapid Commun 1998;19:21–6.

[10] (a) Chatti S, Bortolussi M, Loupy A. Synthesis of diethers derived from dianhydrohexitols by phase transfer catalysis under microwave. Tetrahedron Lett 2000;41:3367–70;
(b) Chatti S, Bortolussi M, Loupy A. Synthesis of new diols derived from dianhydrohexitols ethers under microwave-assisted phase transfer catalysis. Tetrahedron 2000;56:5877–83.

[11] (a) Karas M, Hillenkamp F. Mass spectrometry of synthetic polymers by UV-matrix-assisted laser desorption/ionisation. Anal Chem 1992;64:2866–9;
(b) Montaudo G, Montaudo MS, Puglisi C, Samperi F. Characterization of polymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry: molecular weight estimates in samples varying polydispersity. Rapid Commun Mass Spectrom 1995;9:453–60.

[12] (a) Singer SM, Jow J, DeLong JD, Hawley MC. Comparaison of some mechanical properties of an electromagnetically and thermally processed epoxy resin system. Polym Mater Sci Eng 1989;60:869–74;
(b) Jullien H, Petit A, Mérienne C. The microwave reaction of phenyl glycidyl ether with aniline on inorganic supports: a model for the microwave crosslinking of epoxy resins. Polymer 1996;37:3319–27.

[13] (a) Perreux L, Loupy A. A tentative rationalization of microwave effects in organic synthesis according to reaction medium and mechanism. Tetrahedron 2001;57:9199–223;
(b) Loupy A, Perreux L, Liagre M, Burle K, Moneuse M. Reactivity and selectivity under microwaves in organic chemistry: relation with medium effects and reaction mechanisms. Pure Appl Chem 2001;73(1):161–6.

[14] Keki S, Bodnar I, Borda J, Deak G, Zsuga M. Fast microwave-mediated bulk polycondensation of D.L-Lactic acid. Macromol Rapid Commun 2001;22:1063–5.

[15] Burns DH, Miller JD, Chan HK, Delaney MO. Scope and utility of a new soluble copper catalyst [CuBr–LiSPh–LiBr–THF]: a comparaison with other copper catalysts in their ability to couple one equivalent of a Grignard reagent with an alkyl sulfonate. J Am Chem Soc 1997;119(3):2125–33.