

Thermal polymerization of arylacetylenes:

2. Study of linear dimers

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Four linear dimers of 4-(hexyloxy)phenylacetylene **I** have been synthesized and thermally polymerized under the same conditions which were used for **I**. The polymerization of monomer and linear dimer mixtures was also studied. The reaction products were analysed by chromatography, spectroscopy and spectrometry techniques. The experimental results led us to conclude that the linear dimers are not reaction intermediates of the thermal polymerization of **I**. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In the previous paper¹ we presented the study of the thermal polymerization of 4-(hexyloxy)phenylacetylene **I** used as an arylacetylenic model compound. Some features of its polymerization were determined such as the formation of about 30% of naphthalenic dimers and benzenic trimers (**1–5**) and 70% of oligomeric products which depolymerize under extended heating.

Previous studies^{2–4} have implied linear dimers^{5–7} as reaction intermediates of the arylacetylene polymerization in order to explain the formation of either the benzenic trimers³ or naphthalenic dimers⁴. The proposed reaction mechanisms are given in *Scheme 1*. The formation of 1,2,3-trisubstituted benzenic trimer was explained by a [2+2] cycloaddition.

However, no linear dimer has been clearly evidenced during the polymerization. In addition the backbone geometry of any linear dimer is not favourable to the cyclization into naphthalenic dimers and benzenic trimers. This is due to the presence of the triple bond which implies the alignment of four carbon atoms and will not allow an easy cyclization reaction. In order to elucidate whether linear dimers **II–V** are really intermediates of the monomer **I** polymerization, we undertook their synthesis and their thermal polymerization study.

EXPERIMENTAL

Analyses and polymerization were conducted according to general procedures given in the previous paper¹.

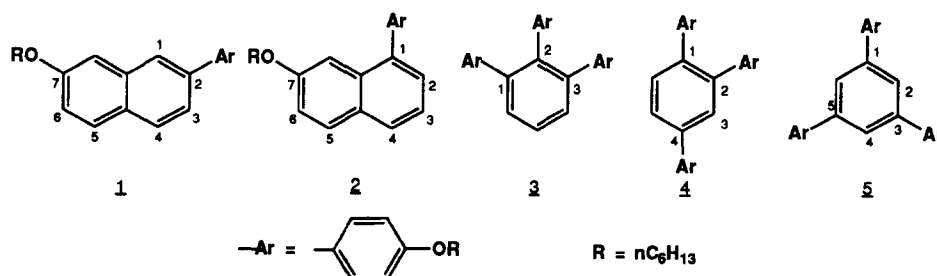
Starting materials

High purity reagents such as methyltriphenylphosphonium bromide, 4-(hexyloxy)benzoyl chloride, cuprous chloride, 1,2-dibromoethane, aluminium chloride, iodine, potassium *tert*-butylate, tetramethylethylenediamine (TMEDA), dimethoxyethane (DME) and the other solvents were purchased from commercial sources and used without further purification. For the synthesis of **III**, rough zinc powder (PROLABO) must be used. Prior to use diethyl ether was dried over molecular sieves (3A).

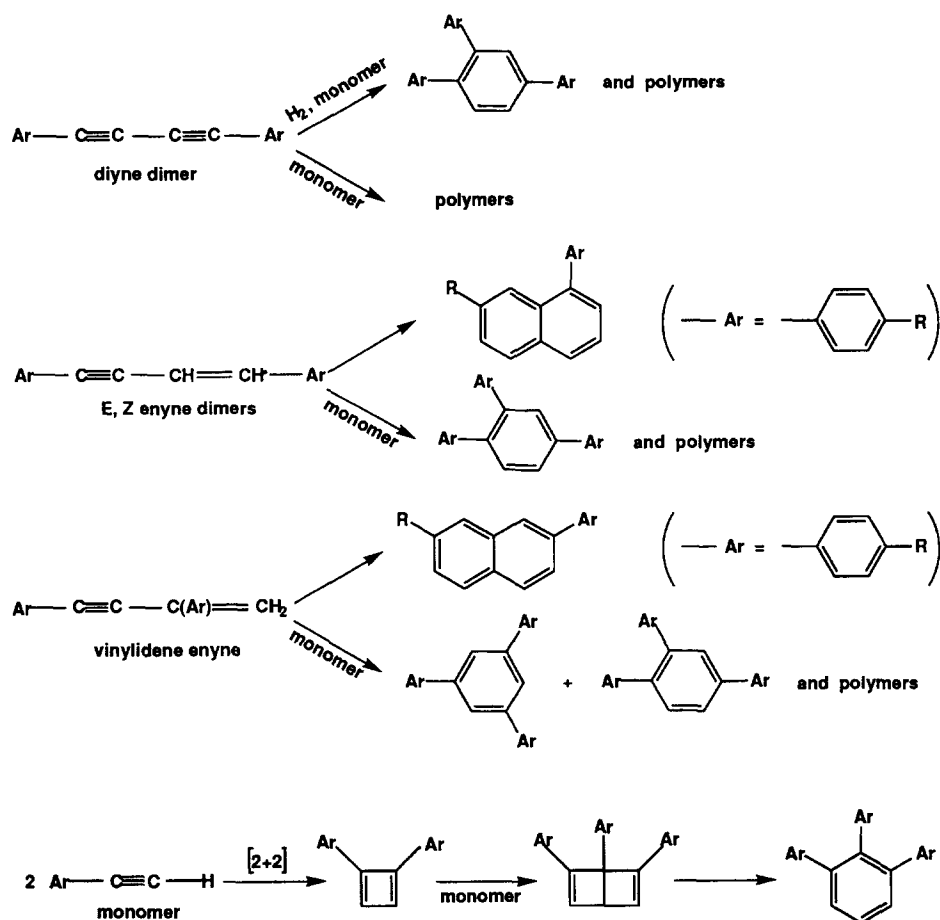
Every reaction was performed under inert atmosphere and with magnetic stirring. The chemical structures of the synthesized products are presented in *Figure 1* as well as an alphabetical indexation of carbon atoms used for ¹³C n.m.r. description.

Preparation of 1,4-di[4'-(hexyloxy)phenyl]-1,3-butadiyne **II**

A solution of 4-(hexyloxy)phenylacetylene **I**¹ (36.81 g, 180 mmol) in DME (45 ml) was added to a mixture of cuprous chloride (3.60 g, 36 mmol) and of TMEDA (7.19 g, 62 mmol) in DME (150 ml). The reaction mixture



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Scheme 1

was vigorously stirred at 40°C for 20 h with air bubbling. The reaction was monitored by t.l.c. analysis (cyclohexane). Some dimer **II** precipitated. Then the reaction mixture was poured into water (200 ml) and extracted with toluene (3 × 200 ml). The organic layers were washed with water and dried over magnesium sulfate. After solvent evaporation, the resulting yellow powder was dried, then crystallized from cyclohexane to yield pure **II** as white needles (34.26 g, 85 mmol, 94%). M.p. = 122–123°C (lit.⁸: 122.5°C); isotropic liquid transition temperature: 153°C (lit.⁸: 149.2°C). I.r.: 2120 (C≡C). ¹H n.m.r.: 7.13 (m, 8H, *H* arom); 3.95 (t, *J* = 6.5, 4H, CH₂O); 1.77 (q, *J* = 6.5, 4H, CH₂CH₂O); 1.30–1.50 (m, 12H, CH₃(CH₂)₃); 0.90 (t, *J* = 6.6, 6H, CH₃). ¹³C n.m.r.: 14.1 (2C, a); 22.6 (2C, b); 25.7 (2C, d); 29.1 (2C, e); 31.6 (2C, c); 68.1 (2C, f); 72.9 (2C, l); 81.3 (2C, k); 113.7 (2C, j); 114.6 (4C, h); 134.0 (4C, i); 159.9 (2C, g).

Preparation of 1,4-di[4'-(hexyloxy)phenyl]-1-butene-3-yne **Z III**

Zinc powder (7.6 g, 116 mmol) was introduced into ethanol (5 ml). After the addition of 1,2-dibromoethane (0.80 g, 4.3 mmol) diluted in ethanol (3 ml), the reaction mixture was heated. When reflux was reached, the heating bath was removed until the self-heating finished. Then a second fraction of 1,2-dibromoethane (0.75 g, 40 mmol) diluted in ethanol (3 ml) was added and the mixture was heated for 10 min under reflux. After cooling down to 50°C the diyne **II** (11.26 g, 28.0 mmol)

was added in two portions and the reaction mixture was homogenized with toluene (25 ml). After 3 h 30 min at 90°C (reflux), a second activated zinc fraction [prepared from zinc (3.70 g, 56.6 mmol) and 1,2-dibromoethane (0.94 g, 5.0 mmol added in twice)] was added to the refluxing reaction mixture. After three additional hours of reflux, the conversion of **II** was complete as was determined by t.l.c. analysis (carbon tetrachloride). Cooled to room temperature, the liquid fraction of the reaction mixture was decanted and poured into an aqueous ammonium chloride solution (4.78 g in 40 ml of water). The organic layer and the liquid fractions used for rinsing the residual zinc with toluene and ethanol, were washed together with 2N hydrochloric acid (100 ml), then with water (4 × 100 ml) until the pH was 7 and finally dried over magnesium sulfate. After filtration and solvent evaporation, the crude product (10.61 g) was purified through silical gel column chromatography using pentane as eluent: 9.44 g (23.3 mmol, 83%) of pure **III** were collected. M.p. = 33–34°C. I.r.: 2180 (C≡C); 670 (CH=CH *cis*). ¹H n.m.r.: 7.36 (m, 4H, *H* arom Ph–C=); 7.14 (m, 4H, *H* arom Ph–C≡); 6.57 (d, *J* = 11.9, 1H, CH–Ph); 5.76 (d, *J* = 11.9, 1H, CH–C≡); 3.96 (t, *J* = 6.4, 2H, CH₂O); 3.93 (t, *J* = 6.4, 2H, CH₂O); 1.77 (m, 4H, CH₂CH₂O); 1.30–1.50 (m, 12H, CH₃(CH₂)₃); 0.90 (t, *J* = 6.5, 6H, CH₃). ¹³C n.m.r.: 14.1 (2C, a and x); 22.6 (2C, b and w); 25.7 (2C, d and u); 29.19 and 29.24 (e and t); 31.6 (2C, c and v); 68.05 and 68.10 (f and s); 87.4 (m); 95.5 (n); 105.0 (l); 114.2 and 114.6 (2 × 2C,

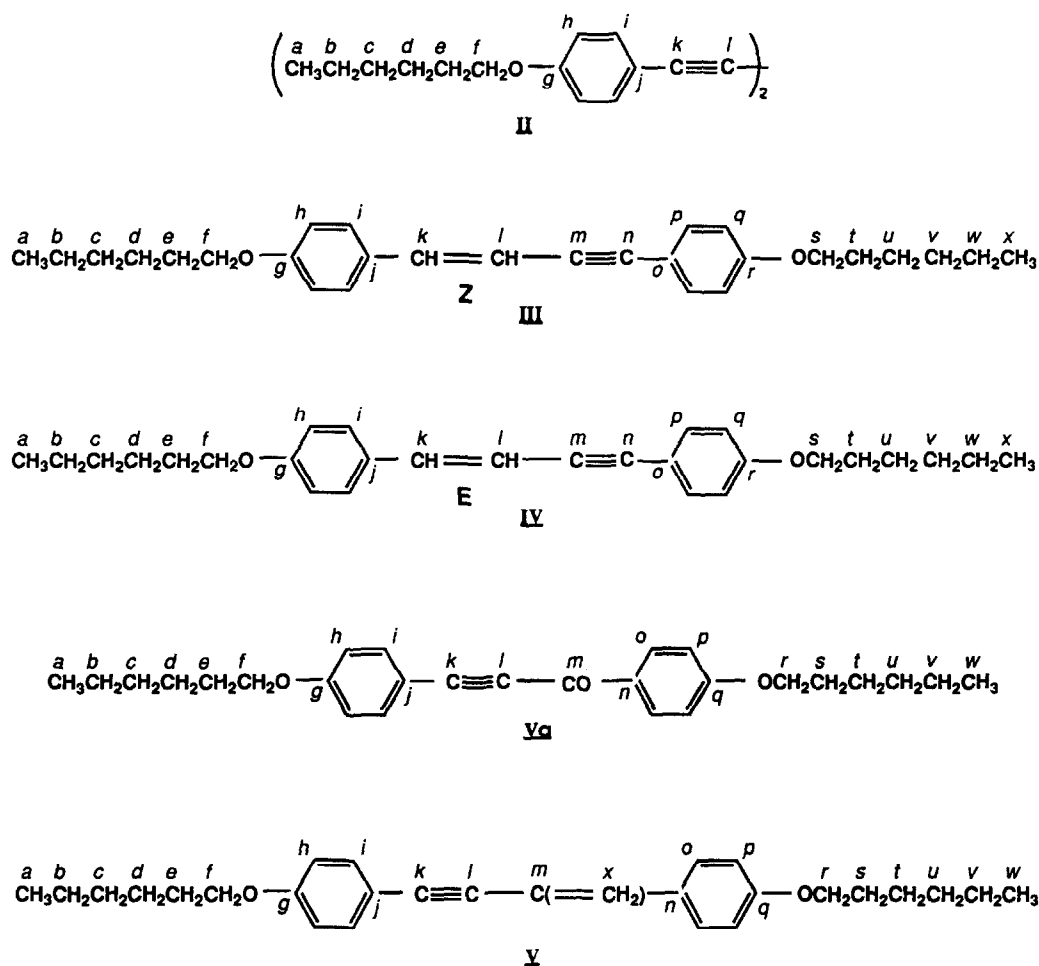
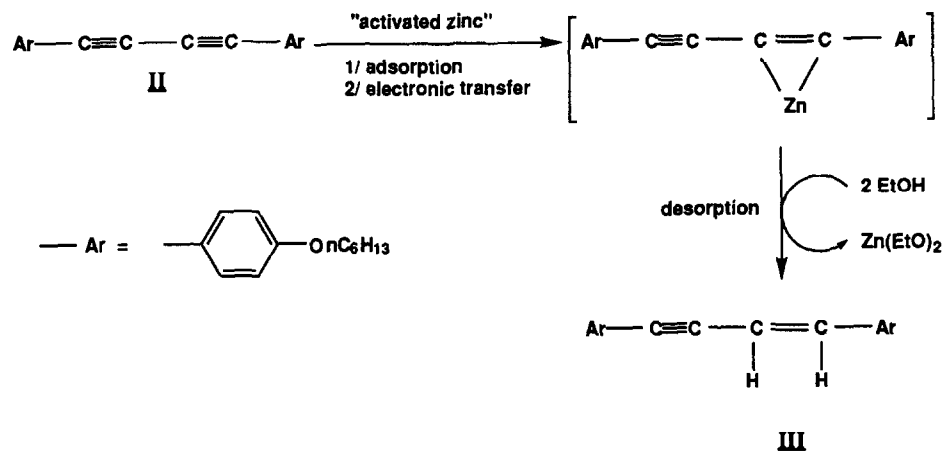


Figure 1 Chemical structures of linear dimers II–V and ynone Va



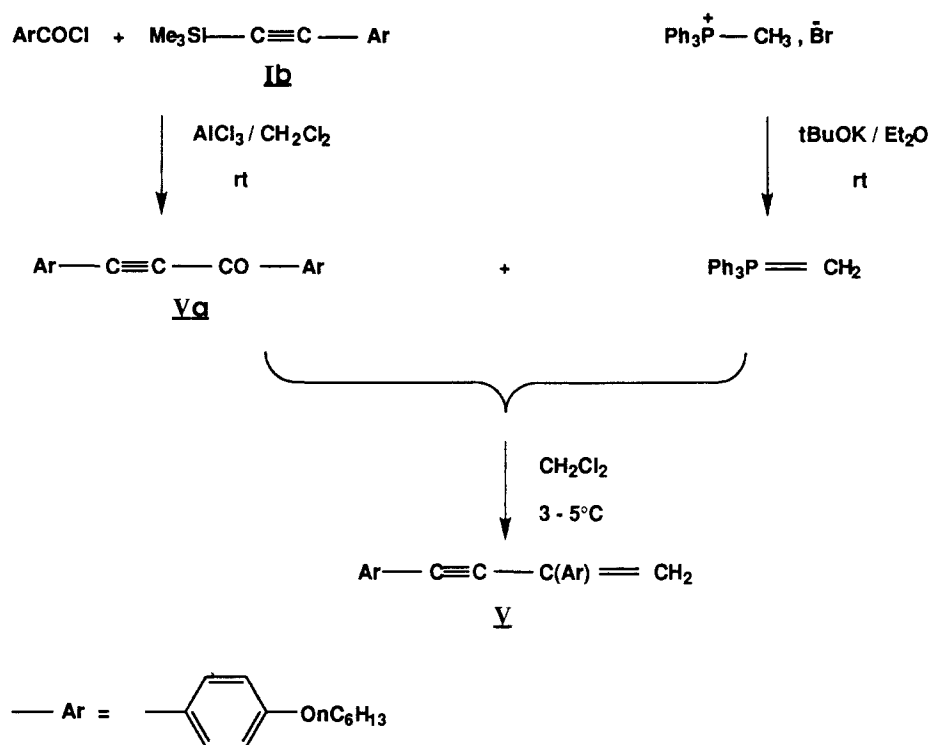
Scheme 2

h and q); 115.6 (o); 129.6 (j); 130.2 (2C, i); 132.8 (2C, p); 137.4 (k); 159.2 (2C, g and r).

Preparation of 1,4-di[4'-(hexyloxy)phenyl]-1-butene-3-yne E IV

In a quartz flask, a solution of the Z isomer **III** (1.90 g, 4.7 mmol) in cyclohexane (25 ml) was first bubbled with argon and then irradiated with a mercury lamp beam (300–400 nm) located at 60 cm away from the reaction flask. After 9 h of irradiation, the solvent was removed

from the reaction mixture to give a residual solid. This solid was washed many times with pentane so that the almost insoluble E enyne **IV** was isolated from the soluble Z dimer **III**. The solid fraction was dried under vacuum to give 1.2 g of crude product. After crystallization in cyclohexane, pure dimer **IV** was collected (0.95 g, 2.4 mmol, 50%). From filtrates the unreacted Z enyne **III** with some E isomer **IV** can be recovered and used again for another isomerization reaction. M.p. = 117–118°C. I.r.: 2200 (C≡C); 950 (CH=CH *trans*). ¹H n.m.r.: 7.11 and 7.10 (2m, 8H, *H* atom); 6.9H (d,



Scheme 3

$J = 16.2$, 1H, =CH-Ph); 6.22 (d, $J = 16.2$, 1H, =CH-C≡); 3.96 (t, $J = 6.5$, 2H, CH₂O); 3.95 (t, $J = 6.5$, 2H, CH₂O); 1.72–1.83 (m, 4H, CH₂CH₂O); 1.30–1.50 (m, 12H, CH₃(CH₂)₃); 0.91 (t, $J = 6.7$, 6H, CH₃). ¹³C n.m.r.: 14.1 (2C, a and x); 22.6 (2C, b and w); 25.7 (2C, d and u); 29.2 (2C, e and t); 31.6 (2C, c and v); 68.1 (2C, f and s); 87.9 (m); 91.1 (n); 105.8 (l); 114.5 and 114.7 (2 × 2C, h and q); 115.5 (o); 127.5 (2C, i); 129.2 (j); 132.9 (2C, p); 140.1 (k); 159.1 and 159.6 (g and r).

Preparation of 1,3-di[4'-(hexyloxy)phenyl]-2-propynone Va

A solution of 1-(hexyloxy)-4-(2-(trimethylsilyl)ethynyl)benzene¹ **Ib** (5.05 g, 18.4 mmol) and of 4-(hexyloxy)benzoylchloride (4.0 g, 16.6 mmol) in dichloromethane (4 ml) was added dropwise to an ice bath cooled suspension of aluminium chloride (2.5 g, 18.7 mmol) in dichloromethane (15 ml). After the addition of rinsing dichloromethane (2 × 4 ml), the reaction mixture was left to return to room temperature and maintained at this temperature for 4 h 30 min. Then a few drops of acid chloride were added to complete the reaction. The reaction mixture was poured into aqueous hydrochloric acid (50 ml, 1.25 N) 30 min later. The organic layer was extracted with dichloromethane (3 × 30 ml) then dried over magnesium sulfate. After solvent evaporation, 7.04 g of crude product were obtained and percolated on silica gel (140 g) using a mixture of petroleum ether/ethyl acetate (from 100/0 to 95/5) as eluent to give pure **Va** (5.26 g, 12.9 mmol, 70%). M.p. = 67–68°C. I.r.: 2180 (C≡C); 1630 (C=O). ¹H n.m.r.: 7.56 (m, 4H, H arom Ph-CO); 7.29 (m, 4H, H arom Ph-C≡); 4.04 (t, $J = 6.5$, 2H, CH₂O); 3.99 (t, $J = 6.5$, 2H, CH₂O); 1.74–1.87 (m, 4H, CH₂CH₂O); 1.30–1.50 (m, 12H, CH₃(CH₂)₃); 0.91 (t, $J = 6.6$, 6H, CH₃). ¹³C n.m.r.: 14.1 (2C, a and w); 22.6 (2C, b and v); 25.7 (2C, d and t); 29.1 (2C, e and s); 31.6 (2C, c and u); 68.3 and 68.4 (f and r); 86.8 and 93.6

(k and l); 111.9 (j); 114.3 and 114.9 (2 × 2C, h and p); 130.3 (n); 131.9 (2C, o); 135.0 (2C, i); 161.2 (g); 164.0 (q); 176.8 (m).

Preparation of 2,4-di[4'-(hexyloxy)phenyl]-1-buten-3-yne V

Methyltriphenylphosphonium bromide (3.06 g, 8.6 mmol) in ether (15 ml) was added to potassium tertbutylate (1.0 g, 8.9 mmol) in ether (5 ml) at room temperature. After disappearance of the phosphonium salt, determined by t.l.c. analysis (ethyl acetate/methanol: 50/50) methyltriphenylphosphonium bromide (0.29 g, 0.8 mmol) was added again. One hour later, the reaction mixture was cooled down to 5°C. Then a cool solution of **Va** (3.06 g, 7.5 mmol) in ether (20 ml) was added. The reaction was monitored with t.l.c. analysis (cyclohexane/ethyl acetate: 95/5). After 6 h at 5°C, the reaction mixture was filtered and the solvent evaporated. The resulting crude product was dissolved in pentane (50 ml) and put in the refrigerator so that triphenylphosphine oxide precipitated. After filtration and evaporation the crude product (2.9 g) was purified on silica gel column (150 g) using a mixture of petroleum ether and ethyl acetate (98/2) as eluent. The enyne **V** was isolated pure (1.9 g, 4.7 mmol, 60%). M.p. = 63–64°C. I.r.: 2190 (C≡C); 880 (=CH₂). ¹H n.m.r.: 7.26 (m, 4H, H arom Ph-C=); 7.15 (m, 4H, H arom Ph-C≡); 5.82 and 5.60 (2d, $J = 0.9$ determined at 400 MHz frequency, 2 × 1H, CH₂=); 3.96 and 3.97 (2t, $J = 6.6$, 4H, CH₂O); 1.72–1.84 (m, 4H, CH₂CH₂O); 1.25–1.52 (m, 12H, CH₃(CH₂)₃); 0.91 (t, $J = 6.7$, 6H, CH₃). ¹³C n.m.r.: 14.1 (2C, a and w); 22.6 (2C, b and v); 25.7 (2C, d and t); 29.22 and 29.17 (e and s); 31.6 (2C, c and u); 68.0 (2C, f and r); 87.5 and 90.7 (k and l); 114.2 and 114.5 (2 × 2C, h and p); 115.0 (m); 117.8 (x); 127.3 (2C, o); 129.8 and 130.1 (j and n); 133.1 (2C, i); 159.28 and 159.33 (g and q).

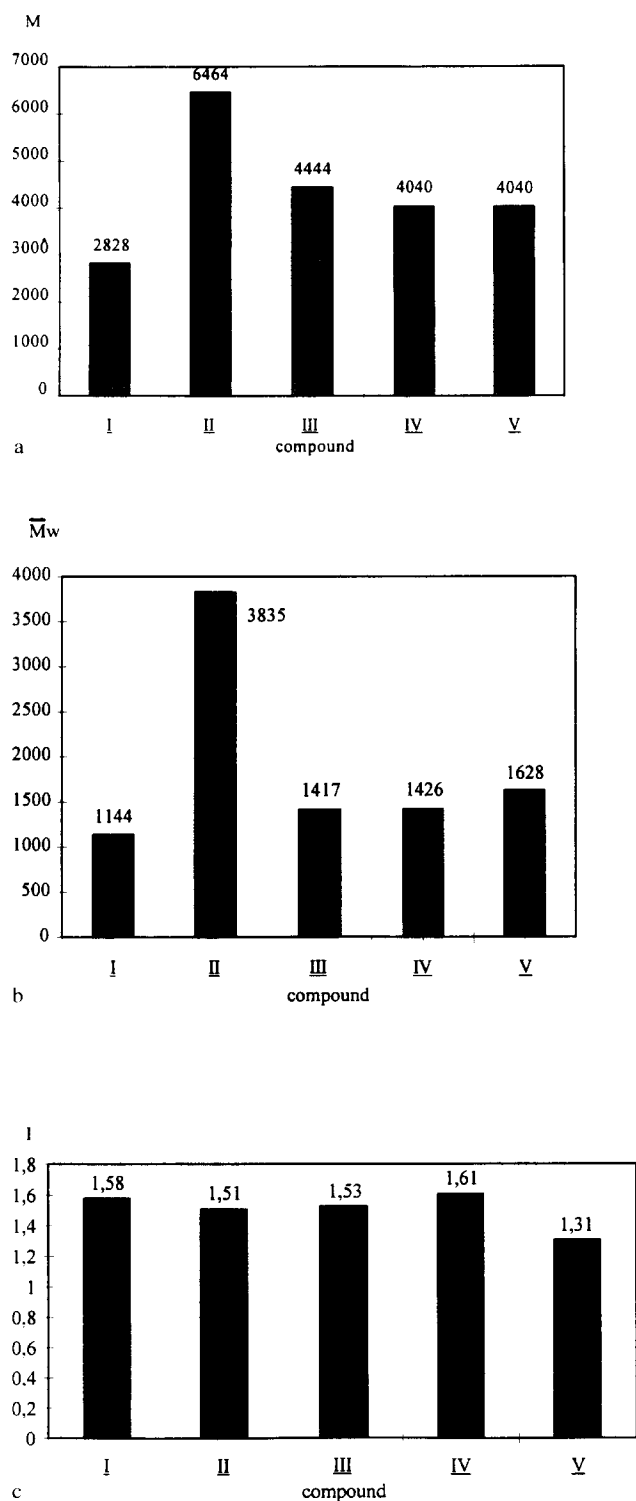


Figure 2 Thermal treatment of dimers II–V and monomer I: highest molecular weight (M) detected by SIMS analysis (a); average molecular weight (\bar{M}_w) and polydispersity ratio (I) measured by s.e.c. analysis (b and c)

RESULTS AND DISCUSSION

Synthesis of linear dimers II–V

The diyne II was synthesized in high yield (94%) from monomer I using the modified oxidative Glaser coupling⁹.

The Z enyne III was prepared with complete diastereoselectivity and good yield (83%) from the selective hydrogenation of one triple bond of the diyne II by activated zinc in ethanol solution¹⁰ (Scheme 2).

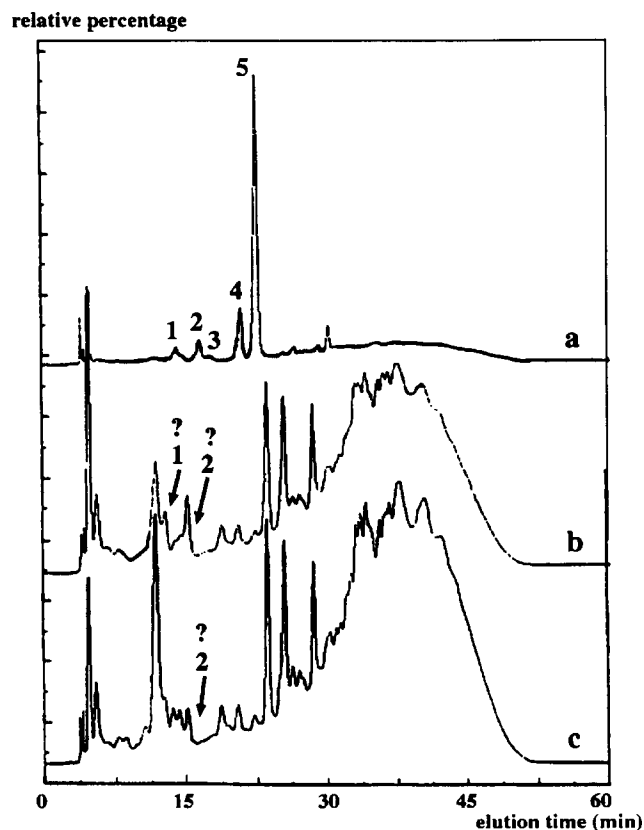


Figure 3 H.p.l.c. chromatograms of crude products of the thermal polymerization of: monomer I (trace a); Z enyne III (trace b); Z enyne III with u.v. detector working at 260 nm (trace c)

The E enyne IV was obtained by the photochemical isomerization of the Z enyne III performed in an apolar solvent in the presence of iodine used as catalyst^{11,12}.

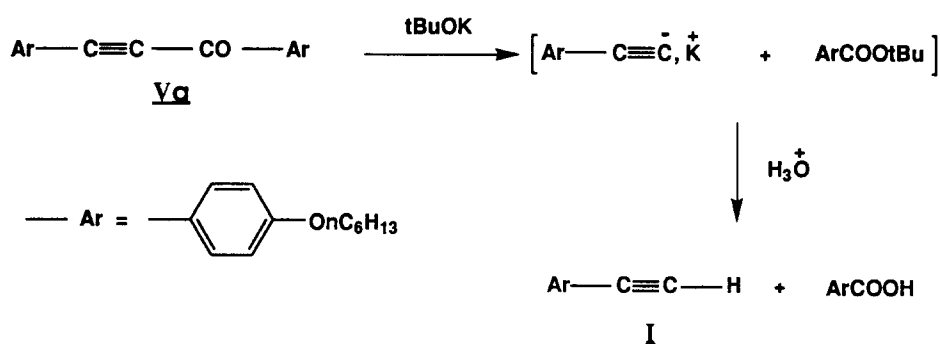
The dimer V was synthesized through a Wittig reaction¹³ between the corresponding α -ynone Va and the methylenephosphonium ylide obtained *in situ* from potassium *tert*-butylate and methyltriphenylphosphonium bromide (Scheme 3). The α -ynone was previously prepared from the acylation of Ib¹ by the 4-(hexyloxy)benzoyl chloride (Aldrich) in presence of aluminium chloride¹⁴. To obtain the enyne V with good yield (60%) it is necessary to prepare and isolate it at low temperature (to prevent its polymerization).

Moreover, before reacting the α -ynone with the ylide, it is also necessary to check that the base used to form the ylide is wholly consumed. If not, the cleavage of the α -ynone¹⁵ takes place leading to the formation of I (Scheme 4).

Thermal polymerization of linear dimers II–V

Dimers II–V were sampled according to the experimental procedure described for monomer I and cured according to a gradual thermal step treatment¹.

The polymerization of linear dimers leads to the formation of oligomers with higher molecular weight than the polymerization of the monomer I (Figure 2). Moreover h.p.l.c. analyses also show this larger proportion of high molecular weight oligomers in the polymerization products of the linear dimers (traces a and b of Figures 3, 4 and 5). The polymerization of II and V gives almost no naphthalenic dimers and benzenic trimers isolated in the cured product of I. When polymerized, the enynes III and IV form some low



Scheme 4

Table 1 S.e.c. analysis: average molecular weight \bar{M}_w and polydispersity ratio I of the thermal polymerization products of monomer/linear dimer mixtures in x/y molar proportions

Linear dimer x/y	Diyne II		Z enyne III		E enyne IV		Vinylidene enyne V	
	\bar{M}_w	I	\bar{M}_w	I	\bar{M}_w	I	M_w	I
10/0	1114	1.58	1114	1.58	1114	1.58	1114	1.58
9/1	1504	1.66	1386	1.70	1347	1.63	1358	1.56
5/5	2655	1.65	1533	1.61	1540	1.57	1528	1.46
0/10	3835	1.51	1417	1.53	1426	1.61	1661	1.26

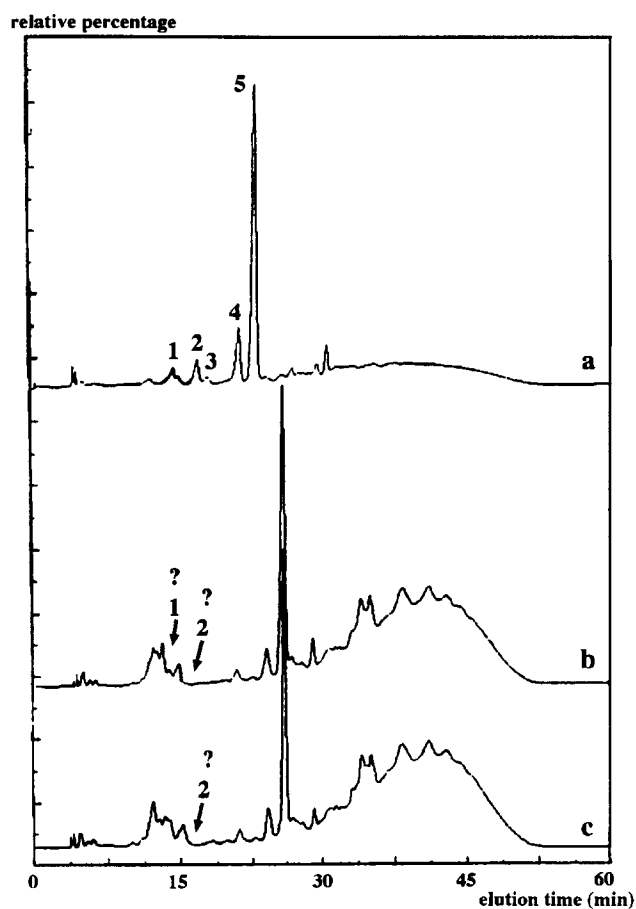


Figure 4 H.p.l.c. chromatograms of crude products of the thermal polymerization of: monomer I (trace a); E enyne IV (trace b); E enyne IV with u.v. detector working at 260 nm (trace c)

molecular weight compounds. One of them could be the 2,7-disubstituted naphthalenic dimer **1**, but in any case cannot be the 1,7-disubstituted naphthalenic dimer **2**, as demonstrated using u.v. detection at 260 nm which is the

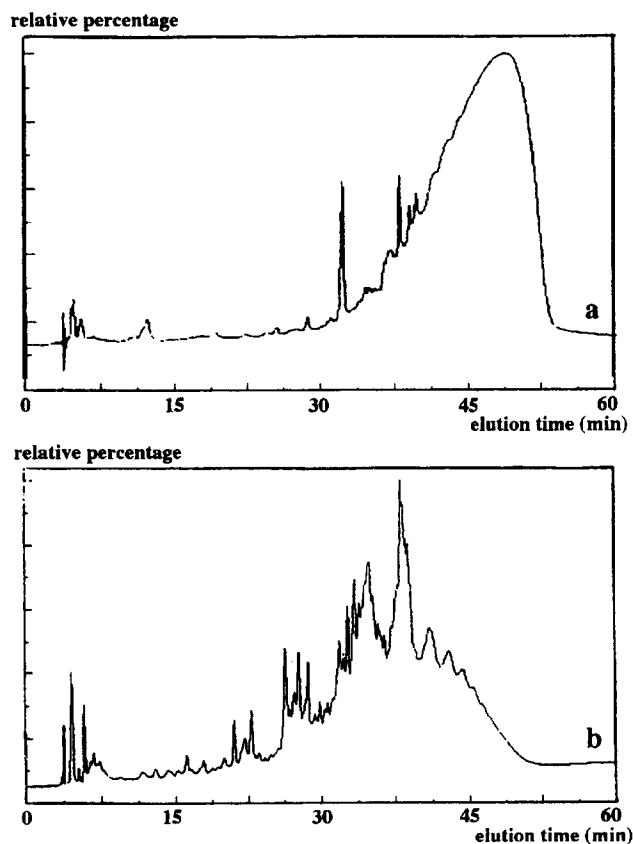


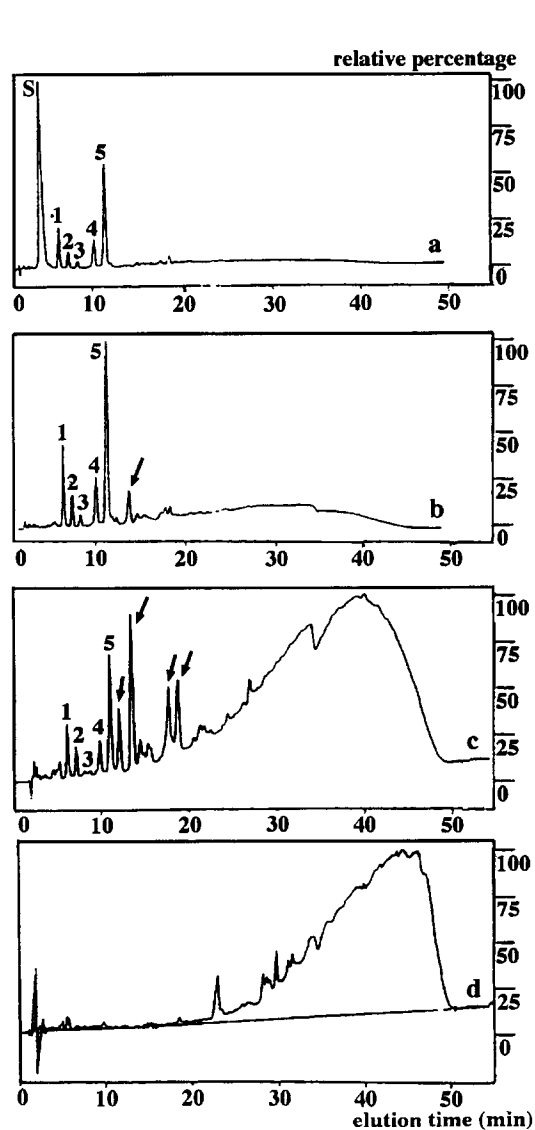
Figure 5 H.p.l.c. chromatograms of crude products of the thermal polymerization of: diyne II (trace a); vinylidene enyne V (trace b)

maximum absorption wavelength of these compounds (traces c of Figures 3 and 4) (unless otherwise specified u.v. detection was at 270 nm).

As the polymerization of linear dimers leads to the formation of high molecular weight oligomers in comparison to the monomer polymerization, we can assume that either the polymerization mechanism is

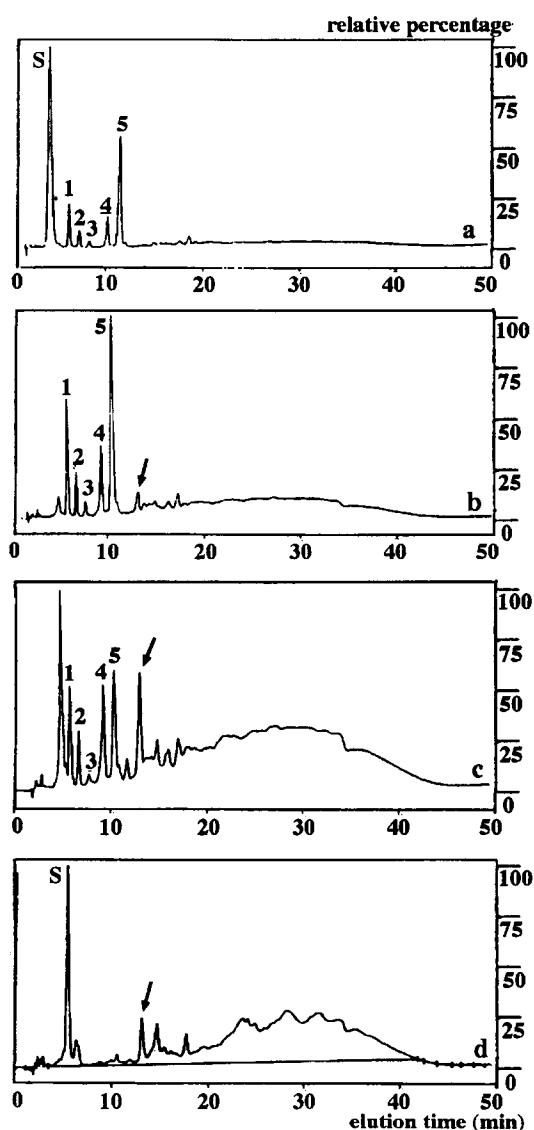
Table 2 S.e.c. analysis: average molecular weight \bar{M}_w and polydispersity ratio I of the products formed during the thermal polymerization of dimers II–V and monomer I

Compound	Time	3 h (180°C)	4 h (220°C)	7 h 24 min (280°C)
Diyne II	\bar{M}_w	455	2138	3629
	I	1.02	1.21	1.57
Z enyne III	\bar{M}_w	324	1255	1416
	I	1.04	1.23	1.25
E enyne IV	\bar{M}_w	983	1171	1578
	I	1.07	1.16	1.25
Vinylidene enyne V	\bar{M}_w	2042	1698 ^a	1628
	I	1.45	1.41	1.31
Monomer I	\bar{M}_w	1495	1534	1252
	I	1.51	1.57	1.57

^a 5 h (220°C)

S : standard
arrows indicate new species

Figure 6 H.p.l.c. chromatograms of crude products of the thermal polymerization of I/II mixtures in molar proportions [u.v. detector working at 254 nm]: 10/0 (trace a); 9/1 (trace b); 5/5 (trace c); 0/10 (trace d)



S : standard
arrows indicate new species

Figure 7 H.p.l.c. chromatograms of crude products of the thermal polymerization of I/III mixtures in molar proportions [u.v. detector working at 254 nm]: 10/0 (trace a); 9/1 (trace b); 5/5 (trace c); 0/10 (trace d)

different or the propagation rate of the reaction of II–V to produce oligomers is higher than the rate of their cyclization into naphthalenic dimers (1, 2) and benzenic trimers (3–5). Besides the formation of small quantities of cyclized oligomers could also come from a thermal decomposition of the enyne leading to the monomer I. Now a question arises: what would be the effect of the monomer presence on the polymerization mechanism of the dimers? So mixtures of monomer and linear dimers in the molar proportion 9/1 and 5/5 have been polymerized.

Polymerization of monomer–linear dimer mixtures

From the s.e.c. results (Table 1) it can be pointed out that the molecular weight increases as a function of the dimer concentration. On the other hand h.p.l.c. analyses show two new features for the polymerization of monomer–dimer mixtures:

- (a) new species are produced (see arrows, Figures 6–9) with each dimer,
- (b) in the case of the mixtures with the enynes III and IV, the ratios of the produced naphthalenic dimers and benzenic trimers are modified.

These results are in agreement with the following conclusions: the linear dimers are not reaction intermediates in the monomer polymerization. Furthermore a reaction between monomer and dimer can occur (probably to some extent) during the copolymerization in addition to individual polymerization of each partner.

Relative thermal reactivity of monomer I and dimers II–V

The thermal reactivity of the linear dimers II–V has been examined and compared with the monomer one. From the d.s.c. measurements (Figure 10), we observed

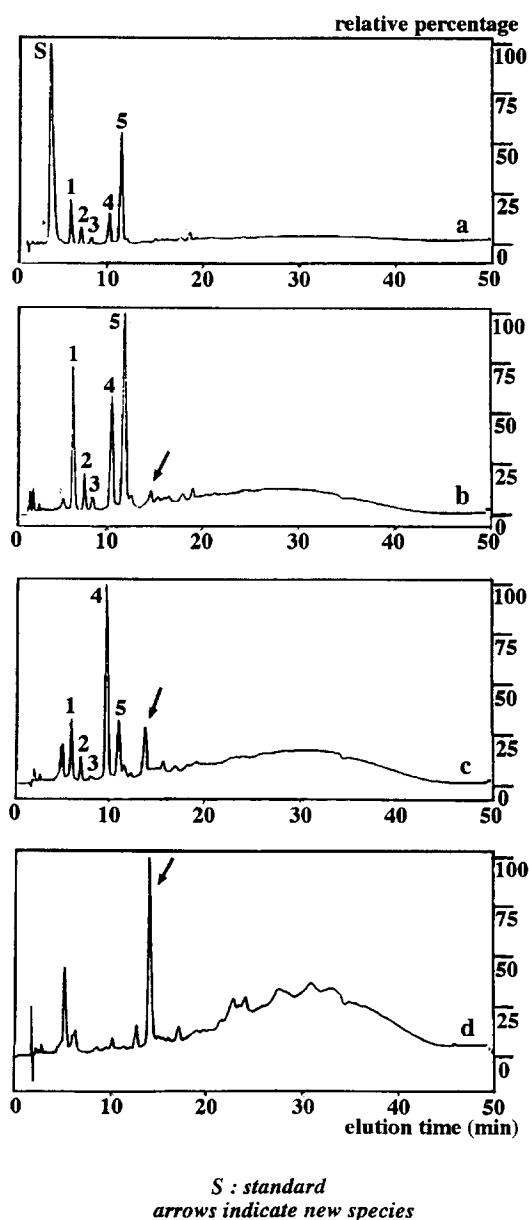


Figure 8 H.p.l.c. chromatograms of crude products of the thermal polymerization of I/IV mixtures in molar proportions [u.v. detector working at 254 nm]: 10/0 (trace a); 9/1 (trace b); 5/5 (trace c); 0/10 (trace d)

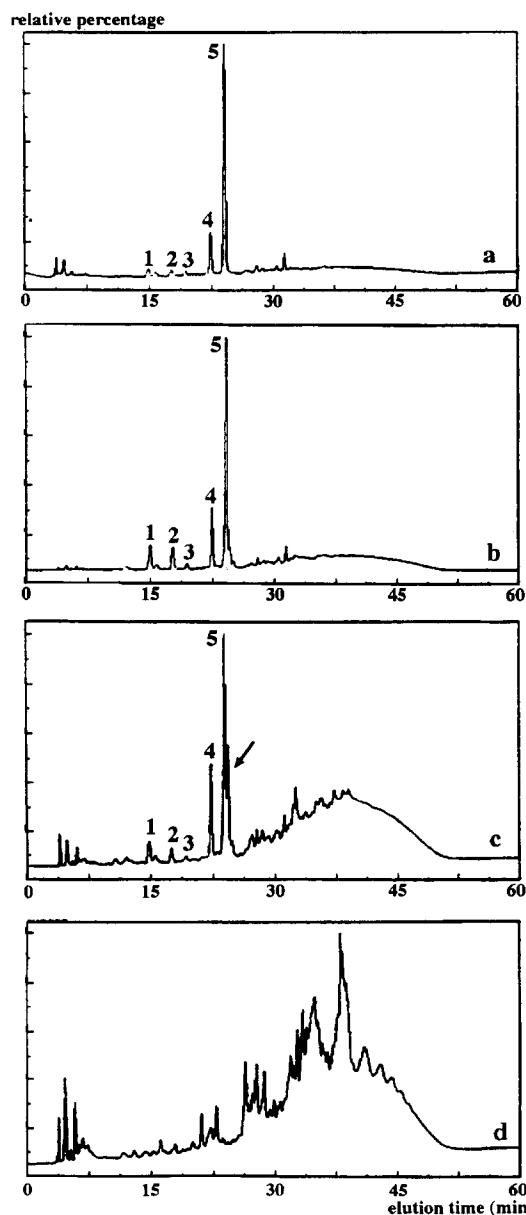


Figure 9 H.p.l.c. chromatograms of crude products of the thermal polymerization of I/V mixtures in molar proportions: 10/0 (trace a); 9/1 (trace b); 5/5 (trace c); 0/10 (trace d)

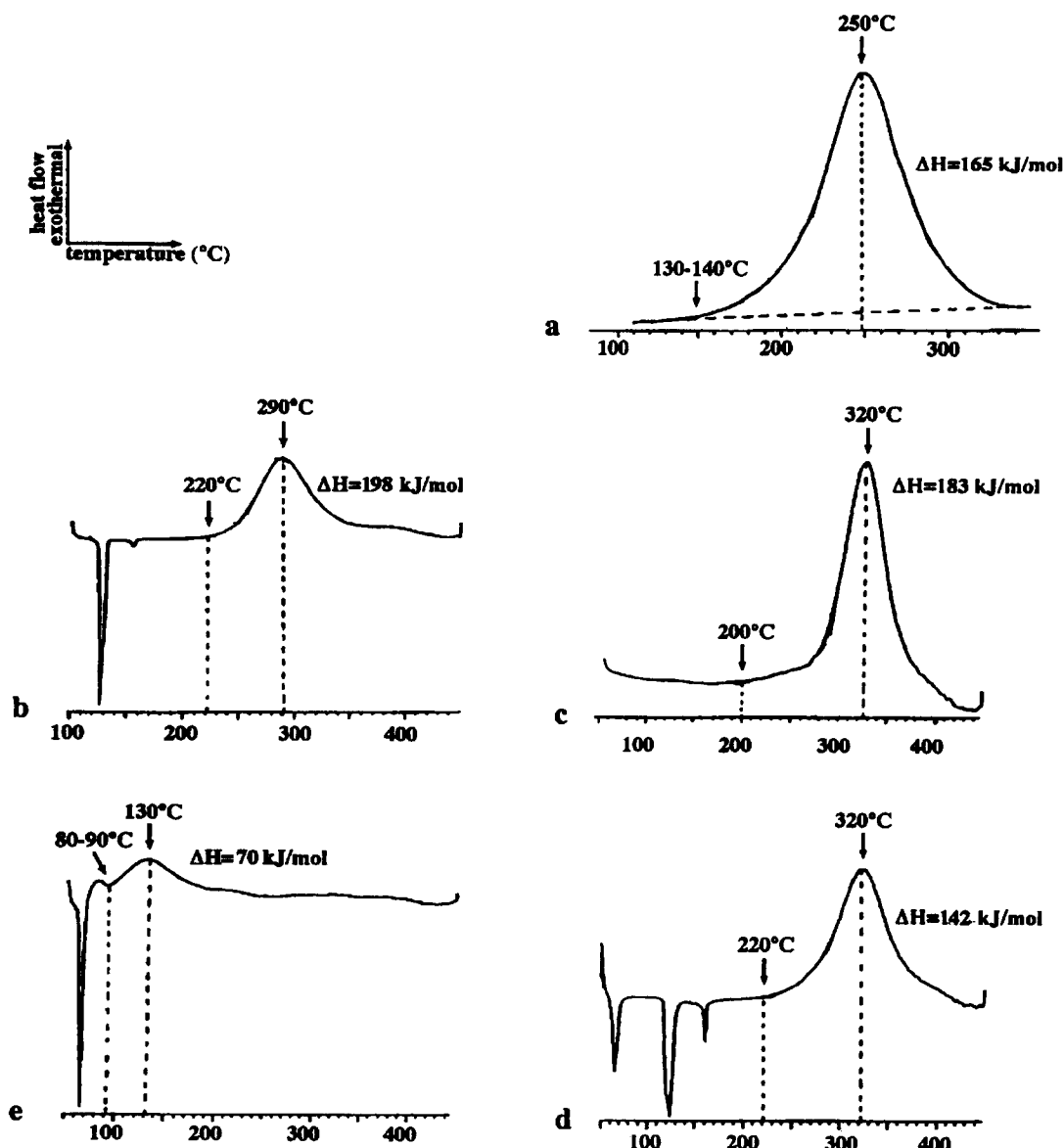


Figure 10 D.s.c. thermograms and polymerization enthalpies ΔH : monomer I (trace a); diyne II (trace b); Z enyne III (trace c); E enyne IV (trace d); vinylidene enyne V (trace e)

that the linear dimers, except V, polymerize at higher temperatures than I.

A kinetic study has confirmed these results: the thermal reactivity of compounds I–V has been studied under the same curing conditions (thermal step treatment), the s.e.c. analyses (Table 2) show that compounds V and I started to react at 180°C, whereas II–IV reacted only at 220°C and they did it slowly. Their conversion gets more important only at 280°C. By the end of the thermal treatment unreacted linear dimer still remains (h.p.l.c. analyses, Figures 11–13). The polymerization of the vinylidene dimer V is very different: after 3 h at 180°C there is no more residual V (Figure 14) and high molecular weight compounds are already produced (Table 2). It seems that similarly to the thermal treatment of I¹, the average molecular weight of the cured product of V decreases along reaction time and temperature as well as the polydispersity (Table 2). Some low retention time species appear by the end of the thermal treatment (see arrows, Figure 14). It may mean that a depolymerization process happens to yield shorter and more stable oligomers.

CONCLUSION

Are the linear dimers reaction intermediates of the thermal polymerization of the arylacetylene?

The experimental results herein described allow us to answer negatively.

Case of the linear dimers II–IV. Their polymerization products (when polymerized with or without the monomer) are very different from the monomer one. Moreover, if they were reaction intermediates, they should accumulate in the cured product of I because of their lowest reactivity. But it is not the case: they are not observed in h.p.l.c. analyses even if the u.v. detection is used at their maximum absorption wavelength.

Case of the dimer V. Its cured product is very different from the monomer one and it does not contain any aromatic dimers and trimers 1–5. So we believe V is not an intermediate of the thermal polymerization of I.

Therefore, to explain our experimental results, another reaction mechanism has to be suggested¹⁶.

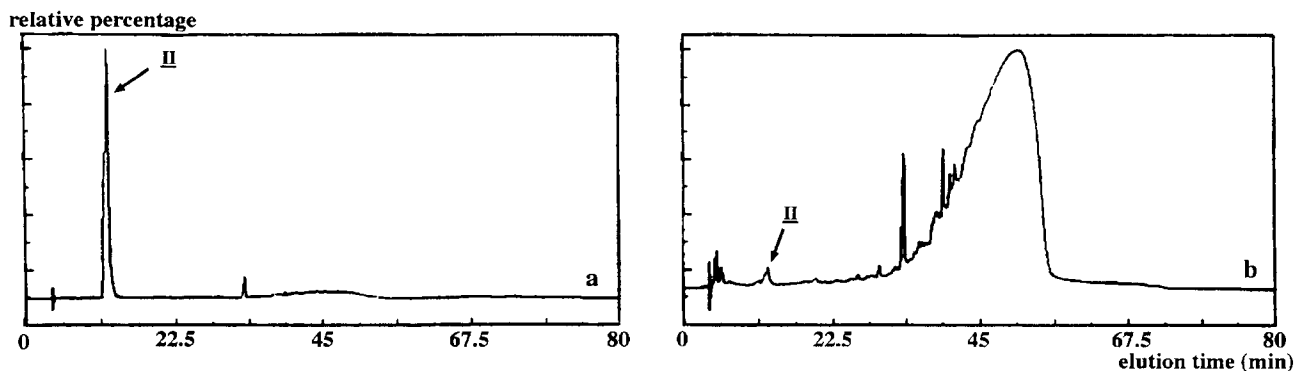


Figure 11 H.p.l.c. chromatograms of crude products of the thermal treatments of II: 3 h at 180°C and 2 h at 220°C (trace a) with additional 2 h at 280°C (trace b)

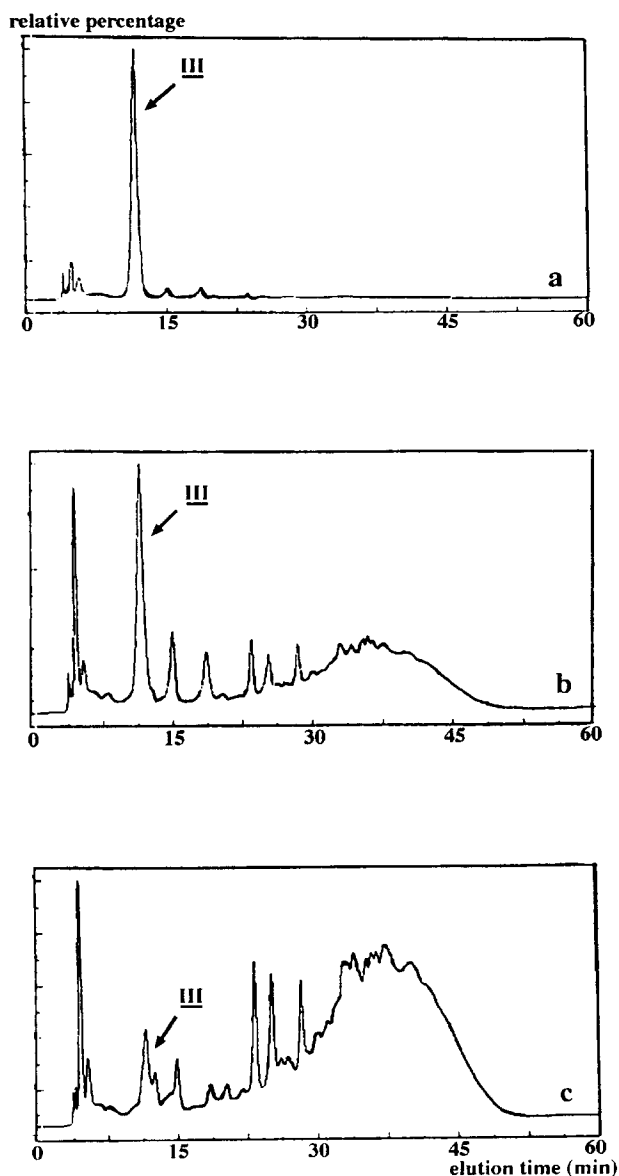


Figure 12 H.p.l.c. chromatograms of crude products of the thermal treatments of III: 3 h at 180°C and 2 h at 220°C (trace a); with additional 1 h at 280°C (trace b); with another additional 1 h at 280°C (trace c)

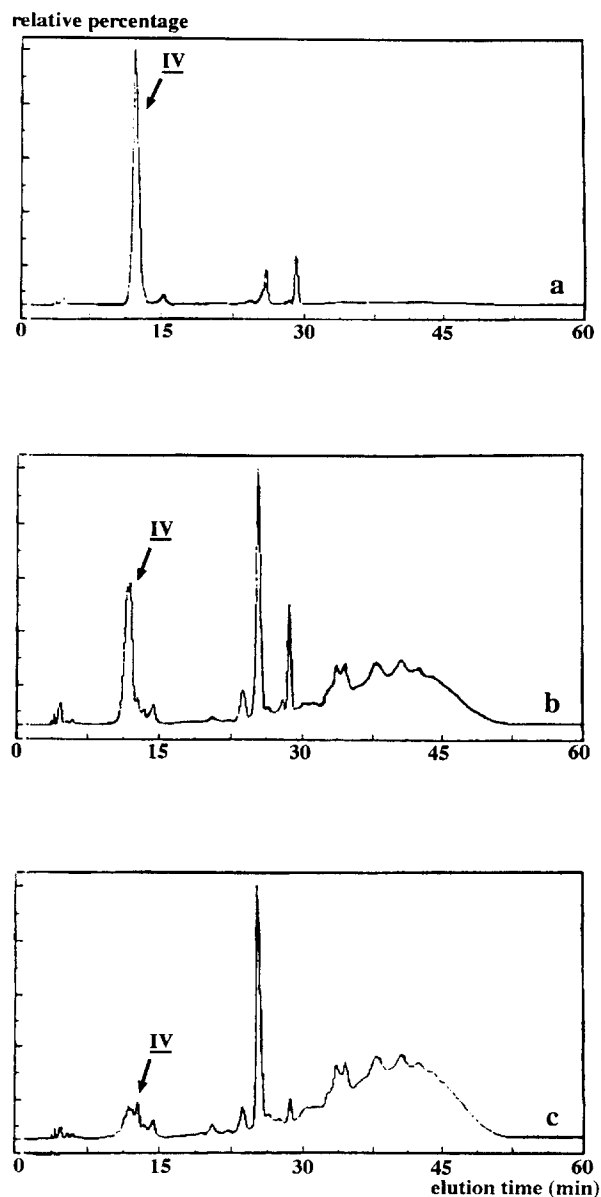


Figure 13 H.p.l.c. chromatograms of crude products of the thermal treatments of IV: 3 h at 180°C and 2 h at 220°C (trace a); with additional 1 h at 280°C (trace b); with another additional 1 h at 280°C (trace c)

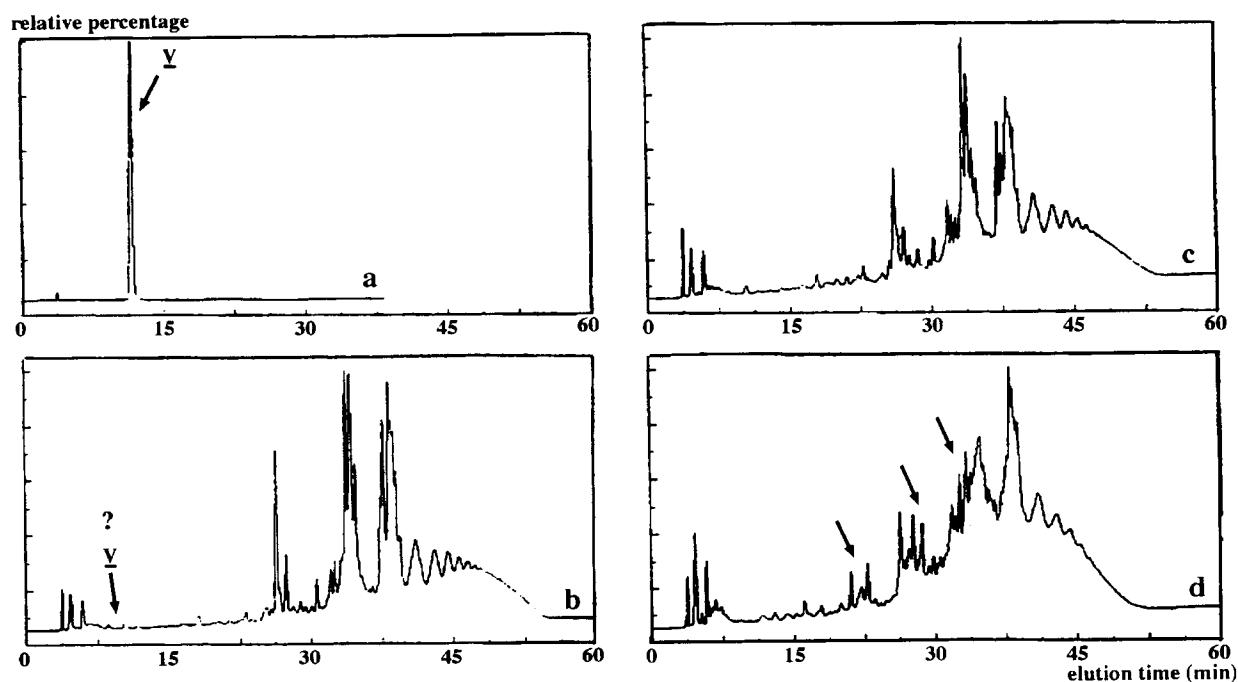


Figure 14 H.p.l.c. chromatograms of crude products of the thermal treatments of V: 3 h at 180°C and 2 h at 220°C (trace a); with additional 1 h at 280°C (trace b); with another additional 1 h at 280°C (trace c)

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