



Synthesis and characterization of a new family of photoactive liquid crystalline polyethers based on α -methylstilbene

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Key Words:	liquid crystalline polyesters, α -methylstilbene, E-Z photoisomerization, photo-active membranes

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7 **Synthesis and characterization of a new family of photoactive liquid crystalline polyethers**
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9 **based on α -methylstilbene**

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ABSTRACT

A liquid crystal polyester and two liquid crystal co-polyesters containing α -methylstilbene moiety and aliphatic or aromatic spacers in the backbone were synthesized in good yields, with the aim of using them for photosensitive microcapsules preparation. The synthesized polymers were fully characterized with respect to thermal stability, type of mesophase, molecular weight, and *E-Z* photoisomerization. Combination of monomers with different structures allowed us to adjust polymer characteristics like crystallinity degree and glass transition temperature, as verified by XRD, POM and DSC measurements. Quantitative ^1H NMR and UV-Vis experiments were performed in order to investigate *E-Z* photoisomerization after photoirradiation at 364 nm. Finally, a membrane based on one of these polymers was prepared and it was found that its wettability increased on photo-irradiation

Keywords: liquid crystalline polyesters; α -methylstilbene; *E-Z* photoisomerization; photo-active membranes.

1. INTRODUCTION

Considerable attention has been recently paid to the possibility of controlling mass transfer through a membrane by stimuli such as pH, ion concentration or temperature. Systems responsive to such stimuli have been proposed as triggered delivery systems, whose applications lie in several fields such as drug delivery, biosensing, biomaterials, catalysis, etc.¹. Photo-irradiation is of especially great interest since it is a remote stimulus which can be imparted in a highly selective way without additional structural chemical changes of the system. Polymer conjugates with azobenzene^{2, 3}, spirobenzopyran^{4, 5}, and diarylethenes^{6, 7} are among the most investigated photo-functional materials. Reversible changes of polymer polarity or conformation by photo-irradiation are caused by photo-isomerization of a photo-chromic unit within the macromolecule.

In a previous paper⁸, we synthesized a new lightly crosslinked, liquid crystalline polyamide, whose state of order could be changed upon the application of external stimuli such as temperature and light, and we subsequently prepared microcapsules, based on this polymer as a shell, by interfacial polymerization. The prepared polyamide underwent E-Z photoisomerization as a consequence of irradiation with UV light at 364 nm. Release experiments performed in water at 20°C on polyamide microcapsules containing β -carotene showed that release could be triggered by photo-isomerization: in the absence of irradiation, release reached a plateau value of about 2.5 % after a few minutes, while, when microcapsules were submitted to continuous irradiation with UV light, β -carotene was quickly released and reached 100% release after five minutes.

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In this paper, we tackled the preparation of UV-sensitive main chain liquid crystalline polyesters based on 4,4'-dihydroxy- α -methylstilbene and aliphatic or aromatic acyl dichlorides. 4,4'-dihydroxy- α -methylstilbene is an interesting mesogen which has been widely reported in the preparation of liquid crystalline epoxy resins, elastomers, polyethers and polycarbonates^{9, 10}. Moreover, stilbenes are highly photosensitive species, which undergo several photoreactions under light exposure. E/Z isomerization is the main photochemical process in low-molecular weight stilbene derivatives; however, [2+2] photocycloaddition and oxidative cyclization of the Z isomer forming phenantrene derivatives may also occur.¹¹ In the literature, many examples exist, which concern the preparation of photo-active polymer-based films containing stilbene as the photo-active unit.¹²⁻¹⁴ Stilbene derivatives in the E state have an extended conformation and are rodlike; on the contrary, in the Z state they do not possess the linear form required for liquid crystallinity: as a consequence of such a drastic conformational change, they isothermally get isotropic under UV radiation. For stilbenes, thermal back-reaction is not reported, since it does not readily take place¹⁵: for this reason, main-chain polymers based on α -methylstilbene were reported to exhibit irreversible photochromic properties.¹⁶

In this paper, we report on the synthesis and the full characterization of different LC polyesters based on α -methylstilbene to be used in the preparation of UV-sensitive microcapsules. We explored different strategies to get a liquid crystalline polymer with a low or no crystallinity, in order to obtain a system which could be efficiently photoisomerized. We also investigated the photoisomerization kinetics in chloroform solution; finally, we prepared a membrane out of one of these polymers and found that its water wettability was increased upon photo-irradiation.

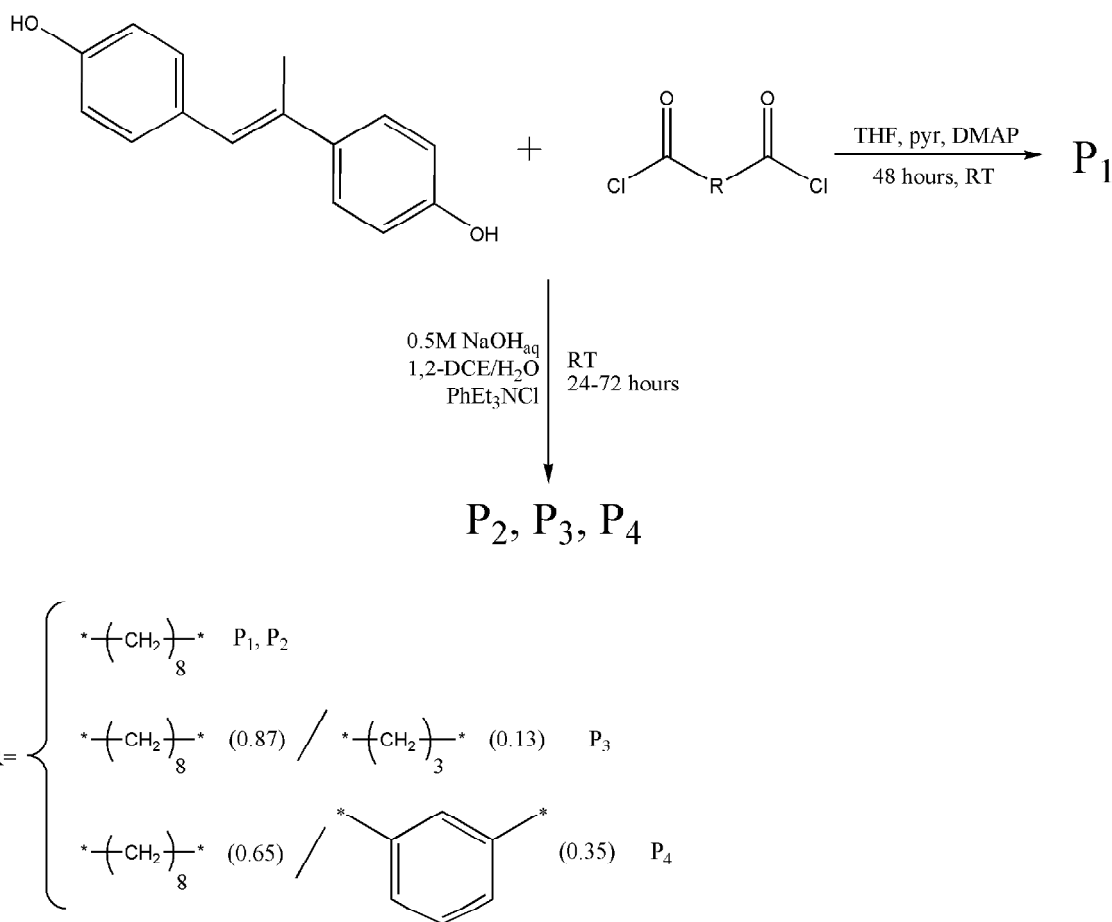
2. MATERIALS AND METHODS

2.1 Materials.

Sebacoyl dichloride (Fluka, 95%), pyridine (Scharlau, synthesis grade), 4-dimethylaminopyridine (Fluka, 99%), benzyltriethyl ammonium chloride (ALFAAesar, 99%), sodium hydroxide (Scharlau, synthesis grade), glutaryl dichloride (Acros Organics, 97%) and isophthaloyl dichloride (Aldrich, 99%) were used as received without any further purification. The solvents were supplied by Scharlau, Aldrich and Fluka were used without previous purification as received. Aqueous solutions were prepared using Milli-Q water.

2.2 Polymer Preparation.

4,4'-dihydroxy- α -methylstilbene was synthesized as previously described.⁹ The reaction scheme is reported in Scheme 1.



Scheme 1

Polymers and copolymers were prepared according to the following procedures. In the case of poly(α -methylstilbenesebacate), polymerization was first attempted in homogeneous phase (polymer P1): 4,4'-dihydroxy- α -methylstilbene (1.0 g, 4.4 mmol) and 4-(dimethylamino)pyridine (0.11 g, 0.9 mmol) were dissolved in 10 mL of dry THF, then pyridine (0.70 g, 8.8 mmol) was added. Afterwards, sebacyl chloride (1.06 g, 4.4 mmol) was added dropwise. The mixture was kept at room temperature for 48 hour under stirring at 900 rpm. The reaction was monitored by TLC chromatography on silica plate. Then, solvent was evaporated

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3 under reduced pressure. The obtained crude solid was dissolved in 50 mL of chloroform, and
4 precipitated from 100 mL of diethyl ether under moderate stirring. It was then filtrated and
5 washed three times using 15 mL of methanol. Purification steps were repeated three times,
6 yielding 286 mg of pure polymer.
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13 Poly(α -methylstilbenesebacoate) P2 and copolymers poly(α -methylstilbenesebacoate-co-
14 α -methylstilbeneglutarate) (P3) and poly(α -methylstilbenesebacoate-co- α -
15 methylstilbeneisophthalate) (P4) were obtained by the conventional liquid-liquid phase transfer-
16 catalyzed interfacial polyesterification, as described by Jegal et al.¹⁷ The ratio phenol
17 group/chlorine was kept 1:1 in all the experiments. In a typical preparation of P2, a solution of
18 4,4'-dihydroxy- α -methylstilbene (1.13 g, 5 mmol, in 20 mL of 0.5 M aqueous sodium hydroxide
19 solution) were added into a blender that contained 31 mL of ice-cold water, 47 mL of 1,2-
20 dichloroethane and benzyltriethyl ammonium chloride (0.35 g, 1.6 mmol) as a phase transfer
21 catalyst. After 10 minutes, a solution of sebacyl chloride (1.20 g, 5 mmol, in 31 mL of 1,2-
22 dichloroethane) was added dropwise. The reaction was performed at room temperature at 400
23 rpm for 67 hours and was monitored by TLC chromatography on silica plate. The resulting
24 polymer was precipitated from ethanol (200 mL), filtered and washed three times using large
25 amount of ethanol. It was purified by repeated dissolution in chloroform (50 mL), and
26 precipitation in ethanol (three times). The product was finally vacuum dried, yielding 1.58 g of
27 pure polymer.
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50 In the case of copolymers P3 and P4, a slight modification of the previously described
51 phase transfer-catalyzed interfacial polyesterification was used, in which a mixture of sebacyl
52 chloride with glutaryl chloride, or isophthaloyl chloride, respectively, were employed. As far as
53 P3 is concerned, 0.56 g (2.5 mmol) of 4,4'-dihydroxy- α -methylstilbene were reacted for 24 hours
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with a solution of sebacoyl chloride (0.42 g, 1.75 mmol) and glutaryl dichloride (0.13 g, 0.75 mmol) in 15.5 mL 1,2-dichloroethane (molar ratio sebacoyl/glutaryl 70/30). 0.62 g of pure polymer was obtained. In the case of P4, 0.56 g, 2.5 mmol, 4,4'-dihydroxy- α -methylstilbene were reacted for 72 hours with a solution of sebacoyl chloride (0.42 g, 1.75 mmol) and isophthaloyl chloride (0.15 g, 0.75 mmol) in 16 mL 1,2-dichloroethane (molar ratio sebacoyl/isophthaloyl 70/30). 0.74 g of pure polymer was obtained. All the polymers were fully characterized by ^1H and ^{13}C NMR, as described in the Results section. The characteristics of the polymers are reported in Table 1.

Table 1. Characteristics of the obtained polymers and copolymers *from ^1H NMR; ^ from SEC-LS; ** polymerization degree from SEC-LS

Polymer	Yield (%)	$M_n \times 10^{-3}$ *	$M_n \times 10^{-3}$ ^	$M_w \times 10^{-3}$ ^	M_w/M_n ^	X_n **
		(g/mol)	(g/mol)	(g/mol)		
P1	14	-	3.1	3.8	1.3	7.9
P2	68	10.2	16.6	41.4	2.5	42
P3	56	20	26.8	66.0	2.5	70
P4	65	16.9	14.6	30.0	2.1	38

Photo-sensitive P2 flat membranes were prepared by solvent-evaporation method. Casting solution was prepared by dissolving 2.5 wt% of P2 polymer in chloroform and stirred for 24h in the darkness. The solution was drawn by a casting knife with 20 μm thickness on a flat and dry glass plate. Then the cast film was placed immediately in a dark place in order to protect the photo-sensitive membrane from light. After 24 h of solvent evaporation at room temperature ($20 \pm 2^\circ\text{C}$), the dried film was carefully peeled-off from the glass surfaces and stored in a dark box.

2.2 Characterization.

Polymers were characterized by ^1H and ^{13}C Nuclear Magnetic Resonance (NMR), which were performed using chloroform (CDCl_3) as a deuterated solvent with a Varian Gemini 400 MHz spectrometer (^1H – 400 MHz, TMS; ^{13}C – 100 MHz, TMS) at room temperature with proton noise decoupling for ^{13}C using pulse delay time of 5 seconds for ^1H NMR spectrum. Measurements were carried out at room temperature on 10-15% (weight/volume) sample solutions. Homonuclear correlation of resonances via through-bond J coupling (CORrelated SpectroscopY, COSY) and Heteronuclear Single Quantum Correlation (gHSQC) experiments were performed according to standard procedures. A study of the kinetics of isomerization for α -methylstilbene moieties of polymers P2-P4 was performed by recording ^1H NMR spectra every 2 minutes during 22 minutes with delay time of 5 s and 32 scans.

Calorimetric studies were performed at the heating rate of $10^\circ\text{C}/\text{min}$ using about 5 mg of sample with a Mettler DSC822e thermal analyzer using nitrogen as a purge gas (100 ml/min) and liquid nitrogen for the system cooling. Equipment was previously calibrated by indium (156.6°C) and zinc (419.58°C) pearls using aluminium standard 40 μl crucibles with pin ME-27331.

Molecular weights of polymers were determined by Size Exclusion Chromatography Coupled to a Light Scattering Detector (SEC-LS). SEC measurements were performed using PL-GPC-50 – system with LS – and RI – Detection (Agilent Technologies, USA) with PL MIXED-B-LS – column, 300 x7,5 mm and 10 μm PSgel, Agilent Technologies. The eluent was chloroform with a flow rate of 1.0 mL/min. The dn/dc value was calculated from the measurements as 0.107 dL/g for P2. Fit of the molecular weight / elution volume dependence or sample specific

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3 calibration¹⁸ were used to estimate the molecular weight distribution of the lower molecular
4 weight samples. The samples were measured at room temperature.
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8 Thermogravimetric analyses (TGAs) were carried out with a Mettler TGA/SDTA 851e
9 thermobalance. Cured samples with an approximate mass of 10 mg were degraded between 30
10 and 600 °C at a heating rate of 10 °C/min in N₂ (100 ml/min) measured at normal conditions.
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15 The liquid crystalline textures were characterized by optical microscopy between crossed
16 polars (POM), by means of an Axiolab Zeiss optical microscope equipped with a Linkam TP92
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23 X-ray experiments at variable temperature were performed with a Siemens D5000
24 diffractometer in the θ - θ configuration, fitted with an Anton Paar TTK temperature chamber.
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CuK α radiation was used and graphite was the second monochromator. The Bragg angle step was
0.05° and the time per step 3 s.

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Infrared spectra on powder of the polymers, were investigated at room temperature on
Fourier transform infrared spectrophotometer (FTIR) 680 Plus from Jasco with resolution of 4
cm⁻¹, scanning speed 2 mm/sec, in the transmittance mode. An attenuated total reflection
accessory (ATR) with thermal control and a diamond crystal (a Golden Gate heated single-
reflection diamond ATR from Specac-Teknokroma) was used to determine FTIR spectra. The
spectra were also collected at higher temperature (200°C) using high stability temperature
controller with RS232 control 300 Series™ from Specac. Spectra were elaborated by means of
Spectra Manager, v. 1.53.04, Jasco Corp. and normalized with respect to the aromatic stretching
peak at 1505 cm⁻¹.

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3 Photoisomerization was investigated by irradiating samples with UV light at 364 nm with
4 a Vilber Lourmat VL-4 LC-230 V UV-lamp at 364 nm for the desired time. The distance
5 between the lamp and the sample was 1 cm.
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11 UV-Vis spectra were recorded at room temperature (20°C) on a UV-Vis
12 spectrophotometer Dinko 8500. First, polymers were dissolved in chloroform to give a
13 concentration in the range 0.9-1.3 mg/mL. Then, the spectra were carried out in the wavelength
14 range 190–600 nm on diluted samples (dilution ratio 1:10).
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21 P2 insoluble fraction after thermal treatment was determined according to the following
22 procedure: 200 mg of P2 powder was placed on a flat ceramic disc covered by conical funnel in
23 oven at 200°C for 15 min. The polymer was then placed on a cellulose filter in Soxhlet apparatus
24 with 200 mL of boiling chloroform. The extraction was performed for 3 hours. After the
25 extraction, the filter was dried in oven at 40°C for 14 hours and finally weighted. This process
26 was repeated till the dry insoluble fraction reached constant weight. Finally 12% (24 mg)
27 insoluble fraction was obtained.
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39 Surface and cross-section morphologies of P2 membranes were observed at 15 kV under
40 low vacuum ESEM FEI Quanta 600 apparatus, without sputter coating. Membrane cross sections
41 were prepared by fracturing in liquid nitrogen. The details of this method were previously
42 reported¹⁹. The real sizes of cross-section of the membrane (10 measures) were calculated by
43 “Image-ProPlus 5[®]” software on ESEM micrographs.
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51 Static contact angles with water on a membrane surface were measured with a Kruss
52 contact angle instrument (Hamburg, Germany) equipped with a motorized pipet (Matrix
53 Technology, Nashua, NH) and deionized water as the probe liquid. The contact angle was
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3 measured immediately after putting the water drop (3 μm) on the membrane surface.
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5 Measurements were repeated using different areas of the film: for each test reported, at least three
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7 drops of water were used.
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10 Dipole moments were calculated with a GAUSSIAN 03 program (Ground State DFT and
11 B3LYP/Set lanL2DZ level).²⁰ Structures, pre-optimized semi-empirically with HYPERCHEM-
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13 7.52 (PM3 Hamiltonian) were used as starting points.
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21 3. RESULTS AND DISCUSSION

24 3.1 Polymer synthesis and characterization.

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27 The aim of this work was the preparation of liquid crystalline polymers, containing a
28 photoisomerizable moiety, to be used as starting material for microcapsules, whose release
29 properties can be triggered by UV light. The reaction scheme is reported in Scheme 1. The
30 characteristics of all the polymers and copolymers obtained are reported in Table 1.
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38 The synthesis of esters and copolyesters based on 4,4'-dihydroxy- α -methylstilbene by
39 interfacial polymerization was reported by Jegal et al.¹⁷ In our case, we first explored the
40 synthesis of poly(α -methylstilbenesebacoate) by polymerization in homogeneous phase (polymer
41 P1 preparation, see Experimental part). By this procedure, only oligomers could be obtained, as
42 shown by SEC-LS analysis (Table 1): as a matter of fact, no light scattering signal could be
43 observed for this sample and the polymerization degree (X_n) resulted as low as 7.9. Moreover,
44 the reaction yield was low (i.e. 14%). ¹H and ¹³C NMR spectra of P1 are reported in the
45 Supporting Information, Figures S1 and S2, respectively. ¹H and ¹³C NMR assignments of P1 are
46 the same as polymer P2, whose detailed NMR discussion is reported below.
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3 Since polymerization in homogeneous phase did not lead to the desired polymer, we tried
4 the liquid-liquid phase transfer-catalyzed interfacial polyesterification. As it can be inferred from
5 Table 1, this procedure resulted successful, since it gave poly(α -methylstilbenesebacoate) with
6 quite high yield and satisfactory polymerization degree. As a matter of fact, SEC-LS analysis
7 showed that, in this case, the weight average molecular weight (M_w) of the resulting polymer
8 was about 41000 g/mol and the polymerization degree about 42.
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18 ^1H and ^{13}C NMR spectra of polymer P2 are reported in Figures 1 and 2. The NMR
19 assignments are reported in Table 2.
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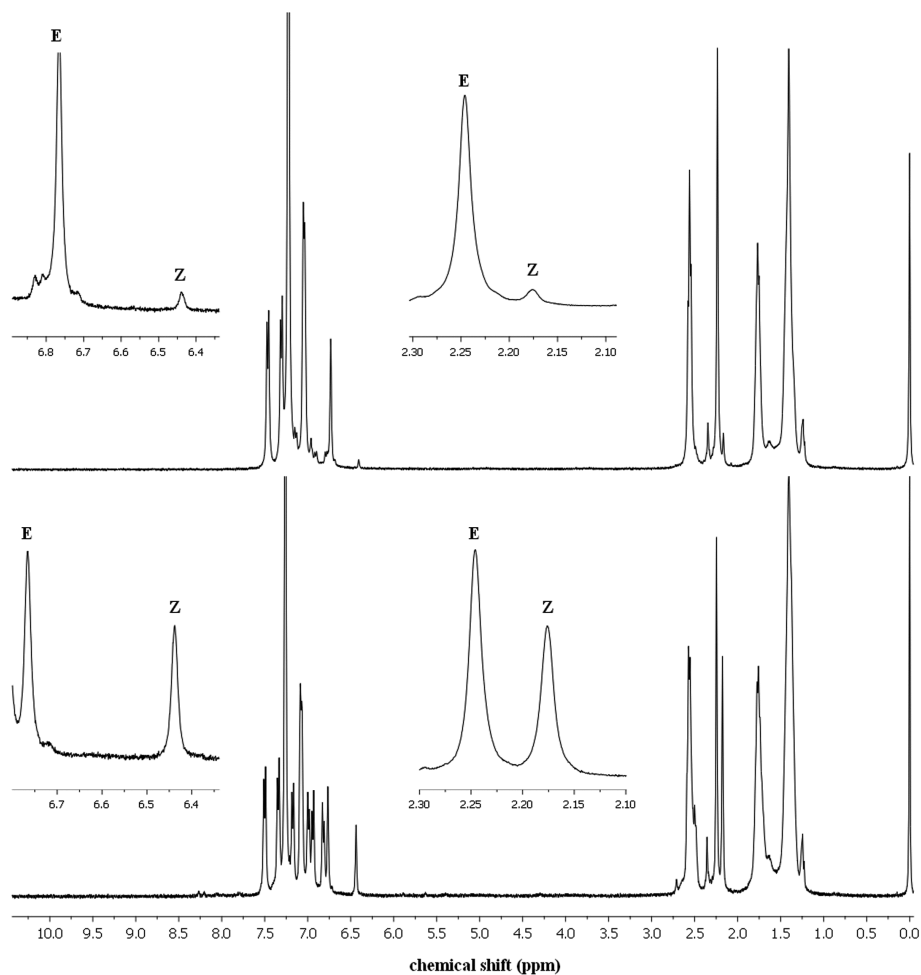


Figure 1 ¹H NMR spectrum in CDCl₃ of P2 before (top) and after (bottom) 20 minutes irradiation. The insets show a magnification of vinyl (6.3- 6.9 ppm) and methylic (2.10-2.30 ppm) protons regions.

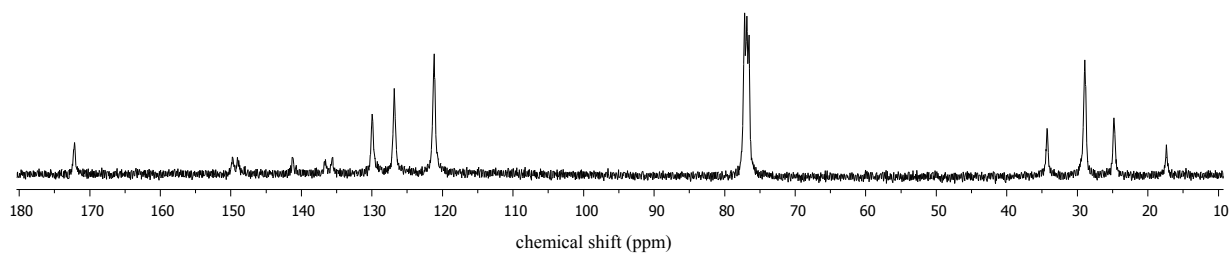
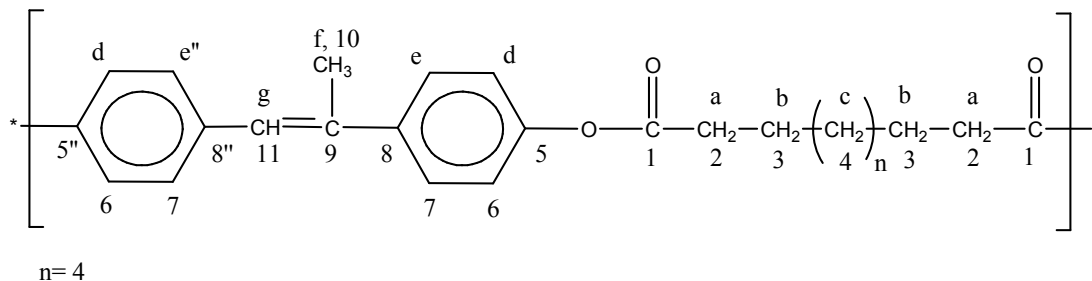


Figure 2. ^{13}C NMR spectrum in CDCl_3 of P2 before photoirradiation.

In ^1H NMR spectra, the signal corresponding to the vinyl proton g and to the methylic protons f appeared as singlets at 6.8 and 2.25 ppm, respectively (Table 2 and Figure 1, top).

Table 2. NMR attributions for polymer P2. The subscripts Z and E correspond to atoms in Z and E form respectively.



$^1\text{H NMR}$		$^{13}\text{C NMR}$	
chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
1.24	c	17.7	10
1.76	b	25.1	4
2.18	f_Z	29.2	3
2.25	f_E	34.6	2
2.57	a	121.5	6
5.59	terminal phenolic	127.2	11
6.44	g_Z	130.3	7
6.77	g_E	135.9, 136.9	8'', 8
7.07	d	141.5	9
7.33	e	149.4, 150.1	5'', 5
7.49	e''	172.5	1
11.13	terminal carboxylic		

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3 They were attributed to α -methylstilbene moiety in the E form. Moreover, two singlets at
4 higher field, i.e at 6.4 and 2.2 ppm, respectively, were found. The latter are attributed to the
5 vinyl proton and to the methylic protons of the α -methylstilbene moiety in the Z form. From the
6 comparison of the integrated areas of the peaks at 2.18 and 2.25 ppm, and 6.4 and 6.8 ppm,
7 respectively, we calculated that the amount of the as-synthesized P2 in Z form was about 3%. It
8 must be pointed out that the ^1H NMR spectrum of 4,4'-dihydroxy- α -methylstilbene monomer
9 (Supporting Information, Figure S3), already showed the presence of 6 % Z form.
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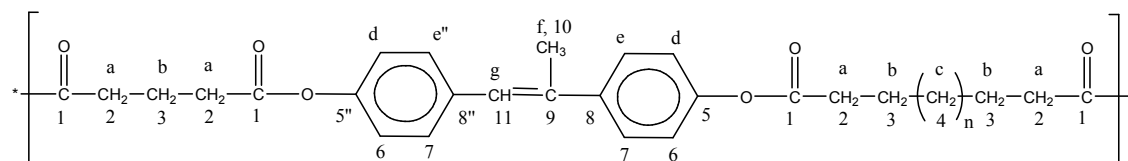
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21 On irradiating P2 at 364 nm for 20 minutes, its ^1H NMR spectra was remarkably changed
22 (Figure 1, bottom) and the intensities of the peaks at 6.4 and 2.2 ppm considerably increased, as
23 we will discuss in section 3.3. The analysis of the ^1H NMR spectrum after UV irradiation also
24 allowed us to exclude the presence of detectable amounts of products deriving from [2+2]
25 photocycloaddition and oxidative cyclization reactions as a consequence of UV-irradiation in the
26 previously described conditions. As far as ^{13}C NMR spectrum is concerned (Figure 2), no
27 variations were found after irradiating P2 at 364 nm for 20 minutes.
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38 In ^1H NMR spectrum before irradiation, two very small peaks were also found at 5.6 and
39 11.1 ppm, respectively: they were attributed to the protons from the terminal phenolic and
40 carboxylic groups, respectively. From the comparison of the integrated areas of these peaks with
41 the ones from the signals of the vinyl protons, we could estimate a molecular weight of about
42 10.2×10^3 g/mol. This value is lower than the one obtained by SEC-LS (16.4×10^3 , see Table 1):
43 this is not surprising, since we must take into account the different sensitivities of the two
44 techniques, as well as that the integration of the peaks at 5.6 and 11.1 ppm is probably affected
45 by a considerable error.
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4 We also prepared copolymers based on the α -methylstilbene moiety, in which the
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6 introduction of some amount of different spacers was expected to lead to a less regular polymeric
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8 structure, to decrease the glass transition temperature, possibly to inhibit crystallization and
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10 modify the nature and stability of the LC phase. For this reason, we first reacted 4,4'-dihydroxy-
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12 α -methylstilbene with a mixture of acyl chlorides, namely sebacoyl and glutaryl chloride, in the
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14 theoretical molar ratio 70/30, in order to have a mixture of shorter and longer flexible spacers in
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16 the final polyester P3. This copolymer was obtained in good yield (56%) and had M_w about $66 \times$
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18 10^3 g/mol.
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22 ^1H and ^{13}C NMR assignments for this copolymer are shown in Table 3. The spectra are
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24 reported in Supporting Information, Figures S4 and S5. In this case, the signals relative to the
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26 methylenic protons in position α and β to the carbonyl of the sebacoyl unit appeared overlapped
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28 with the methylenic protons from the glutaryl unit. However, by comparing the integrated areas
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30 relative to the vinylic proton of α -methylstilbene unit at 6.8 ppm, with the integrated areas of γ -
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32 methylenic protons of the sebacoyl unit at 1.4 ppm, we could calculate that the actual ratio of
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34 sebacoyl and glutaryl units in the final polymer was 87/13. In the case of P3, no signal could be
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36 observed at 6.4 ppm, corresponding to the vinyl proton of the α -methylstilbene in the Z form;
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38 however, the signal at 2.18 ppm, corresponding to the methyl proton of the same unit in the Z
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40 form, could be detected. Therefore, from the comparison of the integrated areas of the peaks at
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42 2.18 and 2.25 ppm, we calculated that the amount of the as-synthesized P3 in Z form was about
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44 6%. Detectable amounts of products deriving from [2+2] photocycloaddition and oxidative
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46 cyclization reactions were not found in ^1H NMR after irradiation.
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Table 3. NMR attributions for polymer P3. The subscripts Z and E correspond to atoms in Z and E form respectively.



$n=4$

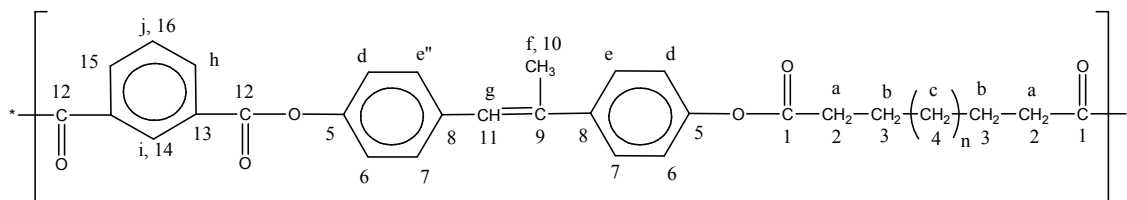
$^1\text{H NMR}$		$^{13}\text{C NMR}$	
chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
1.41	c	17.5	10
1.78	b	24.9	4
2.18	f_Z	29.1	3
2.25	f_E	34.4	2
2.58	a	115.1	6 terminal
4.92	terminal phenolic	121.4	6
6.77	g_E	127.0	11
7.09	d	130.1	7
7.33	e	153.8, 136.8	8", 8
7.49	e''	141.4	9
9.89	terminal carboxylic	149.2, 150.0	5", 5
		172.3	1
		172.3	1

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3 In P3 ^1H NMR spectrum (Figure S4) we could also detect the signals at 4.9 and 9.9 ppm,
4 which correspond to the protons from phenolic and carboxylic end groups, respectively. From the
5 comparison of the integrated areas of these peaks with the area of the vinyl proton at 6.8 ppm, we
6 could estimate the polymerization degree of 53, corresponding to a molecular weight
7 approximately 20×10^3 g/mol. These values are in a good agreement with the results from SEC-
8 LS, which gave a number average molecular weight (M_n) about 27×10^3 g/mol and a
9 polymerization degree of 70 (Table 1), if we take into account the different sensitivity of the two
10 techniques.
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23 In a second preparation, we reacted 4,4'-dihydroxy- α -methylstilbene with a mixture of
24 sebacoyl chloride and isophthaloyl chloride in the theoretical molar ratio 70/30. The presence of
25 the isophthalic unit should, in our hypothesis, force the polymeric chains to bend and could
26 therefore increase the polymer free volume, thus reducing T_g ; the introduction of such
27 irregularities in the structure should also prevent the polymer from organizing in a crystalline
28 structure. The ^1H NMR spectrum of the resulting poly(α -methylstilbenesebacate-co- α -
29 methylstilbeneisophthalate), P4, is reported in Figure 3, while the NMR assignments are reported
30 in Table 4. ^{13}C NMR spectrum of P4 is reported in Supporting Information, Figure S6.
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43 As expected, ^1H NMR spectrum showed, apart from the signal relative to α -
44 methylstilbene and sebacoyl units, three signals at 7.7, 8.5 and 9.0 ppm, respectively, which
45 could be attributed to the protons of isophthaloyl unit. Moreover, the signals relative to the vinyl
46 proton and to the methyl protons, as well as the ones relative to the aromatic protons of the α -
47 methylstilbene unit, appeared split into three peaks of different intensities
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Table 4. NMR attributions for polymer P4. The subscripts Z and E correspond to atoms in Z and E form respectively.



$n=4$

$^1\text{H NMR}$		$^{13}\text{C NMR}$	
chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
1.41	c	17.5	10
1.78	b	24.9	4
2.18	f_Z	29.0	3
2.29, 2.33, 2.38	f_E	34.4	2
2.57	a	121.3	6
4.89	terminal phenolic	127.0	11
6.44, 6.48	g_Z	127.1	16
6.77, 6.81, 6.86	g_E	130.1	7
7.07	d	130.3	13, 14
7.33, 7.38	e	135.0	15, 8
7.49, 7.59	e''	141.4	9
7.71	i	149.9	5
8.48	h	157.9	5 terminal
8.98	j	164.3	12
10.20	terminal carboxylic	172.3	1

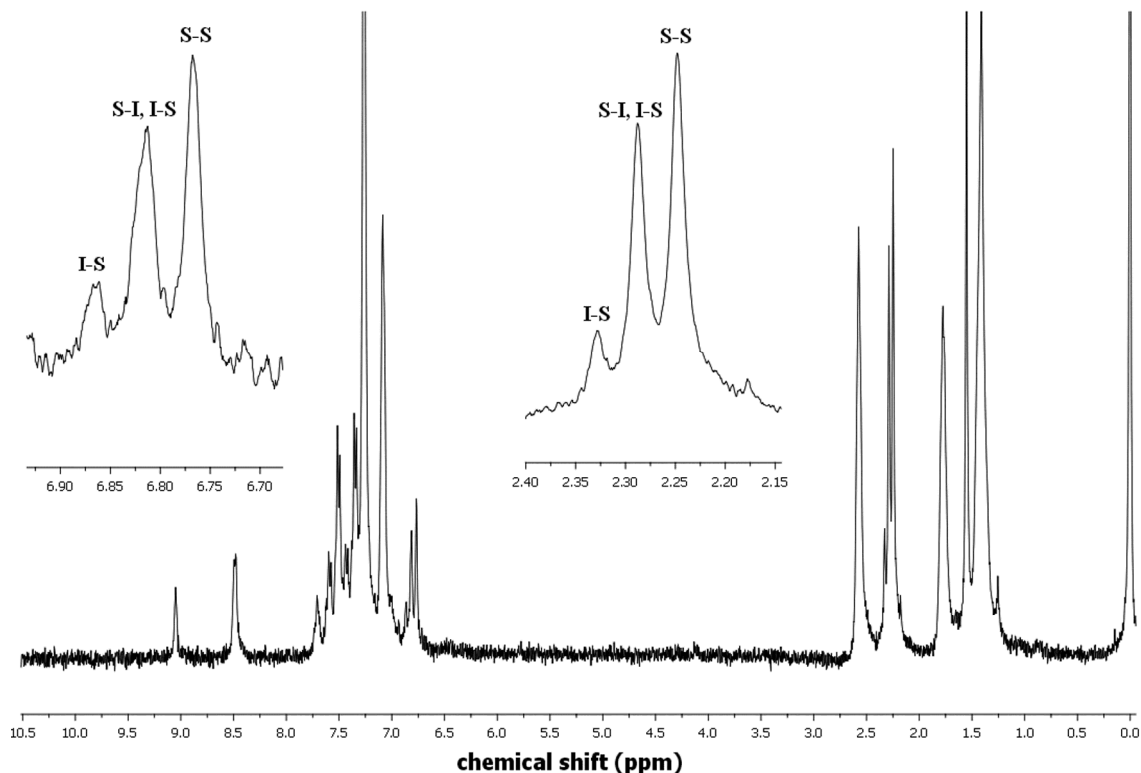


Figure 3. ^1H NMR spectrum in CDCl_3 of P4. The insets show a magnification of vinyl (6.7- 6.9 ppm) and methylic (2.15-2.40 ppm) protons regions.

This was attributed to the fact that each α -methylstilbene moiety can be bound to a sebacoyl group (S) or to an isophthaloyl group (I). This gives rise to the existence of four possible dyads: S-S, I-S, S-I, I-I, which, in principle, correspond to different values of the chemical shift in ^1H NMR spectrum. It is reasonable to assume that, in our case, the chemical shifts of I-S and S-I dyads were very close and gave overlapped signals in the spectrum: for this reason, only three signals were observed. According to the ^1H NMR spectrum of poly(α -methylstilbenesebacate), the peak at 6.78 ppm was attributed to the S-S dyad, while the peaks located at lower fields in P4 spectrum were attributed to the I-S plus S-I dyad (6.81 ppm) and to the I-I dyad (6.86 ppm), respectively.

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3 Similarly to P2, in the case of P4 equivalent signals at higher fields corresponding to the
4 α -methylstilbene moiety in the Z form, were also found. In this case, for instance, a triplet
5 between 6.44 and 6.53 ppm in the case of the vinyl proton could be also detected: this signal was
6 split into a triplet due to the existence of different dyads, as explained before. From the
7 comparison of the integrated areas of the triplets corresponding to the vinyl proton in the E form
8 (centered around 6.8 ppm, as previously explained) and to the vinyl proton in the Z form, we
9 could calculate that the amount of α -methylstilbene moieties in Z form was about 3% in the as-
10 synthesized P4. The analysis of the spectrum recorded after irradiation allowed us to exclude also
11 in the case of P4 the presence of products deriving from [2+2] photocycloaddition and oxidative
12 cyclization reactions.
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28 The actual sebacoyl/isophthaloyl ratio in P4 was calculated from the integrated areas of the
29 peaks corresponding to the isophthaloyl group and of the whole group of signals corresponding
30 to the vinyl proton, and gave a value of 65/35.
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36 The integrated areas of the peaks located at 6.77, 6.81 and 6.86 ppm (Figure 3) allowed us
37 to confirm that the distribution of the two comonomers sebacic (S) and isophthalic (I) was
38 Bernoullian, with a random placement along the copolymer chain. As a matter of fact, if we
39 make this assumption, given that the experimental amount of S versus I is 65/35, then the
40 probability P_{S-S} of finding a dyad S-S is:
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$$48 \quad P_{S-S} = (0.65)^2 = 0.42 \quad (1)$$

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50 while the total probability P_{I-S} of finding a dyad I-S or S-I is:
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$$55 \quad 2 \times P_{I-S} = 2 \times P_{S-I} = 2(0.65 \times 0.35) = 0.46 \quad (2)$$

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3 and finally the probability P_{I-I} of an I-I dyad is:
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$$5 \quad P_{I-I} = (0.35)^2 = 0.12. \quad (3)$$

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10 Therefore, the integrated areas of the signals corresponding to the S-S, I-S+S-I, and I-I
11 dyads should exhibit the ratio 0.42:0.46:0.12. The experimental result was in good agreement
12 with this hypothesis, since the ratio between the areas of the peaks at 6.77, 6.81 and 6.86 ppm
13 gave 0.39:0.44:0.17.
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19 As it can be seen in Figure 3 in P4 ^1H NMR spectrum, two signals at 4.89 and 10.20 ppm
20 could be put into evidence, which corresponded to the phenolic and carboxylic protons from end
21 groups, respectively. From the comparison of the integrated areas of these peaks and the whole
22 set of signals relative to the vinyl protons between 6.9 and 6.4 ppm, we could give an estimation
23 of P4 polymerization degree, which turned out to be about 44. This corresponded to an
24 approximate molecular weight 16.9×10^3 g/mol, which is in agreement with $M_n = 14.6 \times 10^3$
25 g/mol as determined by SEC-LS.
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37 **3.2 Mesomorphic and thermal characterization.**

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40 All the synthesized polymers were characterized by Optical Microscopy between crossed
41 polars (POM), Differential Scanning Calorimetry (DSC) and X-ray diffraction (XRD). DSC
42 thermograms of P1-P4 and the XRD patterns of some selected samples are reported in
43 Supporting Information, Figures S7 and S8.
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51 In the case of P1, only oligomers corresponding to $X_n = 8$ could be obtained. The
52 oligomers exhibited a liquid crystalline behaviour between 111 and 190°C, as shown by DSC,
53 POM and XRD analyses. By POM, the typical Schlieren texture, characteristic of nematic phase,
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3 could be observed (Figure 4a), while XRD performed at 140°C put into evidence a halo centered
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5 at 2θ about 20°. The calorimetric features of P1 are reported in Table 5. The calorimetric analysis
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7 of P2 put into evidence two endothermic peaks, one located at 175°C, and another one at 226°C
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9 (Table 5). Birefringent texture of P2 at 185°C is shown in Figure 4b. According to POM
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11 observation and to XRD analysis, the two endotherms were attributed to the polymer melting to a
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13 nematic phase and to its clearing, respectively. However, from POM observation, a progressive
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15 increase of polymer viscosity was also observed. Furthermore, DSC second heating scan
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17 performed on a sample previously heated above 200°C, put into evidence a slightly higher T_g
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19 value and lower values of clearing temperature and enthalpy. This suggested that, on heating
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21 above 200°C, reactions which involve the central double bond of α -methylstilbene moiety can
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23 occur to some extent; these reactions thus destroy the mesogenic core and lead to a partially
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25 crosslinked material. Figure 5 shows the FT-IR spectrum at room temperature on a P2 powder
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27 before (a) and after (b) heating 15 minutes at 200°C. This spectrum seems to confirm our
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29 hypothesis, since the intensities of the bands at 845 and 1290 cm^{-1} (which can be both attributed
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31 to the phenyl ring + C-H deformation in E- α -methylstilbene) and 1604 cm^{-1} (assigned to the
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33 phenyl out-of-plane vibration of E- α -methylstilbene²¹) are strongly reduced as a consequence of
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35 heating. Furthermore, thermal treatment at 200°C for 15 minutes on P2 sample, followed by
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37 Soxhlet extraction with chloroform, led to 12 wt.% insoluble fraction, thus confirming that
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39 crosslinking of the double bond of the α -methylstilbene moiety takes place to some extent in
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41 those conditions. Similar behavior upon heating above 200°C was found also in the case of P3
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43 and P4.
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Table 5. Calorimetric features of P1-P4 from first heating scan. ¹ Glass transition temperature; ² melting temperature; ³ clearing temperature; ⁴ per mole of repetitive unit; ⁵N: nematic.

Polymer	T_g (°C) ¹	T_m (°C) ²	T_c (°C) ³	ΔH_m (kJ/mol) ⁴	ΔS_m (J/mol K) ⁴	ΔH_c (kJ/mol) ⁴	ΔS_c (J/mol K) ⁴	Mesophase ⁵
P1	71	111	190	9.71	25.3	5.56	12.0	N
P2	135	175	226	6.71	15.0	5.57	11.2	N
P3	78	158	187	2.30	5.3	1.90	4.1	N
P4	45	-	238	-	-	2.43	4.7	N

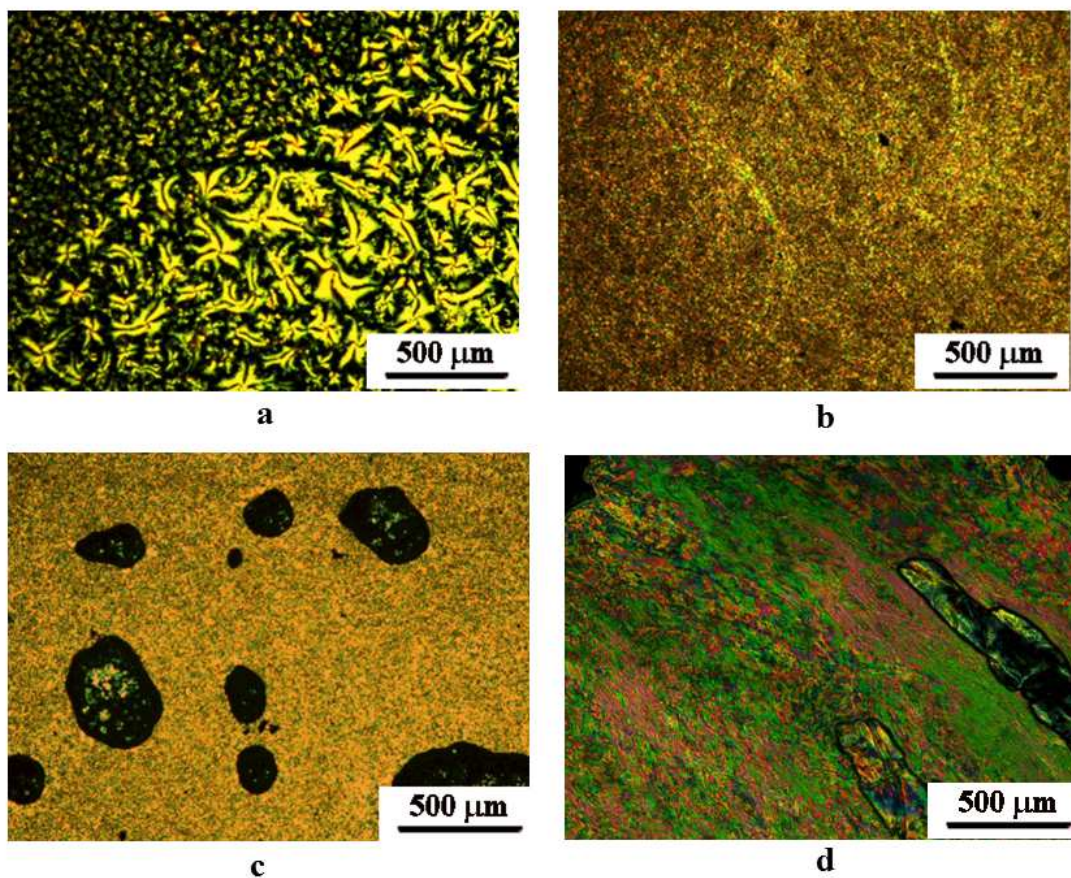


Figure 4. Optical micrographs between crossed polars of: a) P1, 182°C, on cooling from the isotropic phase; b) P2, 185°C, first heating; c) P3, 161°C, second heating; d) P4, 194°C, first heating. Heating or cooling rates: 10°C/min.

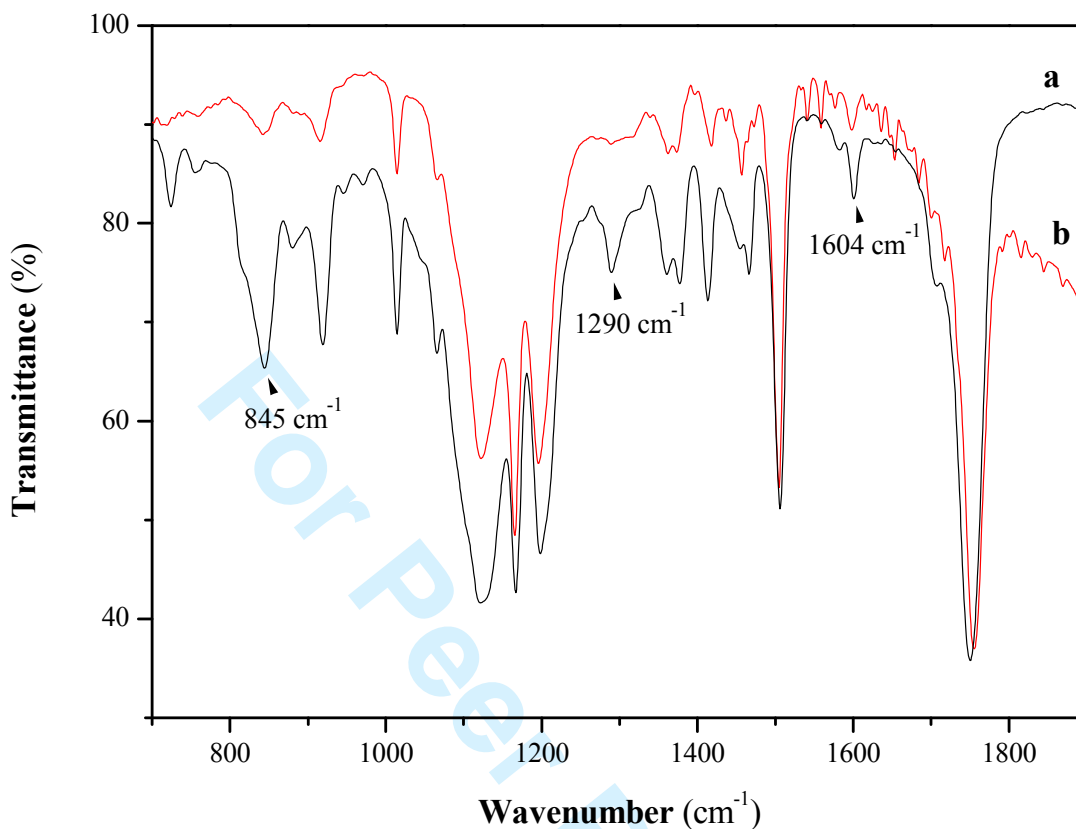


Figure 5. Normalized FT-IR spectra at room temperature on P2 powder before (a) and after (b) heating 15 minutes at 200°C.

The thermal features of P3 are reported in Table 5. As it can be seen, this polymer exhibited a considerably lower T_g with respect to poly(α -methylstilbenesebacate), though its value was still quite high, i.e. 78°C. Moreover, P3 was still partially crystalline, though the extent of crystallinity was reduced, as it can be inferred from the melting enthalpy and entropy reported

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3 in Table 5. Upon melting at 158°C, P3 exhibited a nematic phase up to 187°C, as showed by
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5 POM and XRD. The nematic texture of P3 is shown in Figure 4c.
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9 The introduction of about 30% isophthaloyl moiety was successful in lowering T_g and
10 inhibiting crystallization in the final polymer: DSC analysis performed on P4 showed a T_g at
11 45°C and no melting endotherm; moreover, no crystalline phase could be detected by XRD. DSC
12 analysis showed an endotherm centered at 238°C corresponding to 2.4 kJ/mol. POM analysis put
13 into evidence a nematic thread-like texture (Figure 4d); the clearing point was detected at about
14 240°C. XRD analysis put into evidence a broad halo corresponding at approximately 4 Å, typical
15 of the nematic phase, in the whole temperature range under examination.
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26 Thermal stability of P1-P4 polymers was investigated by TGA under nitrogen atmosphere
27 (Table 6 and Supporting Information, Figure S9). As far as P1 and P2 are concerned, thermal
28 stability increased on increasing molecular weight, as expected, since the temperatures
29 corresponding to 5% weight loss were 292 and 398°C, respectively; $T_{50\%}$ and the weight residue
30 of P2 were also higher than in the case of P1. As far as P2 and P4 are concerned, single step
31 decomposition was found, starting at about 370°C, while in the case of P3 another decomposition
32 step appeared, with an onset at about 300°C; $T_{5\%}$ and $T_{50\%}$ resulted lower for P3 than for P2 and
33 P4. On the other hand, P3, which contained 13% glutaryl spacer, showed higher residue,
34 followed by P4, which contained 35% aromatic spacer, and finally by P2, which had a fully
35 aliphatic quite long spacer. In the case of main chain liquid crystalline polyurethanes based on α -
36 methylstilbene, it was reported that the spacer length and nature significantly influence the
37 decomposition behavior.²² In the case of P2-P4, one should also take into account that heating
38 leads not only to thermal decomposition, but also to reactions of the α -methylstilbene moiety,
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3 which give rise to partially cross-linked products. Thermal decomposition of these products is
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5 not easy to predict, since it can depend, for example, on the tightness of the obtained network.
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9 **Table 6** Results of thermogravimetric analysis of P1-P4. ¹temperature
10 corresponding to 5 wt.% loss; ²temperature corresponding to 50 wt.% loss.
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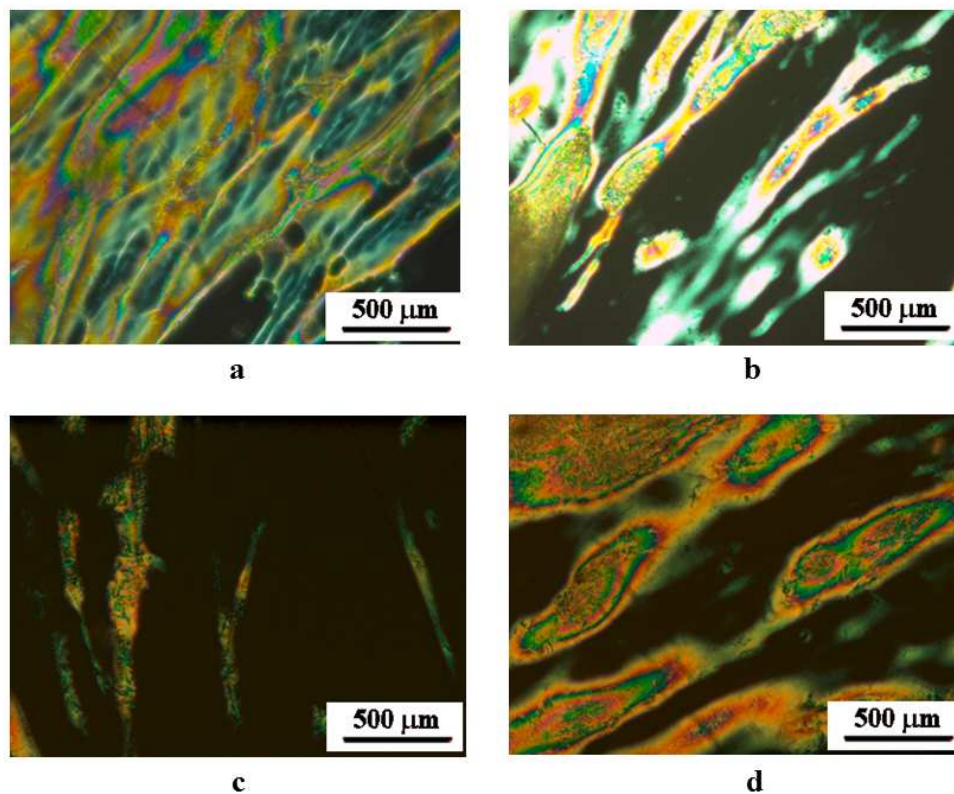
Polymer	T _{5%} (°C) ¹	T _{50%} (°C) ²	Final residue (wt.%)
P1	292	442	3.1
P2	398	455	8.5
P3	307	441	25.3
P4	406	460	18.5

3.3 Polymers photoisomerization.

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36 As already stated, stilbene derivatives in the E state possess the rod-like conformation which is
37 required for liquid crystallinity, while, in the Z state, they have a bent conformation: therefore,
38 they isothermally get isotropic as a consequence of E-Z photoisomerization. Such a drastic
39 conformational change should be accompanied by a remarkable change in transport properties,
40 i.e. on changing the state of order from LC to isotropic, barrier properties should decrease.
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49 On the other hand, thermal Z-E isomerization is not reported in the case of stilbene
50 derivatives, but 254-nm UV light can be used to investigate the Z-E photoisomerization of the
51 stilbene-based compounds.²³ Therefore, on irradiating first with 364-nm and subsequently with
52 254-nm UV light, we should be able to induce first E-Z photoisomerization, followed by
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3 subsequent Z-E photoisomerization. This, in turn, should correspond to isothermal isotropization
4 followed by anisotropization of the polymer under investigation. In order to verify this
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8 phenomenon, we irradiated a P4 film under POM observation, and used the LC texture exhibited
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11 by this sample as a probe to monitor sample isotropization/anisotropization.



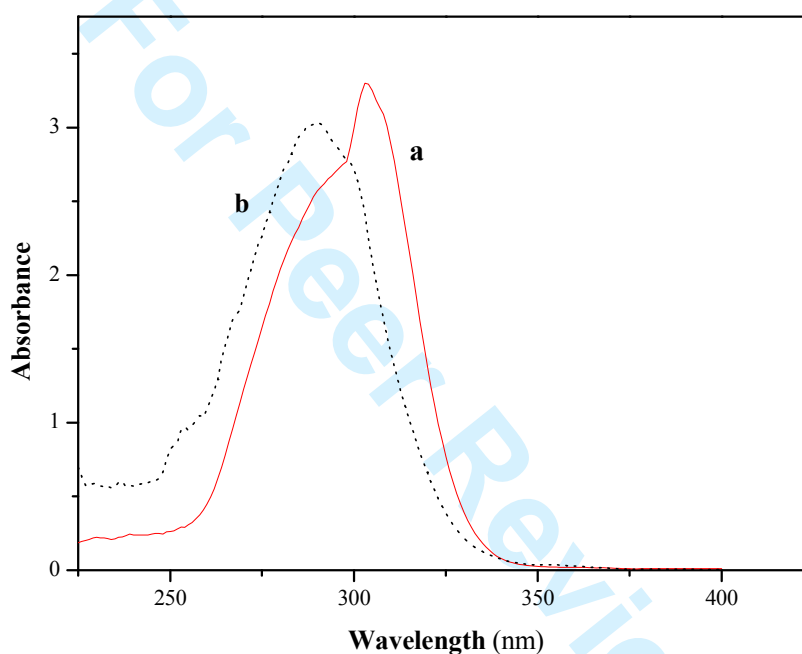
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Figure 6. POM micrographs of P4 film at 180°C: a) before photoirradiation; b) after 10 minutes photoirradiation at 364 nm; c) after 20 minutes photoirradiation at 364 nm; d) after 20 minutes photoirradiation at 364 nm followed by 10 minutes photoirradiation at 254 nm.

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Figure 6 reports the POM micrographs of P4 at 180°C: a) before photoirradiation; b) after 10 minutes photoirradiation at 364 nm; c) after 20 minutes photoirradiation at 364 nm; d) after

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3 20 minutes photoirradiation at 364 nm followed by 10 minutes photoirradiation at 254 nm. It can
4 be noticed that the LC texture of P4 progressively disappears on irradiating at 364 nm, while it is
5 restored after irradiation at 254 nm. These isotropization/anisotropization cycles could be
6 repeated several times.
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43 **Figure 7.** UV absorption spectra of P2 in chloroform before (a) and after (b) 45 minutes UV
44 irradiation at 364 nm .
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52 Figure 7 reports the UV absorption spectra of P2 in chloroform before (a) and after (b) 45
53 minutes UV irradiation at 364 nm. Before irradiation, a peak located at 305 nm, with a shoulder
54 at about 296 nm, was evident. It was reported that at the wavelength of 366 nm, the E form of the
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3 stilbene absorbs to a higher extent than the Z form: as a result, the population of the Z form
4 increases. The resulting decrease in the population of the E form determines a decrease in the
5 absorption band obtained from the system in the wavelength region used in isomerization.²⁴ In
6 the case of thin films of polyimides containing stilbene moieties in the backbone, it was shown
7 that, on UV irradiation, the absorption maximum at 330 nm, characteristic of stilbene units in the
8 E configuration, gradually decreased; at the same time, a band gradually appeared at about 280
9 nm, corresponding to Z stilbene units.²⁵ In the case of P2 in chloroform solution, after irradiation,
10 the maximum of the absorption peak at 302 nm, which can be attributed to the α -methylstilbene
11 moieties in the E form, was displaced at 290 nm. This confirmed that P2 undergoes
12 photoisomerization in these conditions. UV absorption spectra of P3 and P4 in chloroform,
13 before and after 45 minutes UV irradiation at 364 nm, exhibited the same features already
14 discussed for P2. We therefore concluded that all the synthesized polymers underwent
15 photoisomerization in the reported conditions.
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34 Triggering E-Z isomerization can perturb the chemical environments of protons which lie
35 in close proximity to the vinyl bond of α -methylstilbene, and this effect can be quite extended
36 when this moiety is located within a polymer backbone. For cases when these perturbations are
37 sufficiently great, proton NMR spectroscopy can be successfully used to detect the isomerization
38 process. Figure 1b reports the ¹H NMR spectrum of P2 in CDCl₃ after 30 minutes irradiation at
39 364 nm. On comparison with the spectrum obtained before photo-irradiation (Figure 1a), it can
40 be noticed that all the peaks relative to the protons of α -methylstilbene units were clearly
41 duplicated, since signals of similar intensities, with the same multiplicity and shifted up-field,
42 appeared. These peaks were attributed to the Z form of the mesogenic unit. The chemical shifts
43 of Z and E forms were sufficiently far from each other and their peak area provided a good scale
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3 for following quantitatively the progress of photoisomerization with respect to kinetic aspects. As
4 a matter of fact, the comparison of the integrated areas of the vinyl protons at 6.8 and 6.4, and of
5 the methylic protons at 2.25 and 2.2 ppm, allowed us to calculate the amount of the each form
6 after photo-irradiation. The same procedure could be also applied in the case of the ^1H NMR
7 spectrum of P3 and P4 in CDCl_3 .
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11 The relative amount of E form at different irradiation times was calculated according to
12 the following equation:
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$$\pi(t) = \frac{A_E}{A_E + A_Z} \quad (4)$$

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16 where $\pi(t)$ is the amount of E form after irradiation time t , A_E is the peak area of the E
17 form, and A_Z is the peak area of the Z form.
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21 A plot of $\ln [\pi]_t/[\pi]_0$ with respect to irradiation time gave a straight line, whose slope was
22 equal to $-k$, thus confirming that the photoisomerization process followed a first-order rate law,
23 as reported.²⁶ However, in the case of an optically active copolymer of (-)-menthyl acrylate with
24 trans-4-vinylstilbene, it was also reported that E-Z photoisomerization does not obey first-order
25 kinetics, in accordance with the restricted mobility of stilbene chromophores attached to a polymer
26 chain.¹² Table 7 reports rate constants and half-life values calculated at 20°C for the E-Z
27 photoisomerization process of P2-P4 polymers in CDCl_3 . The values of kinetic constants were all
28 in the same range, i.e. around 10^{-4} s^{-1} ; P4 was found to exhibit the lowest value.
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Table 7. Kinetic data for E-Z photoisomerization in CDCl_3 of P2-P4 polymers at 20°C .

Sample	$k \times 10^4 \text{ (s}^{-1}\text{)}$	$\tau_{1/2} \times 10^{-3} \text{ (s)}$
P2	4.8 ± 0.2	1.4
P3	3.66 ± 0.06	1.9
P4	1.64 ± 0.01	4.2

For the low molar mass species, it was reported that on increasing viscosity of the medium, the activation energy involved in the E-Z transformation can increase, thus slowing down the process.²⁷ In the case of photoisomerizable species introduced into a polymer host without chemical linking, it was found that the rigidity of the host matrix largely influences the process rate. In the case of the systems where the active moiety is covalently attached to the polymer, photo-isomerization rate can decrease even further and the activation energy showed temperature dependence.²⁸ Therefore, in order to perform a first check about the occurrence of photo-isomerization also in the bulk state in our systems, we prepared a membrane based on one of the synthesized polymers, namely P2, which exhibited the fastest isomerization kinetics in chloroform solution, and investigated its wetting properties upon UV irradiation.

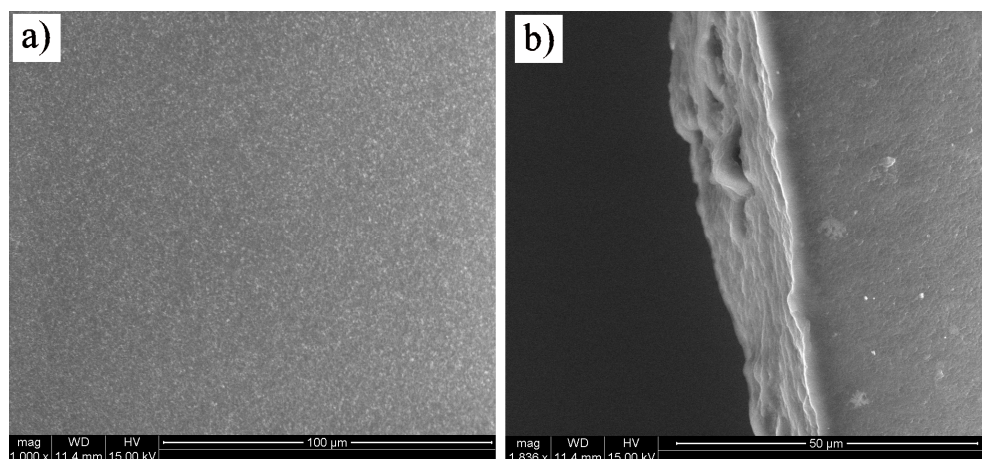


Figure 8. ESEM micrographs of the surface (a) and cross-section (b) of P2 membrane

Figure 8a shows the results of ESEM observation of P2 membrane surface while Figure 8b shows its cross-section morphology. As it is typically expected for membranes prepared by solvent evaporation method, P2 film exhibited dense and non-porous structure.²⁹ Membrane thickness calculated by Image-ProPlus 5[®] software from ESEM micrographs gave the value $6.2 \pm 0.3 \mu\text{m}$.

Wettability of P2 membrane, before and after UV irradiation, was investigated by measuring the static contact angles (CA) with water, which are shown in Figures 9a and 9b, respectively. The value of CA with water of a flat P2 membrane before irradiation (Fig. 9a), resulted $95 \pm 2^\circ$. After exposure to UV light (365 nm) for 30 min the CA was found to be $85 \pm 2^\circ$ (Fig. 9 b), that is, it was decreased about $10 \pm 2^\circ$. This change can be reasonably ascribed to E-to-Z photoisomerization of α -methylstilbene moieties on the membrane surface. In fact, according to our calculations, in the E state, α -methylstilbene moieties have a smaller dipole moment (0.27 D), while E-to-Z isomerization induced by UV light irradiation leads to a large increase in the dipole moment of this molecule (0.56 D). Moreover, the enhanced wettability can be also related to a change in surface roughness on photo-isomerization.³⁰

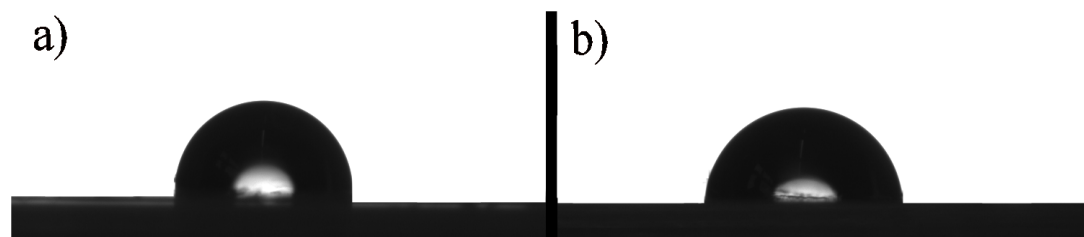


Figure 9. Static contact angles with water of a P2 membrane: (a) before irradiation at 365 nm; (b): after UV irradiation. The angle decrease after irradiation reveals that the membrane is more hydrophilic after the irradiation.

The wettability change of P2 membrane is just a first clue on the possibility of triggering the properties of membrane and microcapsules based on the synthesized polymers. A forthcoming paper will deal with the preparation and characterization of membranes and microcapsules out of P2-P4, as well as with the change of their properties (such as morphology, roughness and permeability) upon photo-irradiation.

4. Conclusions

In this paper we report on the synthesis and characterization of three nematic liquid crystal polyesters containing α -methylstilbene moiety in the main chain and aliphatic or aromatic spacers. Their structure and molecular weights were fully characterized by means of NMR and SEC-LS. XRD, POM and DSC analyses showed that admixture of different chlorides had a significant impact on the behavior of polymers, reducing their crystallinity, or even suppressing it completely, and decreasing the value of glass transition temperature. In all cases we observed some changes in polymers structure around 200°C, which seemed to be due to crosslinking reaction of the vinyl bond, as showed by FTIR. These polymers exhibit E-Z photoisomerization,

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3 as proved by UV and NMR spectra performed after UV irradiation at 364 nm.
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5 Photoisomerization kinetics was also studied at 20°C in CDCl₃ by ¹H NMR and it was found to
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7 obey first order, with constants of the order of 10⁻⁴ s⁻¹. A dense membrane based on P2 polymer
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9 was also prepared by casting and showed an increase of wettability upon photo-irradiation. These
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11 polymers could therefore be candidates to constitute the shell of photoactive microcapsules for
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13 light-triggered release.
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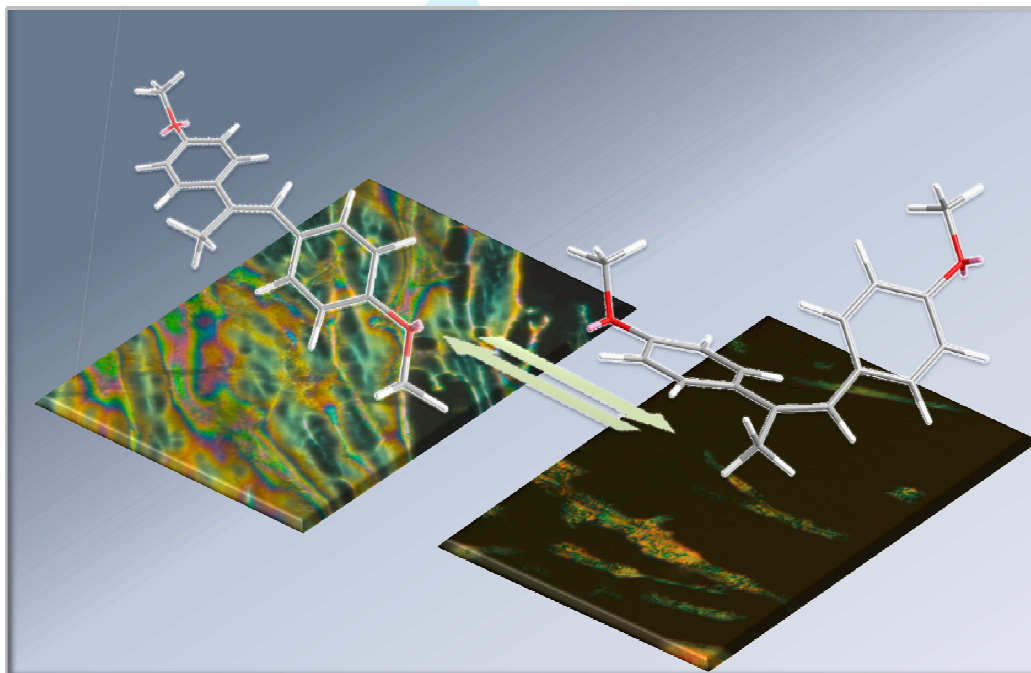
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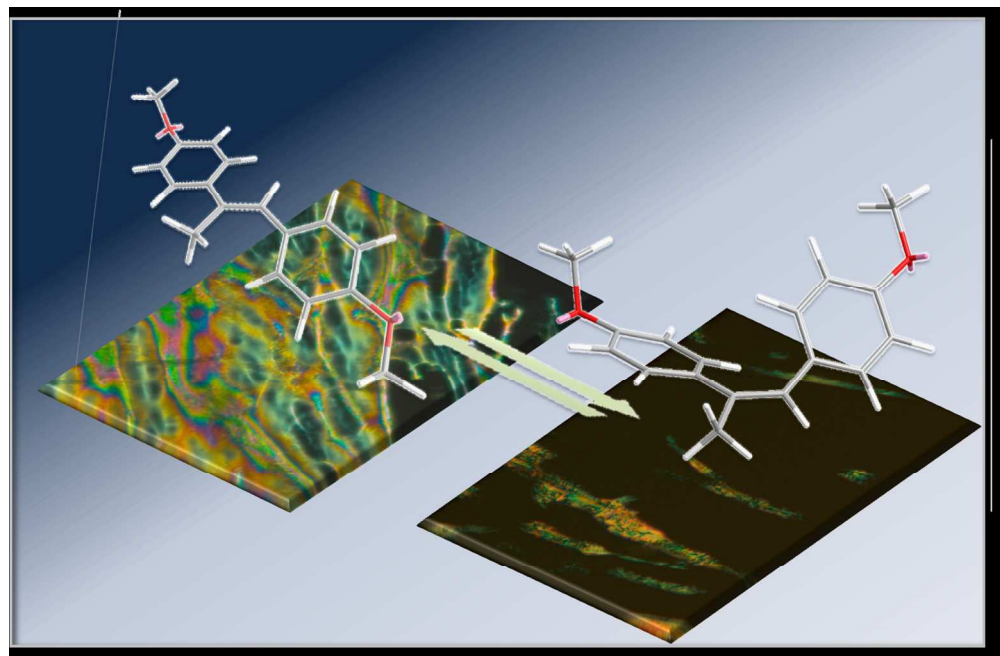
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Graphical abstract**Synthesis and characterization of a new family of photoactive liquid crystalline polyethers based on α -methylstilbene**

Bartosz Tylkowski, Krzysztof A. Bogdanowicz, Veronica Ambrogi, Albena Lederer, Violetta Patroniak, Marta Giamberini*

A family of Liquid Crystal co-polyesters containing α -methylstilbene moiety and aliphatic or aromatic spacers were synthesized. They exhibited E-Z photo-isomerization and increased wettability on photo-irradiation.





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Review

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Supporting Information

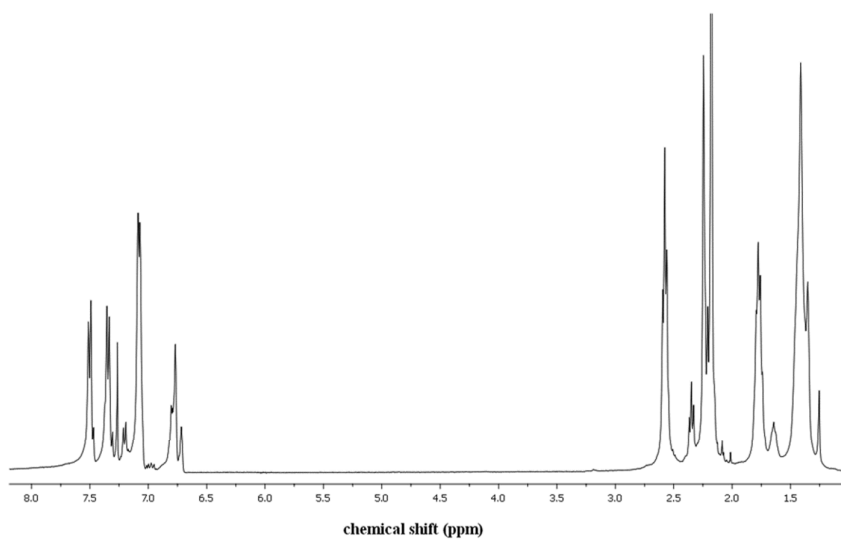


Figure S1 ^1H NMR spectrum in CDCl_3 of P1

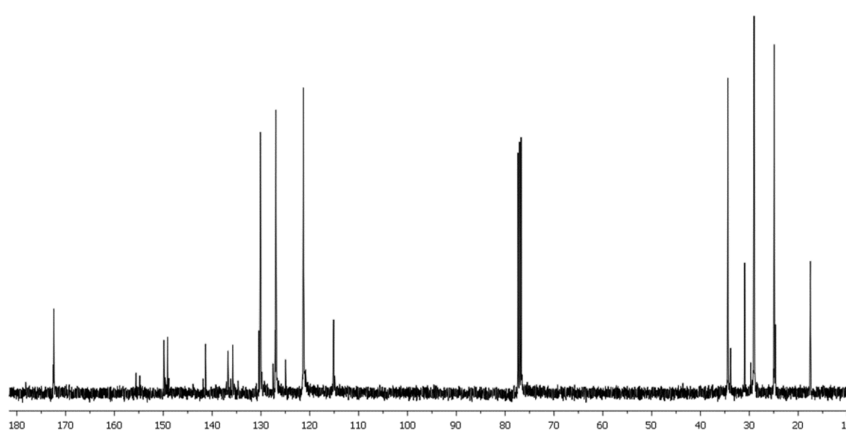
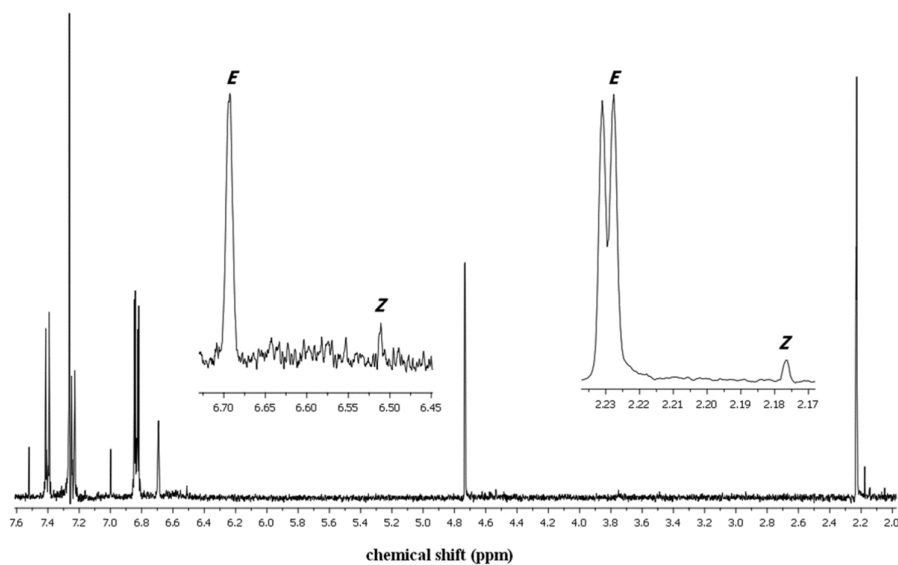
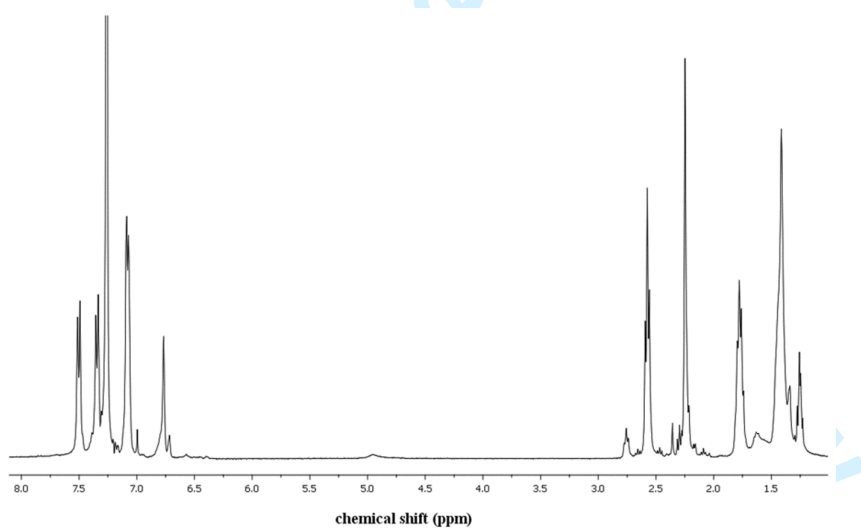


Figure S2 ^{13}C NMR spectrum in CDCl_3 of P1.



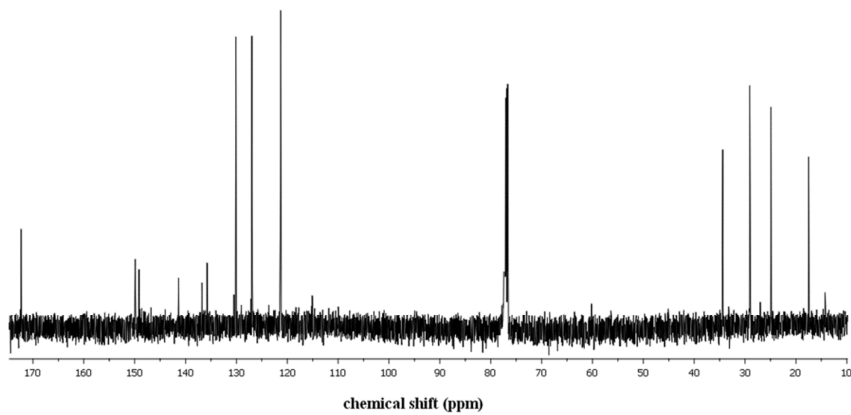
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Figure S3 ^1H NMR spectrum in CDCl_3 of α -methylstilbene. The insets show a magnification of vinyl (6.45- 6.75 ppm) and methylic (2.17-2.24 ppm) protons regions.

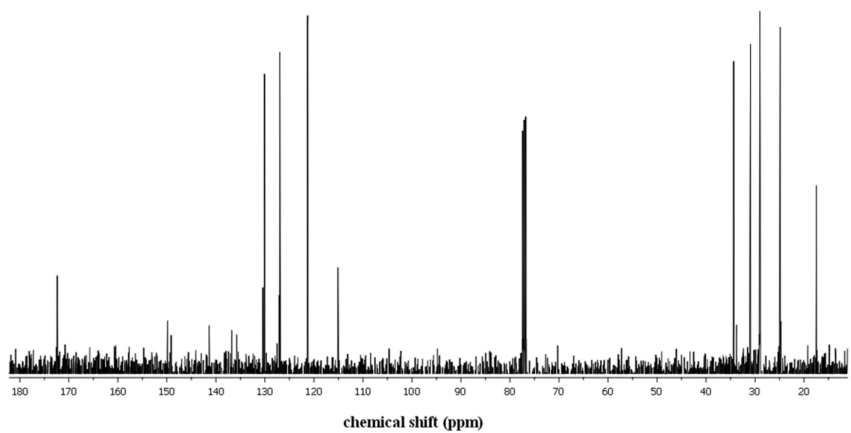


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Figure S4 ^1H NMR spectrum in CDCl_3 of P3



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21 **Figure S5** ^{13}C NMR spectrum in CDCl_3 of P3.
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44 **Figure S6** ^{13}C NMR spectrum in CDCl_3 of P4.
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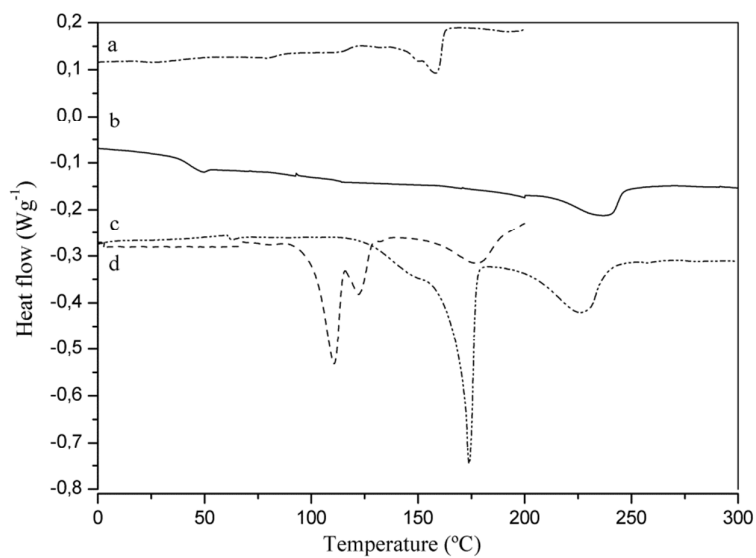


Figure S7 DSC thermograms of: (a) P3, second heating scan; (b) P4, first heating scan; (c) P2, first heating scan; (d) P1, second heating scan. Scan rate: 10°C/min.

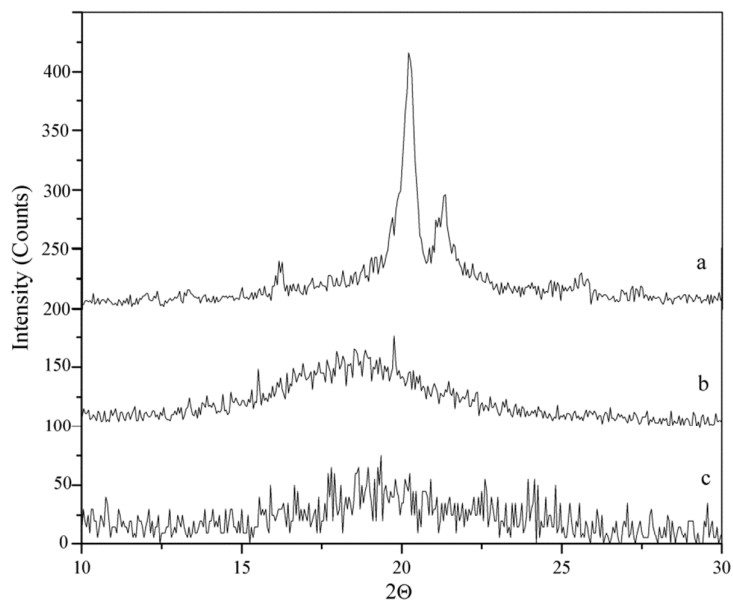


Figure S8 XRD pattern of: (a) P2, 30°C; (b) P2, 180°C; (c) P4, 30°C

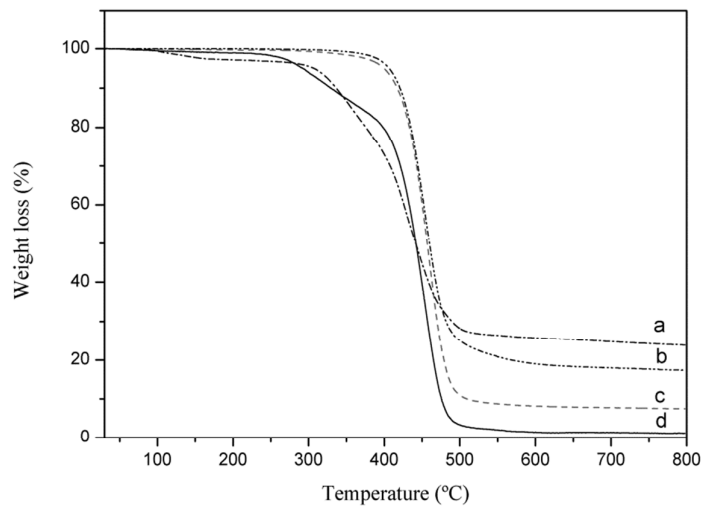


Figure S9 Thermogravimetric analysis in nitrogen of: (a) P3; (b) P4; (c) P2; (d) P1.