PII: S0032-3861(96)00658-1

Thermal polymerization of arylacetylenes: 1. Study of a monofunctional model compound

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(Received 17 June 1996)

The thermal polymerization of arylacetylene compounds has been studied from a monofunctional model compound, 4-(hexyloxy)phenylacetylene **I**. **I** was synthesized and bulk polymerized under several experimental conditions. The reaction products were analysed by chromatography, spectroscopy and spectrometry techniques. The observed average polymerization degree is low. The lowest molecular weight compounds were isolated and identified: they are two naphthalenic dimers and three benzenic trimers. They represent 30 wt% of the whole polymerization product. We have shown also that the thermal polymerization of **I** is temperature and time dependent and that a depolymerization process takes place at high temperature. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: arylacetylene; thermal polymerization; thermal depolymerization process)

INTRODUCTION

Many acetylene terminated resins have been described[1,2]. Although some α,ω-diethynylimide oligomers were commercialized in the seventies, the mechanism of the thermal polymerization of the arylacetylene group is not yet fully established.

The polymerization takes place above $130°C$[1,2] without catalyst and the properties of the resulting networks depend on the length and the nature of the aromatic or heterocyclic moieties as well as on the conditions of polymerization and post cure.

Different assumptions concerning the polymerization mechanism have been proposed to explain kinetic results. Different determinations such as electron spin resonance (e.s.r.) data, structure determination of low molecular weight species and nuclear magnetic resonance (n.m.r.) studies of the oligomeric products were used to obtain experimental data.

The radical nature of the polymerization was evidenced early[3] and confirmed later with organic cure inhibitors[4] or initiators[5], effect of air[6], and e.s.r. determination[7]. Free radical species concentration was plotted as a function of the conversion degree and it was observed that the acetylene group consumption was faster than the radical species appearance[8]. During the polymerization of the ethynylpyridine, dimers with quinoline and isoquinoline structure were isolated besides benzenic trimers. The authors[9] pointed out that the trimers were produced by elimination from the growing chain.

Pickard *et al.*[10] mentioned that the molecular weight of the polymeric fractions were rather insensitive to the reaction temperature and they suggested a polymerization through a biradical mechanism. The same authors[11] using ¹H and ¹³C n.m.r. data assumed that the polymeric products were polyenic systems with a *trans*-cisoid structure.

Barkalov *et al.*[3] and later Amdur *et al.*[12] pointed out that the reactivity decreased while the molecular weight was increasing.

Swanson *et al.*[13] using solid state ¹³C n.m.r. cross polarization magic angle spinning and isotopically labelled samples, suggested that the polymerization could occur according to different mechanisms: cyclotrimerization, biradical mechanism, Glaser and Straus coupling and Friedel–Craft alkenylation.

Linear dimers resulting from Straus or Glaser reactions might be formed during the first step of the reaction[14,15]. However these potential intermediates were not isolated in the reaction mixture.

Three benzenic trimers which had been proposed earlier by Hergenrother[15] and two naphthalenic dimers have been isolated using preparative high pressure liquid chromatography (h.p.l.c.) and their structures established on the basis of ¹H and ¹³C n.m.r. criteria[16].

The important literature data do not allow a complete understanding of such unusual radical polymerization. Many questions are still without answer. In this paper we will discuss the thermal polymerization of an arylacetylenic monomer.

As telechelic oligomers produce insoluble materials when polymerized, we decided to work with a monofunctional model compound to circumvent solubility

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problems. 4-(Hexyloxy)phenylacetylene **I** was chosen for its low volatility for the thermal stability of the aliphatic chain which provided an internal standard for n.m.r. studies.

We will try to elucidate the following points:

(a) determination of the nature and the proportion of the polymerization products;
(b) effect of polymerization temperature on the molecular weight and the molecular distribution of the polymer.

EXPERIMENTAL

Except where otherwise specified, reactions and analyses were accomplished under the following conditions. Every reaction was conducted under argon atmosphere and was magnetically stirred. The mesh of silica gel used for column chromatography was 0.063–0.2 nm (Merck 60 F_{254}). Thin layer chromatography (t.l.c.) was performed with 60A silica gel plates (Whatman MK 6F). H.p.l.c. and size exclusion chromatography (s.e.c.) analyses were carried out with a Shimadzu SCL-6A device including two pumps and a mixing chamber. Weight concentration of the sample solutions was 0.1% in chloroform. Prior to use, solvents (h.p.l.c. grade) were degased with helium bubbling.

H.p.l.c. analyses

The stationary phase of the column was Spherisorb C18 ODS II silica gel (mesh: $5 \mu m$); the column length was 250 mm and the interior diameter 4.6 mm. Eluent phase was a linear gradient in methanol and chloroform so that the methanol proportion linearly decreased from 100% down to 20% in 50 min. Elution was then maintained for 10 min with a 20/80 methanol/chloroform mixture. The flow rate was $0.7 \, ml \, min^{-1}$ with a pressure around 60 bar.

S.e.c. analyses

The stationary phase of the column was a polystyrene gel (Eurogel 100, mesh: $5 \mu m$); the column length was 300 mm and the interior diameter 8 mm. A filtration column (Eurogel PRP 250, mesh: $10 \mu m$, length 30 mm and interior diameter 8 mm, Knauer, Berlin) was used. The eluent phase was chloroform, the flow rate was $0.3 \, ml \, min^{-1}$ with a pressure around 20 bar. For each analysis series, the column was first standardized with polystyrene isomolecular mass.

Other characterizations

Differential scanning calorimetry (d.s.c.) analyses were achieved with a Mettler-TA 3000 apparatus, with indium calibration in aluminium crucibles. The measurements were recorded in argon with temperature ramp of $10°C \, min^{-1}$. Infra-red (i.r.) spectra were recorded with a Perkin–Elmer 398 spectrophotometer (KBr pellet). Absorption band positions are given in cm^{-1}.

Secondary ion mass spectrometry (s.i.m.s.) analyses were performed with a ZAB-SEQ caesium emitter device using 2-nitrophenyloctylether as a matrix. Caesium ion beam was accelerated with a 35 kV potential. Electron spin resonance (e.s.r.) analyses were accomplished with a Bruker-100 D apparatus using a 10 000 G electromagnet; the resonance chamber was temperature controlled. ^{1}H and ^{13}C n.m.r. spectra were recorded in deuterated

chloroform on a Bruker AC-250 device operating at 250 MHz (^{1}H) and 62.8 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to tetramethylsilane used as internal standard. The abbreviations s, d, t, q, Q and m were used for singlet, doublet, triplet, quartet, quintet and multiplet respectively. The coupling constants (J) are given in Hertz. ^{13}C n.m.r. signal multiplicity due to the $^1J_{CH}$ coupling constant with hydrogen atoms was determined by a distortionless enhancement by polarization transfer (DEPT-135) sequence and in some cases precised by a DEPT-90 sequence. Integration value of the number of carbon atoms is specified only from 2.

Starting materials

High purity reagents such as *n*-hexylbromide, 4-iodophenol, trimethylsilylacetylene (TMSA), potassium carbonate, cuprous iodide, triphenylphosphine, dichlorobis(triphenylphosphine)palladium, dimethylformamide (DMF) and the other solvents were purchased from commercial sources and used without further purification.

The chemical structures of the synthesized molecules are presented in *Figure 1*, as well as an alphabetical indexation of carbon atoms used for the ^{13}C n.m.r. description.

Preparation of 1-hexyloxy-4-iodobenzene **Ia**

A *n*-hexylbromide (74.26 g, 450 mmol) solution in DMF (250 ml) was added dropwise to a solution of 4-iodophenol (66.08 g, 300 mmol) and potassium carbonate (51.20 g, 370 mmol) in DMF (300 ml). T.l.c. (cyclohexane/ethyl acetate: 70/30) allowed us to monitor the conversion and the reaction was stopped after 5 h of stirring at 130–135°C (reflux). After filtration and evaporation of DMF, the filtrate was poured into water (150 ml) and extracted with dichloromethane (3 × 80 ml). The organic layers were washed first with soda (0.75 N, 1 × 60 ml), then with water (3 × 100 ml) and finally dried over magnesium sulfate. After evaporation of dichloromethane the crude product (90.0 g) was distilled to give pure **Ia** (84.0 g, 276 mmol, 92%); $bp_{0.01 \, mb} = 92–94°C$ ($bp_{3–5 \, mmHg} = 133°C^{17}$). ^{1}H n.m.r: 7.06 (m, 4H, *H* arom); 3.86 (t, $J = 6.5$, 2H, CH_2O); 1.73 (Q, $J = 6.5$, 2H, CH_2CH_2O); 1.27–1.45 (m, 6H, $CH_3(CH_2)_3$); 0.89 (t, $J = 6.7$, 3H, CH_3). ^{13}C n.m.r:
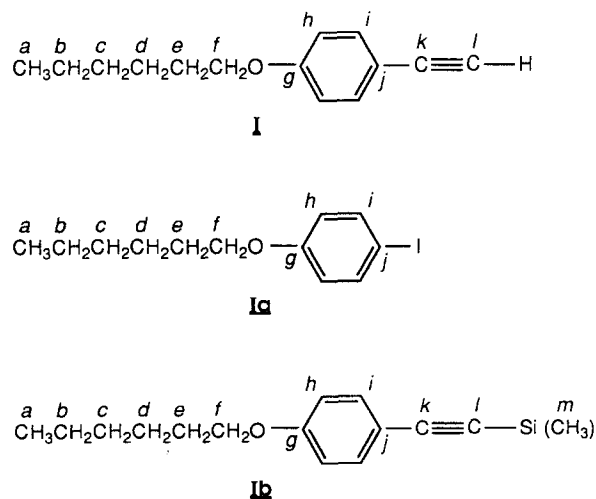

Figure 1 Chemical structures of products **I**, **Ia** and **Ib**

14.1 (a); 22.6 (b); 25.7 (d); 29.1 (e); 31.6 (c); 68.1 (f); 82.4 (j); 116.9 (2C, h); 138.1 (2C, i); 159.0 (g).

Preparation of 1-(hexyloxy)-4-[2-(trimethylsilyl)-ethynyl]benzene Ib

In a one litre steel tight-fitting reactor equipped with a mechanical stirrer and purged with argon we introduced **Ia** (120.41 g, 396 mmol) in triethylamine (300 ml, bubbled with argon) and TMSA (42.95 g, 437 mmol) in the presence of a catalytic system composed of triphenyl-phosphine (202.3 mg, 0.77 mmol), dichlorobis(triphenyl-phosphine)palladium (771.5 mg, 1.10 mmol) and cuprous iodide (185.9 mg, 0.98 mmol). Under argon pressure (7 bar), the reactor mixture was heated at 73°C. After 18 h 30 t.l.c. analysis (cyclohexane) showed that some **Ia** remained unreacted. So dichlorobis(triphenylphosphine) palladium (367.2 mg, 0.52 mmol), cuprous iodide (95.3 mg, 0.50 mmol) and TMSA (5.05 g, 50 mmol) were added and after four additional hours at 73°C, the reaction was completed (t.l.c.). After filtration of the triethylammonium salt and solvent evaporation, the reaction product was poured into water (1 l), extracted with dichloromethane (4 × 100 ml). The organic layers were dried on magnesium sulfate. After filtration and evaporation of dichloromethane, the crude product (116.71 g) was percolated through a silica gel column (500 g) with the help of pentane and then dichloro-methane. In order to remove the by-product 1,4-bis(trimethylsilyl)-1,3-butadyine, the percolated crude product (109.82 g) was first sublimed and then distilled to give pure **Ib** (87.18 g, 320 mmol, 80%). bp$_{0.01\,mb}$ = 115–118°C. I.r.: 2140 (C≡C). ^{1}H n.m.r.: 7.10 (m, 4H, *H* arom); 3.92 (t, *J* = 6.5, 2H, C*H*$_2$O): 1.77 (Q, *J* = 6.5, 2H, C*H*$_2$CH$_2$O); 1.30–1.47 (m, 6H, CH$_3$(C*H*$_2$)$_3$); 0.92 (t, *J* = 6.6, 3H, C*H*$_3$CH$_2$; 0.26 (s, 9H, (C*H*$_3$)$_3$Si). ^{13}C n.m.r.: 0.1 (3C, m); 14.1 (a); 22.6 (b); 25.7 (d); 29.2 (e); 31.6 (c); 68.0 (f); 92.2 (l) 105.4 (k); 114.3 (2C, h); 115.0 (j); 133.4 (2C, i); 159.3 (g).

Preparation of 4-(hexyloxy)phenylacetylene I

Potassium carbonate (3.2 g, 23 mmol) was added to a solution of **Ib** (6.5 g, 24 mmol) in methanol (16 ml) at 30°C. The conversion was monitored with t.l.c. analysis (cyclohexane/ether: 90/10) and i.r. analysis (absorption band at 2140 cm^{-1} disappeared while absorption band at 3300 and 2100 cm^{-1} appeared). After 2 h 30 min at 30°C, the reaction was worked up. After filtration of carbonate and evaporation of methanol, the reaction product was poured into water (25 ml) and extracted with pentane (5 × 15 ml). The organic layers were washed with water (3 × 15 ml) and dried over magnesium sulfate. Pentane was removed under vacuum. Finally 4.71 g of pure **I**

were obtained (23 mmol, 97%). I.r.: 2100 (C≡C); 3300 (H–C≡); ^{1}H n.m.r.: 7.10 (m, 4H, *H* arom); 3.92 (t, *J* = 6.5, 2H, C*H*$_2$O); 2.98 (s, 1H, *H*C≡); 1.76 (Q, *J* = 6.5, 2H, C*H*$_2$CH$_2$O); 1.28–1.46 (m, 6H, CH$_3$(C*H*$_2$)$_3$); 0.90 (t, *J* = 6.6, 3H, C*H*$_3$). ^{13}C n.m.r.: 14.0 (a); 22.6 (b); 25.7 (d); 29.1 (e); 31.6 (c); 68.0 (f); 75.7 (l); 83.7 (k); 113.9 (j); 114.4 (2C, h); 133.5 (2C, i); 159.5 (g). Freshly synthesized **I** was used for the thermal polymerization studies without further purification.

Sampling for the thermal treatments of monomer I

Tubes of 7 and 15 mm i.d. were used where around 200 mg and 4 g samples of monomer were polymerized respectively. The reactor tube was filled with argon before and after weighing the sample. The tube was then sealed and heated in a programmed oven.

Quantitative analysis of thermal treatment

Monomer (4.0 g) was heated according to the thermal step treatment as indicated in *Figure 2*. The step at 280°C was maintained for 30 min longer. Part of the thermal treatment product (1.86 g) was mixed with silica gel (7 g) and cyclohexane (5 ml), and deposited on top of the dry silica gel column (110 g). Percolation was carried out with petroleum ether (500 ml), then with 1 l of a 98/2 petroleum ether/ether mixture (the first 350 ml was allowed to elute the 30 wt% **A** and **B** fractions); oligomers were eluted next with a 3/1 petroleum ether/dichloromethane mixture (450 ml) and with pure ethylacetate (400 ml). The overall weight of residual products after evaporation of solvents was 1.85 g.

RESULTS AND DISCUSSION

Synthesis of 4-(hexyloxy)phenylacetylene I

The synthetic route is summarized in *Scheme 1*.
The first step[17,18] is a Williamson reaction performed from 4-iodophenol and *n*-hexylbromide. A better yield was produced using potassium carbonate as base and DMF as solvent. The second step[19] was the most difficult to complete; to obtain the full conversion of **Ia** into **Ib**, it was necessary to work under a small pressure of argon (7 bar) with an excess of TMSA. Moreover during the reaction an extra addition of the palladium catalyst, copper iodide and TMSA was done. This procedure led to the formation of the TMSA dimer, which was separated from **Ib** through a sublimation step.
As **I** was used as crude product of the deprotecting step, the purification of **Ib** was the key stage to obtain pure **I**. **Ib** was stored in a refrigerator without alteration for a long period. This was not the case for **I**. So the
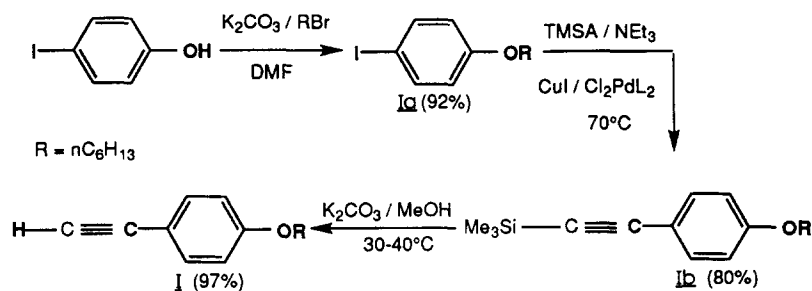
Scheme 1

deprotection[20] of **Ib** to **I** was realized just before each thermal polymerization study. The overall yield of the preparation of **I** is 71% and the intermediate **Ib** was also used to prepare an enyne dimer of **I**[21].

Characterization of I

I is described in the literature[22,23], but **Ib** is not. N.m.r. data given in the Experimental section are in agreement with such structures and with ^{1}H n.m.r. literature data[23]. The i.r. absorption bands at $2140 \, cm^{-1}$ for **Ib** and $2100 \, cm^{-1}$ for **I** are in accordance with disubstituted and monosubstituted triple bond absorption, respectively.

Thermal polymerization of I

The onset and the end of polymerization temperatures, which were 160–170°C and 320–330°C respectively (maximum at 240–250°C), were measured by d.s.c. analysis. The polymerization enthalpy value is $165 \, kJ \, mol^{-1}$: the polymerization of **I** is among the most exothermic reactions described in the literature[16,24].

Three curing procedures were used: two isothermal treatments at 180 and 280°C respectively; and a gradual thermal step treatment according to *Figure 2*.

The reaction products resulting from the thermal treatments were chromatographically (h.p.l.c. and s.e.c.), spectroscopically (^{1}H n.m.r.) and spectrometrically (s.i.m.s.) analysed.

Chromatographic analyses

The general shape of the h.p.l.c. chromatograms in *Figure 3* is similar for the three thermal treatments. Preparative h.p.l.c. experiments allowed us to isolate the compounds 1–5 corresponding to the signals numbered 1 to 5, respectively. From their ^{1}H and ^{13}C n.m.r. analyses (*Tables 1* and *2*), we established that they present naphthalenic (**1** and **2**) and benzenic (**3–5**) structures (*Scheme 2*). These assignments are in agreement with literature data[15,16].
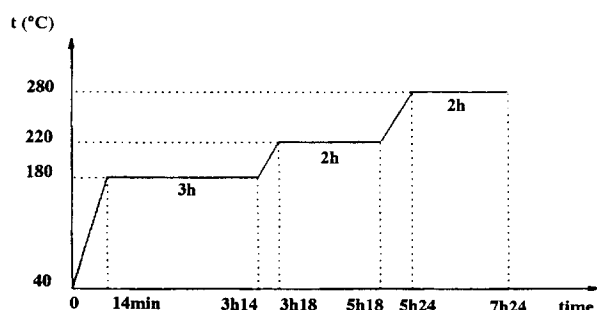
Depending on the curing mode, only minor variations of relative amounts of products 1–5 are observed. However a question is to be elucidated: what is the ratio of naphthalenic dimers and benzenic trimers over the oligomeric species?

Naphthalenic dimer and benzenic trimer 1–5 study

The curing (by steps) of **I** was performed on a 4 g scale and the resulting crude reaction mixture was column-chromatographed on silica gel. The aromatic species 1–5 were eluted first and they represented 30 wt% of the whole reaction mixture. The other elution fractions (70%) did not contain compounds 1–5, but only oligomers. The yield of this chromatography was almost quantitative.

^{1}H n.m.r. analysis of the low molecular weight fraction shows that **1** and **5** are the major components of this fraction (40% each). The other main component (15%)
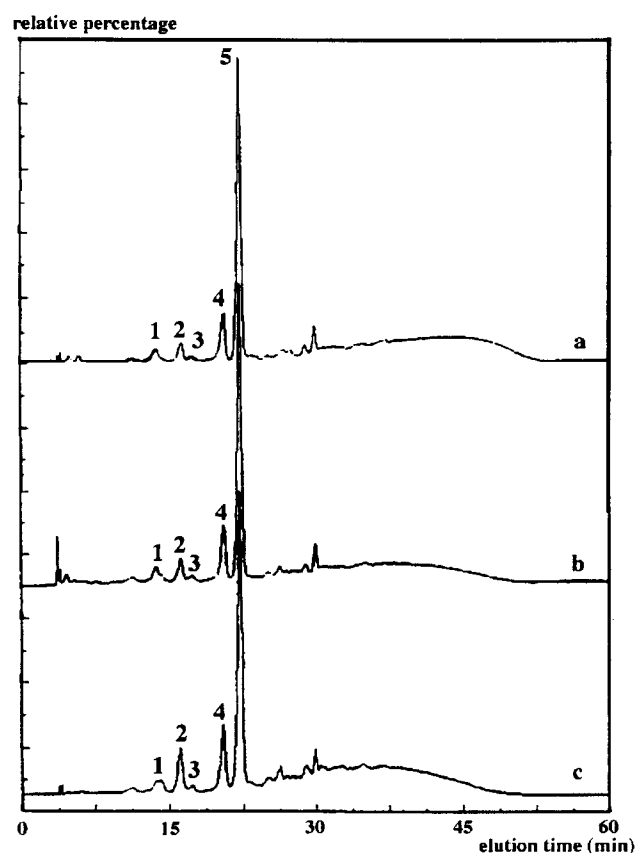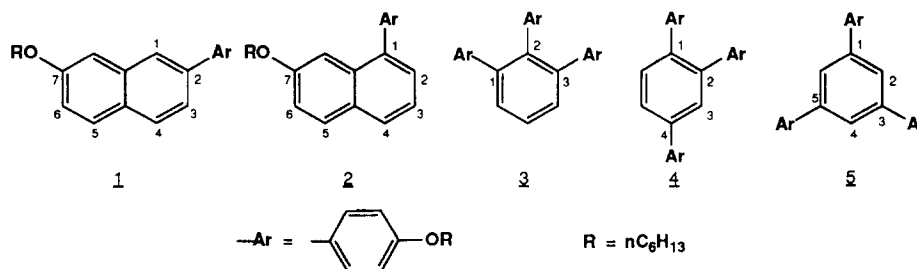

Figure 3 H.p.l.c. chromatograms of crude products of the thermal polymerizations of **I**: trace a, 180°C for 64 h (isotherm); trace b, gradual curing (*Figure 2*); trace c, 280°C for 7 h (isotherm)

Figure 2 Graphical representation of the gradual curing used for the thermolysis studies of **I**

Scheme 2

Table 1 ^1H and ^{13}C n.m.r. chemical shifts [δ scale relative to internal tetramethylsilane (TMS)] for compounds **1** and **2** (CDCl$_3$ solution; 400.1 and 100.6 MHz respectively)

1   **2**

	1	2	3	4	4a	5	6	7	8	8a	a	b	c	d	OCH_2-	CH_2-	CH_2	CH_2-	CH_2-	CH_3
^1H **1**	7.35 m[a]	—	7.75 m[a]	7.35 m[a]	—	7.79 d[b]	7.15 dd[b]	—	7.24 d[b]	—	—	7.42 d[c]	7.02 d[c]	—	4.05 3.91 t	1.85 1.76 Q	1.51 1.49 m	1.38 1.32 m	m	0.93 0.90 t
^{13}C **1**	127.4*	138.7	123.0	127.1*	129.3	129.6	118.6	157.2†	105.3	132.2†	132.9†	130.9	114.3	158.4‡	67.9 68.1	29.3 29.2	25.8 25.7	31.64 31.62	22.7 22.6	14.1 14.0
^1H **2**	—	6.82 d[d]	7.34 dd[d]	7.41 d[d]	—	7.83 d[e]	7.71 dd[e]	—	8.44 d[e]	—	—	7.67 d[f]	7.02 d[f]	—	4.20 4.06 t	1.95 1.82 Q	1.50 m	1.37 m	m	0.93 0.92 t
^{13}C **2**	g	125.7*	119.3†	125.8*	g	127.9	119.7†	g	104.9	g	g	128.4	114.8	g	68.3 68.1	29.3 29.2	26.0 25.8	31.6	22.6	14.0

Additional designations in the **R,R** column (hexyloxy chain assignment): **R,R** for all four rows.

a ABX pattern
b $^3J_{H5H6} = 8.9$; $^4J_{H6H8} = 2.5$
c $^3J_{HbHc} = 8.6$ (AB pattern)
d $^3J_{H2H3} = 7.3$; $^3J_{H3H4} = 7.6$
e $^3J_{H5H6} = 8.6$; $^4J_{H6H8} = 1.8$
f $^3J_{HbHc} = 8.8$ (AB pattern)
g These signals have not been detected
*,†,‡ Assignments can be reversed

Table 2 ^{1}H and ^{13}C n.m.r. chemical shifts [δ scale relative to internal tetramethylsilane (TMS)] for compounds **3**, **4** and **5** (CDCl$_3$ solution: 400.1 and 100.6 MHz respectively)

Structures shown: compound **3** (OR^1, OR^2, Ar^3; Ar^1 = Ar^3); compound **4** (OR^1, OR^2, ^{4}RO); compound **5** (OR^1, Ar^3, Ar^5; Ar^1 = Ar^3 = Ar^5).

	1	2	3	4	5	6	a	b	c	d	OCH$_2$	CH$_2$–	CH$_2$–	CH$_2$–	CH$_2$	CH$_3$	
^{1}H **3**	—	—	—		7.35 m		—	6.96 d^a / 6.73 d^a	6.69 d^a / 6.53 d^a	— / —	3.89 t / 3.83 t			1.9–0.9 m			} R^1, R^{3} ^{3,b} } R ^{2,b}
^{1}H **4**			7.57 d^c		7.55 dd^e	7.43 d^c		7.08 / 7.11 d^d / 7.58 d^d	6.77 / 6.78 d^d / 6.98 d^d		3.93 t / 4.01 t	1.78 m / 1.79 m		1.4 m		0.91 t / 0.92 t	} R^1, R^2 } R^4
^{13}C **4**	138.5	140.4*	125.3	139.6*	128.9	131.0	134.0† / 133.5† / 133.0†	130.9‡ / 130.8§ / 128.1‡	114.0§ / 113.9§ / 113.8§	157.9‖ / 157.8‖ / 157.7‖	67.9 / 68.1	29.7 / 29.8	25.8	31.6	22.6	14.1	} R^1, R^2 } R^4
^{1}H **5**	—	7.65 s	—	7.65 s	7.65	7.65 s	—	7.61 d^e	7.00 d^e	—	4.01 t^f	1.82 Q^f	1.49 m	1.36* m	1.35* m	0.92 t^g	
^{13}C **5**	141.9	123.7	141.9	123.7	141.9	123.7	133.6	128.3	114.8	158.9	68.1	29.3	25.8	31.6	22.6	14.1	

^{a} $^3J_{b1c1} = {}^3J_{b2c2} = 8.6$
^{b} Assignments based on relative intensities
^{c} $^4J_{H3H5} = 2.0$; $^3J_{H5H6} = 7.8$
^{d} $^3J_{hc} = 8.7$
^{e} $^3J_{hc} = 8.8$
^{f} $^3J = 6.5$
^{g} $^3J = 6.7$
*, †, ‡, §, ‖ Assignments can be reversed
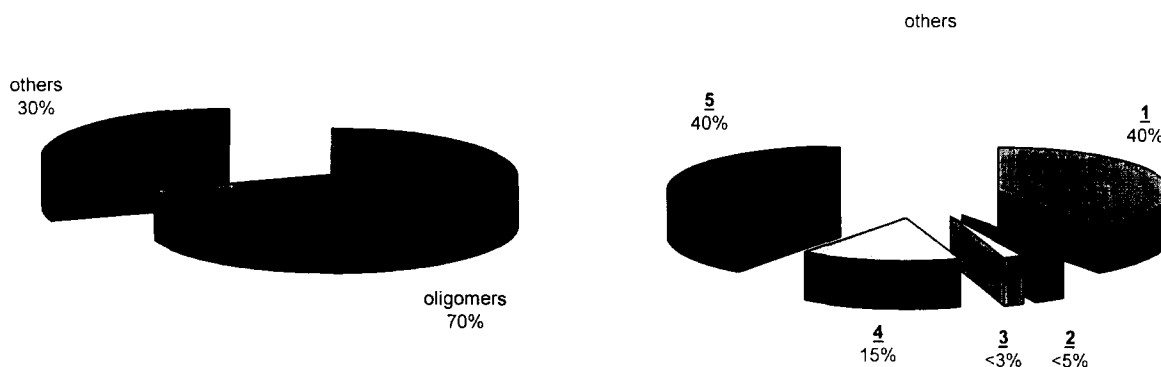
Figure 4 Relative proportions of naphthalenic dimers, benzenic trimers and oligomers in the cured product of **I** (wt%)
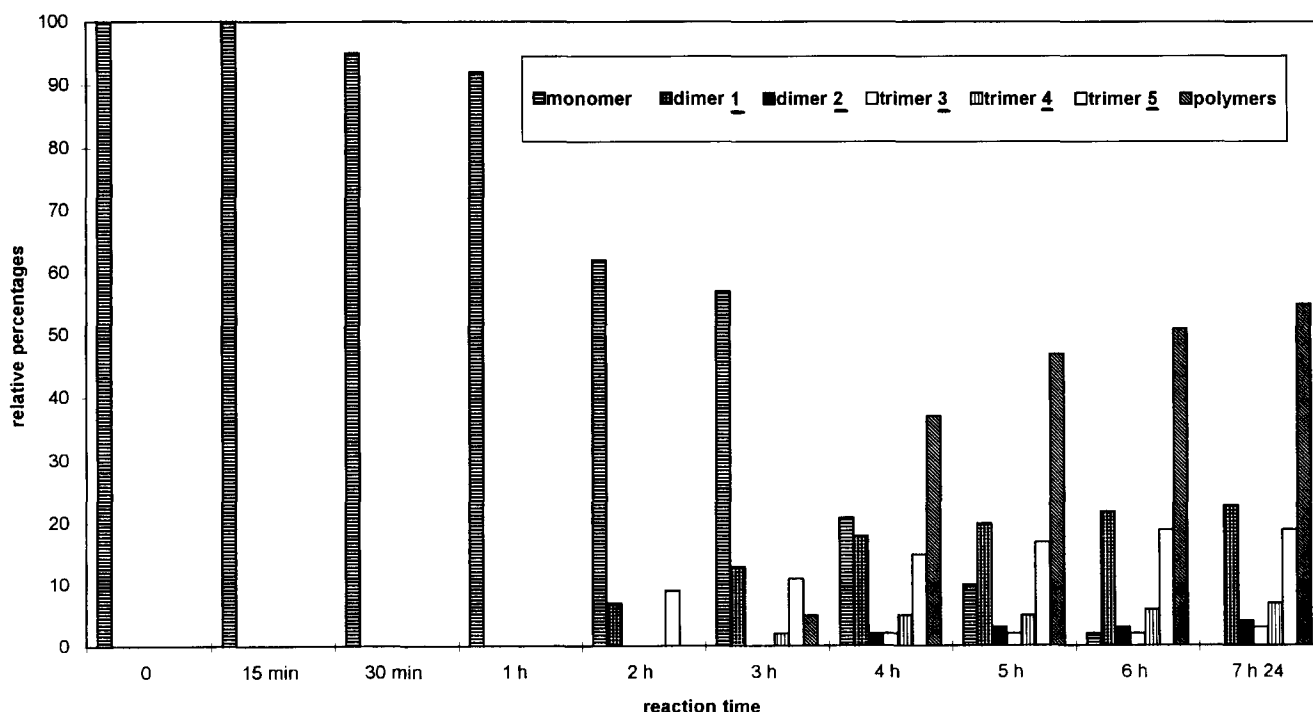

Figure 5 H.p.l.c. kinetic profile of the thermal polymerization of **I**: relative amounts of products as a function of reaction time

is **4**. Compound **2** is easily evidenced with the resonance of the H-8 proton ($\delta = 8.44$ ppm), but its contribution is lower than 5%. [1]H n.m.r. does not allow us to quantify **3** contribution, which can be estimated lower than 3% (*Figure 4*).

The [1]H n.m.r. analysis and relative quantifications of dimers, trimers and oligomers were confirmed by a kinetic study of the thermal polymerization of **I** (thermal step treatment) (*Figure 5*). Within experimental errors, they are both in agreement. The low h.p.l.c. estimation of relative amounts of naphthalenic dimers to benzenic trimers should be assigned to the difficulty to standardize the u.v. detection. Moreover it is worth noting that the overall amounts of the naphthalenic dimers and benzenic trimers (20–40%) relative to the total reaction product, are not very sensitive to the substituent borne by the phenyl group of the starting arylacetylene[25–27]. Nevertheless, the structure of the major product among these naphthalenic dimers and benzenic trimers is different according to the nature of the arylacetylene:

(a) the 1,7-distributed naphthalenic dimer has been isolated as the major component (50–60%) when

the phenyl group substituent is an electron withdrawing group (MeCO, PhCO, ROCO)[25];
(b) the 2,7-disubstituted isomer and 1,3,5-trisubstituted benzenic trimer are the major products when the substituent is an electron donating group, as observed with **I**,
(c) the 1,3,5-trisubstituted benzenic trimer is the major component in the case of the thermal polymerization of ynones[26].

Besides we also checked if the aromatic species proportions were dependent on the atmospheric nature. We performed our experiments under inert atmosphere (argon); Hergenrother[15] worked in nitrogen; other workers performed the polymerization in air[25,26].

The h.p.l.c. analyses (*Figure 6*) of the thermal polymerization of **I** in argon and air showed only minor variations in the relative intensities of the signals of the naphthalenic dimers (peaks 1 and 2). The formation of the 2,7-disubstituted isomer (peak 1) is favoured in air relative to the 1,7-disubstituted isomer (peak 2).

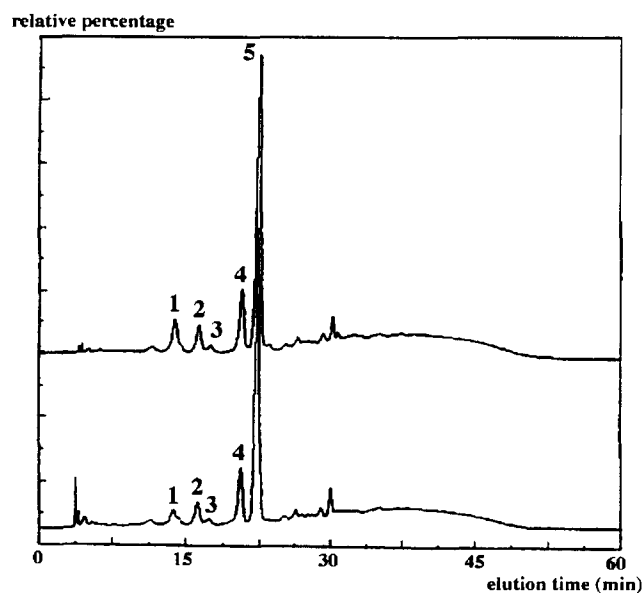The s.e.c. analyses (*Figure 7*) also showed that the formation of the naphthalenic dimers (peak A) is

relative percentage

Figure 6 H.p.l.c. analyses of the thermal polymerization of **I** in argon (lower trace) and air (upper trace)
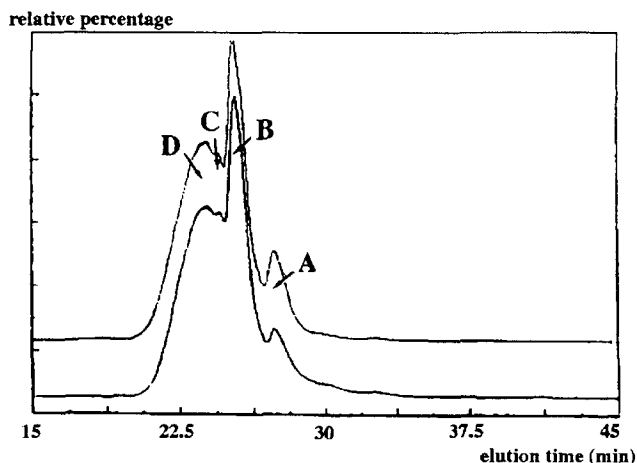
relative percentage

Figure 7 S.e.c. analyses of the thermal polymerization of **I** in argon (lower trace) and air (upper trace)

favoured in air. These observations are in agreement with literature data[25].

An explanation of the formation of the naphthalenic dimers and benzenic trimers was first proposed by Hergenrother[15] and put forward by other authors[16]. It mainly implies the intermediate formation of linear dimers (a diyne and enynes called Glaser and Straus dimers respectively) of the starting acetylenic compound.

Depending on the electronic effect of the substituent of the aromatic group and on the experimental conditions (temperature, air or inert atmosphere, ...) we may expect different proportions of linear dimers and the subsequent forming of different proportions of aromatic derivatives. However, such intermediates will not fulfil the fact that an e.s.r. signal is observed as soon as 100°C. This signal is very strong at 150°C. So the radical nature of the thermal arylacetylenic polymerization is proven.

Mass spectrometry analysis: characterization of the cured product

The cured crude product of **I** (after thermal step treatment) was analysed by s.i.m.s. This technique makes

possible the observation of the molecular ions of species contained in the analysed sample[28]. Although some fragmentations occur (loss of 85 mass unit fragment), it is only a minor process. Large intensity molecular ions of dimers ($m/z = 404$) and trimers ($m/z = 606$) are observed. Oligomeric molecular ions (4 to 14 repetitive units) are also formed, but their relative intensities decrease. These results corroborate those of s.e.c. analyses measuring an average polymerization degree of 6.

Depolymerization process

We observed only minor variations of relative amounts of products **1–5** according to the curing mode. However, as far as the oligomeric fraction is concerned, s.e.c. chromatograms (*Figure 8*) show an elution shape depending on the thermal treatment. This dependence is mainly due to the change in the parts labelled C and D which correspond to the elution of oligomers (A and B correspond to the elution of naphthalenic dimers and benzenic trimers).

As the temperature of the polymerization increases, the C and D signals have their width narrowing down and they shift towards bigger elution volumes: lower molecular weight species are eluted. From these observations we suggest that a depolymerization process may take place.

A kinetic study performed at 280°C confirmed it (*Figure 9*). As the reaction time increases, the average molecular weight $\bar{M}_w$ and polydispersity ratio I decrease, and after around 11 h of reaction they remain constant ($\bar{M}_w \approx 1230 \pm 30$; $I = 1.48 \pm 0.03$). We can assume that the polymerization of **I** gives a polyene chain which is broken to form irreversibly shorter aromatic entities.

CONCLUSION

The study of the thermal polymerization of the model compound **I** confirmed literature data about the structures and the concentration of low condensation aromatic species which are formed. Furthermore we
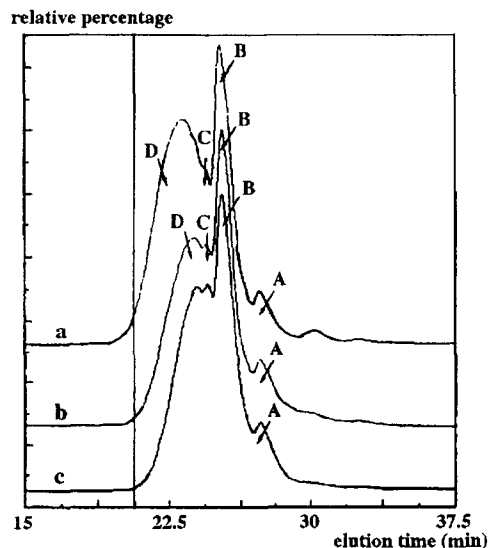
relative percentage

Figure 8 S.e.c. chromatograms of crude products of the thermal polymerizations of **I**: trace a, 180°C for 64 h (isotherm); trace b, gradual curing (*Figure 2*); trace c, 280°C for 7 h (isotherm)
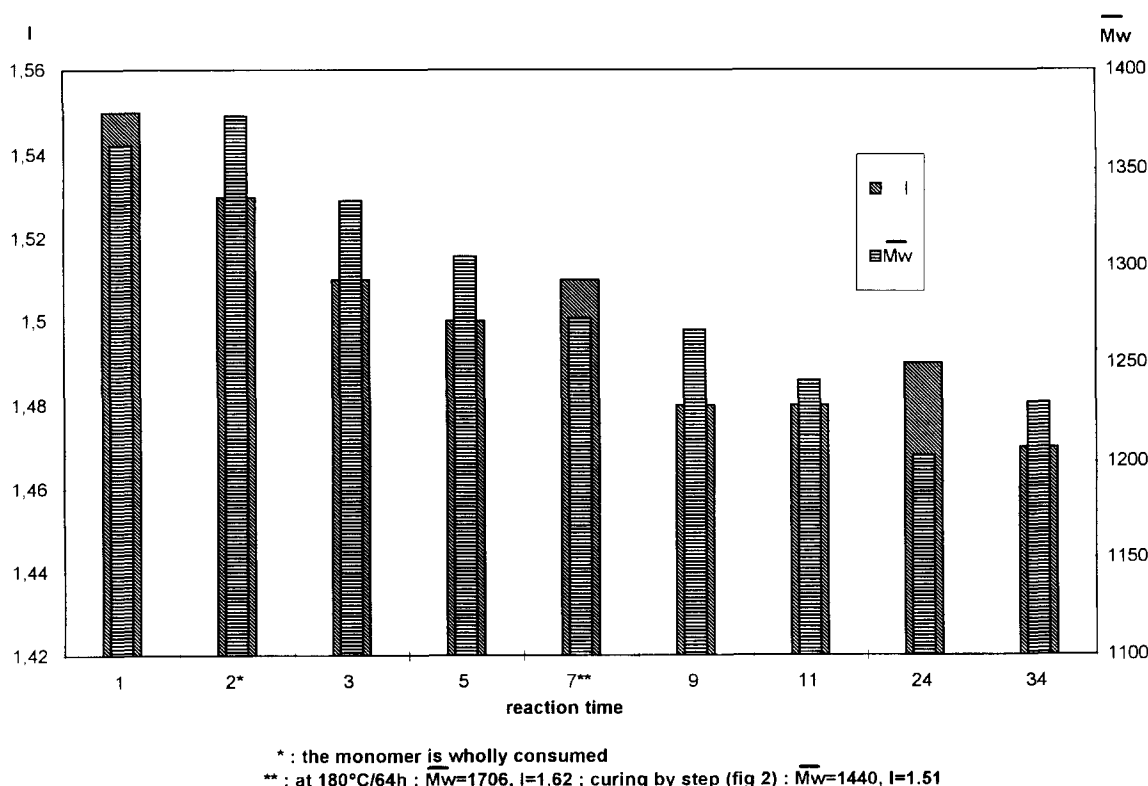
* : the monomer is wholly consumed
** : at 180°C/64h : $\overline{Mw}$=1706, I=1,62 ; curing by step (fig 2) : $\overline{Mw}$=1440, I=1.51

Figure 9 S.e.c. analyses of cured (280°C) crude product of **I**: average molecular weight ($\bar{M}_w$) and polydispersity ratio (*I*) variations as a function of reaction time (polystyrene standards)

evidenced a new reaction feature: a depolymerization process occurs under extended reaction time or increased reaction temperature. This process produces thermally more stable compounds.

The versatile formation of linear dimers as reaction intermediates has already been proposed. However, no experimental data are available to prove their involvement in the thermal polymerization of arylacetylenes. So, in a future paper, we will undertake the study of thermal polymerization of these linear dimers.

ACKNOWLEDGEMENTS

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