Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Characterization of Thermotropic Polyesters-Block-Polyethers

Pascal Thuillier [a] , Manine Tessier [a] & Ernest Maréchal [a]

[a] Laboratoire de Synthèse Macromoléculaire - Boite 184 - Université, P. et M. Curie 4, Place Jussieu -, 75252, Paris Cedex 05, France

Version of record first published: 24 Sep 2006.

To cite this article: Pascal Thuillier , Manine Tessier & Ernest Maréchal (1994): Synthesis and Characterization of Thermotropic Polyesters-Block-Polyethers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 254:1, 1-16

To link to this article: http://dx.doi.org/10.1080/10587259408036066

Mol. Cryst. Liq. Cryst. 1994, Vol. 254, pp. 1–16
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC POLYESTERS-BLOCK-POLYETHERS

Pascal Thuillier, Martine Tessier, Ernest Maréchal

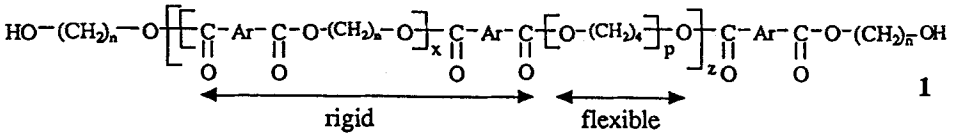
Laboratoire de Synthèse Macromoléculaire - Boite 184 - Université P. et M. Curie
4, Place Jussieu - 75252 Paris Cedex 05 - France

(Received: February 7, 1994)

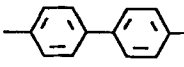
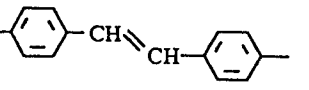
Abstract : Polyesters-block-polyethers whose rigid blocks are thermotropic polyarylates are prepared and studied. Rigid polyarylates are poly(1,5-pentanediyl-4,4'-biphenyl-dicarboxylate) or poly(1,5-pentanediyl-4,4'-trans-stilbenedicarboxylate) ; the corresponding homopolymers are studied and they contain macrocycles which are characterized. Flexible blocks are oligooxytetramethylenes ($\overline{M_n}$ =620 or 2030). The block-copolymers are characterized by ^1H and ^{13}C NMR spectroscopies ; the use of 500 MHz ^1H NMR permits their complete structural analysis showing that they contain a cyclic oligomer. SEC, polarizing microscopy and X-ray studies show that their mesophase is smectic. Their viscoelastic properties are compared to those of some aromatic polyesters-block-polyethers.

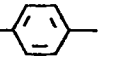
INTRODUCTION

Most thermoplastic elastomers are block copolymers containing rigid blocks such as polyamides[1,2] or polysulfones[3-5] and flexible blocks such as polyenes[3], polyisobutylenes[2], polysiloxanes[4-6] or polyethers[1]. More recently block copolymers with thermotropic rigid blocks were described[6]. In this article we describe several poly(alkylene arylates)-block-polyethers which have the following structure :



1

Ar is  (B) ,  (S)

or  (T) , n = 5 or 6

Some poly(alkylene arylates), which are models of the rigid blocks, were already described[7-9, 13] ; additional information is given.

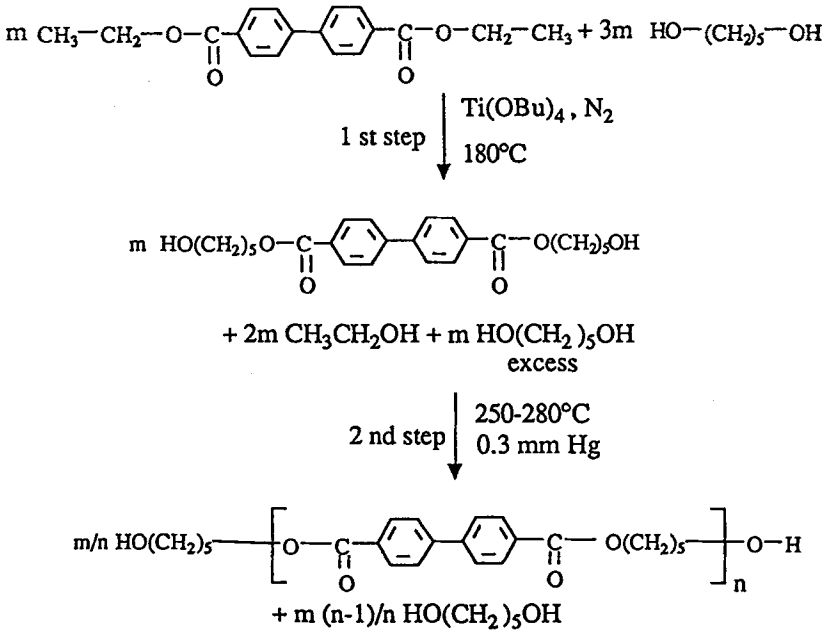
POLY(ALKYLENE ARYLATES)

Several articles relative to poly(α,ω-alkylenediyl-4,4'-biphenyldicarboxylate), particularly X-ray diffractometry, have been published[7-9] ; however these results and ours differ to some extent : we find that the structure depends on the molar mass of the polyesters. Morever, a thorough analysis of these polymers shows that they contain macrocyclic oligoesters ; we could identify them through NMR and mass spectrometry.

Poly (1,5-Pentanediyl-4,4'-Biphenyldicarboxylate) (B5)

Synthesis :

B5 is prepared by reaction of diethyl-4,4'-biphenyldicarboxylate with 1,5-pentanediol :



NMR

^{1}H and ^{13}C NMR spectra are reported in Figure1. Starred peaks at 7.54 and 8.04 ppm (^{1}H) and 22.3, 27.9 and 65.7 ppm (^{13}C) belong to macrocyclic compounds which will be studied further down. Methylene group in α of hydroxy esterified by trifluoroacetic acid gives a peak at 68 ppm (solid triangle).

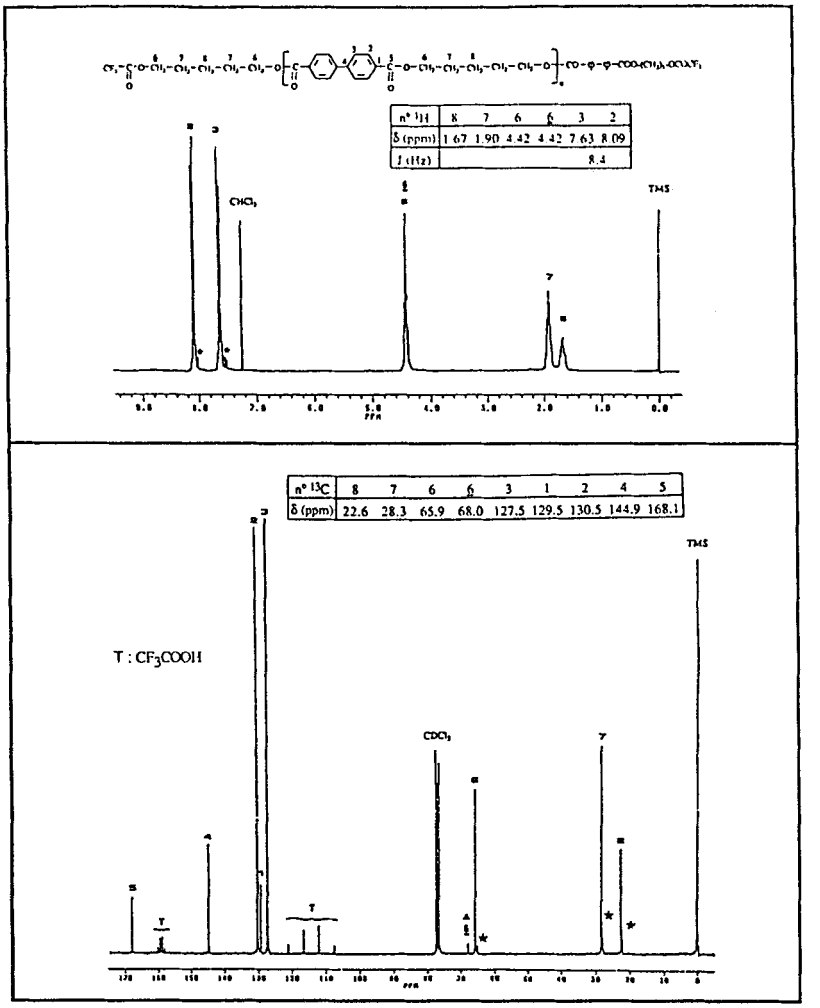


FIGURE 1 - ^{1}H and ^{13}C NMR spectra of B5 in $CDCl_3/CF_3COOH$

DSC

On first heating (20°C min^{-1}) thermogram of a sample whose $\overline{M_n}$ =6000 shows two endotherms at 173 (ΔH=12.6 $J.g^{-1}$) and 210°C (ΔH=17.1 $J.g^{-1}$); they are relative to melting and to clearing and their position dœs not change on second heating (10°C min^{-1}) after cooling. Cooling (10°C min^{-1}) shows two exotherms at 93 (ΔH=7.7 J.g-1) and 195°C (ΔH=15.9 $J.g^{-1}$).

Optical polarizing microscopy

Observation of the samples on cooling from isotropic state, and after maintained at 192 and 175°C during three days, shows focal-conic textures which are characteristic of smectic organization (A or C)

X-Ray diffractometry

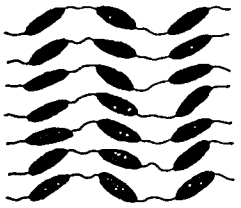
Diffractograms were registered from powder or from fibers prepared from the melt.

The theoretical length (d_{th}) of the mesogenic unit in its fully streched-out conformation ranges between 17.3 and 18.6.Å.

In all cases they lead to a smectic C mesophase. However the position of the layers with respect to the the fiber axis depends on $\overline{M_n}$ as shown below : .

- *Sample whose $\overline{M_n}$ is 2800 (η = 0.5 dlg^{-1} ; phenol (60) / $C_2H_2Cl_4$ (40) ; 25°C).*

The layers are parallel to the fiber axis.

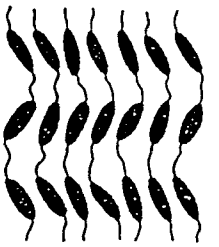


Lines	Distances (Å)	Tilt angle Θ
1st order	15.44	30.7
2nd order	7.71	
Halo	4.29	

FIGURE 2 - B5 ($\overline{M_n}$ = 2800). Smetic C ; relative position of the layers.

- *Sample whose $\overline{M_n}$ is 6000 (η = 0.90 dlg^{-1} ; phenol (60) / $C_2H_2Cl_4$ (40) ; 25°C).*

The layers are perpendicular to the fiber axis.



Lines	Distances (Å)	Tilt angle Θ
1st order	15.46	30.7
2nd order	7.74	
Halo	4.37	

FIGURE 3 - B5 ($\overline{M_n}$ = 6000) Smetic C ; relative position of the layers (ref.8 and 9).

The dependence of the structure on molecular weight was already observed by Krigbaum [10,11] who provided an analysis of the phenomenon.

Dependence of B5 characteristics on reaction parameters.

The results are reported in Table I. p, $\overline{DP_n}$, $\overline{M_n}$, T_m and T_i are relative to reaction extent, number average degree of polymerization, number average molar mass, melting temperature and clearing temperature. T°C is the reaction temperature.

There is a good agreement between $\overline{M_n}$ values obtained from NMR and SEC. On the other hand, $\overline{M_n}$ values determined from effluent volume are below those derived from the two other methods ; some part of the effluents remains in the reactor which undervalues their actual volume. Sample 6 was prepared in the same run as samples 1 to 5 but the temperature was raised from 250 to 280°C when p is 0.84. ; both SEC and ^1H

NMR show that degradation takes place at this temperature ; this phenomenon was observed for other smetic systems [12].

Sample 7 was obtained at 250°C but the reaction time is 12 h instead of 6 h for sample 5. In fact, it is difficult to obtain high molar mass as the viscosity of the reaction mixture is very high and increasing temperature above 250°C leads to degradation.

TABLE I -Characteristics of B5 - (a) $\overline{M_n}$ from effluent volume; (b) $\overline{M_n}$ determined by SEC (as standard polyoxytetramethylene ; 1,3,5-trichlobenzene at 140°C) ; (c) $\overline{M_n}$ from ^1H NMR spectra.

Sample	T°C	p	$\overline{DP_n}$ (a)	$\overline{M_n}$ (a)	$\overline{M_n}$; I(b)	$\overline{M_n}$ (c)	T_m(°C)	T_i (°C)
1	250	0.10	1.12	450	730 ; 1,8		118	
2	"	0.45	2	670	940 ; 1.9		139	
3	"	0.64	2.8	970	2010 ; 2.2		166	
4	"	0.73	2.7	1260	2100 ; 30	1995	172	203
5	"	0.84	6.4	2100	2870 ; 3.2	2740	173	204
6	280	0.87	7.9	2550	2340 ; 3.5		170	192
7	250					6000	173	210

However, it was possible to increase $\overline{M_n}$ by using solid state polycondensation : sample 5 was ground then maintained at 110°C (63°C below the initial melting temperature), under 0.2 torr, during 12 h ; 1,5-pentanediol was evolved and $\overline{M_n}$ reaches 9000. Although the thermogram has the trend before and after the treatment at 110°C, Ti increased from 204 to 211°C.

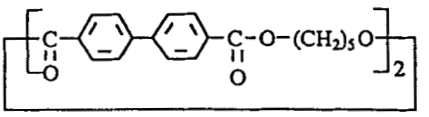
All SEC chromatograms show the presence of a peak corresponding to a low compound ($\overline{M_n} \approx 400$) ; it will be analyzed in next part.

Cyclic Oligoesters.

Several observations (NMR, SEC) show that the samples contain low molar weight compounds which were extracted with boiling propanone from the finely powdered polyester.

^{13}C and ^1H NMR spectra of the extract from sample 6 (Figure 4) show two characteristic peaks at 7.6 and 8.05 ppm which were already observed in the non extracted polymer (Figure 1) ; on the other hand their intensity is drastically decreased in the extracted polymer.

The extract contains mainly a macrocyclic compound and several degradation-products which give peaks at 2.18, 5.05, 5.86 ppm (^1H NMR) and 115.4 ppm (^{13}C NMR) and corresponding to allylic end-groups. Mass spectrum of the extract shows a peak at 620 $g.mol^{-1}$ which corresponds to the macrocycle below :



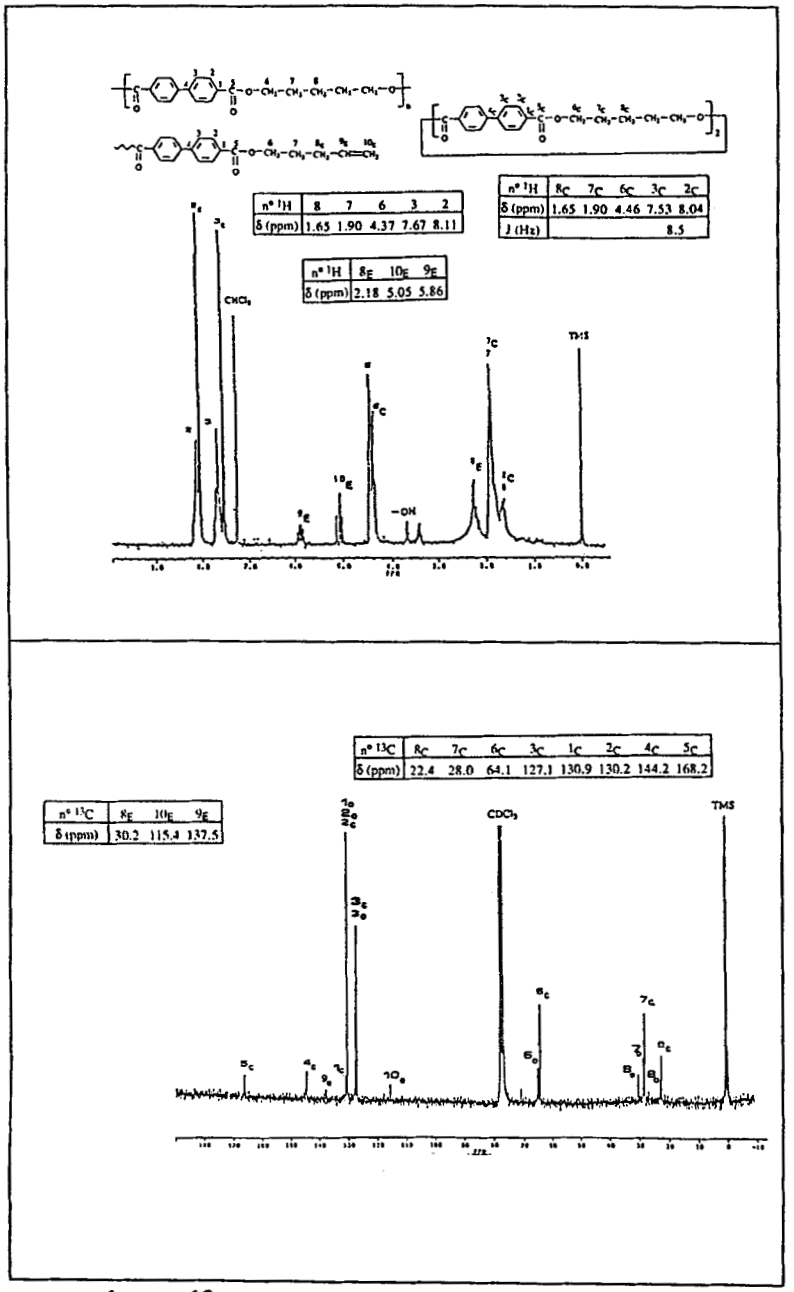


FIGURE 4 - ^{1}H and ^{13}C NMR spectra of fraction of B5 extracted by propanone ($CDCl_3$).

Such cyclic compounds are observed in various polyesters, particularly poly(alkylene terephtalates).

In order to obtain degradation-products free macrocycle we prepared sample 7 at 250°C (degradation takes place only above this temperature). The extract accounts for weight 0.6 % of the polymer ; its ^1H NMR shows no longer peaks of degradation products .

Positive chemical ionisation mass spectrometry gives peaks at 621 and 638 g. mol^{-1} which corresponds at MH^+ and $M(NH_4)^+$. Negative chemical ionisation gives a peak at 620 $(M)^{\cdot-}$.

DSC and polarizing microscopy examination of the macrocycle show that it dœs not exhibit anisotropy. However the observation is perturbed by degradation on heating ; it begins at around 300°C.

Poly(1,6-Hexanediyl-4,4'-Biphenyldicarboxylate) (B6).

The characteristics of poly (1,6-hexanediyl-4,4'-biphenyldicarboxylate) are relative to a sample whose inherent viscosity is 1.1 dlg^{-1} (solvent as B5; 25°C). It has been prepared as with B5.

NMR.

^1H and ^{13}C NMR spectra show the signals which could be expected from the structure proposed ; moreover peaks relative to a cyclic oligoester are observed ; however we did not separate the macrocyclic compound from the linear polymer. ^1H NMR leads to $\overline{M_n}$ value : 5690 (n = 17.2).

DSC.

Two transitions are observed on first heating (20°C min^{-1}) : 212°C (melting) and 239°C (clearing). These transitions appear at 153.5 (ΔH=21.6 $J.g^{-1}$) and 221°C (ΔH=28.2 $J.g^{-1}$) on cooling (10°C min^{-1}). Three endotherms 212, 219 and 237°C are observed on second heating (10°C min^{-1}) ; such a pattern is characteristic of polymorphism.

Optical Polarizing Microscopy

Samples are maintained at 239°C, during 24 h from cooling. They show batonnets and focal-conic textures which are characteristic of smectic lamellar mesophases (A or C).

X-Ray Diffractometry.

The pattern leads to the same conclusion as Watanabe[9] : the mesophase is smectic A ; the layers are perpendicular to the fiber axis as in the case of B5 with $\overline{M_n}$ = 6000 ; however we did not prepare B6 samples of low molar mass.

Poly(1,5-Pentanediyl-4,4'-tr.Stilbenedicarboxylate) (S5)[13].

Synthesis.

S5 is obtained by polytransesterification of diethyl-4,4'-tr.stilbenedicarboxylate with 1,5-pentanediol at 250°C.

NMR.

The low solubility of S5 does not permit to register a ^{13}C NMR spectrum. ^{1}H NMR spectrum (Figure 5) shows starred peaks (7.2, 7.44 and 7.90 ppm) which correspond to a macrocyclic structure and gives $\overline{M_n}$ = 7200.

Mass spectrometry

Mass spectrum of the extract (boiling propanone) shows a peak at 672 g. mol^{-1} which corresponds exactly to a macrocycle with two 1,5-pentamethylene-4,4'-stilbenedicarboxylate units.

DSC.

On first heating (20°C min^{-1}), S5 thermogram shows endotherms relative to melting at 183°C (5 $J.g^{-1}$) and to clearing at 265°C (ΔH = 11.25 J.g-1). On cooling (10°C min-^{1}) two exotherms are respectively relative to the transition from isotropic phase to mesophase at 240°C (ΔH = 10 $J.g^{-1}$) and to crystallisation at 110°C (ΔH = 18 $J.g^{-1}$). On second heating (10°C min^{-1}) the endotherms relative to melting and to clearing are observed at 187.5°C and 262°C respectively.

Optical polarizing microscopy

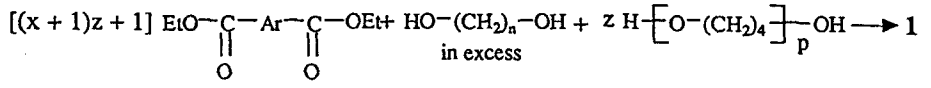
Observation of the samples on cooling from isotropic state, after maintained at 227°C during several hours, shows batonnets and focal-conic textures which are characteristic of A or C smetic organization.

X-Ray Diffractometry

We used a pattern obtained from a fiber ; it is relative to a C smetic structure but this shows two perpendicular layers whose characteristics are in table II.

BLOCK-COPOLYMERS

The copolymers were prepared according to the following reaction :



and prepared and characterized as B5.

Two α,ω-dihydroxypolyoxytetramethylene samples were used : PE620 ($\overline{M_n}$ = 620) and PE2030 ($\overline{M_n}$ = 2030).

Copolymers are labelled BnE and tSnE(W_r) ; followed by polyether $\overline{M_n}$: 620 or 2030 ; n = 5 or 6. $\overline{M_r}$ and $\overline{M_f}$ are the average molar mass of rigid (R) and flexible (F) blocks respectively

$$\overline{W_r} = \overline{M_r} / (\overline{M_r} + \overline{M_f}) ; \overline{W_f} = \overline{M_f} / (\overline{M_r} + \overline{M_f})$$

In all cases we carried out a preliminary study of the polycondensation of α,ω-dihydroxyoligoether with diethyl α,ω-aryldicarboxylate and the characterization of the resulting homopolymers.

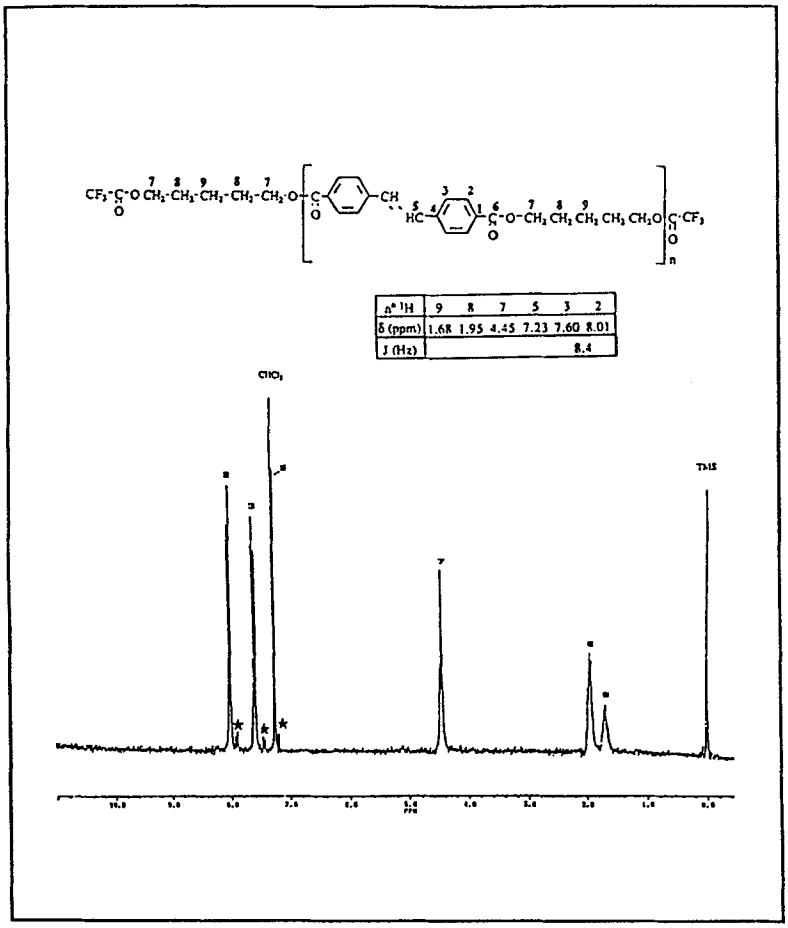


FIGURE 5 - ^1H NMR spectrum of S5 ($CDCl_3/CF_3COOH$)

TABLE II - Characteristic parameters of the X-ray pattern relative to S5. (19.75 Å < d_{th} < 21.2Å)

Lines	Distances (Å)	Tilt angle Θ
1 st order	17.66	30.4
2nd order	8,70	
halo	4.31	
1 st order	17.25	32.6
2nd order	8,52	
halo	4.37	

Poly (α,ω-polyoxytetramethylenediyl-4,4'-biphenyldicarboxylate (BE620).

Effluents contain very small amounts of 1-butanol and THF. Experimental value of

$\overline{M_f}$ (^{1}H NMR) is 640, showing that no significant degradation takes place. Both end-groups are ethoxycarbonyl (1.42 ppm), there is no signal of hydroxy end groups; this is due to the fact that low-molecular-weight fractions of the polyether are distilled off leading to an excess of ethoxycarbonyl functions. Integration of the spectrum and use of the peak at 1.42 ppm allow the determination of the molar mass of the polymer : 7000 ; SEC (polyoxytetramethylene standardization; THF as solvent) : 7450. DSC shows that BE620 is amorphous (T_g = -49 °C) contrarily to the precursor oligoether (PE620) which is crystalline (T_m=17°C).

Block Copolymers B5E(W_r)620

^{1}H NMR spectroscopy shows that no degradation takes place and allows the determination of $\overline{M_r}$; the characteristics of B5E(W_r)620 are reported in Table III.

DSC results are reported in Figure 7. Thermograms obtained on heating show only one melting endotherm with contrast to B5 which exhibits several endotherms characteristic of polymorphism. On the other hand copolymers B5E(W_r)620 exhibit several transitions on cooling as long as F content is below 25% ; they are monotropic. Comparison of the characteristics of the copolymers and B5 shows that the segregation is only partial.

TABLE III -Structural characteristics of copolymers B5E(W_r)620- $\overline{W_r}$, $\overline{x}$: see text.

	$\overline{W_r}$ %		$\overline{x}$		$\overline{M_r}$	
Copolymer	theor.	exp.[a]	theor.	exp.[a]	theor.	exp.[a]
B5E(92)620	91.5	91.7	20.7	20.9	6630	6700
B5E(84 620	84.1	84.4	9.9	9.8	3300	3250
B5E(78)620	77.6	78.1	6.3	6.3	2150	2150
B5E(55)620	54.6	55	1.7	1.7	740	735

[a] by ^{1}H NMR

Poly(α,ω-polyoxytetramethylenediyl-4,4'-biphenyldicarboxylate) (BE2030) :

$\overline{M_f}$ is 1840 instead of 2030, showing that a slight degradation takes place : heating PE2030 in the presence of $Ti(OBu)_4$ gives of a small amount of butyrolactone. BE2030 molar mass (SEC) is 26000 (I=2.2) ; no accurate value could be obtained from ^{1}H NMR as the end group signal is very weak. Contrarily to PE620, PE2030 is able to crystallise when engaged in homopolyester BE2030 : T_m=24 °C ; ΔH=50 J.g^{-1}; T_g = -70 °C.

Block Copolymers B5E(W_r)2030

Their characteristics are reported in Table IV and Figure 7. Copolymers B5(W_r)2030 exhibit anisotropy on heating when W_r>65%; their thermal characteristics are close to those of B5. On the other hand thermograms registered on cooling show two transitions :

isotropic liquid → mesophase and mesophase → crystal when W_r>30% ; the anisotropy temperature domain increases with increasing W_r. T_g of flexible blocks (~ -75°C) depends little on W_r showing that the segregation is high.

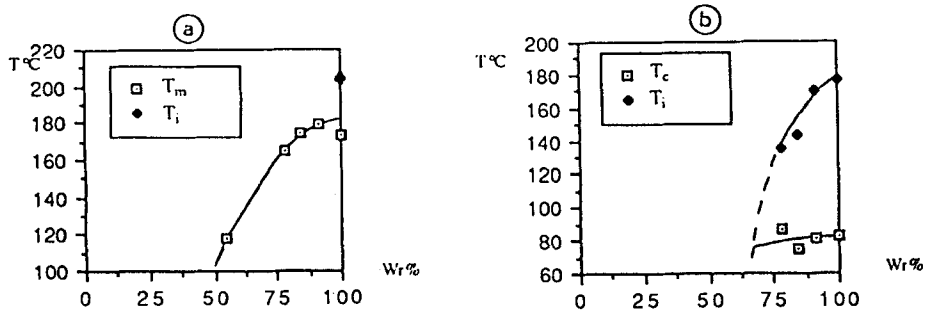


FIGURE 6 : Variation of rigid phase transitions T_m, T_i, and T_c of copolymers B5E(W_r) 620 with respect W_r % (DSC).- a) heating (10°C/min) - b) cooling (10°C/min) ; T_m : melting point - T_i : clearing point - T_c : crystallization point

Polarizing microscopy and X-ray diffraction show that the mesophase of B5E(76)2030 is smectic C (tilt angle ~ 30°) ; the layers are perpendicular to the fiber axis as in the case of B5 ($\overline{M_n}$ = 6000).

TABLE IV-Structural characteristics of copolymers B5E(W_r)2030-Symbols as in table III.

	$\overline{W_r}$ %		$\overline{x}$		$\overline{M_r}$	
Copolymer	theor.	exp.[a]	theor.	exp.[a]	theor.	exp.[a]
B5E(76)2030	76.3	76.1	20.9	20.8	6500	6670
B5E(65)2030	65.1	63	11.5	10.5	3800	3450
B5E(60)2030	59.6	58.1	9.0	8.4	3000	2810
B5E(50)2030	49.3	45.6	5.7	4.8	1970	1700
B5E(42)2030	41.7	39.6	4.0	6.3	1500	1330
B5E(28)2030	27.9	25.6	1.9	1.6	800	700

[a] by ^{1}H NMR

Block Copolymers B6E(W_r)2030

In the same way we prepared copolymers derived from 1,6-hexanediol and PE2030 ; they are anisotropic when W_r is above 55%; the mesophase is smectic A, a high phase segregation is observed.

Poly (α,ω-polyoxytetramethylene diyl-4,4'-trans-stilbenedicarboxylate) (SE2030)

Homopolyester SE2030 results from the polycondensation of the PE2030 with diethyl 4,4'-trans-stilbenedicarboxylate; experimental determination of $\overline{M_f}$ (^{1}H NMR) showed that little degradation took place (1960 instead of 2030). The molar mass of the copolymer (SEC) is 14000; I_p=4.6; the value obtained by ^{1}H NMR is 9900.

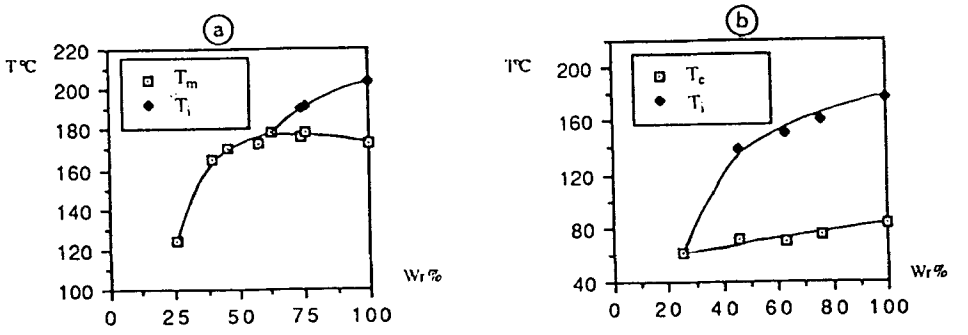


FIGURE 7 : Variation of rigid phase transitions T_m, T_i and T_c of copolymers B5E(W_r)2030 with respect W_r % (DSC) - a) heating (10°C/min) - b) cooling (40°C/min) (for symbols see Figure 6)

Block copolymers SE5(W_r)2030

^{1}H NMR determinations (Table V) show that the block length is below theory particularly when the rigid monomers content is high ; this results from an incomplete polycondensation due to the high viscosity of the reaction medium.

TABLE V-Structural characteristics of copolymers SE5(W_r)2030-Symbols as in table II

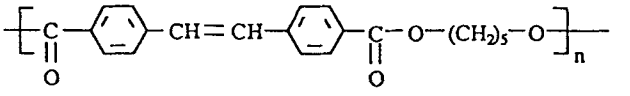
	$\overline{W_r}$ %		$\overline{x}$		$\overline{M_r}$	
Copolymer	theor.	exp.[a]	theor.	exp.[a]	theor.	exp.[a]
S5E(76)2030	76.3	73.2	18.8	15.8	6500	5540
S5E(66)2030	66.3	57.4	11.2	7.4	4000	2730
S5E(60)2030	59.3	57.1	8.1	7.3	3000	2700
S5E(56 2030	56.3	53.6	7.1	6.3	2600	2340
S5E(50)2030	50	52.1	5.3	5.9	2000	2210
S5E(41)2030	40.6	31.7	3.4	2.1	1400	940
S5E(35)2030	35	29.5	2.6	1.8	1100	850
S5E(30)2030	29.5	27.5	1.8	1.6	850	770
S5E(28)2030	28	-	1.7	-	800	-
S5E(24)2030	24	19.1	1.2	0.7	640	480

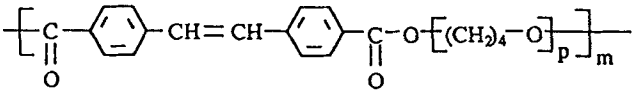
[a] by ^{1}H NMR

The presence of double bonds in the chain permits a thorough analysis of the polymer structure using 500 MHz ^{1}H NMR spectroscopy. The aromatic and ethylenic regions (7 to 8.2 ppm) of spectra of polymers with W_r=100, 66, 50, 30 and 10% are reported in Figures 8 and 9. A progressive shift of the signals toward low fields is observed when rigid blocks content decreases; it is accompanied by a significant splitting of the peaks which is maximal for the intermediate composition (W_r=30%). All these spectra, with the exception of those of SE2030, show a small peak at 0.05 ppm before the double bond

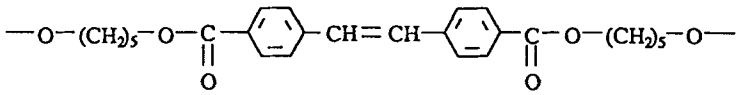
singlet and another one at 0.1 ppm before each aromatic proton doublet. These small peaks are due to small amounts of cyclic molecules in polymers. These observations are discussed below.

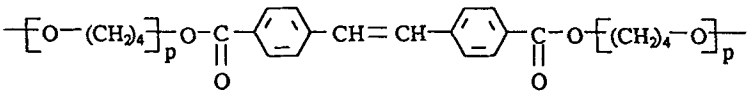
Any chain contains N_A blocks A and N_B blocks B :

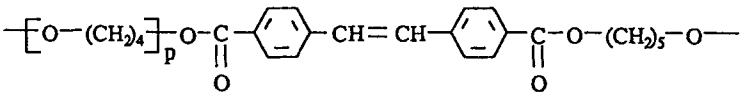


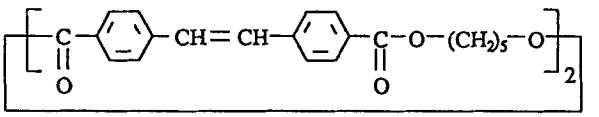


which can be present in four arrangements :









$N_A/N_B = (I+III/2+IV)/(II+III/2)$

Evolution of the spectra (Figure 8) led to the following assignments : peaks 5, 6, 7 to I; peak 2 to II; peaks 3 and 4 to III; peak 8 to IV. Integration gave the following distribution (%): I 38.4, II 17.10, III 41.05 and IV 3.45 leading to N_A/N_B=1.7 (theory = 1.8). Assuming a statistical distribution of polyether and pentanediyl units, the theoretical contents of I+IV, II and III are respectively 41.35, 12.75 and 45.9 close to experimental values : 42.85, 17.10 and 41.05, thus showing the possibility of determining the average number of successive S5 units in each sample.

DSC results are reported in Figure 10. Copolymers with W_f above 45% are anisotropic; the X-ray diffractogram of S5(76)2030 shows that it is smectic C (tilt angle : 31.4 °) between 180 and 262°C; all layers are perpendicular to the fibre axis whilst in S5 they are either parallel or perpendicular to the fiber direction. Segregation of rigid and flexible blocks was observed as long as W_f was below 40%.

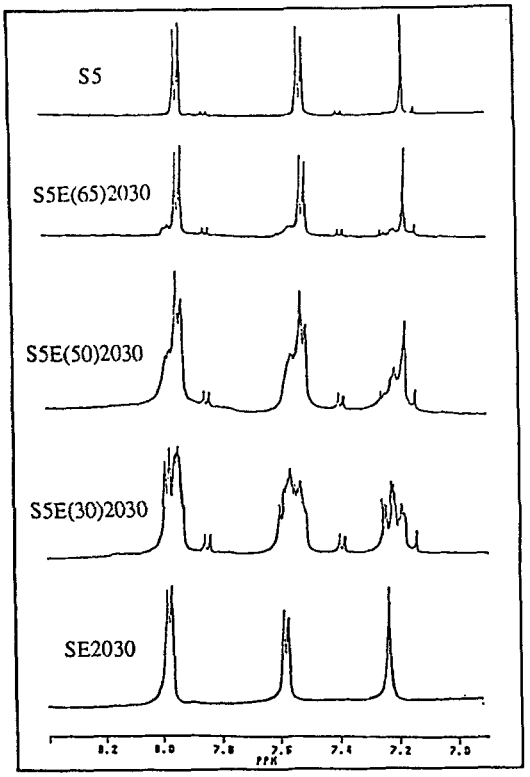


FIGURE 8 : ^1H NMR spectra (500 MHz) of S5, S5E(66)2030, SE5(50)2030, SE5(30)2030 and SE2030

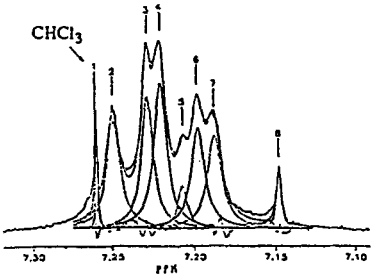


FIGURE 9 : Extending and deconvolution of ^1H NMR spectrum area between 7.1 and 7.3 ppm of copolymer S5E(30)2030

VISCOELASTIC PROPERTIES OF COPOLYMERS BnE(W_r)2030 AND S5E(50)2030

The determination of the elastic modulus E' of copolymers BnE(W_r)2030 at different temperatures showed that their rigidity increases with W_r regardless the temperature. Several E' drops were observed : around -70 °C (flexible phase T_g), between 10 and 20 °C (flexible phase melting) and between 30 and 40 °C (rigid phase T_g). The value of tg δ is maximal at T_g(F ; tg δ) and its intensity decreases with increasing W_r. In all cases tg δ maximum is around -60 °C whatever the copolymer composition is; this behaviour differs from that of Hytrel® whose tg δ maximum increases with rigid block content showing that substituting 4,4'-biphenyldicarboxylate for terephthalate units increases the phase segregation and leads to materials with smectic rigid phase. Table VI compares the variation of rigid phase crystallinity degree χ , at 25°C , and the modulus drop between -100 and 60 °C for various B5E(W_r)2030 copolymers as well as for S5E(50)2030 and B6E(50)2030 copolymers. The characteristics of B6E(50)2030 are above those of the other two copolymers with W_r = 50%. The modulus drop increases with decreasing χ.

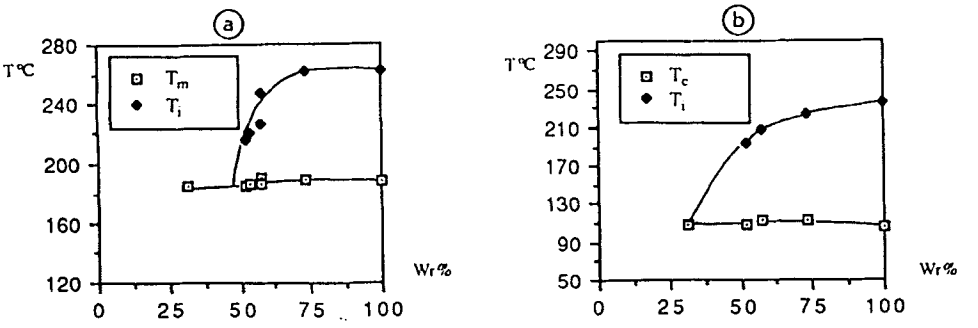


FIGURE 10 : Variation of rigid phase transitions T_m, T_i and T_c of copolymers S5E(Wr)2030 with respect Wr % (DSC) - a) heating (10°C/min) - b) cooling (10°C/min)- Symbols see Fig.6)

TABLE VI : Dependence of the elastic modulus drop ΔlogE'=logE'(-100°C) - logE'(+60°C) on the crystallinity degree χ for various block copolymers

Copolymer	χ (%)	ΔlogE'
B5E(76)2030	25	1.26
B5E(60)2030	-	1.60
B5E(50)2030	10	2.30
B6E(50)2030	12	1.60
S5E(50)2030	0	2.40

TABLE VII-Thermal and viscoelastic characteristics of block copolymers prepared from oligo(oxytetramethylene) 2030 and pentanediol with T, B and S diesters (see text). T_g(F ; E"), T_g(R ; E") and T_g(F ; tg δ) are the glass transition temperatures corresponding to the maximum of E" and tg δ, respectively. R and S as before.

Copolymer	W_r (exp)	T_g(R;E")	T_g(R;tg δ)	T_m (f)	T_g (r;E")	T_m (r)	χ	ΔlogE'
		°C	°C	°C	°C	°C	%	
T5E(66)2030	65.2	-	-5	-	-	124	-	1.5
B5E(66)2030	63	-65	-50	10	-	178	-	1.6
5ES(66)2030	57.4	-63	-53	-	-	187	-	1.7
T5E(50)2030	47.3	-68	-60	-	-30	124	11	1.5
B5E50)2030	45.6	-70	-55	15	40	170	10	2.3
S5E50)2030	52.1	-67	-53	10	50	185	0	2.4

The characteristics of block copolyesters prepared by polycondensation of PE2030 and 1,5-pentanediol with diethylterephthalate (T) or 4,4'-biphenyldicarboxylate (B) or 4,4'-tr.stibenedicarboxylate (S) are reported in Table VII.

T copolymers have thermomechanical characteristics above those of B and S copolymers although their melting points are 35 to 60 °C below those of the latter two. The values for B copolymers could be increased by increasing polymerization degree.

REFERENCES

1- G. Deleens, P. Foy, E. Maréchal, Eur. Polym. J. **13**, 337, 343, 353 (1977)

2- M. Tessier, E. Maréchal, J. Polym. Chem., Polym. Chem. Ed. **27**, 539 (1989)

3- A. Pourdjavadi, P.J. Madec, E. Maréchal, Eur. Polym. J. **20**, 305, 311 (1984)

4- D. Gagnebien, P.J. Madec, E. Maréchal, Eur. Polym. J. **21**, 273, 289, 301 (1985)

5- G. Torrès, P.J. Madec, E. Maréchal, Makromol. Chem. **190**, 203, 2789 (1989)

6- P.J. Madec, R. Pérès, E. Maréchal, Makromol. Chem., Makromol. Symp. **47**, 357 (1991)

7- W.R. Krigbaum, J. Asrar, PH. Toriumi, J. Preston, J. Pol. Sci., Polym. Lett. Ed. **20**,109 (1982).

8- J. Watanabe, M. Hayashi, Macromolecules, **21**, 278, (1988).

9- J. Watanabe, M. Hayashi, Macromolecules, **22**, 4083, (1989).

10- D. Acierno, F.P. La Mantia, G. Polizzoti, A. Ciferri, W.R. Krigbaum and R. Kotek, J. Pol. Sci., Polym., **21**, 2027 (1983).

11- W.R. Krigbaum and J. Watanabe, Polymer, **24**, 1299 (1983).

12- S.G. James, P. Navard, C. Noël, Rheol. Acta. **29**, 366 (1990).

13- W.J. Jackson Jr., J.C. Morris, J. Appl. Polym. Sci. Appl. Polym. Symp., **41**, 307 (1985).