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Coupling order and conductivity. Liquid crystalline conjugated polymers

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Coupling order and conductivity
Liquid crystalline conjugated polymers

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Acetylenic and diacetylenic liquid crystalline monomers have been prepared in order to obtain conjugated polymers with an orientational character. Unlike the polydiacetylene derivatives obtained and which do not exhibit any mesomorphic behaviour, a smectic phase, stable over a large temperature range, occurs in the case of all the polyacetylenes. This mesophase appears to be stabilized by an *in situ* polymerization of the monomers oriented in the nematic state. After iodine doping, a nematic phase appears in the polymer in addition to the smectic phase. AC complex conductivity measurements, realized over a large frequency range, are reported for some doped and undoped polyacetylenes. Preliminary results concern both non-oriented polymers and an undoped polymer in which the mesogenic groups have been oriented after polymerization.

1. Introduction

Association of electrical conduction and microscopic or macroscopic order has been proved promising in recent years. Different methods may be used to couple order with other physical properties. For instance polyacetylene films prepared by polymerization in a liquid crystal solvent exhibit an enhanced conductivity as well as an anisotropic electrical behaviour [1, 2]. In the same way, mechanical stress is commonly used to achieve a crucial improvement in one-dimensional character [3, 4], and a clear correlation has been found between conductivity and tensile strength [5]. Both these methods improve the physical properties of the polymer, introducing order during or after polymerization through an external constraint (ordered solvent or mechanical stress). However the polymers obtained do not exhibit intrinsic orientability.

In order to obtain a strong and permanent coupling between order and electroactive properties, orientable groups have to be directly linked to the polymer. Side-chain liquid crystalline polymers are known to allow orientation of mesogens [6] by a magnetic field, for example, and consequently an induced anisotropic conformation of the backbone arises. Furthermore if the mesogenic moiety is chemically bonded to the monomer leading to a liquid crystalline entity, we can expect to achieve polymerization in an oriented mesophase. This has been proved to give highly ordered

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polymers [7]. Side-chain liquid crystalline polymers, obtained from conjugated backbones, have been recently considered, and some mesogenic acetylenic and diacetylenic monomers have been synthesized [8–14] and first polymerizations reported. Likewise, some liquid crystalline polynitriles or polydipropargylacetate derivatives have lately been obtained [15, 16]. Some of these polymers are mesomorphic, but for none of them has the benefit of the liquid crystalline properties been used either during polymerization or for anisotropic conductivity measurements.

Concerning the electronic properties, measurement of the complex conductivity is a suitable way of studying conduction mechanisms in the solid state and it can be used for conducting polymers [17]. Many results published up to now concern the DC conductivity, and a few papers on the AC behaviour are available in the literature. Furthermore, only a few data are reported on the DC conductivity anisotropy of oriented conducting polymers [1–5].

In this paper we report on the synthesis and polymerization of new acetylenic and diacetylenic monomers substituted by mesogenic groups. The monomers prepared are shown to exhibit thermotropic mesomorphic behaviour over a temperature range allowing polymerization in an oriented phase. Preliminary results on the AC frequency dependence of the complex conductivity are given for a substituted polyacetylene, both in a non-oriented state and in an oriented mesophase.

2. Materials and polymorphism

2.1. *Acetylenic derivatives*

2.1.1. *Acetylenic monomers*

Classical mesogenic phenylbenzoate moieties have been chosen to substitute acetylenic monomers

(A_3C_m)

Two parameters are adjustable in these systems: the length of the spacer and the length of the end chain. To ensure coupling between the chain conformation and the mesogenic order, a short spacer with three carbons has been used. The length of the end chain (m) allows tuning of the liquid crystalline properties. The polymorphism of a series of acetylenic monomers with a spacer of three carbons and an end chain length equal to 1, 4 or 8 is presented in table 1.

With methoxy and butoxy tails, the monomers present only a metastable (monotropic) nematic phase. Lengthening of the aliphatic chain induces enantiotropic mesophases: the last compound ($m = 8$) exhibits enantiotropic smectic A and nematic phases. The temperature range over which these phases are stable is compatible with the polymerization conditions used for such compounds and allowed us to consider polymerization in an oriented phase. Usually, however, the polymerization of acetylene

Table 1. Phase transition temperatures (°C) for the acetylenic monomers (A_3C_m).

m	C		S_A		N		I
1	●	93			●	[53]†	●
4	●	91			●	[72]	●
8	●	45	●	57	●	73	●

†[ ] denotes a monotropic transition.

compounds is performed in solution, excluding the possibility of taking advantage of the mesogenic ordering. Polymerization in an oriented thermotropic mesophase requires the use of a bulk polymerization method.

2.1.2. *Polyacetylenes*

The monomers with $m=1$ and 4 exhibit only monotropic phases. Their polymerization was performed by metathesis in solution using a $WCl_6/SnMe_4$ catalyst/cocatalyst system. The monomer with $m=8$, presenting a stable nematic phase, has been more extensively studied. In order to achieve polymerization in bulk, in the ordered nematic phase, polymerization was planned on the basis of the experiments made in solution. The reaction temperature was chosen within the temperature range of the nematic state. It was observed that, in this case, polymerization could be successfully performed using WCl_6 alone, without any cocatalyst. So this monomer has been successively polymerized not only in solution, but also in bulk with or without cocatalyst and in a nematic monodomain state. In this latter case, the monomer is first macroscopically aligned by a uniform magnetic field of 1 Tesla (see figure 1). In order to assure alignment, the sample is heated into the isotropic state, then held constant at a chosen temperature inside the nematic range. The polymerization is initiated by introducing the catalyst. The magnetic field and the temperature are kept constant during the whole polymerization process.

The characteristics of the polymers PA_3C_m so obtained are summarized in table 2. Toluene induces low molecular weight materials due to the low solubility of the polymer in this solvent. The use of tetrahydrofuran leads to higher molar mass

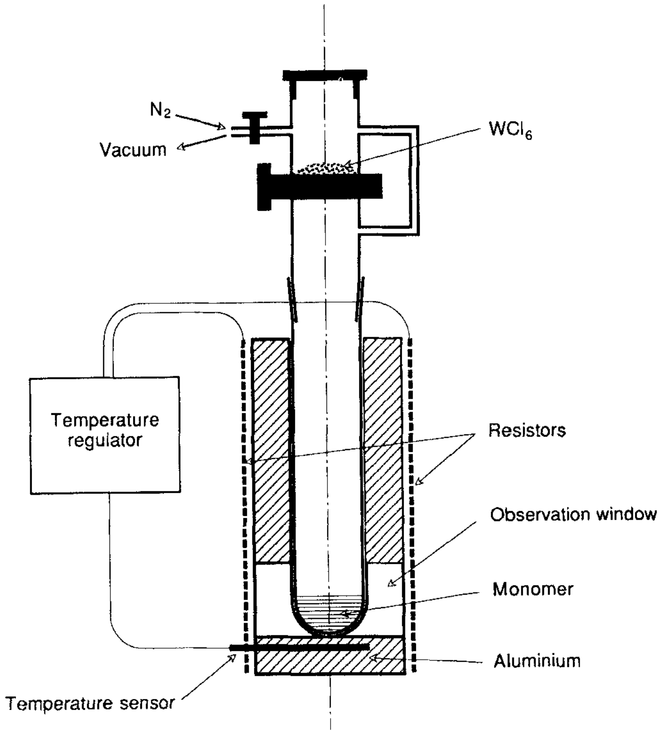


Figure 1. Apparatus for polymerization in a magnetic field.

Table 2. Polymerization of acetylenic derivates (PA_3C_m).

Polymerization conditions					Polymer characteristics				
m	Solvent or bulk	Catalyst	Temperature/ °C	Time/ h	Molecular weight† M_{peak}/g mol^{-1}	T_g/ °C‡	Polymorphism/°C§ S		I
1	Toluene	WCl_6/S_nMe_4	50	18	14000	20	●	138	●
1	THF	WCl_6/S_nMe_4	50	18	30000	20	●	142	●
4	THF	WCl_6/S_nMe_4	50	18	30000	36	●	135	●
8	THF	WCl_6/S_nMe_4	50	18	35000	46	●	144	●
8	Bulk	WCl_6/S_nMe_4	65	18	30000	38	●	137	●
8	Bulk	WCl_6	65	18	26000	37	●	156	●
8	Oriented N phase¶	WCl_6	65	96	25000	32	●	166	●

† Average molecular weight corresponding to the top of the peak obtained by gel permeation chromatography, with respect to polystyrene.

‡ Glass transition temperature determined by differential scanning calorimetry (DSC).

§ Transition temperature determined by microscopic observation.

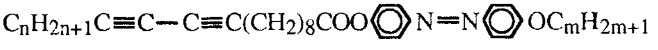
¶ Alignment of monomer by a magnetic field.

polymers. It is noteworthy that the polymers obtained by bulk reaction have molecular weights in the same range. In the same way, the molecular weights of the polymers obtained without cocatalyst remain comparable to those of the other polymers. Therefore, owing to the simplification of the initiation procedure without cocatalyst, this method has been used for the polymerization in the oriented phase. The polymerization reaction in the oriented phase, where stirring must be avoided, is notably slower due to the high viscosity of the sample.

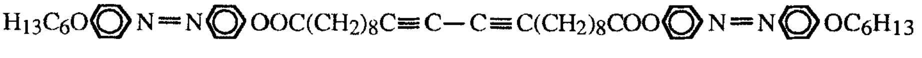
All the polymers, whether synthesized in bulk or in solution, are red–orange materials and exhibit smectic behaviour over a large temperature range. The layer spacing (38 Å), determined by X-ray diffraction experiments on powder samples, is slightly larger than the molecular length of the side group in its most extended conformation (32 Å). The octyloxy monomer ($m=8$), polymerized under a magnetic field in its oriented nematic phase, shows an enhancement of the clearing temperature, suggesting that the polymer has a better organization. Structural analysis of these materials is in progress in order to clarify the influence of the polymerization conditions on the mesophase stability.

2.2. *Diacetylenic derivatives*

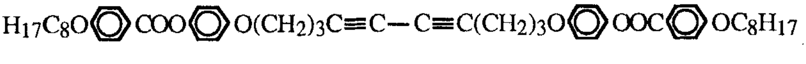
Diacetylenic derivatives appear promising owing to their ability to polymerize in bulk under radiation (UV, X, γ). Unsymmetrical and symmetrical diacetylenic molecules incorporating either one or two identical mesogenic moieties have been synthesized and their characterization is given in table 3.



(DA_nN_m)



($DA(_8N_6)_2$)



($DA(_3C_8)_2$)

Table 3. Phase transition temperatures (°C) for diacetylenic monomers.

Compound	C		S_B†		N		I
DA_nN_m							
n m							
4 1	●	61					●
4 6	●	82					●
5 1	●	78					●
$DA(_8N_6)_2$	●	126					●
$DA(_3C_8)_2$	●	136·5	●	145·5	●	149	●

† Ordered smectic phase characterized by textural observation only.

It is clear from table 3 that all the azo derivatives, both mono- and di-substituted, display only crystalline phases. On the other hand, the diacetylenic monomer disubstituted by phenyl benzoate moieties ($DA(_3C_8)_2$) exhibits two stable mesomorphic states, a smectic phase and a nematic phase. From observation of the texture by optical microscopy, the smectic phase has been identified as an ordered B phase.

The polymerization of the diacetylenic derivatives has been attempted using irradiation (UV, γ) or by heating. Compound DA_4N_1 was successfully polymerized using UV or γ irradiation. The resulting orange material is insoluble in common solvents. The colour change and the insolubility are evidence of the occurrence of polymerization leading to conjugated double bonds. However the orange colour corresponds to a rather short conjugation length [18]. No mesomorphic behaviour was detected by optical observation in the polarizing microscope. For the other monomers, polymerization failed in the solid state using UV or γ irradiation. These results agree with those already reported for similar compounds [11]: the polymerization of diacetylenic derivatives following a 1–4 topochemical mechanism, small variations in the architecture of the monomer can completely modify the polymerization reactivity. A thermal polymerization was carried out on the $DA(_3C_8)_2$ material in its isotropic state ($T = 160°C$). This resulted in a soluble, dark brown material. Purification by gel permeation chromatography gave a polymer of average molecular weight, $M_{\text{peak}} = 10\,000\,\text{g mol}^{-1}$. This polymer, when observed by optical microscopy, did not exhibit thermotropic mesomorphic behaviour. Structural analysis, using NMR, is in progress in order to elucidate the type of polymerization reaction (1–4 or 1–2 addition) undergone by this material.

3. Electronic conductivity

We report here preliminary results on the frequency dependence of the complex conductivity of the substituted polyacetylene PA_3C_8 (undoped or iodine doped samples, and an undoped sample in which orientation of the mesogenic groups had been achieved by a magnetic field).

The conductivity is a complex quantity usually defined as $\sigma^* = \sigma' + j\sigma''$, where σ' is the real part of the sample conductivity, and σ'' the imaginary component. Formally, σ^* is related to the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ by the relation $\sigma^* = j\omega\varepsilon_0\varepsilon^*$, where ω is the angular frequency of the applied field and ε_0 the vacuum permittivity. In this article, data are presented using traditional parameters:

—real conductivity: $\sigma' = \sigma = \omega\varepsilon_0\varepsilon''$

—relative dielectric constant: $\varepsilon' = \varepsilon = \sigma''/\omega\varepsilon_0$

Typical data for the frequency dependence of σ and ε are shown for the three samples that follow:

(i) *Undoped PA_3C_8*

This polymer has been synthesized in bulk using WCl_6 as catalyst. The DC conductivity is about $10^{-11}\,\Omega^{-1}\,cm^{-1}$, and the relative dielectric constant is 2·5–3 (see figures 2(*a*) and (*b*)).

(ii) *Doped PA_3C_8*

The iodine doping of the above polymer was performed by exposure to the vapour during 2 days. The UV spectrum (in CH_2Cl_2) of doped PA_3C_8 is shown in figure 3(*a*) and it exhibits three absorption peaks: 260 nm from the conjugated backbone, and 365 nm and 500 nm assigned respectively to the I_3^- and I_2 species [19]. As shown in figure 3(*b*), free I_2 can be removed from doped PA_3C_8 under a dynamic vacuum. The final amount of I_3^-, determined by weighing, is about 1 for every 4 monomer units.

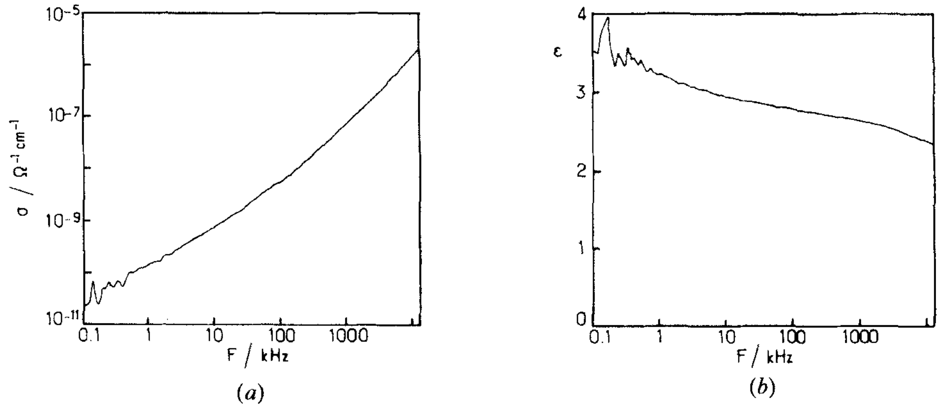


Figure 2. Conductivity (*a*) and relative dielectric constant (*b*) versus frequency for PA_3C_8.

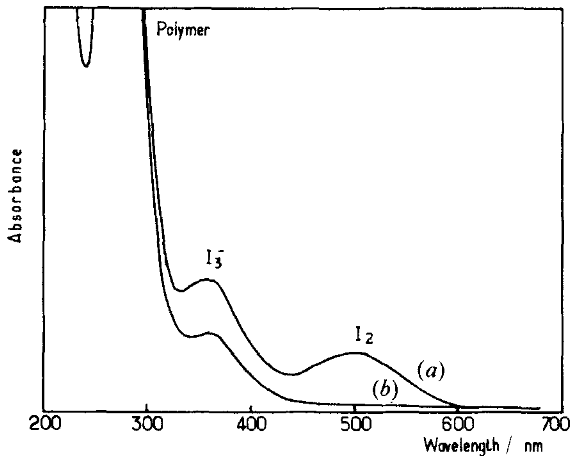


Figure 3. UV spectra of PA_3C_8 upon iodine doping before (*a*) and after (*b*) evaporation of I_2 under vacuum.

The corresponding doped polymer remains mesomorphic. However, this character is changed, since the clearing temperature is determined as 112°C, and a nematic phase replaces the smectic phase at high temperature

Doped PA_3C_8: S 85°C N 112°C I.

The emergence of a nematic phase should make the orientation of the mesogenic groups easier. On the other hand, the smectic phase should induce a notable conformational anisotropy of the polymer aligned by a magnetic field [20].

Figure 4 (*a*) shows that the conductivity of the I_3^- doped polymer increases ($\sigma_{DC} = 5 \times 10^{-8}\,\Omega^{-1}\,cm^{-1}$), and can be separated into a frequency-independent contribution corresponding to σ_{DC}, which is predominant in the low frequency region, and a frequency-dependent contribution σ_{AC}, which becomes appreciable at high frequencies. Then, the total conductivity can be expressed by: $\sigma(\omega) = \sigma_{DC} + \sigma_{AC}(\omega)$. The importance of each component depends on the doping level.

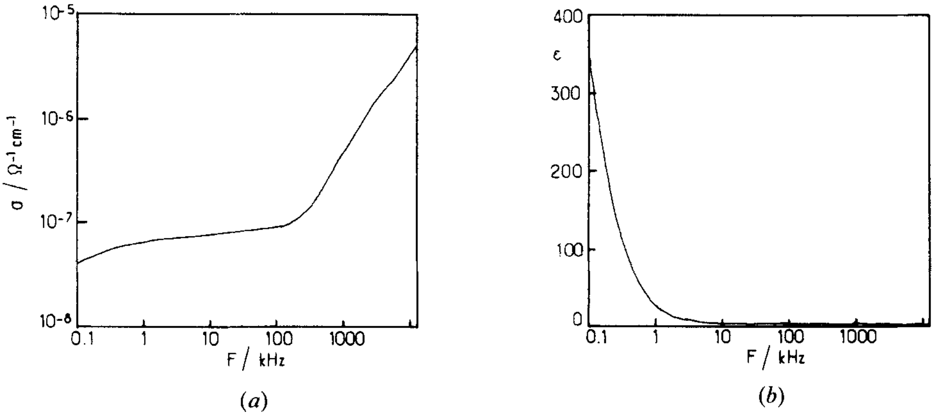
The relative dielectric constant of I_3^- doped polymer increases rapidly as the frequency decreases (see figure 4 (*b*)), following the losses due to the conductivity.

(iii) *Oriented (homeotropic alignment), undoped PA_3C_8*

The cell (thickness: 200 μm) is set up in a magnetic field of 4·7 Tesla and heated into the isotropic state of the polymer. Homeotropic orientation of the mesogenic groups is achieved by slowly cooling in the mesophase at 4°C h^{-1}, and is finally frozen in below the glass transition temperature.

The conductivity of the oriented undoped polymer ($\sigma_{DC} \approx 10^{-9}\,\Omega^{-1}\,cm^{-1}$) is higher than that of the non-oriented sample, while the dielectric constant remains at 2–2·5, without heavy losses through conductivity (see figures 5 (*a*) and (*b*)). Doping should be achieved in this oriented polymer in order to determine the effective contribution of the orientation to the conductivity value.

These preliminary results show that orientation of a side-chain conjugated polymer enhances its conductivity. Future prospects will consist of optimization of doping and the orientation of a doped sample. Thus, parallel and perpendicular orientation of the mesogenic groups (relative to the applied electric field) should be achieved in order to carry out complete measurements and reveal any conductivity anisotropy.



(*a*) (*b*)

Figure 4. Conductivity (*a*) and relative dielectric constant (*b*) versus frequency for I_3^- doped PA_3C_8.

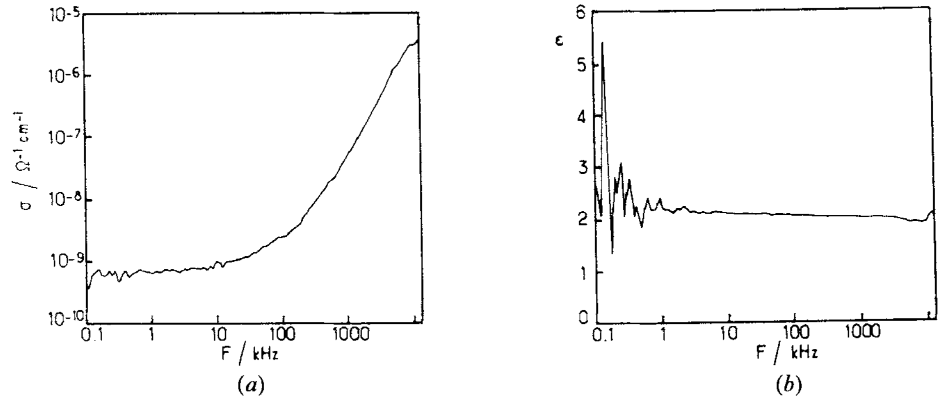


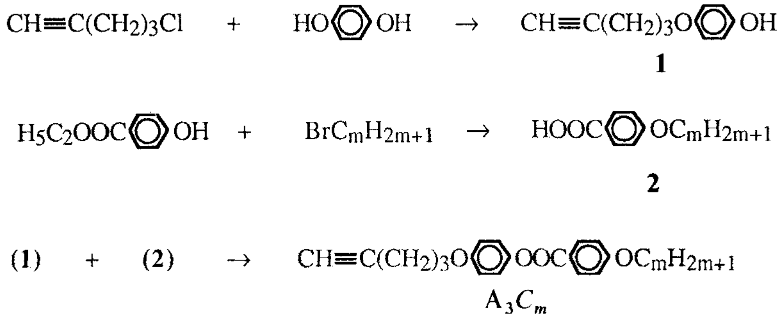
Figure 5. Conductivity (*a*) and relative dielectric constant (*b*) versus frequency for homeotropically oriented PA_3C_8.

4. Experimental

4.1. *Synthesis of acetylenic derivatives*

4.1.1. *Monomers*

A_3C_m monomers were obtained by the following chemical scheme:



A typical procedure for which $m = 8$ is given below.

4-(Pent-4-ynoxy) phenol (**1**): 10·1 g (0·18 mol) of KOH were dissolved in 100 ml of ethanol, and 33·6 g (0·305 mol) of hydroquinone were added. The solution was heated under reflux while a solution of 12·6 g (0·12 mol) of 5-chloropent-1-yne in 250 ml of ethanol was slowly added. The reaction mixture was boiled for 20 h. The solvent was then evaporated off and the residue added to 100 ml of water/ice. The product was filtered off, washed with water, dissolved in ether, and dried over Na_2SO_4. Purification was effected on a silica gel column, with a 1 : 1, hexane/ether mixture as eluent. Yield: 8·1 g (38 per cent). ^1H NMR (CD_3COCD_3, δ) : 2–2·1 (2 H, C–CH_2–C; 1 H, C≡CH), 2·5 (2 H, C≡C–CH_2), 4 (2H, OCH_2), 6·8 (4 H arom.), 7·8 (1 H, OH).

4-Octyloxybenzoic acid (**2**): 7·8 g (0·14 mol) of KOH were dissolved in 300 ml of ethanol, and then 16·6 g (0·1 mol) of ethyl 4-hydroxybenzoate were added [21]. The solution was heated under reflux while a solution of 18·1 ml (0·105 mol) of 1-bromooctane in 200 ml of ethanol was slowly added. The reaction mixture was boiled for 5 h, when more KOH (28 g, 0·5 mol) was added and the solution heated and stirred for 3 h. The solvent was evaporated, the residue was acidified with 50 ml of 12M-HCl (pH = 1), and the product filtered off and washed with water (until pH = 7). The product was purified by recrystallization from ethanol. Yield: 15·1 g (60 per cent). ^{1}H NMR ($CDCl_3$, δ): 1 (3 H, CH_3), 1·4 (10 H, C–CH_2–C), 1·8 (2 H, O–C–CH_2), 4 (2 H, OCH_2) 6·9 (2 H arom. *ortho* to O*R*), 8 (2 H arom. *ortho* to COO).

4-(*Pent-4-ynoxy*)*phenyl 4-n-octyloxybenzoate* (A_3C_8): 2·5 g (0·01 mol) of (**2**) were dissolved in 15 ml of thionyl chloride, and boiled for 2 h. The excess of $SOCl_2$ was removed during 1 h under vacuum, and the residual acid chloride was immediately added to a solution of 1·76 g (0·01 mol) of (**1**) in 10 ml of freshly distilled pyridine. The reaction mixture was stirred, excluding light, at room temperature for 20 h, and then added to 20 ml of HCl/ice. The product was extracted with ether, washed with water until pH = 7, dried over Na_2SO_4, and recrystallized twice from ethanol. Yield: 1·7 g (42 per cent). ^{1}H NMR ($CDCl_3$, δ): 1 (3 H, CH_3), 1·4 (10 H, C–CH_2–C), 1·8 (2 H, O–C–CH_2), 2–2·1 (2 H, C≡C–C–CH_2–C–O; 1 H, C≡CH), 2·5 (2 H, C≡C–CH_2), 4 (4 H, OCH_2), 6·9–7·1 (6 H arom. *ortho* to O*R*), 8·1 (2 H arom. *ortho* to COO).

4.1.2. *Polymerization in oriented nematic phase*

Monomer (~ 1 g) was introduced into the lower part of the reactor (see figure 1) and kept under nitrogen. WCl_6 (3 per cent mol/monomer) was introduced into the upper part under a nitrogen flow. The apparatus was set in a magnetic field, and the temperature was slowly reduced from 80 to 65°C (nematic phase of monomer). By opening the tap, WCl_6 was brought into contact with the monomer and polymerization took place slowly (4 days). The reaction was stopped by addition of methanol. The polymer was dissolved in dichloromethane and precipitated into a large excess of acetone; it was then filtered off, purified on Celite, and dried under vacuum. Yield: 25 per cent.

4.2. *Synthesis of diacetylenic derivatives*

4.2.1. *Monomers*

DA_nN_m monomers were synthesized according to the following scheme:

$$C_nH_{2n+1}C{\equiv}CH + HOBr \rightarrow C_nH_{2n+1}C{\equiv}Br$$

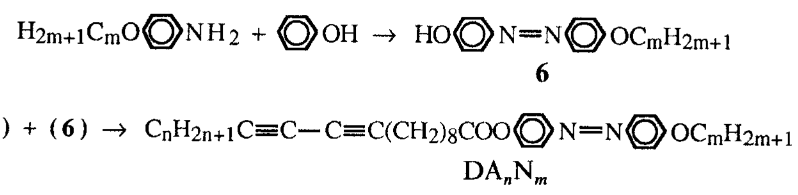
3

$$CH{=}C(CH_2)_8COOH \rightarrow CH{\equiv}C(CH_2)_8COOH$$

4

$$(\mathbf{3}) + (\mathbf{4}) \rightarrow C_nH_{2n+1}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$$

5



6

DA_nN_m

A typical procedure for which *n* and *m* are 4 and 6, respectively is given below.

1-*Bromohex-1-yne* (**3**): 10 g (0·25 mol) of NaOH in water (10 M) and 66·4 g (0·415 mol) of bromine were added to 200 g of ice. More NaOH was added until the mixture turned yellow, and then 6 g (0·422 mol) of hex-1-yne were added [22]. The reaction mixture was stirred at room temperature for 20 h, the organic product extracted with ether, and the extract dried over Na_2SO_4. The product was recovered by evaporating the ether. Yield: 51·9 g (76 per cent). ^{1}H NMR ($CDCl_3$, δ): 0·9 (3 H, CH_3), 1·2 (4 H, CH_2), 2·2 (2 H, CH_2–C≡C).

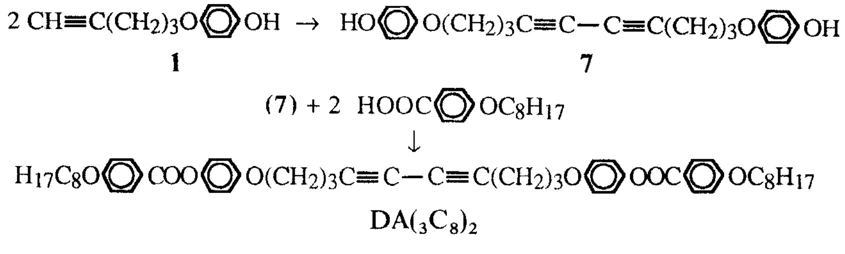
Undec-10-ynoic acid (**4**): 77·3 g (0·420 mol) of undec-10-enoic acid were dissolved in 210 ml of freshly distilled CCl_4, and the mixture was then cooled by NaCl/ice. 68 g (0·425 mol) of bromine were added slowly while the mixture was stirred vigorously [23]. The mixture was allowed to warm up to room temperature and CCl_4 was removed under vacuum. A solution of 184·8 g (3·3 mol) of KOH in 50 ml of H_2O was added to this product, the mixture was heated to 160°C for 8 h, then cooled, and 800 ml of H_2O/H_2SO_4 added until pH = 3. The product was extracted by ether; the extract was washed with water, dried over Na_2SO_4, and the ether evaporated. The product (yellow oil) was distilled under vacuum. Yield: 30·8 g (40 per cent). ^1H NMR ($CDCl_3$, δ): 1·2 (10 H, CH_2), 1·3 (2 H, CH_2–C–COOH), 2 (1 H, CH≡C), 2·2 (2 H, CH_2–COOH; 2H, CH_2–C≡C). IR: 2200 cm^{-1} (C≡C).

Heptadeca-10,12-diynoic acid (**5**): a mixture of 40 ml of 30 per cent aqueous dimethylamine (0·27 mol), 200 mg (0·002 mol) of copper (I) chloride, 650 mg (0·009 mol) of hydroxylamine hydrochloride, and 22·6 g (0·124 mol) of **4** in 400 ml of 10 per cent aqueous KOH was cooled to 0°C [22]. Then, while stirring, a solution of 20 g (0·124 mol) of (**3**) in 50 ml of methanol was slowly added. The reaction mixture was stirred at room temperature for 1 h, and then acidified with 400 ml of M-H_2SO_4. The product was extracted into ether; the extract was washed with M-H_2SO_4 and water, dried over Na_2SO_4, and the ether evaporated. The product was purified by recrystallization from light petroleum. Yield: 17·9 g (55 per cent). ^1H NMR ($CDCl_3$, δ): 0·9 (3 H, CH_3), 1·2 (14 H, CH_2), 1·3 (2H, CH_2–C–COOH), 2·2(4 H, CH_2–C≡C; 2 H, CH_2–COOH).

4-(4-Hexyloxyphenylazo)phenol (**6**): 3·78 g (19·5 mmol) of 4-hexyloxylaniline, recrystallized from light petroleum, were dissolved in 8 ml of H_2O and 20 ml of 3 M-HCl slowly added [24]. The mixture was cooled to 0°C. A solution of cooled 6 M-$NaNO_2$ was then added, and the reaction mixture stirred for 2 h at 0°C. This solution was added to a solution of 1·84 g (19·5 mmol) of phenol, 0·8 g of NaOH and 2·3 g of Na_2CO_3 in 26 ml of H_2O at 0°C. The mixture was stirred for 1 h at 0°C, and acidified with 20 ml of 3 M-HCl until pH = 2–3. The product was extracted into ether, and the extract washed with water and dried over Na_2SO_4. The residue after removal of ether was purified by recrystallization from a hexane/ethanol 9/1 mixture. Yield: 4·3 g (74 per cent). ^1H NMR (CD_3COCD_3, δ): 1 (3 H, CH_3), 1·4 (6 H, C–CH_2–C), 1·8 (2 H, O–C–CH_2), 4 (2 H, OCH_2), 7 (2 H arom. *ortho* to O*R*), 7·1 (2 H arom. *ortho* to OH), 7·9 (4 H arom. *ortho* to N=N), 9 (1 H, OH).

4-(4-Hexyloxyphenylazo)phenyl heptadeca-10,12-diynoate DA_4N_6): esterification of (**5**) and (**6**) was carried out as in the case of the acetylenic monomer, using oxalyl chloride instead of thionyl chloride. Purification was carried out on a silica gel column, with a hexane/dichloromethane 1/1 mixture as eluent, followed by recrystallization from ethanol. Yield: 21 per cent. ^1H NMR ($CDCl_3$, δ): 1 (6 H), CH_3), 1·2–1·4 (22 H, CH_2), 1·8 (2 H, O–C–CH_2), 2·2(4 H, CH_2–C≡C; 2H, CH_2–COO), 4 (2 H, OCH_2), 7 (4 H arom. *ortho* to O*R*), 7·9 (4 H arom. *ortho* to N=N).

$DA(_3C_8)_2$ was synthesized according to the following scheme:



1,10-Di-(4-hydroxyphenoxy)deca-4,6-diyne (**7**): to 9·15 g (45·9 mmol) of copper (II) acetate monohydrate, dissolved in 35 ml of a pyridine/methanol 1/1 mixture, were added 5·6 g (32 mmol) of **1**; the reaction mixture was heated under reflux for 1 h and acidified with 100 ml of 9M-H_2SO_4, with stirring and cooling at 0°C [25]. The product was extracted into ether, and the extract washed with water and dried over Na_2SO_4. The diyne was purified by recrystallization from toluene. Yield: 2·6 g (49 per cent). ^1H NMR (CD_3COCD_3) δ: 2 (4 H, C–CH_2–C), 2·5 (4 H, C≡C–CH_2), 4 (4 H, OCH_2), 6·8 (8 H arom.), 7·8 (2 H, OH). IR: no C≡CH at 3300 cm^{-1}.

Bis-4-n-octyloxybenzoate of the bis-phenol (**7**) ($DA(_3C_8)_2$): the same esterification procedure was used as for the acetylenic monomer, using 2 mol of the acid chloride of (**2**) per mol of (**7**). Yield: 38 per cent. ^1H NMR ($CDCl_3$, δ): 1 (6H, CH_3), 1·4 (20H, C–CH_2–C), 1·8 (4 H, O–C–CH_2), 2 (4 H, C≡C–C–CH_2–C–O), 2·5 (4 H, C≡C–CH_2), 4 (8 H, OCH_2), 6·9–7·1(12 H arom. *ortho* to O*R*), 8·1 (4 H arom. *ortho* to COO).

$DA(_8N_6)_2$ was synthesized by first coupling undec-10-ynoic acid (**4**), using copper acetate (see synthesis of **7**), followed by condensation of 2 mols of phenol (**6**) with 1 mol of the diacid (see synthesis of $DA(_3C_8)_2$.

4.2.2. *Polymerization of diacetylenic derivatives*

γ radiation: DA_4N_1 was polymerized using 1·5 Mrad (accelerated electrons, yield: 10 per cent), DA_4N_6 and $DA(_3C_8)_2$ did not polymerize on irradiation using 16 Mrad.

UV radiation: $DA(_3C_8)_2$ was crystallized by evaporating a THF solution under a slight vacuum, and polymerized by exposure to UV radiation during 20 h (high pressure Hg lamp, 450 W, distance: 30 cm without filter). Yield: 1–2 per cent.

Thermal polymerization: crystals of $DA(_3C_8)_2$ were heated at 160°C for 15 h. The polymer obtained was purified by semi-preparative GPC using a 19 × 300 mm Ultrastyragel column (500 Å) from Waters Associates and toluene as eluent.

4.3. *Characterization of the materials*

Gel permeation chromatography: the molecular weights of the polymers were determined by GPC analysis using toluene and three 7·8 × 300 mm Ultrastyragel columns from Waters Associates (10^4, 10^3, 500 Å) with polystyrene standards for calibration.

Optical microscopy: the characterization of the mesophases was achieved by polarizing optical microscopy (Leitz–Dravert) coupled with a Mettler FP 52 hot stage. The transition temperatures reported for the polymers were obtained by cooling from the isotropic phase.

Differential scanning calorimetry: the optical observations were confirmed by DSC analysis carried out using a DSC 7 Perkin–Elmer apparatus at 5°C min^{-1}. Glass transition temperatures were systematically determined at a heating rate of 10°C min^{-1}.

4.4. *Conductivity measurements*

The equipment consists of three parts:

(i) the measurements of σ and ε' were made in the frequency range 5 Hz–13 MHz. The measurement device was an impedance analyser HP 4192A piloted by an HP 330 computer. More than 20 measurement points per decade could be obtained. Data could be easily plotted or stored on floppy disks for further analysis.

(ii) the experimental cell was a parallel plate capacitor located at the end of a coaxial line (APC 7 standard). This cell has been fully described elsewhere [26]. It is made of glass electrodes coated with transparent conductive ITO ($R < 50\,\Omega$). The sample was introduced into the free inter-electrode volume by using capillary filling.

(iii) additional apparatus to this set-up consisted of a polarizing microscope, to achieve an *in situ* check on the sample orientation, and an EI 822 Eurotherm programmable thermal regulator to control the sample temperature.

5. Conclusions

Substituted polyacetylenes and polydiacetylenes have been synthesized from liquid crystalline thermotropic monomers. Polymerization of the acetylenic derivatives has been achieved in the non-oriented as well as in the oriented nematic state. All polyacetylene derivatives exhibit a smectic phase whose transition temperatures depend on polymerization conditions.

Despite the low values of the observed conductivity, preliminary dielectric measurements have shown an enhancement of conductivity for the undoped oriented polyacetylene compared to the non-oriented polymer. Since doping preserves the mesomorphic behaviour and induces a nematic phase above the smectic one, the influence of the orientational character has to be studied on doped material.

Furthermore, a more efficient orientation of the mesogenic moieties could be achieved by *in situ* polymerization of aligned monomers. This orientation could be preserved either by direct polymerization in the measurement cell, or by cross linking the material using difunctional monomers. On the other hand, polymerization should also be achieved in the aligned smectic phase, in order to improve coupling between polymer backbone and the mesogenic moieties.

Conductivity measurements have to be made in parallel and perpendicular planes with respect to the orientation direction in order to reveal an anisotropic conductivity.

Substituted polyacetylenes having low intrinsic conductivity, this study will be extended to other backbones, for which conductivity is less affected by attachment of large groups.

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