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APPLICATION OF THE PHASE TRANSFER CATALYSIS TO THE SYNTHESIS OF NEW FURANIC POLYESTERS

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ABSTRACT: The phase transfer catalysis (PTC) process involving solid-liquid systems has been applied to the synthesis of new polyesters containing furan moieties by polycondensation of various alkylidene-bis(2-furoic acid) salts with dibromo compounds. The influence of several reaction parameters such as the nature of liquid phase, temperature, reaction time and the nature and concentration of catalyst was investigated. The polyesters were characterized in terms of backbone structure, molecular weights and thermal stability, showing that the solid-liquid PTC method is very well-suited to the preparation of such polyesters.

Key words: polyesters, phase transfer catalysis, furanic polymers

INTRODUCTION

During the last few years, we synthesized and studied various new furan-based polymers in a general study on the valorization of 2-ethylfuroate, a biomass derivative [1]. In this context, polyesters having regular structure and high molecular weight were prepared by the following methods: (i) melt polycondensation of alkylidene-bis(2-furoic acid) diesters and aliphatic diols, (ii) liquid-liquid interfacial polymerization of alkylidene-bis(2-furoic acid) dichlorides with bisphenols, and (iii) solution polycondensation of alkylidene-bis(2-furoic acid) dichlorides with aliphatic diols or with bisphenols [2-4]. However specific problems limited the success of these techniques to furano-aliphatic and furano-aromatic polyesters.

Solid-liquid phase-transfer reactions, well-known in the polycondensation field [5-10], have been successfully applied to the synthesis of a number of polyesters containing monomer units such as malate, tartrate, maleate, fumarate or phthalate [11-14]. As a continuation of our investigation on the synthesis of furanic polyesters, we present here our recent work on the use of this procedure to preparing some other furan-based polyesters by polycondensation of various alkylidene-bis(2-furoic acid) salts with α,α'-dibromo-p-xylene (**DBX**) and (Z)1,4-dibromo-but-2-ene (**DBB**).

EXPERIMENTAL

Materials

Commercial phase transfer catalysts (PTA), triethylbenzylammonium chloride (TEBAC), tetrabutylammonium bromide (TBAB), bis-tetrabutylammonium sulfate (TBAS), hexadecyltrimethylammonium bromide (HTAB), trioctylmethylammonium chloride (TOMAC), and cis-dicyclohexano-18-crown-6 (DCHC) (Aldrich) were used as received. Toluene, bromobenzene, chloroform, nitrobenzene, dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP) and dimethylacetamide (DMA) were purified by standard techniques and redistilled prior to their use.

Commercial samples of (Z)1,4-dibromo-but-2-ene (DBB) (Aldrich 99%) and α,α'-dibromo-p-xylene (DBX) (Aldrich 98%) were recrystallized thrice from dry toluene before use.

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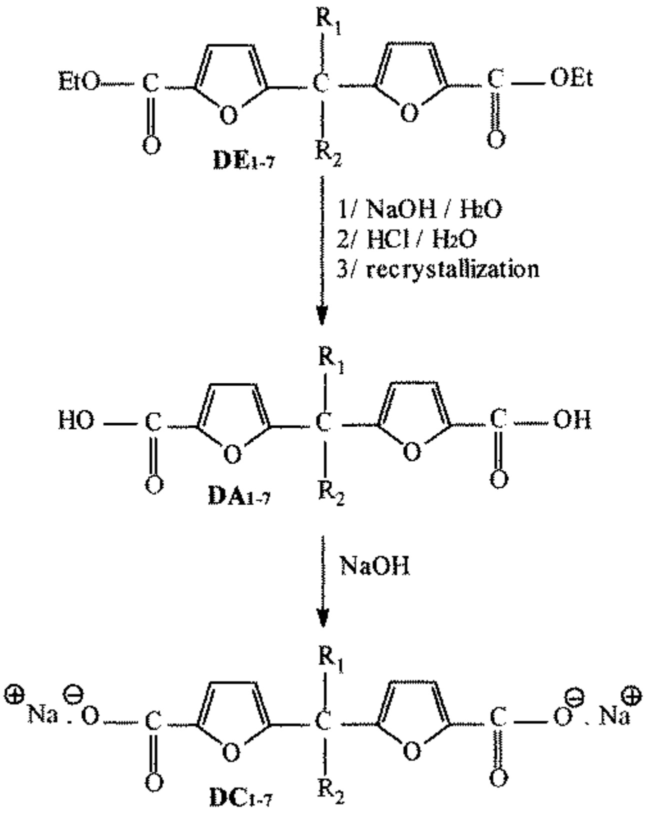
* corresponding author

Synthesis of furanic monomers

The synthesis of furanic monomers is depicted in Scheme 1. Diesters **DE**$_{1-7}$ were synthesized and characterized as previously described [3]. Diacids **DA**$_{1-7}$ were in turn quantitatively obtained by hydrolysis of the corresponding diesters in basic medium followed by acidification and recrystallization from water. Dicarboxylates **DC**$_{1-7}$ were prepared by neutralization of the corresponding diacids with a stoichiometric amount of NaOH.



	R_1	R_2
DC$_1$	CH_3	CH_3
DC$_2$	CH_3	H
DC$_3$	CH_3	n-C_3H_7
DC$_4$	CH_3	n-C_5H_{11}
DC$_5$	C_2H_5	C_2H_5
DC$_6$	CH_3	C_6H_5
DC$_7$	CH_3	CH_2-C_6H_5

Scheme 1: Synthesis of Furanic Dicarboxylates **DC**$_{1-7}$

General procedures

Diacids: A solution of 0.0312 mol of **DE** in 12 mL of methanol was slowly added to a stirred solution of 0.0625 mol NaOH in 25 mL of water and 12 mL of methanol and the mixture was refluxed for 3 h. The mixture was evaporated to dryness under reduced pressure and the solid residue was treated with 300 mL of 0.1 M HCl. **DA** was filtered, recrystallized thrice from distilled water and vacuum dried at 60°C until constant weight. **DA**$_4$ which could not be recrystallized was used without purification.

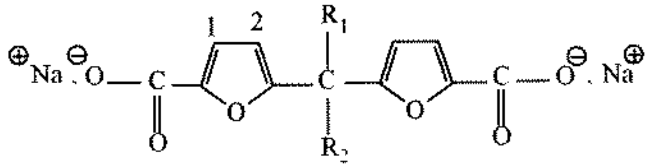
Compound	**DA**$_1$	**DA**$_2$	**DA**$_3$	**DA**$_5$	**DA**$_6$	**DA**$_7$
Yield (%)	95	90	88	92	94	90
mp (°C)	240	235	249	244	274	270

Dicarboxylates: To a solution of 0.005 mol of **DA** in 5 mL of methanol, was added a solution of 0.4 g (0.010 mol) NaOH in 5 mL of water. The mixture was stirred during 30 min at 60°C and then evaporated to dryness under reduced pressure to give **DC** which was used as obtained.

Characterizations

DC_{1-7} compounds and corresponding diacids (except **DA_4**), characterized by FTIR and ^1H and ^{13}C-NMR spectroscopy, displayed the expected structures without detectable impurities. ^1H-NMR data (chemical shifts and assignments) of **DC_{1-7}** are summarized in Table I.

Table I. Chemical shifts (δ, in ppm), integrations (number of protons) and assignments of the ^1H NMR resonances of **DC_{1-7}** (CD_3OD, 300 MHz, ref. TMS). *solvent: DMSO-d_6



Dicarboxylate	H_1	H_2	$H(R_1)$	$H(R_2)$
DC_1	6.91	6.23	1.80	1.80
DC_2	6.90	6.25	4.40	1.68
DC_3	6.91	6.22	1.66	0.92; 1.10; 2.63
DC_4	6.92	6.23	1.42	2.08; 1.55; 1.12; 0.75
DC_5*	6.47	6.11	0.71; 1.99	0.71; 1.99
DC_6	6.91	6.21	2.20	7.20 ; 7.26 ; 7.39
DC_7*	6.61	6.08	1.40	3.34 ; 6.81 ; 7.15

General polymerization procedure

5.05 mmol of **DC**, 0.12 mmol of **PTA** and 5 mmol of **DBX** or **DBB** were added to 4 mL of solvent (NMP, DMSO or DMA) under nitrogen. The resulting mixture was heated under magnetic stirring for 3 h at 110 °C. The mixture was then poured in 300 mL of ethanol. After filtration, the polyester was washed with a 0.1 M HCl aqueous solution until the filtrate gave a neutral pH value. Finally, the polyester was washed with distilled water, acetone and diethyl ether and vacuum dried at 60 °C to constant weight. Experiments were carried out at various temperatures, PTA concentrations and monomer stoichiometric ratios.

Measurements

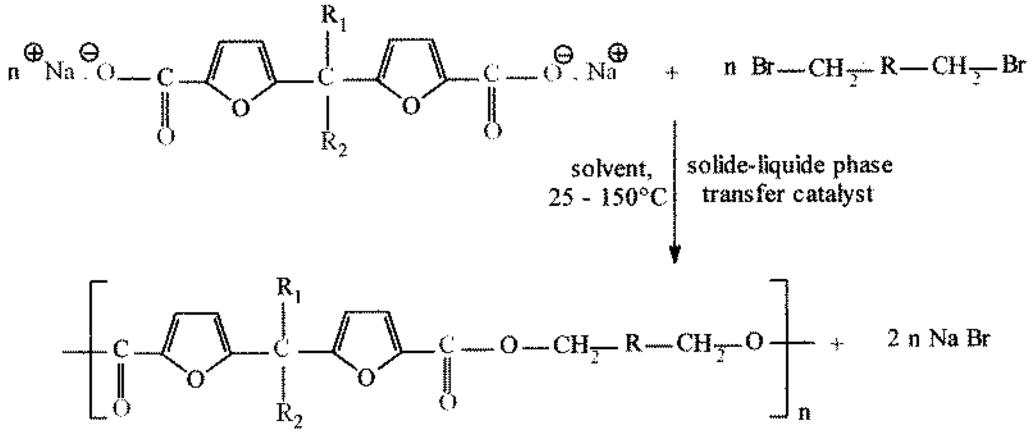
^1H NMR spectra were recorded on a Bruker AM-300 spectrometer (DMSO-d6 or $CDCl_3$ solutions, ref TMS). Infrared spectra were recorded on a Bruker 300 FTIR spectrometer. Inherent viscosities (η_{inh}) of polymers were measured using a Ubbelhode microviscosimeter in $CHCl_3$ solutions (3 $g.L^{-1}$) at 25 °C. Size exclusion chromatography (SEC) analyses were carried out in THF at 20 °C on a Waters equipment and two ultra-styragel columns (10^3 and 10^4 Å). Differential scanning calorimetric (DSC) and thermogravimetric analyses were performed on a TGA 92 SETARAM apparatus under nitrogen with a heating rate of 10 °C min^{-1}. DSC was calibrated with indium standard sample and glass transition temperatures were taken at the inflexion point of the second heating curves. Decomposition temperatures were recorded at 10% mass loss.

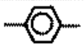
RESULTS AND DISCUSSION

Polyesters **P_{1-10}** were prepared by polycondensation of dicarboxylates **DC_{1-7}** with **DBX** or **DBB** in the presence of PTA as shown below in Scheme 2. **DC_{1-7}** salts are slowly dissolved in the medium during the reaction, while the polyesters - soluble in reaction medium - are formed.

In order to optimize the synthesis of these polyesters we undertook a systematic study of various parameters using the model system (**DC_1** + **DBX**). This monomer system was chosen because similar polyesters had been previously prepared by reacting 1,4-

bis(hydroxymethyl)benzene with 2,2'-bis(2-ethoxycarbonyl-5-furyl) propane (melt reaction) [3] or with 2,2'-his(5-chloroformyl-2-furyl)propane (solution reaction) [4]. The results obtained on these polyesters will be used for comparison purposes.

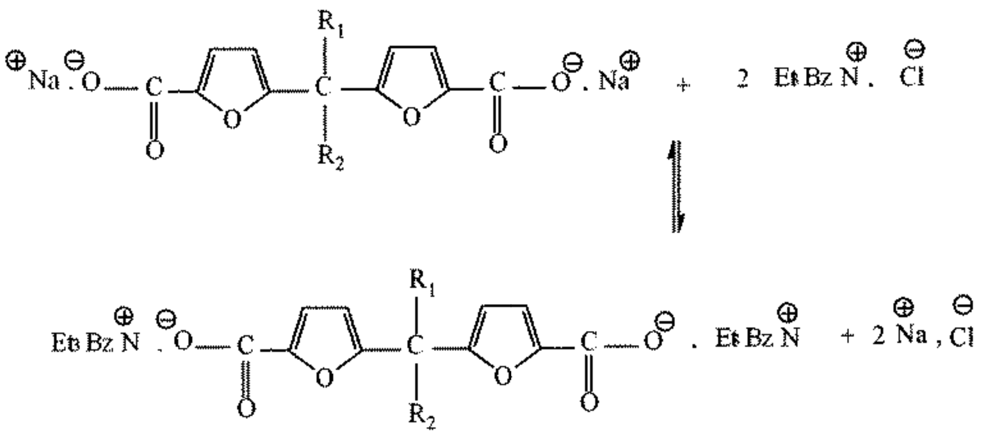


Polyester	**P₁**	**P₂**	**P₃**	**P₄**	**P₅**	**P₆**	**P₇**	**P₈**	**P₉**	**P₁₀**
R_1	CH_3	CH_3	CH_3	C_2H_5	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
R_2	CH_3	n-C_3H_7	n-C_5H_{11}	C_2H_5	C_6H_5	CH_2–C_6H_5	CH_3	H	n-C_5H_{11}	C_6H_5
R							-CH=CH-	-CH=CH-	-CH=CH-	-CH=CH-

Scheme 2: Synthesis of Furanic Polyesters **P₁₋₁₀**

Several experiments were carried out at varying temperature, reaction time, monomer concentration and molar ratio, the nature of organic solvent and the nature of the phase transfer catalyst (**PTA**). Interfacial polycondensation progress was followed in terms of polymer inherent viscosities and yields.

The effect of solvents on the two-phase polycondensation is shown in Table II. The synthesis of polyester **P₁** was successful only in polar solvents. In fact, in these solvents, we noted a progressive disappearance of solids (monomer **DC₁**) in reaction medium, resulting from its diffusion and solubilization in the liquid phase, where it can react with **DBX**. Therefore, the first step of reaction mechanism could reasonably involve a transfer of the anionic reagent (solid phase) to the organic solvent favored by a sodium - onium cation exchange (Scheme 3).



Scheme 3

Table II. Influence of the nature of organic solvent on the polycondensation of (**DC$_1$** + **DBX**)
*Viscosity measured in $CHCl_3$ at 25 °C (polymer concentration = 3 g.L^{-1}).
DC$_1$: 5 mmol **DBX**: 5 mmol TEBAC: 0.12 mmol solvent: 5mL T: 25 °C time reaction: 2hr

Polyester **P$_1$**	Solvent						
	C_6H_5-CH_3	C_6H_5-Br	$CHCl_3$	C_6H_5-NO_2	DMSO	NMP	DMA
Yield (wt.-%)	0	0	0	25	30	38	45
η_{inh}* (L.g^{-1})	-	-	-	0.012	0.015	0.017	0.022

Figure 1 illustrates the role of reaction temperature on polyester **P$_1$** synthesis. The reaction is very sensitive to temperature variations since a dramatic decrease of both η_{inh} and yield was observed when temperature was increased above the optimum value of 110 °C. This could be assigned to the thermal instability of TEBAC above 110 °C [6].

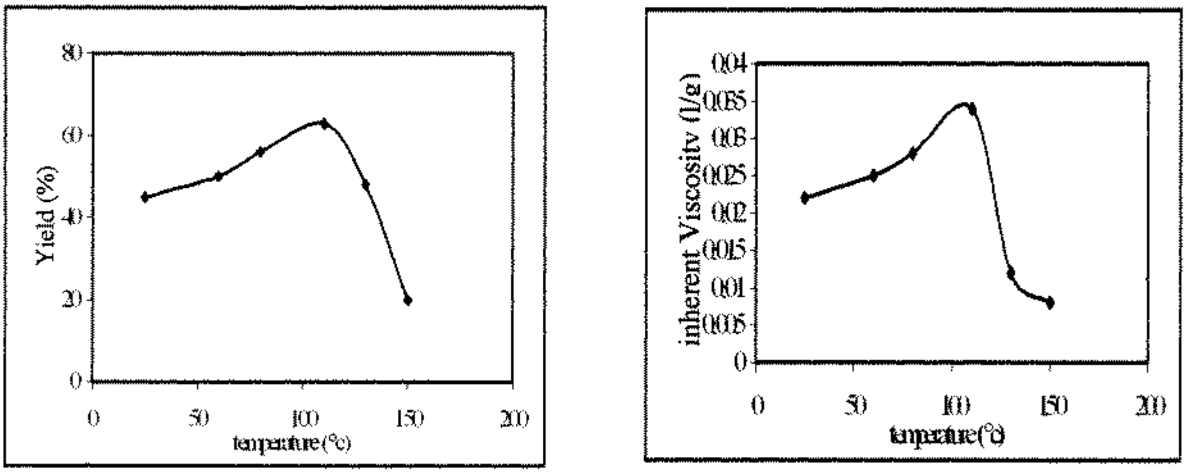


Figure 1. Influence of temperature on the polycondensation of (**DC$_1$** + **DBX**)
DC$_1$ = **DBX** = 5 mmol, TEBAC : 0.12 mmol, time reaction : 2 hr, V (DMA) = 5mL

The maximum η_{inh} and yield was reached at t = 3 h as shown in Figure 2. A longer reaction time at 110 °C resulted in a slight reduction in η_{inh} and yield.

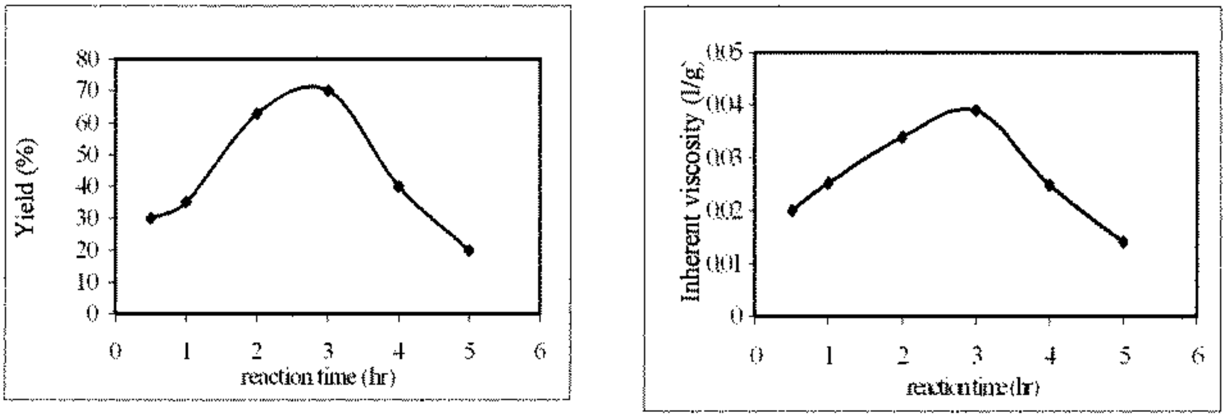


Figure 2. Influence of reaction time on the polycondensation of (**DC$_1$** + **DBX**)
DC$_1$ = **DBX** = 5 mmol, TEBAC : 0.12 mmol, T = 110°C, V (DMA) = 5mL

As can be seen in Figure 3 the use of a ca. 5% **DC$_1$** molar excess of about of over the dibromide compound **DBX** yielded the best polyester yield and η_{inh}. A similar result was obtained by Sepulchre et al. [13] on the polycondensation reaction between potassium maleate and 1,4-dihalogenobutanes.

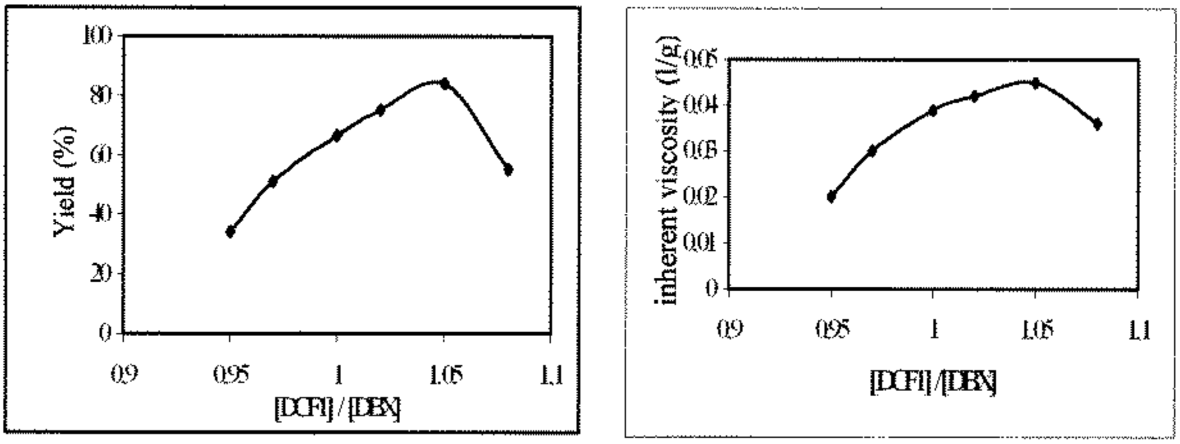


Figure 3. Influence of the bulk monomer molar ratio on the polycondensation of (**DC**$_1$ + **DBX**)
DBX = 5 mmol, TEBAC : 0.12 mmol, T = 110°C, V (DMA) = 5mL time reaction : 3 h

Figure 4 illustrates the influence of **DBX** concentration on polymer yield and η_{inh}. The best results were obtained with **DBX** concentration close to 1.25 mol.L^{-1}. A dramatic decrease of both polymer yield and inherent viscosity was observed when the reaction was carried out at high **DBX**, **DC**$_1$ and PTA concentration. In this case the amount of solvent is low and a part of carboxylate **DC**$_1$ remains as a separate solid phase during the whole course of reaction, leading to an unfavourable stoichiometric balance of reactants in the organic phase. On the other hand, at low monomer concentration, carboxylate **DC**$_1$ progressively dissolves in reaction medium. However, the resulting low monomer concentrations results in low reaction rate. The value of [**DBX**] = 1.25 mol.L^{-1} represents the best compromise between these two antagonist effects.

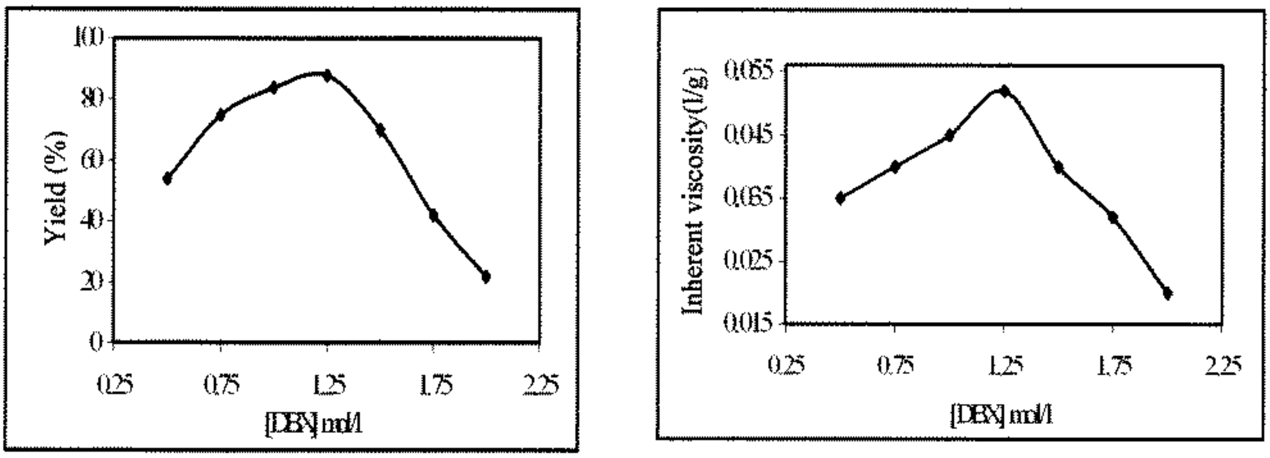


Figure 4. Influence of **DBX** concentration on the polycondensation of (**DC**$_1$ + **DBX**)
DC$_1$: 5.05 mmol **DBX** = 5 mmol TEBAC : 0.12 mmol T = 110°C solvent: DMA = 5mL time reaction : 3 h

The last variable examined in this experiments series of was the nature and the use or not use of PTA. The results are summarized in Table III. When the catalyst was not used, only a low molecular weight polyester was obtained, whereas the addition of quaternary onium salts and crown ethers increased polymer molecular weight. Crown ether DCHC was the most efficient PTA for the preparation of high molecular weight polyester, as evidenced by the high value of inherent viscosity.

The best conditions determined on the (**DC**$_1$ + **DBX**) system (**DMA**, 110°C, 3h, [**DA**$_1$]/[**DBX**] = 1.05, [**DBX**] = 1.25 mol.L^{-1}, **DCHC** as **PTA**) were used to synthesize polyesters **P**$_{2\text{-}10}$. The values of yields, η_{inh} and $\overline{M_n}$ are reported in Table IV. All polymers **P**$_{1\text{-}10}$ were obtained in good yields and exhibited molecular weight higher than polyester **P**$_1$ one synthesized in the bulk

[15] or in solution [4]. This clearly shows that the reaction in heterogeneous solid-liquid medium is a better preparation method for such polyesters. The lower $\overline{M_n}$ values obtained for **P$_3$** and **P$_9$** could be assigned to the purification problems of intermediate bis(2-furoic acid) **DA$_4$** (see experimental part).

Table III. Influence of the PTA nature on the (**DC$_1$** + **DBX**) polycondensation
*Viscosity measured in $CHCl_3$ at 25 °C (polymer concentration = 3 g.L^{-1}).
DC$_1$: 5.05 mmol DBX: 5 mmol PTA: 0.12 mmol solvent: 4mL T: 110 °C time reaction: 3h

Polyester **P$_1$**	PTA						
	None	TEBAC	TBAB	TBAS	HTAB	TOMAC	DCHC
Yield (wt.-%)	35	88	80	70	90	95	97
η_{inh}^{*} (L.g^{-1})	0.010	0.052	0.039	0.022	0.055	0.062	0.074

Table IV. Results of polyesters **P$_{1\text{-}10}$** synthesis
* Viscosity measured in $CHCl_3$ at 25 °C (polymer concentration = 3 g.L^{-1}).
** From SEC in THF (eq.polystyrene)
***Polydispersity index, from SEC.
#Polyester of similar structure obtained by bulk polycondensation.[15]
##Polyester of similar structure obtained by solution polycondensation.[4]

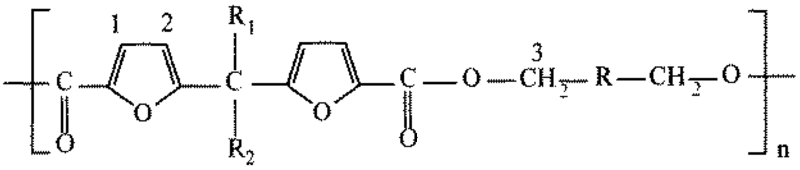
Polyester	Yield (wt.-%)	η_{inh}^{*} (L.g^{-1})	$\overline{M_n}^{**}$	Ip***
P$_1$	97	0.074	24000	2.2
P$_1^{\#}$	97	0.016	2100	3.1
P$_1^{\#\#}$	97	0.048	8400	2.5
P$_2$	74	0.045	17000	2.2
P$_3$	72	0.027	9700	2.3
P$_4$	90	0.060	22000	2.5
P$_5$	88	0.030	10800	2.0
P$_6$	85	0.042	18500	2.4
P$_7$	80	0.050	20000	1.9_5
P$_8$	85	0.032	12400	2.7
P$_9$	84	0.025	8000	2.5
P$_{10}$	90	0.029	10000	2.2

STRUCTURAL STUDY

The ^1H NMR spectra of **P$_{1\text{-}10}$** agree with the expected structures (Table V). It is should be pointed out that the butene double bonds are clearly identified, close to 6 ppm. The ^{13}C NMR spectra of **P$_1$**, **P$_5$**, **P$_7$**, **P$_8$** and **P$_{10}$** are in good agreement with their structures (Table VI).

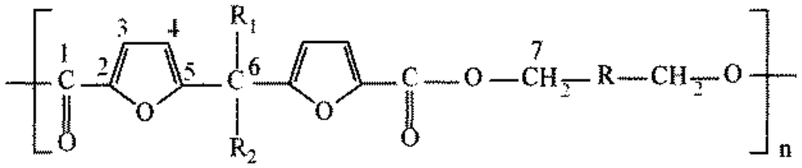
The relevant IR features are easily recognizable at 3126 cm^{-1} for the furanic =CH, around 2980 cm^{-1} for the CH_3 and CH_2 peaks, below 1720 cm^{-1} for the strong carbonyl band, at 1315 cm^{-1} and 1125 cm^{-1} for the C-O ester vibration, at 1022 cm^{-1} for the heterocycle breathing and 980, 802 and 765 cm^{-1} for the characteristic 2,5-disubstituted furanic out-of plane wagging modes.

Table V. Chemical shifts (δ, ppm) and assignments of the ^1H NMR resonances of polyesters $\mathbf{P_{1\text{-}10}}$



Polyester	NMR Solvent	δ, ppm					
		H_1	H_2	H_3	$H(R_1)$	$H(R_2)$	$H(R)$
P_1	DMSO-d_6	7.26	6.55	5.37	1.74	1.74	7.51
P_2	CF_3COOD	7.39	6.45	5.25	1.60	2.65 ; 1.10 ; 0.90	8.10
P_3	$CDCl_3$	7.10	6.11	4.74	1.68	2.11 ; 1.60 ; 1.10 ; 0.70	7.23
P_4	DMSO-d_6	7.25	6.55	5.37	2.10–0.85	2.10–0.85	7.51
P_5	$CDCl_3$	7.11	6.12	5.27	2.12	7.24 ; 7.33	7.38
P_6	$CDCl_3$	7.11	6.12	5.27	2.12	3.70 ; 7.24 ; 7.38	7.33
P_7	$CDCl_3$	7.04	6.15	4.73	1.67	1.67	5.93
P_8	$CDCl_3$	7.09	6.19	4.76	1.66	4.31	5.96
P_9	DMSO-d_6	7.10	6.12	4.88	1.43	2.00 ; 1.50 ; 1.02 ; 0.70	5.93
P_{10}	$CDCl_3$	7.10	6.11	4.74	2.11	7.06 ; 7.23	5.93

Table VI. Chemical shifts (δ, ppm) and assignments of the ^{13}C NMR resonances of polyesters



Polyester	NMR Solvent	δ, ppm									
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	$C(R_1)$	$C(R_2)$	$C(R)$
P_1	DMSO-d_6	163	157	119	107	142	37	65	25	25	128; 135
P_5	$CDCl_3$	161	158	118	110	143	47	65	24	126; 127; 128; 143	128
P_7	$CDCl_3$	163	158	118	107	143	38	63	25	25	127
P_8	$CDCl_3$	159	158	119	108	143	33	64	17	-	128
P_{10}	$CDCl_3$	161	157	118	110	143	47	63	24	126; 127 128; 143	128

Thermal analyses

All synthesized polyesters are amorphous. The DSC thermograms of the $\mathbf{P_{7\text{-}10}}$ series display glass transition temperatures between −20 and 15 °C, while T_g of the $\mathbf{P_{1\text{-}6}}$ series are much higher (25 to 90°C), as expected regarding the structure rigidity of **DBX** compared to **DBB** one. The TGA analysis of all polyesters $\mathbf{P_{1\text{-}10}}$ shows a similar behavior with an onset of degradation consistently higher than 260 °C (Table VII).

Table VII. Glass transition temperatures (T_g) and temperatures of decomposition of polyesters $\mathbf{P_{1\text{-}10}}$.

T (°C)	Polyester									
	P_1	**P_2**	**P_3**	**P_4**	**P_5**	**P_6**	**P_7**	**P_8**	**P_9**	**P_{10}**
T_g	60	58	25	60	90	88	-9	-12	-20	13
T_d	298	287	294	305	357	398	283	272	268	300

CONCLUSION

The synthesis of unsaturated polyesters based on various alkylidene-bis(2-furoate) salts and 1,4-dibromobut-2-ene was successfully carried out in the conditions of solid-liquid phase transfer polycondensation. The method appears to be much more efficient than the acid dichloride/diol solution polycondensation or the diacid/diol melt polycondensation for the preparation of such polyesters.

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