Polymer Bulletin 41, 525–532 (1998)

Polymer Bulletin

Functional polythiiranes 9: Stilbene mesogen side chain polythiirane

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Received: 11 May 1998/Revised version: 17 September 1998/Accepted: 24 September 1998

Summary

Polythiirane containing pendant mesogenic stilbene units was synthesized by ring opening polymerization of the corresponding monomer. The synthetic convergent pathway used for the monomer synthesis involved several steps including a Wittig reaction in order to obtain the stilbene unit. The insoluble polymer was characterized by high resolution CP/MAS 13C NMR. The thermotropic liquid crystalline mesomorphism of the polymer was studied by conventional methods. A mechanical dynamical thermal analysis completes the polymer characterization.

Introduction

We have previously reported on a new class of side chain liquid crystalline polymers (SCLCP) polythiiranes, bearing alkyloxybiphenyl mesogens. The anionic ring opening polymerization of thiirane monomers, provided these new materials (1,2). In this series, a significant result was that large spacers were needed to obtain liquid crystal properties. In the previous studies, we have varied the length and the nature of the spacer, and also the nature of the alkoxy terminal group. Only smectic mesophases (SmA and SmE) were observed in this series. The goal of this new paper is to study the influence of the nature of mesogens on phase transitions in SCLC polythiiranes. The stilbene group was chosen as a mesogen because only a few studies deal with stilbene SCLCP (3,4,5). Though some stilbene derivatives do not exhibit any mesomorphic properties (6), others derivatives reported as low molecular mass liquid crystals provided Sm C*mesophases (6). So, using the constant strategy previously detailed and preparing at a first time a suitable monomer **M** which was then polymerized, we synthesized a polythiirane with mesogenic stilbene side chains **P**. On account of the low solubility of the product in organic solvents, the polymer **P** was identified by ^{13}C NMR in the solid state. The thermotropic behaviour of the polymer was studied by classical methods (DSC, RX, polarized optical microscopy) and a mechanical dynamical thermal analysis was carried out to complete the characterization.

Results and Discussion

The whole convergent synthesis used to prepare the suitable monomer **M** is described in Figure 1. It involves four main steps : introduction of the alkoxy terminal group in p-cresol and modification of the methyl group in methylene triphenylphosphonium leading to **6** ; introduction of a polymethylene spacer in the 4-hydroxybenzaldehyde ; Wittig reaction in order to build the stilbene group ; and introduction of the polymerisable thiirane group by reaction of the bromoacetate with mercaptomethylthiirane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (8). In order to allow some comparisons with the previous SCLC polythiiranes, we chose a six methylene spacer and a butoxy terminal group on the mesogen. The characteristics of the intermediate compounds are given in the experimental section. The monomer was identified by ^{1}H and ^{13}C NMR. The attribution

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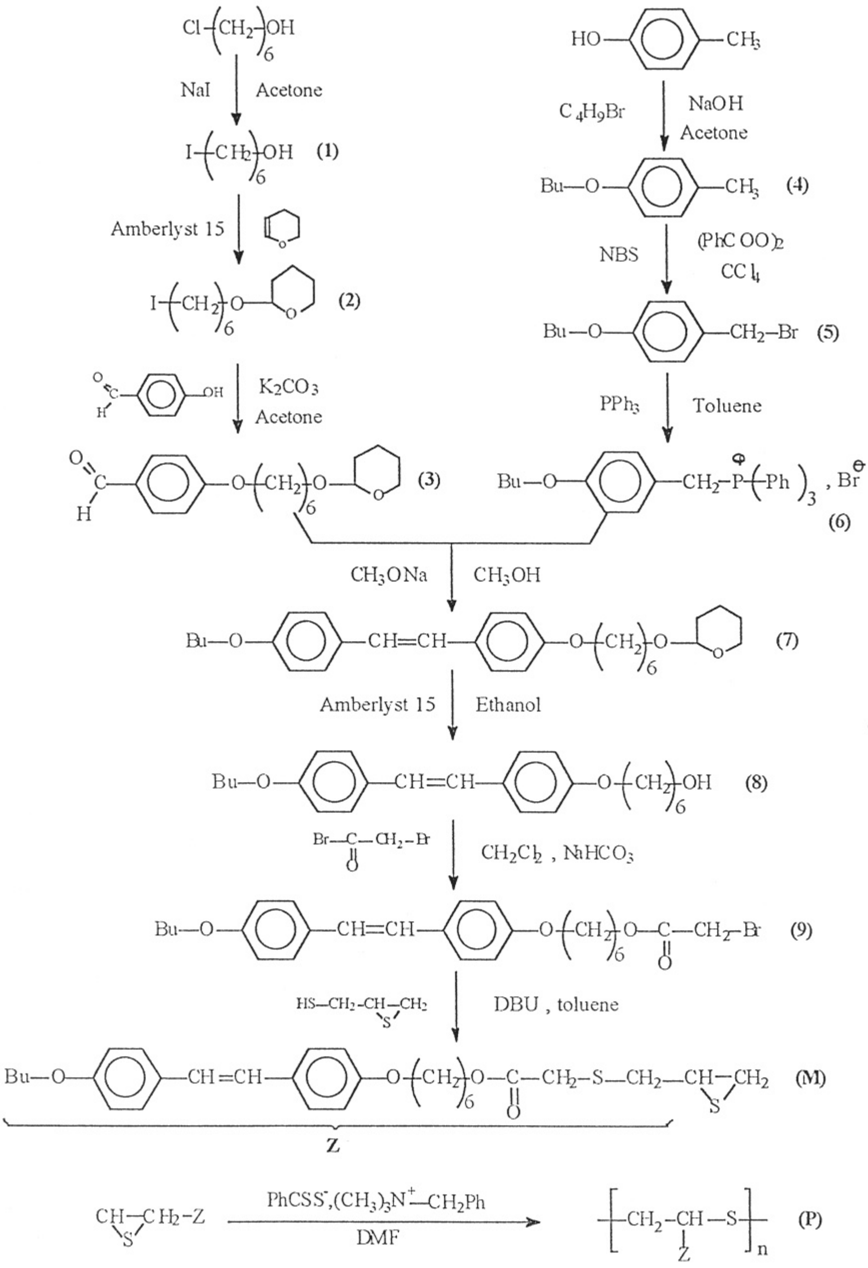


Figure 1 : convergent synthesis of polymer **P**

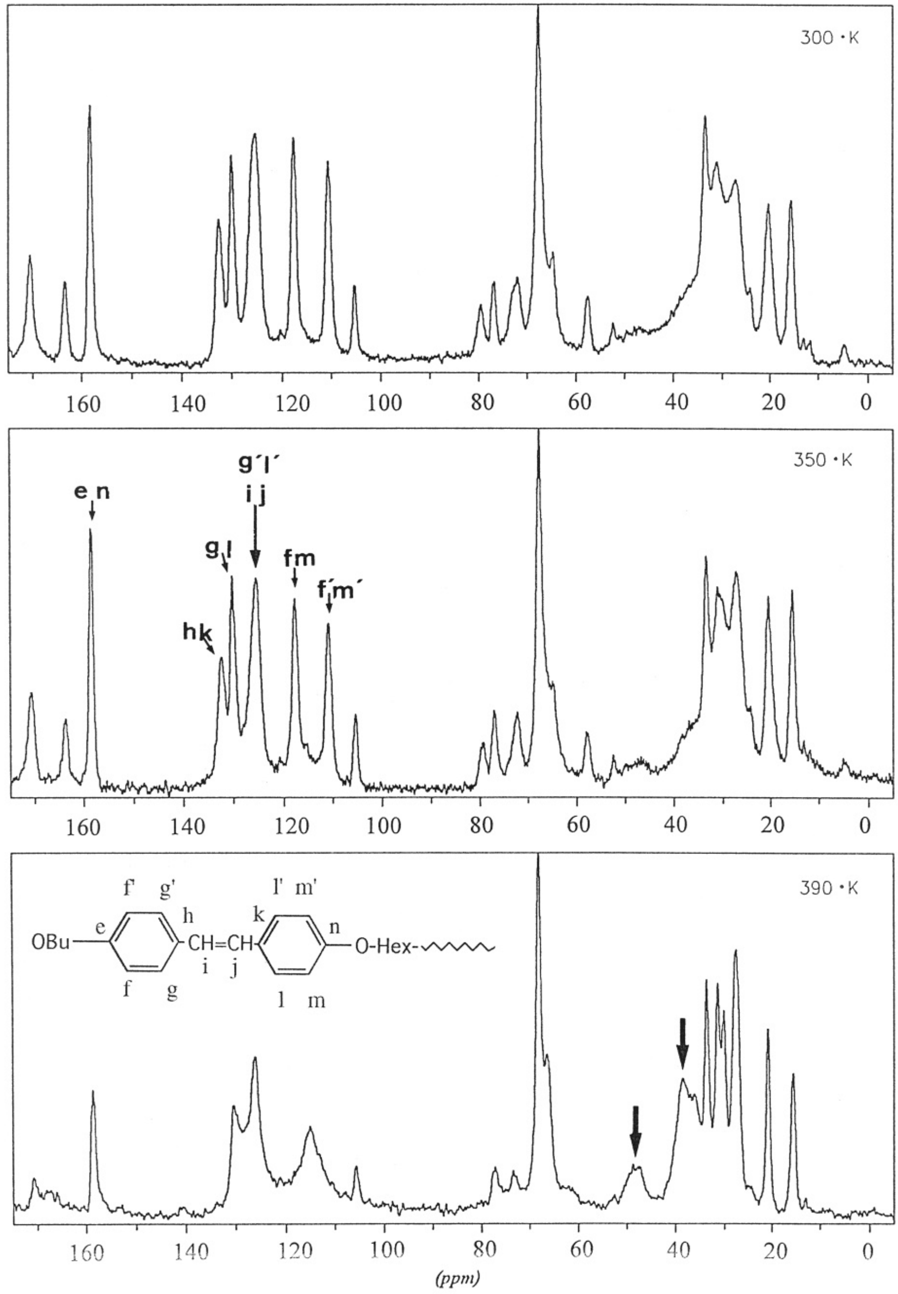


Figure 2 : High resolution CP/MAS ^{13}C NMR of polymer **P** in the solid state at different temperatures

of the signals results from a $^{1}H/^{13}C$ correlation. The configuration of the double bond in the stilbene group was difficult to assign. However, the chemical shifts of the ethylenic protons and the equivalence of some aromatic carbons led us to consider an *E* configuration for **M**. The preferred formation of the *E* stereoisomer was occasionally observed in Wittig reaction (9) : steric constraints in the intermediary betain and oxaphosphorane, both arising from aromatic groups, may account for this result.

The anionic ring opening polymerization of **M** was run as customarily in our laboratory with benzyltrimethyl ammonium dithiobenzoate as an initiator and dimethylformanide (DMF) as a solvent. The monomer/initiator ratio was 100 /2 which leads to a theorical DP_n = 50 as in our previous studies (1,2). We obtained **P** in quantitative yield but as a weakly soluble product; it was soluble only in polar solvents such as refluxing pyridine and N-methylpyrrolidone near 150°C. As previously prepared SCLC polythiiranes were soluble in usual solvents, the low solubility of polymer **P** might be explained by strong Van der Waals interactions between the stilbene groups with the same configuration and/or a high DP_n (>> 50) resulting from the presence of impurities which “killed” some amounts of the initiator. The elementary analysis of **P** was in accordance with the empirical formula.

So, **P** was characterized by high resolution CP/MAS ^{13}C NMR in the solid state at different temperatures (figure 2); these spectra were compared with those of the monomer and those of other polymers of the series (1). These comparisons allowed an identification of polymer **P**. The main results in the solid state NMR are observed between 350 and 390 K. Signals at 38.3 and 48.6 ppm appear ; they are absent in monomer spectrum and their positions, in accordance with other polythiiranes, are characteristic of carbons in the main chain of polythiiranes: the presence of these signals confirms the thiirane ring opening. At lower temperature the main chain is motionless and these signals do not appear. Other modifications occur in the ^{13}C NMR spectrum between 350 and 390 K; they involves some motions of the functional groups of the molecule and are characteristic of theses different groups. Signals at 158 and 132 ppm, as in the monomer, could be attributed to the aromatic carbons **e, h, k, n** (figure 2). The decrease of these signals shows the starting of the rotation of aromatic cycles : there is a decrease of the polarisation transfer between ^{1}H and ^{13}C. Both signals at 110 and 117 ppm coalesce into a single one at 114 ppm at 390 K; these signals could be assigned to carbons **f, f', m, m’** which become equivalent at this temperature : this coalescence is due to the rotation of the aromatic cycles but more particularly to the motion of butoxy and hexyloxy chains. The signals of the carbons **g, g’, l , l’**, observed at 125 and 130 ppm are also coalescing at 390 K but in a less extent because the farther butoxy and hexyloxy chains have a weak influence. The unmodified signal at 126 ppm could be attributed to the ethylenic carbons **i** and **j**. Motional narrowing are also viewed on the peak at 30 ppm which splits into two lines as the temperature is increasing.

The thermal properties of the polymer were investigated by usual techniques. In DSC both enantiotropic transitions are observed but as usual in this series, we can not detect the glass transition (figure 3). The corresponding textures were determined by observation on the optical polarizing microscope. At the upper temperatures, a focal-conic texture characteristic of a smectic phase is observed; at lower temperatures a striated texture appears. The X-ray diffraction pattern of both mesophases allows their assignement.

At 170°C a single peak in the wide angle region (2 θ = 20.1°) is consistent with a Sm B mesophase ; from the diffraction ray in the small angle region (2 θ = 4.87°), the lamellar thickness is evaluated at 36.4 Å. At 160°C, in the wide angle region two diffractions at θ = 21.2° and 2 θ = 19.8° are consistent with a Sm E mesophase. The d-spacing is then evaluated at 37.8 Å. The length of the side chain was calculated for a polymer with the same spacer and the same terminal group, but a biphenyl unit as mesogen core (1) : 27.98

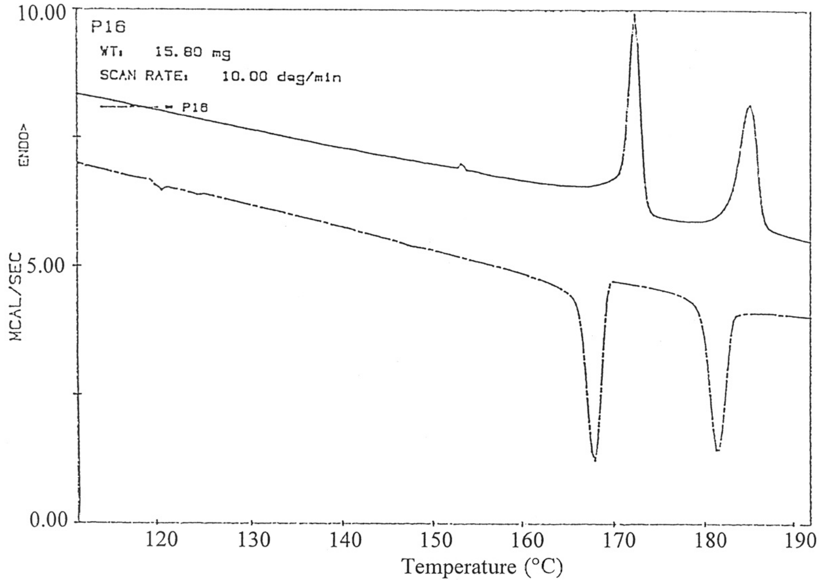


Figure 3 : DSC curves for polymer **P**

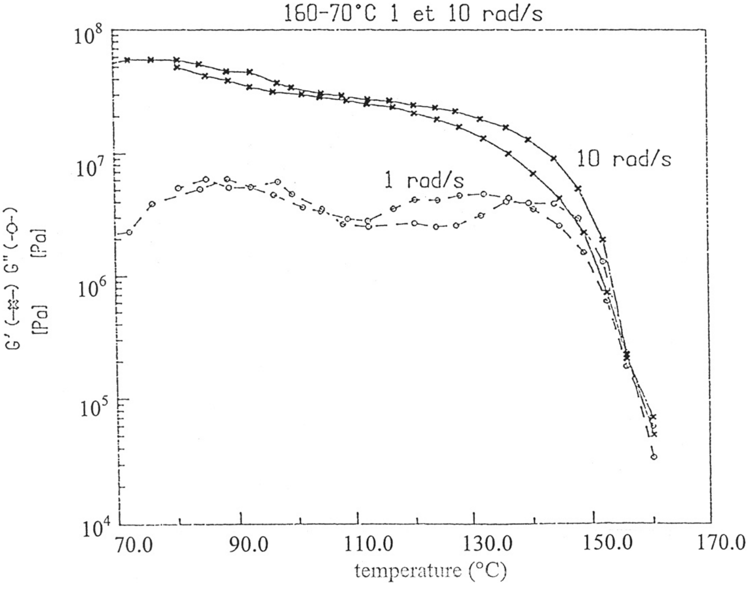
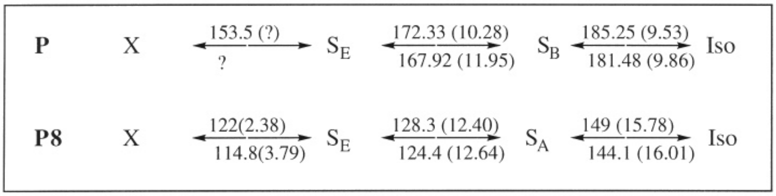


Figure 4 : Dynamical mechanical thermal behaviour of polymer **P**



P	X	$\underset{?}{\overset{153.5\ (?)}{\longleftrightarrow}}$	S_E	$\underset{167.92\ (11.95)}{\overset{172.33\ (10.28)}{\longleftrightarrow}}$	S_B	$\underset{181.48\ (9.86)}{\overset{185.25\ (9.53)}{\longleftrightarrow}}$	Iso
P8	X	$\underset{114.8(3.79)}{\overset{122(2.38)}{\longleftrightarrow}}$	S_E	$\underset{124.4\ (12.64)}{\overset{128.3\ (12.40)}{\longleftrightarrow}}$	S_A	$\underset{144.1\ (16.01)}{\overset{149\ (15.78)}{\longleftrightarrow}}$	Iso

X = crystalline ; S_A = smectic A ; S_E = smectic E ; S_B = smectic B ;Iso : isotropic liquid
Table 1 Phase transition temperatures in °C (enthalpy in $J.g^{-1}$)

Å. So, we can conclude that this SCLC polythiirane is probably arranged in a monolayered structure.

A noteworthy result of this study is the emergence of mesomorphism in this polythiirane bearing 4,4'-alkoxy stilbene units, while stilbene derivatives like 4,4'- dihexyloxystilbene do not exhibit any liquid crystalline mesomorphism (5). As well as the other polythiiranes, this polymer exhibits smectic mesophases while polyacrylates or polymethacrylates with stilbene mesogens exhibit mainly nematic mesophases and lower transitions temperatures (3,4).

The comparison between the thermotropic behaviour of polymer **P** and the previously prepared polymer **P8** (1) (Table 1) shows some important results :

- the modification of the nature of the mesogen leads to a different Sm phase in the upper temperatures.
- the general trend observed about the influence of the mesogene length on phase transitions (10) is confirmed : an increase of the mesogene length leads to an increase of the thermal stability.
- the transition to a SmX phase which was characterized as a crystalline phase (2) was observed in **P8** at the lower temperatures ; its only appears slightly near 150 °C on the heating DSC curve of **P** and is not obviously observed on the optical polarizing microscope.

The dynamical mechanical thermal properties of polymer **P** were also investigated. The molten polymer was squeezed between 8 mm diameter parallel plates with a thickness around 1 mm. The elastic moduli G' and G" were measured at a given frequency (0.1, 1, 10 rad/s) at temperatures decreasing by steps of 4 °C. As shown in figure 4, a strong increase of the moduli is observed between 160 and 150°C which is accompanied by a maximum of the loss modulus located at lower temperatures as the frequency decreases. This transition might be attributed to the apparition of a smectic mesophase in which the layers are less mobile than in a Sm E, a crystalline phase, affording some stiffness to the polymer. A second transition less pronounced from a mechanical point of view is observed at lower temperatures (90°C) which might correspond to the glass transition of **P**.

In conclusion, although low molecular mass alkyloxy stilbene does not give rise to liquid crytalline properties, its attachment as side group to polythiirane main chain lead to enantiotropic liquid crystalline polymer. In the SCLC polythiirane, the mesogenic stilbene unit only bring slight modifications to the thermotropic properties with regard to biphenyl unit. The influence of the polymer backbone on phase transitions can be discussed by comparison with the literature.

Experimental Part

^1H and ^{13}C NMR spectra were recorded on a Brucker AC 400 NMR spectrometer; tetramethylsilane was used as a standard. ^{13}C NMR spectra in the solid state were recorded on a Brucker MLS 300 spectrometer working at 75 MHz for ^{13}C. A Perkin-Elmer DSC 4 differential scanning calorimeter was used to determine the thermal transitions ; heating and cooling rates were 10°C min-1. A Leitz Ortho-Plan polarizing microscope equipped with a Mettler FP 82 hot stage was used to observe the textures of mesophases. The X-ray diffraction patterns were obtained using a CPS-120 curved counter from inel. The localized CuK_{α_1} X-ray beams were produced by a XRG-2500 generator (inel). Thermomechanic analysis was carried on a Rheometric Dynamic Analyser RDA II.

6-iodohexanol : **1**: was previously prepared and characterized (1)

6-iodo-1-(2-oxanyloxy)hexane : **2** : was prepared according a process described in (11). The product was recovered as an oil. Yield : 82 %

4-[6-(2-oxanyloxy)hexyloxy]benzaldehyde : **3** : was prepared accordindg to (12). The crude product was purified by silica gel chromatography (cyclohexane/acetone; 90/10). Yield: 65 %

4-butoxytoluene : **4** : was prepared from p-cresol and ethyl bromide according to (13)

1-(bromomethyl) -4-butoxybenzene : **5** : *w*as prepared according a process described in (14).

4-butoxybenzyltriphenylphosponium bromide : **6** : was prepared following the method described in (15). Yield 65 % ; mp : 180-183°C
The ^1H NMR spectra of the whole products were in accordance with their structure.

2-[6-(4-(2-(4-butoxyphenyl)vinyl)phenoxy)hexyloxy]oxane : **7**
Sodium methylate was prepared by reacting sodium (0.36 g; 15.6 mmol.) with dry methanol (40 ml) under a nitrogen flow. 4-butoxybenzyltriphenylphosponium bromide (**6**) (5.3 g ; 10.4 mmol.) was added in small amounts while stirring. 4-[6-(2-oxanyloxy)hexyloxy]benzaldehyde (**3**) (3.1 g ; 10 mmol.) dissolved in dry methanol was then added. The mixture was refluxed for 5 hours. The white solid was filtred off, dissolved in dichloromethane. The solution was washed with water, dried and evaporated. Yield : 32 %. mp : 170°C ; ^1H NMR ($CDCl_3$) : $\delta = 0.95$ (s, 3H, CH_3), 1.35-1.85 (m, 18H, CH_2), 3.40 and 3.70 (2 q, 2H, CH_2O in oxane), 3.5 and 3.85 (2 t,2H, CH_2O -cycle) , 3.95 (2 t, 4H, CH_2O-Ar), 4.55 (s, 1H, O-CH-O); stilbene group $\delta = 6.83$ (s, 2H, vinylic), 6.78 (d, 4H, aromatic) 7.32 (d, 4H, aromatic).

6-[4-(2-(4-butoxyphenyl)vinyl)phenoxy]hexanol : **8**
7 was treated by Amberlyst according a process described in (11) in order to de-protected the alcohol function. Yield : 85 %; mp : 172°C; the ^1H NMR spectra showed the disappearance of the tetrahydropyranyl group and a triplet at 3.6 ppm (2H) for the CH_2OH. The other parts of the spectrum were strictly identical with those of **7**.

6-[4-(2-(4-butoxyphenyl)vinyl)phenoxy]hexyl bromoacetate : **9** and *6-[4-(2-(4-butoxyphenyl)vinyl)phenoxy]hexyl (2,3-epithiopropylthio)acetate* : **M**

The crude product **8** was used to lead to monomer **M**. The reactions were carried out as we have described them in our previous work (1), the synthesis of bromoacetate proceeding in dichloromethane. **9** and **M** were obtained in both last steps in quantitative y¡elds.

9 was obtained as a white solid : mp : 138°C ; its ^{1}H NMR spectrum was identical with **8** and a triplet at 4.1 ppm (CH_2O) and a singlet at 3.75 ppm (CH_2Br) confirmed the presence of the bromoacetate group.

M was purified by silica gel chromatography (cyclohexane/ acetone: 95/5) ; mp : 120-122°C.

^{1}H NMR ($CDCl_3$) : δ : 0.90 (t, 3H, CH3), 1.42 (m, 6H, CH2), 1.65-1.71 (m, 6H, CH_2), 2.20 and 2.48 (2d, 2H, CH_2 thiirane), 2.62 and 3.05 (m, 3H, CH_2S et CH thiirane), 3.24 (s, 2H, $OCOCH_2S$, 3.89 (t, 4H, CH_2O-Ar), 4.07(t, 2H, CH_2OCO-), 6.80 (2d, 4H, aromatic), 6.85 (s, 2H, CH=CH), 7.32 (d, 4H, aromatic H)

^{13}C NMR ($CDCl_3$) : δ 12.85 (CH_3), 18.22 (CH_2-CH_3), 24.63 (CH_2CH_2OCO), 25.63 (CH_2 thiirane), 25.69 (CH_2CH_2O), 27.47 and 28.11 (CH_2 in hexyl), 30.30 ($CH_2CH_2CH_3$), 32.32 (CH thiirane), 32.72 (CH_2COO), 32.72 (CH_2COO), 37.51 (CH_2S), 64.47 (CH_2OCO), 66.70 and 66.72 (CH_2OAr), 113.62, 133.64, 126.33, 129.21, 129.37, 157.41, 157.55, (aromatic C), 124.98 and 125.13 (ethylenic C)

Polymerization and polymer

The polymerization was performed in DMF as previously described (1). The insoluble product obtained **P** was carefully washed with ether and dried.

$(C_{29}H_{38}O_4S_2)n$ $(514,7)_n$	Calc.	C 67.67	H 7.44	S 12.46
	Found	C 67.61	H 7.45	S 12.11

Acknowledgements

DSC, optical polarising microscopy, RX measurements were realized at IPCM, Strasbourg with the collaboration of Dr A. Skoulios. Prof. J.F. Tassin (Université du Maine, Le Mans) and Prof. G. Levesque (Université de Bretagne Sud, Lorient) contributed to this work by helpful discussions.

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