Synthesis of New Polyethers Derived from Isoidide Under Phase-Transfer Catalysis: Reactivity and Selectivity Under Microwaves and Classical Heating

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ABSTRACT: Microwave irradiation was applied to the synthesis of polyethers from 1,8-dibromo- and 1,8-dimesyl-octane under solid–liquid phase-transfer catalytic conditions. To evaluate the influence of microwaves on the reaction rates and polyether properties, we carried out the polymerization reactions under similar conventional conditions (oil bath) with the same temperature profiles. First, the microwave-assisted syntheses proceeded more rapidly in comparison with conventional heating, and the reaction time was reduced from 24 h to 30 min with higher yields of polyethers. Second, the structure of the polymers strictly depended on the activation mode. Under microwave conditions, the polyethers were characterized by higher molecular weights with better homogeneity. Third, the mechanism of chain termination was different under microwave and conventional conditions. The polyethers prepared with conventional heating possessed shorter chains with mainly hydroxylated ends, whereas under microwave irradiation, the polymer chains were longer with mainly ethylenic group ends. In fact, under microwave irradiation, ethylenic group ends were formed rather rapidly and set up a hindrance to further polymer growth. In contrast, under conventional conditions terminations were essentially constituted by hydroxyl functions; however, further polymerization was terminated as well. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1255–1266, 2003

Key words: polyethers; phase transfer catalysis

INTRODUCTION

Among the important byproducts of biomass are the dianhydrohexitols obtained in the sugar industry by the double dehydration of starch.[1] These chiral compounds exist as three stereoisomers according to the relative configuration of their two hydroxyl functions [1,4 : 3,6-dianhydro-D-sorbitol, or isosorbide (**A**); 1,4 : 3,6-dianhydro-D-mannitol, or isomannide (**B**); and 1,4 : 3,6-dianhydro-L-iditol, or isoidide (**1**; **C** in the structure):[2]
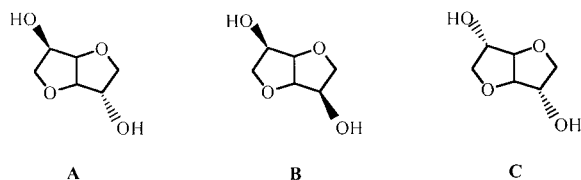
These three isomers have been used as monomers for the manufacture of new biodegradable polymers, including polyesters,[3] polyurethanes,[4] and polycarbonates[5] based on natural and renewable raw materials. These polymers presented promising high glass transitions, excellent thermal stabilities, and interesting physical properties.[6] In the literature, only a few polyethers have been considered.[7]

Among this class of compounds, **1** is the less studied isomer as the less accessible one within four steps from D-mannose.[7] However, it is certainly the most interesting for polymer synthesis due to the improved accessibility of the two hydroxyl groups lying in exo (pseudoequatorial) positions. Furthermore, on the basis of thermal measurements [differential scanning calorimetry (DSC)], it has been shown that the exo substituent increases the ring thermal stability.[1,7]

In this article, we describe the synthesis of new polyethers by the microwave (MW)-assisted polycondensation of **1** with 1,8-dibromo- or 1,8-dimesyl-octane under phase-transfer catalytic (PTC) conditions. This technique has been shown to be of special interest in polycondensation procedures and the chemical
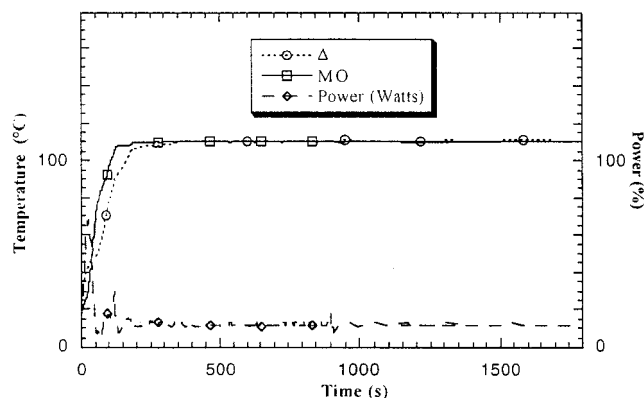
Figure 1 Profile of the rise in temperature under MW irradiation for the reaction of **1** with **2a**.

modification of polymers involving nucleophilic substitutions.[8,9]

In other respects, it was shown recently that the MW activation of polymer synthesis[10] allowed enhancements in reactivity and selectivity. When these two techniques (i.e., PTC and MW irradiation) are combined, this may result in a large decrease in reaction time and an improvement in the yields and purity of the products.[9]

For the sake of comparison, in this study, the reactions were performed under both types of activation [i.e., MW and conventional heating (Δ)] with identical reaction media, vessels, temperature, pressure, and reaction times with even same profiles of rises in temperature. For this purpose, a monomode MW reactor (Prolabo, Synthewave 402, Fontenay-sous-Bois, France)[11] with accurate measurement of temperature by IR detection during the reaction course was used. This equipment allowed us to also monitor the temperature at a constant value by the modulation of emitted MW power.

EXPERIMENTAL

Reagents and equipment

The starting materials were purchased from Aldrich or Acros and were used without any purification. **1** (from Roquette-Frères, Lestrem, France) was previously recrystallized from acetone. The MW 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 IR detector, which indicated the surface temperature (we calibrated the IR lecture by tuning the emissivity factor with an optical fiber introduced into the reaction mixture). The temperature was maintained constant at a chosen value by the modulation of emitted power. Mechanical stirring all along the irradiation provided good homogeneity (in power and temperature). All of the data treatments

were followed with a computer. All of the reactions were performed in cylindrical Pyrex open vessels. There was no need to use an upright condenser, as only small amounts of solvent were involved and as the vessel walls remained at a low temperature.

To compare MW irradiation with Δ, the reactions were performed under similar sets of experimental conditions (weight of reactants, reaction time, and temperature). When a thermostated oil bath was used, the temperature was measured with a Quick digital thermometer introduced inside the reaction mixture. The rate of the raise in temperature was adjusted to be similar to that measured under MW irradiation. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 250 and 62.91 MHz (Bruker WP 250). Chemical shifts were given in parts per million downfield from the internal standard tetramethylsilane (δ = 0.00 ppm). IR spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer).

Preparation of *n*-octyl 1,8-methanesulphonate[12]

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 syringe at a rate of 0.25 mL min^{-1}. The reaction was allowed to stir for 1 h at this temperature and was then quenched with 250 mL of ice water. The mixture was washed successively with 1.5M HCl (200 mL) and 10% $NaHCO_3$ (200 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo,* and the raw product was recrystallized from absolute ethanol (yield = 13.2 g (87%), white solid, melting point = 78°C; ref. 13 melting point = 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).

General procedure for the synthesis of polyethers

The syntheses of polyethers derived from isosorbide were performed under MW irradiation or Δ. In a Pyrex cylindrical open reactor adapted to the Synthewave reactor, 5 mmol (0.73 g) of isosorbide were

TABLE I
FP MeOH and FP Hex for the Reaction of 1 with 2a or 2b at 110°C (30 min)

	FP MeOH (%)		FP Hex (%)		Total yield (%)[a]	
	MW	Δ	MW	Δ	MW	Δ
2a	39	5	42	47	81	52
2b	67	12	18	81	85	93

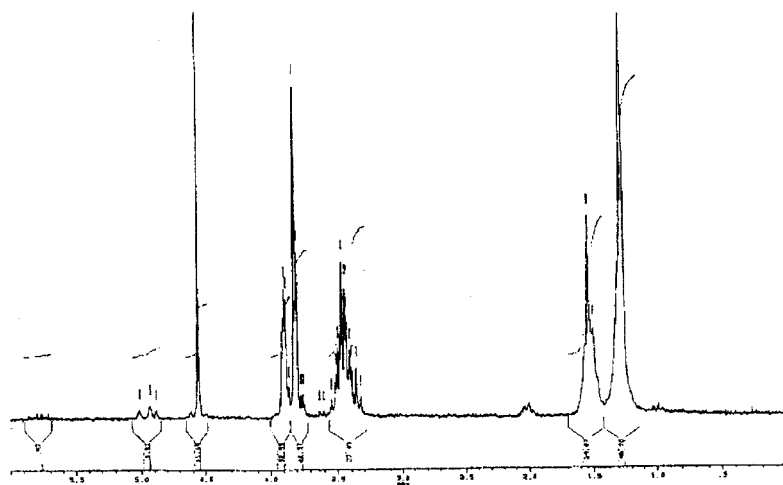[a] Completion to 100% was constituted by the starting materials.

Figure 2 ^{1}H-NMR spectrum of the FP MeOH recorded for the reaction of **1** with **2a**.

mixed with 5 mmol of *n*-octyl-1,8-dibromide (1.36 g) or *n*-octyl-1,8-methanedisulphonate (1.51 g), 1.25 mmol (0.4025 g) of tetra-*n*-butylammonium bromide (TBAB), 12.5 mmol of powdered KOH (0.8125 g; containing roughly 15% water), and 1 mL of toluene. The mixture was then homogenized and submitted to MW 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 the polymers. The precipitate was dried overnight *in vacuo* to give a white powder:

^{1}H-NMR (250 MHz, CDCl$_3$, δ): 1.26 (m, 4 CH$_2$, H-6 and H-7), 1.51 (m, 2 CH$_2$, H-5), 3.49 (m, 4H, H-1), 3.81 (m, 4H, H-4), 3.89 (m, 2H, H-2), and 4.55 (s, 2H, H-3); ^{13}C-NMR (62.5 MHz, CDCl$_3$, δ): 26.02 (CH$_2$, C-7), 29.22 (CH$_2$, C-6), 29.61 (CH$_2$, C-5), 69.72 (C-4), 72.11 (C-1), 83.46 (C-2), and 85.31 (C-3); FTIR (ν, cm^{-1}): 3436, 2931, 2855, 1119, 1095, and 786.

Micro-analysis: (C$_{14}$H$_{24}$O$_4$)$_n$ MW = n × 256; Calcd: C 65.62; H 9.37; O 25.00; Found: C 66.54; H 9.68; O 23.78.

Size exclusion chromatography (SEC)

SEC was performed using a Knauer apparatus working at 30°C with tetrahydrofuran (THF) eluent at a flow rate of 1 mL min^{-1} and equipped with a set of 5–10-μm PLgel columns (8 × 250 mm). Polymer solution (200 μL) in THF (concentration ≈ 1%) was then injected. A differential refractive index detector was used, and the molecular weights were derived from a calibration curve based on matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) molar mass determination[11] of isomolecular fractions (0.5 μL) collected every 30 s.

MALDI-TOFMS

MALDI-TOF mass spectra were recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument was equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated
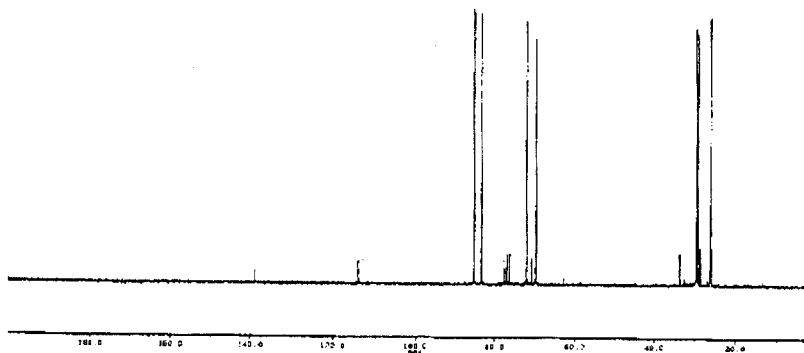

Figure 3 ^{13}C-NMR spectrum of the FP MeOH recorded for the reaction of **1** with **2a**.

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 with the two-point calibration software version 3.07.1 from PerSeptive Biosystems.

The polymer solutions were prepared in THF at a concentration of 2 g L^{-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 g · L^{-1}). Polymer solution (5 μL) was mixed with 50 μL of matrix solution. Sodium iodide solution (5 μL; 5 g L^{-1} in THF) were added in some experiments to induce cationization. The final solution (1 μL) was deposited onto the sample stage and allowed to dry in air.

RESULTS AND DISCUSSION

Polymer synthesis

The reactions were carried out with equivalent amounts of **1** and a dialkylating agent (i.e., 1,8-dibromo- or 1,8-dimesyl-octane) in the presence of potassium hydroxide (2.5 equiv, i.e., 1.25 equiv/hydroxyl function) and 10 mol % of TBAB with a small amount of toluene . The role of toluene, which is a nonpolar solvent transparent to MWs, was twofold: to allow a decrease in the viscosity of the reaction medium and to ensure good temperature constancy and control (Fig. 1):

$$ \tag{1} $$
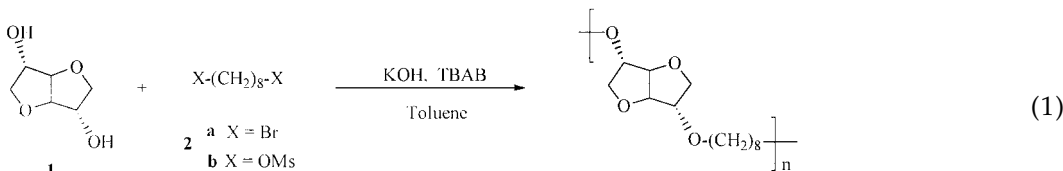
At the end, the reaction mixture was dissolved in a minimum amount of chloroform (roughly 5 mL) and filtrated to separate the insoluble materials. The solution was then poured into 100 mL of methanol to precipitate the heavy fraction of polyethers [the fraction of polyethers precipitated from methanol (FP MeOH)]. The light fraction (oligomers) remained soluble in methanol, so it was subsequently removed, and the residue was treated with *n*-hexane to afford the rest of the polyethers [the fraction of polyethers precipitated from *n*-hexane (FP Hex)].

For the reactions performed at 110°C, within 30 min under identical conditions for both types of activation (MW or Δ), and with similar profiles of the rise in temperature (Fig. 1), the most significant results are given in Table I.

The heavy fractions of polyethers (FP MeOH) were essentially obtained under MW irradiation with yields of 39 and 67% for **2a** and **2b**, respectively. Under conventional thermal conditions, the yields of the heavy fraction (FP MeOH) were 5 and 12% for **2a** and **2b**, respectively. Mesylate appeared to be a better leaving group than bromide and gave a higher yield of FP MeOH's (67%) under MW conditions. The light fractions of polyethers (FP Hex) were obtained under both conditions (i.e., MW and Δ), but the total conversions were moderate (**2a**, Δ = 52%) to excellent (81–93% in all other cases), and the reactivity and the selectivity were clearly affected by the activation mode.

Analysis of the polymers

All of the polymers were analyzed by complementary techniques [i.e., ^{1}H-NMR and ^{13}-NMR, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF), and DSC] to establish their structures and molecular weights and to evaluate their behaviors.

^{1}H-NMR and ^{13}-NMR spectroscopies

The NMR spectra of the FP MeOH fraction obtained from either **2a** or **2b** under MW irradiation were identical and consistent with foreseen structures. They clearly indicated the presence of a terminal ethylenic double bond (^{1}H-NMR: two signals at 4.95 and 5.80 ppm; cf. Fig. 2; ^{13}C-NMR: two peaks at 114.16 and 138.87 ppm; cf. Fig. 3). The signals relative to free OH on isodide rings groups were absent.

However, the NMR spectrum of the FP Hex indicated the formation of the lightest polymers in the growing phase containing OH groups, that is, those able to undergo subsequent reactions. This point was essentially evident from the ^{1}H-NMR spectrum where H in the α position to OH group was present at δ = 4.25 ppm. In contrast, in the FP MeOH fraction obtained under MW irradiation, the signal corresponding to these hydrogen atoms was absent (Fig. 2).

Average molecular weights (FP MeOH)

The weight- and number-average molecular weights (M_w and M_n, respectively) and the polydispersity in-
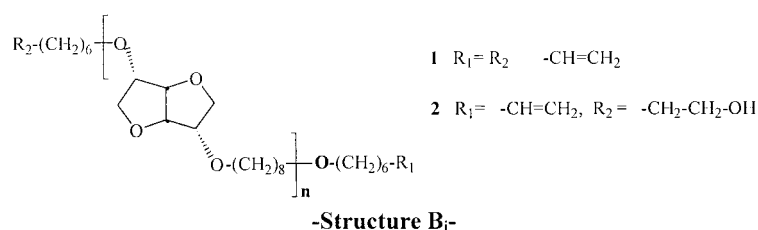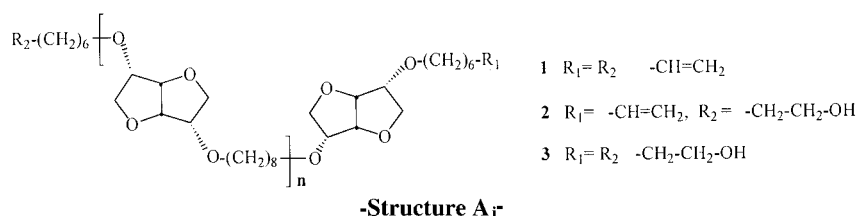
dex (M_w/M_n) of the polyethers derived from **1** were estimated by SEC with THF as a solvent with low-mass polystyrene standards. The values were subsequently revisited after calibration by MALDI-TOFMS[14] (Table II).

The analysis of the results presented in Table II indicated three essential points. First, the molecular weights of polyethers obtained with mesylate as an alkylating agent were higher than those obtained with bromide. Second, when the same alkylating agent (i.e., mesylate) was applied, MW activation was more prone to produce higher molecular weights (probably due to polycondensation kinetics). Third, the polydispersity of polyesters (M_w/M_n) remained rather identical in all of the cases (from 1.27 to 1.32), showing that there was no effects of activation mode and leaving group on the homogeneity of the polymers.
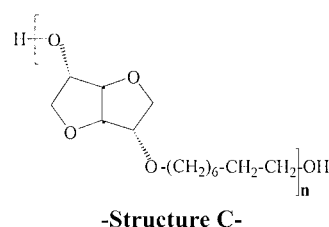
MALDI-TOFMS spectrum

The polyethers were further analyzed by MALDI-TOFMS, which allowed characterization of the individual constituents of the polymer.

MW-assisted reactions. **Methanol-insoluble fraction (FP MeOH).** The mass spectra of the FP MeOH (Fig. 4) clearly showed the presence of a main series of peaks (repeating unit = 256.17 u). The spectra were identical when started from **2a** or **2b**. Two main families of structures (Fig. 4, Table III) could be attributed. First, normal polyethers (type **A**) which differs by chain terminations as either an ethylenic double bond or an hydroxyl group (**A₁**, **A₂**, and **A₃**). Second, polyethers with an oxygen bridge (type **B**; **B₁** and **B₂**):

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

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

3 $R_1 = R_2$ $-CH_2-CH_2-OH$

-Structure A₁-

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

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

-Structure B₁-

In structures **A₂** and **B₂**, one termination was composed of an ethylenic moiety, and the other was composed of a hydroxyl end group resulting from S_N2 reactions by HO^- rather than β elimination, whereas in structure **A₃**, the chain terminations consisted of hydroxyl groups from S_N2 reactions by HO^-.

Hexane-insoluble fraction (FP Hex). The MALDI-TOF mass spectrum of the FP Hex obtained under the MW-activated reaction of **1** and **2a** revealed the presence of one major series of peaks (repeating unit = 256.17 u) attributed to sodium cationized structures (**C**). In this case, only hydroxyl end groups were obtained, one from **1** and the other from the S_N2 reaction by HO^-:
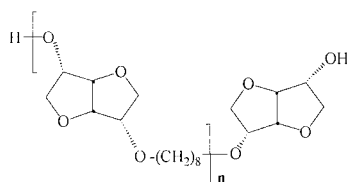

-Structure C-

n		3	4	5
$(M+Na)^+$	*Calc.*	809.55	1065.23	1321.88
	Meas.	808.89	1065.04	1321.50

Δ

Methanol-insoluble fraction. The results obtained by MALDI-TOFMS analysis for the FP MeOH fractions were noticeably different from those resulting from MW activation (Fig. 5). Four major series of peaks (repeating unit = 256.17 u) were obtained and attributed to structures **A₁**, **C**, and two new structures, **D** and **E**.

TABLE II
Distribution Parameters of the FP MeOH by SEC with a MALDI-TOFMS Calibration

2	Activation mode	Calibration polyether		
		M_n	M_w	M_w/M_n
2a	MW	2670	3400	1.27
2b	MW	3530	4650	1.32
2b	Δ	2600	3400	1.31

-Structure D-

N		2	3	4	5	6	7
(M+Na)+	Calc.	681.46	937.63	1193.21	1448.95	1705.29	1961.45
	Meas.	681.26	937.62	1193.17	1448.98	1705.17	1961.36
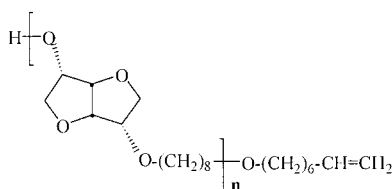
-Structure E-

n		1	2	3
(M+Na)+	Calc.	663.51	919.65	1175.91
	Meas.	663.45	919.58	1175.82

Hexane-insoluble fraction. With regard to the FP Hex, by far the most abundant (81%), they were essentially composed of a mixture of the three previously described structures **C**, **D**, and **E** (mostly hydroxylic functions).

Mechanism of polycondensation

All of the structures of the polyethers that we identified (A_1, A_2, A_3, B_1, B_2, **C**, **D**, and **E**) resulted from
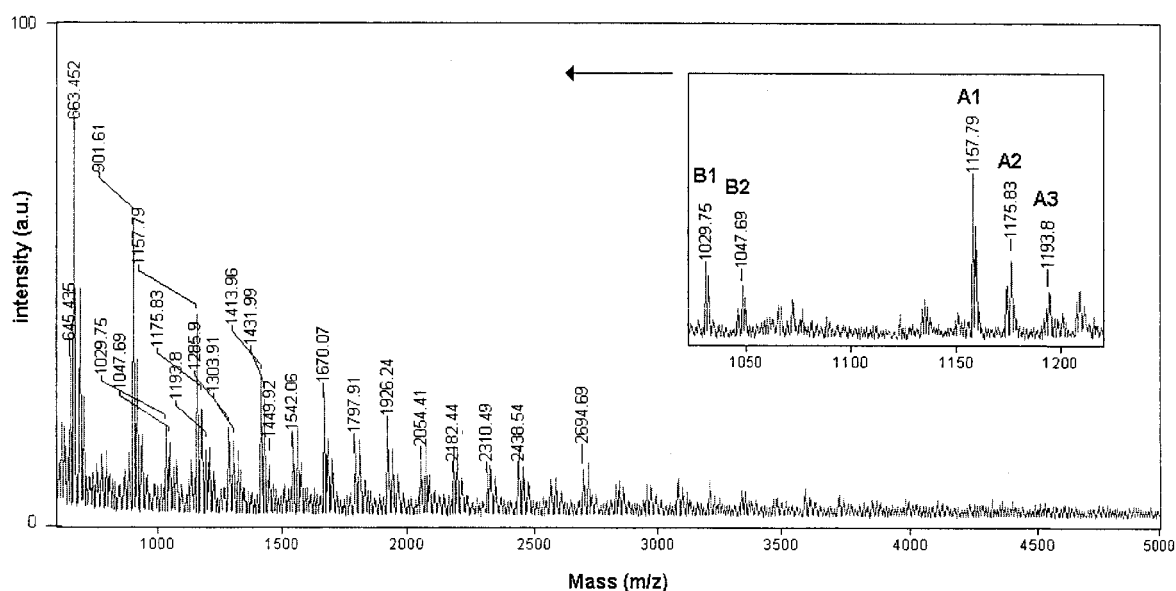

Figure 4   MALDI-TOF spectrum of the FP MeOH obtained for the reaction of **1** with **2a** under MW (yield = 39%).

a multistep reaction mechanism that we could describe here in terms of a step-growth polymerization reaction. At the beginning, it consisted of successive nucleophilic substitutions (repeated n times) leading to the precursor polymer **I** with a repetitive unit (256.17 u):
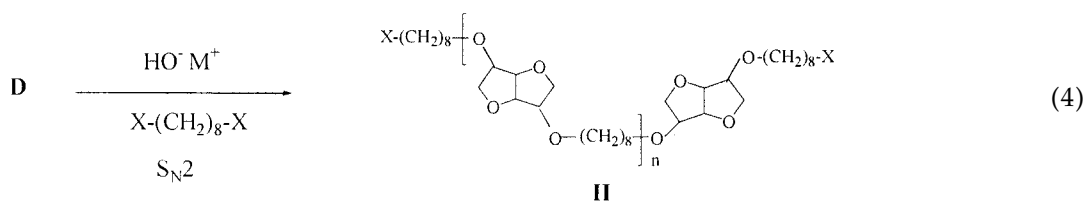

$$\tag{2}$$
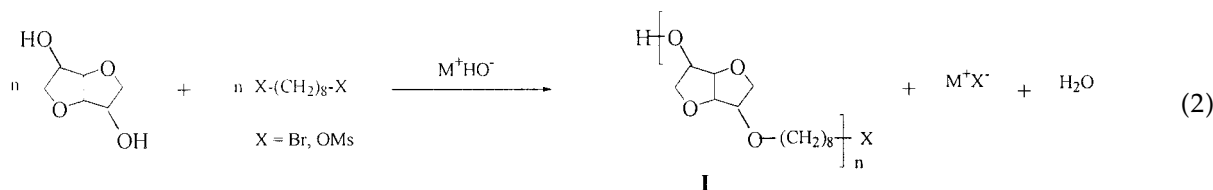
In the next phase, we expected two different pathways starting from the precursor polymer **I** . First, the so-called normal propagation consisted of a three-step procedure from precursor **I**:
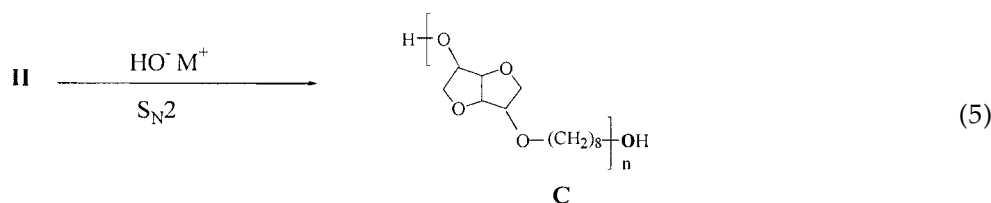
An S_N2 reaction with isoidide alkoxide (RO^-)

$$\tag{3}$$
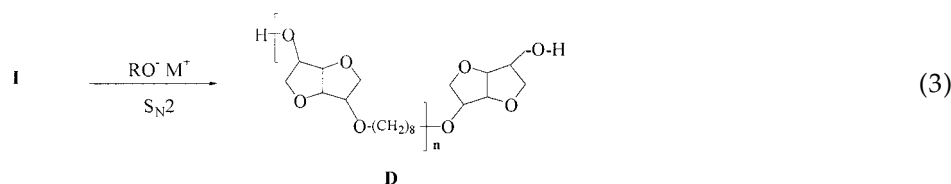
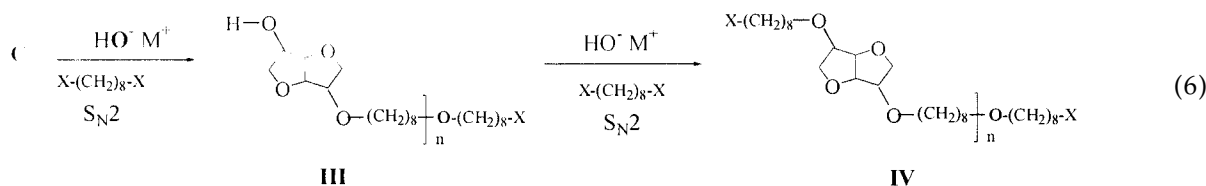A subsequent alkylation on **D** leading to the intermediate **II**

$$\tag{4}$$

The hydrolysis of **II** leading to structure **C**
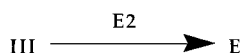

$$\tag{5}$$

Second, propagation with the introduction of a complementary oxygen atom, that is, the alkylation of **C** that led to intermediate **III** was followed by another alkylation to intermediate **IV**:

$$\tag{6}$$

In the final stage, each of the intermediates, **II, III,** and **IV,** were subjected to either S_N2 reactions by the base

$$III \xrightarrow{\text{E2}} E$$

HO⁻M⁺ (hydrolysis) or β elimination (E2) by RO⁻M⁺ or HO⁻M⁺:

$$II\ (IV) \begin{cases} \xrightarrow{S_N2\ +\ S_N2} & A_1\ (B_1) \\ \xrightarrow{S_N2\ +\ E2} & A_2\ (B_2) \\ \xrightarrow{E2\ +\ E2} & A_3\ (B_3) \end{cases} \qquad (7)$$

Influence of the extension of the reaction time

Among all of the suggested structures resulting from the MALDI-TOFMS analysis, most of them contained hydroxyl functions as termination chains (A_2, A_3, B_2, **C D,** and **E**). These polymers were, therefore, under a growth phase. These functional groups could, in turn, lead to subsequent reactions in our conditions.
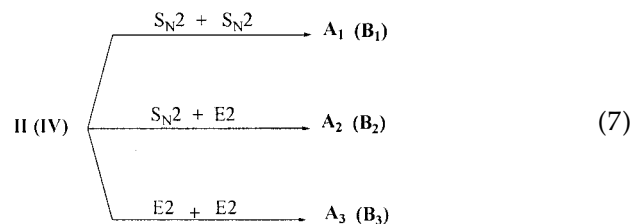
Yields

The influence of the extension of the reaction time was studied next, and the main results are given in Table IV.

The extension of the reaction time showed only a slight effect when the reactions were carried out under MW conditions. The total yield of polyethers increased only slightly from 85 to 90% for 30 and 60 min of irradiation, respectively.

However, when the reactions were performed under Δ conditions, the prolonging of the reaction time caused a large increase in the proportion of the heavy fraction (FP MeOH) to light fraction (FP Hex). After 1 month of Δ, it was possible to remove only the FP MeOH fraction with an excellent yield (91%). However, if after 30 min, the total yield of the polyethers

was 93%, it was only 12% FP MeOH but 81% FP Hex (Table IV). This is typical for step-growth polymerization reactions such as polycondensation, in which monomers are consumed rapidly at the beginning of reaction to afford low-molecular-weight oligomers with reactive end groups that can undergo further reactions to give higher molecular weight polymers.

Molecular weight

The influence of the reaction time on the molecular weights of the polyethers and their distributions are indicated in Table V.

The main conclusions we could draw from the results given in Table V are as follows. The M_w and M_n values of the polyesters increased with the extension of the reaction time from 30 to 60 min and from 30 min to 1 month under MW irradiation and Δ, respectively, which is again a typical feature of a polycondensation reaction. Low-molecular-weight oligomers with reactive ends that are formed at the beginning of the reaction undergo further condensation reactions to afford higher molecular weight polymers. Thus, the polymer molecular weight rises steadily throughout reaction, and rather long reaction times are essential

TABLE III
Attribution of Sodium-Cationized Structures of the FPMeOH by the MALDI-TOF Spectrum Obtained in the Reaction of 1 with 2a under MW (Yield = 39%)

|	1	2	3	4	5	6	7
A₁							
Calcd	645.44	901.61	1157.77	1413.94	1670.11	1926.27	2182.45
Found	645.43	901.61	1157.79	1413.96	1670.07	1926.24	2182.44
A₂							
Calcd	663.55	919.47	1175.50	1431.71	1687.78	1943.66	2200.41
Found	663.45	919.43	1175.83	1431.63	1687.71	1943.71	2200.39
A₃							
Calcd	681.41	937.51	1193.57	1449.64	1705.75	1961.71	2218.31
Found	681.39	937.46	1193.52	1449.60	1705.70	1961.70	2218.37
B₁							
Calcd	—	—	1029.75	1285.86	1542.03	1798.20	2054.36
Found	—	—	1029.75	1285.90	1542.06	1797.91	2054.41
B₂							
Calcd	—	—	1047.48	1303.58	1559.65	1815.36	2071.89
Found	—	—	1047.69	1303.91	1559.68	1815.44	2071.98
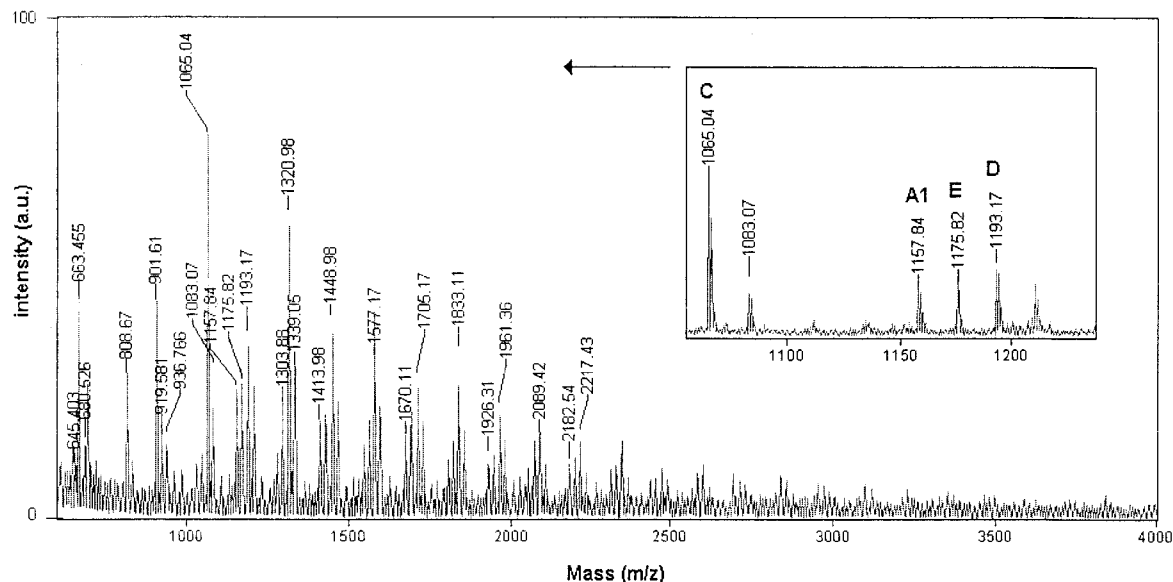
Figure 5 MALDI-TOF mass spectrum of FP MeOH obtained for the reaction of **1** with **2b** under conventional heating (yield = 12%).

for obtaining high-molecular-weight polymers. The polydispersity of the polymers was not significantly affected whatever the mode of activation, but higher molecular weights were obtained under MW irradiation (60 min). To obtain good yields and good-quality polyethers, at least 1 week under Δ was needed.

Polymer structures (heaviest polymers: FP MeOH)

MW-assisted reactions. For the reactions carried out for 30 and 60 min under MW conditions, the mass spectra are given in Figure 6(a,b).

We obtained the same structures in both cases whatever the reaction time (A_1, A_2, A_3, B_1, and B_2). Furthermore, the average molecular weights were noticeably enhanced in contrast to the SEC measurements. This was surely due to the subsequent reactions of functionalized polyethers bearing at least one hydroxyl group (structures A_2, A_3, and B_2).

Δ. The MALDI-TOF mass spectrum of the FP MeOH obtained in the reaction of **1** with **2b** under Δ for 1 month is given in Figure 7.

The spectrum recorded after 1 day of reaction time indicated that the Gaussian repartition of peaks was centered around molecular weights of 1300–1400 g mol^{-1}, whereas this maximum became centered around 2500–2700 g mol^{-1} for 1 month of reaction time. The enhancement in molecular weights was in agreement with the SEC measurements and the detection of intermediate polyethers functionalized with hydroxyl groups. After 1 month of Δ, a similar structure as found under MW irradiation for 1 hour was obtained but with lower molecular weights.

Thermal behavior (DSC)

DSC of the two polymers [Fig. 8 (30 min under MW irradiation) and Fig. 9 (1 month under Δ)] revealed similar thermal behavior of both polymers. The DSC curve of the poly-MW (Fig. 8) showed a glass-transition temperature (T_g) at 35°C and a melting range between 65–75°C (T_{max} = 72°C). The DSC curve of the poly-Δ (Fig. 9) showed a T_g at 36°C and a melting

TABLE IV
Influence of the Reaction Time on the Yields of the FP MeOH and FP Hex for the Reaction of 1 with 2b

Time	Mode of activation	FP MeOH (%)	FP Hex (%)
30 min	MW	67	18
60 min	MW	71	19
30 min	Δ	12	81
1 day	Δ	64	25
1 week	Δ	83	5
1 month	Δ	91	0

TABLE V
Influence of the Reaction Time on the Average Molecular Weights of the FP MeOH for the Reaction of 1 with 2b (Estimated by SEC with a MALDI-TOFMS Calibration)

Time	Mode of activation	M_n	M_w	M_2/M_n
30 min	MW	3500	4700	1.34
60 min	MW	5100	6900	1.35
30 min	Δ	2600	3400	1.31
1 day	Δ	3200	4100	1.28
7 days	Δ	3900	5100	1.31
1 month	Δ	4100	5000	1.22
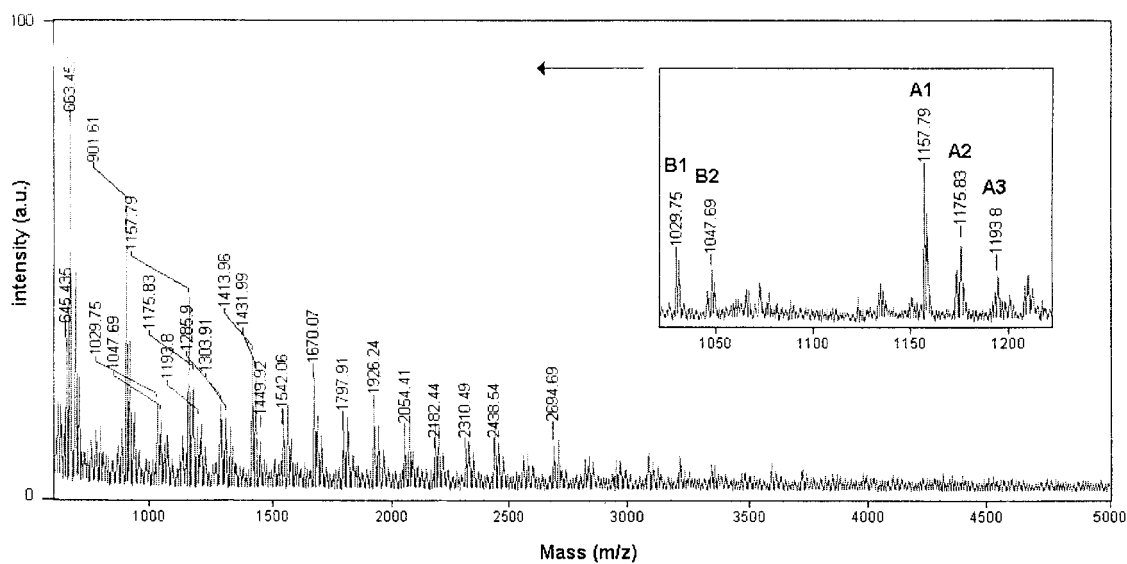
(a)
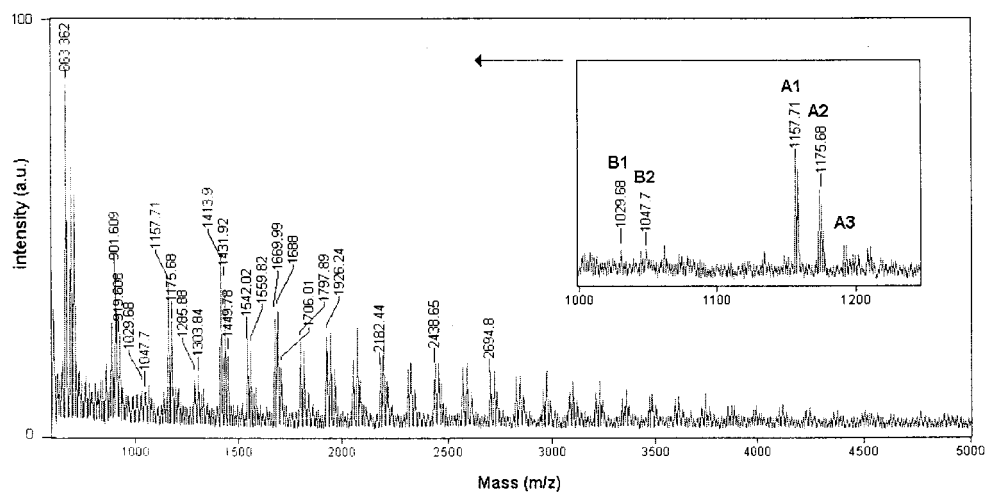
(b)

Figure 6 MALDI-TOF mass spectrum of the FP MeOH obtained for the reaction of **1** with **2b** under MW conditions: (a) 30 and (b) 60 min.
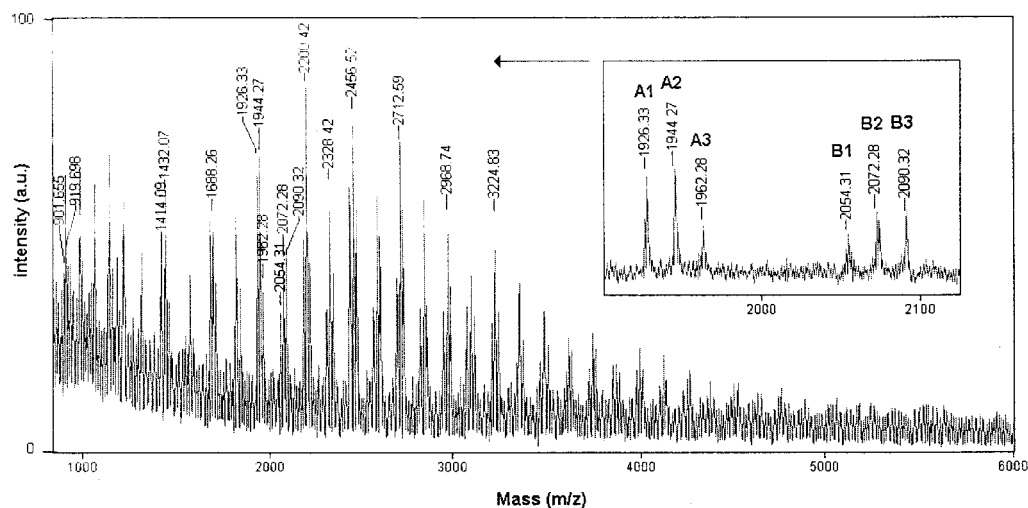

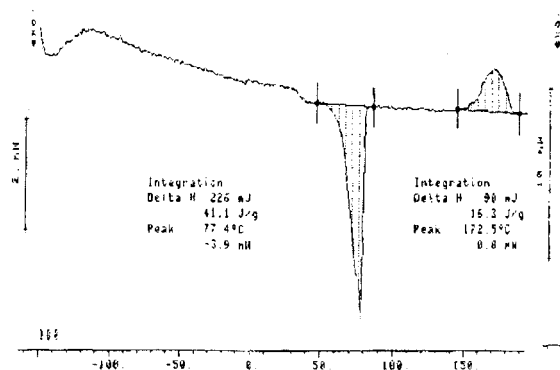**Figure 7** MALDI-TOF mass spectrum of the FP MeOH for the reaction carried out for 1 month.

Figure 8 DSC curve of poly-MW (30 min under MW irradiation).

Figure 9 DSC curve of poly-Δ (1 month under Δ).

range between 69–82°C (T_{max} = 77.5°C). These results demonstrate that the poly-MW or poly-Δ was partly crystalline (50%) with some amorphous parts (50%).

Comparison of the two techniques

As shown, noticeably different results were obtained when polycondensation was performed under MW irradiation instead of Δ:

1. Reaction times largely decreased as already advocated for such types of alkylation. This effect was attributed to an increase in the system polarity from the ground state of the reaction, which consisted of tight ions pairs (involving hard alkoxide anions), toward the transition where loose ion pairs were concentrated due to negative-charge delocalization. It resulted in an enhancement in polarity during the reaction progress and, consequently, in an increase of the magnitudes of MW materials electrostatic (dipole–dipole) interactions responsible for the observed acceleration:[15]

2. Higher molecular weight polymers were obtained with better homogeneity. This effect could have originated from some dipole orientation influence in the presence of an electromagnetic field that induced some mutual special orientation of reagents. Such a conclusion was already drawn in some studies in the literature.[13]
3. The structure of polymers were quite different, with essentially large discrepancies in the chain terminations, as shown by the MALDI-TOF mass spectra.
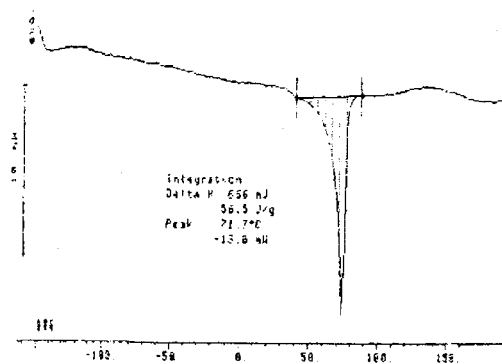
In fact, under MW irradiation, ethylenic end groups were formed rather rapidly and set up a hindrance to the further growth of polymers. Reciprocally, under Δ the terminations were essentially constituted of hydroxyl functions that nevertheless did not allow further polymerization. These conditions are shown clearly in Table IV, as MW led to the ethylenic polymers **A**, **B**, and **C** and Δ gave mainly the hydroxylated polymers **D** and **E**.

Ethylenic formation appeared to be favored under MW when compared to Δ. This could be considered an example of a specific MW effect on selectivity, with the competitive β elimination enhanced toward nucleophilic substitution when the reaction was performed under an electromagnetic field. This observation can be interpreted as consistent with an enhanced MW stabilization by dipole–dipole interactions of the more polar transition state (TS). In the elimination TS (over five atoms), due to a greater delocalization of negative charge when compared to the substitution TS (over three atoms), polarity is enhanced in connection with looser ion pairs (Figs. 10 and 11).[15]

CONCLUSIONS

We developed a new method for the rapid synthesis of linear polyethers from **1** by MW irradiation under solid–liquid PTC conditions in the presence of a small amount of toluene. The use of a small amount of solvent was crucial to ensure good temperature control and a decrease in the viscosity of the reaction medium. We demonstrated that the MW-assisted syn-
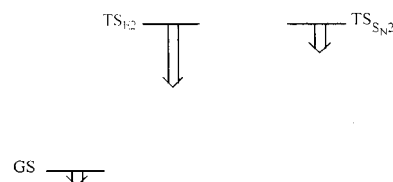

Figure 10 Relative stabilizations of the ground state (GS) and TSs for E2 and S_N2 reactions due to dipole–dipole interactions with MW irradiation.
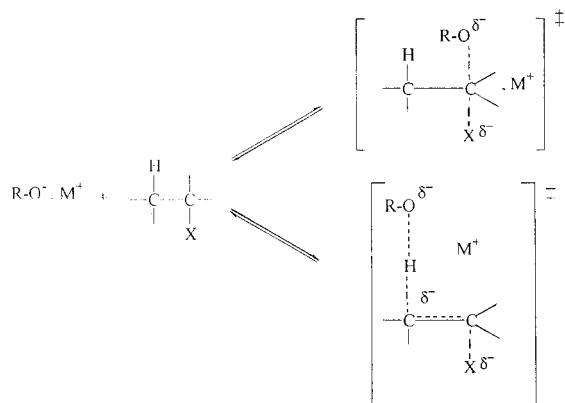
Figure 11 Competitive E2-S$_N$2 reaction mechanisms.

thesis proceeded more rapidly, compared with Δ, and the reaction time was reduced to 30 min with yields of approximately 81–85%, in which 39–67% of the polymer consisted of the heavy fraction of the polyethers (FP MeOH). Under conventional conditions, the polyethers were afforded within 30 min with 52–93% yield, but the heavy fraction (FP MeOH) was obtained with only a 5–12% yield (Table I). Similar yields of the heavy fractions (FP MeOH) were obtained under Δ, whereas the reaction time was extended to 1 week. These yields remained practically unchanged, even though the synthesis was carried out for another month (Table IV).

The analysis of the properties of the synthesized polyethers revealed that the structure of the products strictly depended on the activation mode (i.e., MW or Δ activation). Under MW conditions, the polyethers were characterized by higher molecular weights with better homogeneity. For example, within 30 min of the reaction under Δ, the polyethers with higher molecular weights were observed only in small yields (Table IV). Moreover, that the mechanism of chain termination was different under MW and Δ conditions. The polyethers prepared with Δ possessed shorter chains with mainly hydroxylated ends (**A$_1$, C, D,** and **E**), whereas under MW irradiation, the polymer chains were longer with mainly ethylenic group ends (**A$_1$, A$_2$,**

A$_3$, B$_1$, B$_2$, and **C**). In fact, under MW irradiation, ethylenic group ends were formed rather rapidly and set up a hindrance to further polymer growth. In contrast, under Δ conditions, the terminations were essentially constituted by hydroxyl functions; however, further polymerization was terminated as well. In conclusion, this method should become important from the viewpoint of its high efficiency.

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