PII: S0032-3861(96)00936-6

New alternating donor–acceptor type conjugated copolymer: poly[bicarbazolylene-*alt*-phenylene-bis(cyanovinylene)]. Synthesis and properties

V. Boucard, T. Benazzi, D. Adès, G. Sauvet* and A. Siove

Laboratoire de Recherches sur les Macromolécules (Unité associée au CNRS), Institut Galilée, Université Paris-Nord, F-93430 Villetaneuse, France
(Received 31 July 1996; revised 10 October 1996)

The Knoevenagel condensation has been applied to the synthesis of ([bicarbazolylene]-*alt*-[phenylene-bis(cyanovinylene)]) copolymers. These materials are mostly insoluble in organic solvents but, depending on the reaction conditions a small amount of soluble oligomers could be obtained. The alternation of electron-donor carbazolylene units and electron-withdrawing phenylene-cyanovinylene entities is believed to be partly responsible for the rigidity of the macromolecular chains, so explaining their insolubility. Moreover, this regular alternation of donor–acceptor moieties is thought to be responsible for the lowering of the bandgap of the soluble oligomers and for decreasing the stability of the bicarbazolylium radical-cations of the doped state. Lastly, materials were fairly resistant to thermal degradation, up to 450°C. © 1997 Elsevier Science Ltd.

(Keywords: conjugated poly(bicarbazolylene-phenylene cyanovinylene) copolymer; donor–acceptor alternance; Knoevenagel condensation)

INTRODUCTION

Since the discovery of electroluminescence in poly(*p*-phenylene vinylene) (PPV)[1], a number of polymers used as an active element in light-emitting diodes (LEDs) have been reported. Various π-conjugated structures, emitting in different regions of the visible spectrum have been used. Over the last few years, improvements have been made concerning the control of colour, efficiency, durability, brightness and processibility of such materials. Among successful examples are soluble poly(2,5-dialkoxy-*p*-phenylene vinylene)s[2,3], poly(3-alkylthiophene)s[4], (phenylene vinylene-*co*-alkoxyphenylene vinylene) copolymers[5] and polymer blends composed of a PPV derivative as the electron-transporting layer and a hole-transporting matrix of poly(*N*-vinylcarbazole)[6].

We previously reported on the synthesis of soluble poly[*N*-alkyl-3,6-carbazolylene)₂-b-(3-octylthiophene)$_m$]$_n$ copolymers[7] displaying tunable electronic properties such as electrochromism and thermochromism. Moreover these copolymers, which possess both a wide-bandgap block (bicarbazolylene) and a low-bandgap block (thiophene) in the backbone, exhibit electroluminescence (from yellow-orange to red) as a function of the comonomer composition[8]. It has been shown that the electronic properties of these materials arise from both the bicarbazolylene segments and the polythiophene blocks[8]. Nevertheless, it was not possible to obtain copolymers with thiophene blocks shorter than six repeat units owing to the unfavourable reactivity ratios in the carbazole–thiophene oxidative copolymerization. Hence, in order to attain new electronic properties and in particular a blue-shifted emission, we designed a novel electroactive copolymer consisting of an alternating arrangement of bicarbazolylene and [1,4-phenylene-bis(1-cyanovinylene)] units, **1** (*Figure 1*). These donor–acceptor type copolymers were obtained by a Knoevenagel type condensation, a route which has been recently applied to the synthesis of PPV derivatives[9]. This first report presents the synthesis, characterization and study of some physico-chemical and electronic properties of these copolymers in the neutral and the doped states. Electroluminescence of these materials will be the subject of a forthcoming paper.

EXPERIMENTAL

N-*Octylcarbazole (2)*

N-Octylcarbazole was prepared from carbazole according to the method described by Pielichioswki *et al.*[10] for the synthesis of *N*-vinylcarbazole. Carbazole (Aldrich) was recrystallized from hexane and obtained as slightly brownish needles.

In a 250 ml two-necked flask fitted with a reflux condenser, 10 g of carbazole (60 mmol) were dispersed in 75 ml of a sodium hydroxide solution (16 mol l⁻¹). 2.5 ml of an aqueous solution of triethylbenzylammonium chloride (TEBAC, 2.5 mol l⁻¹), as a phase transfer

---

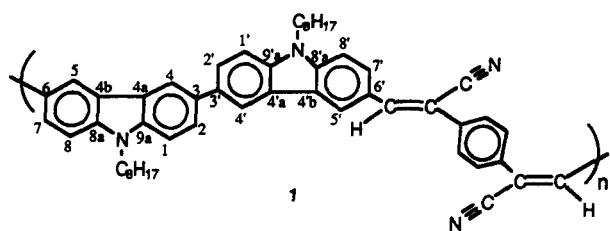*To whom correspondence should be addressed

Figure 1 Poly{[6,6'-(N, N'-dioctyl-3,3'-bicarbazyl)ylene]-*alt*-[1,4-phenylene-bis(1-cyanovinylene)} (**1**)

catalyst, and 75 ml (430 mmol) of distilled 1-bromooctane were added. The mixture was heated to reflux under vigorous stirring for 4 h and then decanted. The organic layer was isolated, washed with water and dried over magnesium sulfate. Finally, **2** was purified by distillation under reduced pressure (bp 150–155°C at 10^{-2} mmHg) and recovered as a yellow viscous liquid with an almost quantitative yield. ^{1}H n.m.r. (CDCl$_3$): δ 8.07 (d, H4, H5); 7.38–7.36 (m, H2, H3, H6, H7); 7.22 (t, H1, H8); 4.21 (t, 2H); 1.81 (q, 2H); 1.24 (m, 10H); 0.85 (t, 3H). ^{13}C n.m.r. (CDCl$_3$): δ 140.4 (C8a,9a); 125.5 (C3,6); 122.8 (C4a,4b); 120.3 (C4,5); 118.6 (C2,7); 108.2 (C1,8); 43.0, 31.8, 29.4, 29.2, 28.9, 27.3, 22.8 (seven CH$_2$); 14.1 (CH$_3$).

N,N'-Dioctyl-3,3'-bicarbazyle (3)

N,N'-Dioctyl-3,3'-bicarbazyle was prepared as previously reported[7]. In a two-necked flask fitted with a reflux condenser, a dropping funnel and a magnetic stirrer, a solution of 10 g of N-octylcarbazole (**2**) (36 mmol) in 50 ml of freshly distilled chloroform was added dropwise to a solution of 23.3 g of iron (III) chloride (144 mmol) in 200 ml of chloroform. After stirring overnight, at room temperature, the resulting greenish solution of bicarbazolylium radical-cations was poured in a large excess of methanol and the white precipitate was collected in a Büchner funnel and washed with acidified water and methanol successively. The target compound (**3**) (mp 67°C) was obtained in quantitative yield as a white powder. ^{1}H n.m.r. (CDCl$_3$): δ 8.43 (s, H4,4'); 8.18 (d, H5,5'); 7.81 (d, H1,1'); 7.22–7.46 (m, H2,2',8,8',7,7'); 4.28 (t, 4H); 1.88 (q, 4H); 1.28 (m, 20H); 0.86 (t, 6H). ^{13}C n.m.r. (CDCl$_3$): δ 140.9 (C9a,9'a); 139.5 (C8a,8'a); 133.3 (C3,3'); 125.6 (C4a,4'a); 125.5 (C6,6'); 123.4 (C2,2'); 123.0 (C4b,4'b); 120.4 (C5,5'); 118.9 (C4,4'); 118.7 (C7,7'); 108.8–108.7 (C1,1' and C8,8'); 43.1, 31.8, 29.4, 29.2, 29.0, 27.3, 22.6 (CH$_2$); 14.1 (CH$_3$).

N,N'-Dioctyl-3,3'-bicarbazyl-6,6'-dicarbaldehyde (4)

The dicarbaldehyde (**4**) was prepared according to the method used for the synthesis of N-ethylcarbazole-3-carbaldehyde[11]. In a three-necked flask fitted with a condenser, a nitrogen inlet and a magnetic stirrer, a solution of 8 g of **3** (14 mmol) in 10 ml of freshly distilled *o*-dichlorobenzene (ODCB) was added dropwise to a mixture of 1.3 ml of phosphorus oxychloride (14 mmol) and 1.2 ml of N,N-dimethylformamide (15 mmol) at 0°C. After addition, the reaction medium was heated to 90–100°C for 4 h and, after cooling to 25°C, poured into water. The organic layer was isolated and evaporated under vacuum. The resulting solid brownish dicarbaldehyde, **4**, was purified by column chromatography (eluent: chloroform/hexane, vol. ratio 3/1). Yield: 4.7 g (55%) of a yellow powder. Recrystallization from diethylether gave 4.1 g of yellow crystals (mp = 117°C). C$_{42}$H$_{48}$N$_2$O$_2$

(612), Calc.: C 82.35, H 7.84, N 4.58, O 5.23; Found: C 82.00, H 8.06, N 4.47, O 5.45. ^{1}H n.m.r. (CDCl$_3$): δ 10.09 (s, CHO); 8.64 (s, H4,4'); 8.42 (s, H5,5'); 7.98 (d, H1,1'); 7.85 (d, H2,2'); 7.49 (d, H8,8'); 7.43 (d, H7,7'); 4.28 (t, 4H); 1.86 (m, 4H); 1.23 (m, 20H); 0.85 (t, 6H).

^{13}C n.m.r. (CDCl$_3$): δ 191.7 (CHO); 144.4 (C8a,8'a); 140.3 (C9a,9'a); 134.1 (C6,6'); 128.5 (C3,3'); 127.1 (C4b,4'b); 126.3 (C4a,4'a); 124.1 (C5,5'); 123.6 (C7,7'); 123.1 (C2,2'); 119.1 (C4,4'); 109.7 (C8,8'); 109.1 (C1,1'); 43.5 to 22.6 (seven CH$_2$ signals); 14.0 (CH$_3$). FTi.r. (powder): 1350 cm^{-1} (N-CH$_2$); 2726 and 1672 cm^{-1} (CHO); 902 and 799 cm^{-1} (C-H carbazole) (*Figure 3a*).

Benzene-1,4-diacetonitrile (5)

Benzene-1,4-diacetonitrile (Aldrich) was recrystallized from hexane and obtained as colourless crystals (mp 98°C). ^{1}H n.m.r. (deuterated DMSO): δ 7.4 (s, 4H); 4.0 (s, 4H). ^{13}C n.m.r. (deuterated DMSO): δ 139.9 (-C≡N); 128.8 (C$_{1,4}$); 119.1 (other C aromatic); 22.1 (-CH$_2$-). FTi.r. (powder): 2248 cm^{-1} (-C≡N); 2917 and 2937 cm^{-1} (-CH$_2$-); 3036 and 782 cm^{-1} (C-H phenylene) (*Figure 3b*).

Synthesis of copolymers 1

Equimolar quantities of the dialdehyde, **4**, and benzene-1,4-diacetonitrile, **5** (2 mmol), were dissolved in 20 ml of dry tetrahydrofuran (THF) and introduced into a flask fitted with condenser, nitrogen inlet and magnetic stirrer. The system was then purged with a nitrogen stream. A 0.1 M solution of the catalyst, tetrabutylammonium hydroxide (Fluka) in an isopropanol–methanol mixture (vol. ratio 10/1) was then added to the solution (see concentrations in *Table 1*). The reactions were carried out at various temperatures for 24 h, under a nitrogen blanket. Samples were withdrawn at intervals for FTi.r. analysis. The resulting red-brown precipitate of **1** was filtered, washed several times with THF and dried under vacuum. When the polycondensation was carried out in mild conditions, the copolymer was partly soluble in THF. The soluble fraction was precipitated in methanol, filtered and analysed by size exclusion chromatography (s.e.c.) and n.m.r.

Copolymer oxidation

Analytical reagent grade nitrobenzene (Acros organics) and nitrosonium tetrafluoroborate NOBF$_4$ (Alfa) were used as received. The doped copolymer samples were prepared under nitrogen by mixing separate nitrobenzene solution of oligomers and NOBF$_4$ in a ratio of one NOBF$_4$ per repeat unit. Upon mixing the two solutions,

Table 1 Synthesis of poly[bicarbazolylene-*alt*-phenylene-bis(cyanovinylene)]s[a] by polycondensation of **4** and **5** catalysed by tetrabutylammonium hydroxide in an isopropanol–methanol mixture (10/1 in volume) (reaction time: 24 h)

Sample	[catalyst] [monomer] mol ratio (%)	Temperature (°C)	Overall yield (%)	Soluble fraction[b] (%)
A	100	reflux	100	0
B	100	20	70	14.5
C	100	55	79	9
D	50	55	72	11.3
E	20	55	54.5	17.4
F	5	55	42	28.7

[a] For details, see Experimental
[b] Soluble in THF (precipitated in methanol)

the colour turned dark green, indicating the formation of carbazolylium radical-cations.

Electrochemical oxidation

Electrochemical studies were performed with a Solea-Tacussel apparatus (PJT 35-2 potentiostat, GSTP 4 generator). Cyclic voltammetry (c.v.) of solution-cast films of **1** onto conducting support were carried out with a one-compartment cell equipped with three electrodes. Working anode was either glassy carbon (surface $7 \, mm^2$) or ITO glass ($10 \times 30 \, mm$). The counter-electrode was platinum wire ($1.2 \, cm$; $0.38 \, cm^2$) while the reference electrode was a saturated calomel electrode (s.c.e.). Electrochemical and electrochromic behaviours of films were studied in acetonitrile (polarographic grade, Fluka) containing $0.3 \, mol \, l^{-1}$ of $LiClO_4$ (Alfa) as supporting electrolyte.

Physico-chemical characterization

All nuclear magnetic resonance (n.m.r.) spectra were recorded on a Bruker AC200 spectrometer (200 and 50 MHz for ^1H and ^{13}C, respectively), using $CDCl_3$ or deuterated dimethylsulfoxide (DMSO) as solvent. Optical spectroscopy was performed with a DMS100 Varian. Fourier transform infra red (*FT*i.r.) spectra were recorded in KBr pellets on a Perkin-Elmer 1600. Molar masses were determined by size exclusion chromatography (s.e.c.) in THF with Ultrastyragel columns (100, 500 and $10^3 \, Å$), using a R 401 differential refractometric detector (Waters). Polystyrene samples were used as standards.

RESULTS AND DISCUSSION

Synthesis and characterization

A Knoevenagel condensation polymerization has been used previously for the synthesis of insoluble cyano-substituted poly(arylene-vinylene)s[12,13]. Recently,

Friend *et al.*[9] have successfully synthesized soluble poly(*p*-phenylene vinylene) cyano-based derivatives. Solubilization was obtained by substituting the phenylene unit by two hexyloxy substituents. In a similar manner we used this route to synthesize the alternating copolymer **1** with *N*-octyl substituted carbazole units by the condensation of *N,N'*-dioctyl-3,3'-bicarbazyl-6,6'-dicarbaldehyde (**4**) with benzene-1,4-diacetonitrile (**5**). *Figure 2* shows the various steps of this synthesis.

The dialdehyde, **4**, was prepared in three steps. In the first step, carbazole was N-alkylated with octylbromide through a phase transfer reaction catalysed by triethyl-benzylammonium chloride (TEBAC). The resulting *N*-octylcarbazole, **2**, was then dimerized via an oxidative coupling reaction using $FeCl_3$ in $CHCl_3$ solution. The resulting stable, deep green-coloured bicarbazolylium radical-cation[7], was treated with methanol to yield the neutral (de-doped) dimer, **3**. In the third step, the dialdehyde, **4**, was obtained by reacting **3** with phophorus oxychloride and *N,N'*-dimethylformamide in *o*-dichlorobenzene (ODCB). The overall yield obtained after work-up was close to 55%.

The polycondensation of **4** with **5** was catalysed by tetrabutylammonium hydroxide in an isopropanol–methanol mixture (10/1 in volume) (*Table 1*). Whatever the catalyst concentration and temperature, the reaction mixture became dark green to brown and precipitation occurred immediately. The precipitated polymer was totally insoluble in organic solvents such as tetrahydrofuran or 1,1,2,2-tetrachloroethane. Except when the reaction was carried out at reflux, the THF solution contained a fraction of oligomers which could be precipitated in a large excess of methanol.

Polymers were analysed by *FT*i.r. and the spectra compared with those of the monomers **4** and **5**. In the spectrum of the dialdehyde, **4** (*Figure 3a*), the carbonyl groups show a strong absorption at $1672 \, cm^{-1}$, whereas the signal is slightly shifted ($1683 \, cm^{-1}$) in the case of the insoluble polymer **1** (*Figure 3c*) and its intensity is
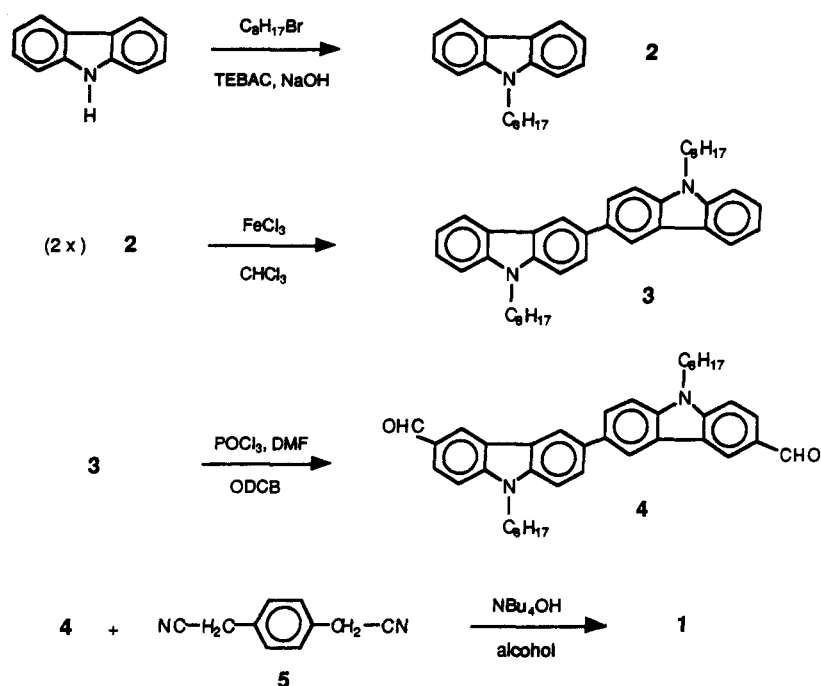

Figure 2 Reaction scheme for monomer and copolymer syntheses

drastically decreased. For the dinitrile **5** (*Figure 3b*), an absorption at 2248 cm^{-1} is characteristic of a cyano group linked to a saturated sp^3 carbon. This signal is not present in the spectrum of the polymer which may indicate the absence of end groups of this type. However, a new signal at 2208 cm^{-1} corresponds to cyano groups borne by an ethylenic carbon as expected for cyanovinylene groups. The weak absorption near 3400 cm^{-1}
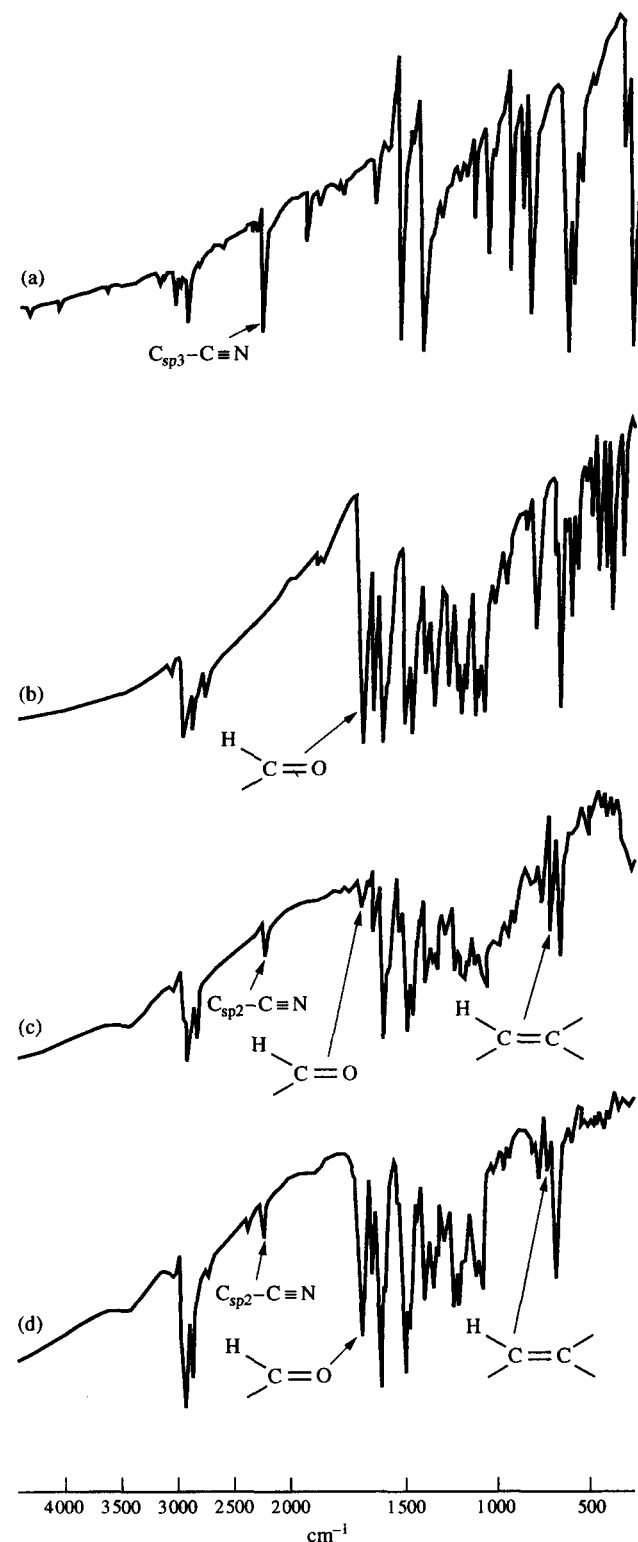
indicates that hydroxyl groups, if present, are in very small proportion. The formation of a trisubstituted vinylene bond is confirmed by the presence of a sharp signal at 835 cm^{-1}. When the polymer is partly soluble in THF (low catalyst concentration, low temperature), the insoluble fraction has the same characteristics as indicated above. However, the soluble fraction shows only a weak signal at 835 cm^{-1} (*Figure 3d*) which seems to indicate a different type of linkage between carbazolylene and phenylene moieties. This is difficult to conciliate with the observation of a single type of CN at 2208 cm^{-1}.

On the other hand, the DP_n of the copolymer could be estimated by comparing the *FT*i.r. carbonyl absorption of the –CHO chain ends (1684 cm^{-1}) with that of the n-octyl groups of the repeating units (2924 cm^{-1}), assuming two aldehyde end groups per chain. In the case of the soluble fraction of **1**, such an evaluation suggests $DP_n \sim 7$–9. In the case of the insoluble fraction, the same calculation could not be applied because the aldehyde signal was very weak. For polymers obtained at 55°C or lower temperatures, values of DP_n of about 40 were calculated. For polymers prepared at reflux temperature, the aldehyde signal was not measurable and the DP_n is therefore assumed to be higher than 40.

The soluble fraction was examined by s.e.c. The chromatogram was polymodal (*Figure 4*). According to i.r. which shows only aldehyde end groups, odd values of DP are expected. If the main peak is attributed to trimer, the next signals obtained by curve resolution would correspond to $DP = 5, 7, 9, \ldots$, up to a limit of about 25. The proportion of soluble polymer was found to increase with decreasing catalyst concentration; the overall yield was also found to decrease. The reaction was fast even in mild conditions (exp. F, *Table 1*) and no significant change in composition was observed between 30 min and 24 h.

The soluble fraction was also examined by ^{1}H n.m.r. (*Figure 5*). The ratio of aldehyde function (at 10.06 ppm) and dicarbazyle groups (aliphatic or aromatic protons, see *Figure 5*) was close to 1 which is compatible with a trimer. The signal corresponding to the ethylenic proton in the cyanovinylene appears at 8.57 ppm. The n.m.r. spectrum of this soluble fraction is in agreement with the expected structure shown in *Figure 1*.
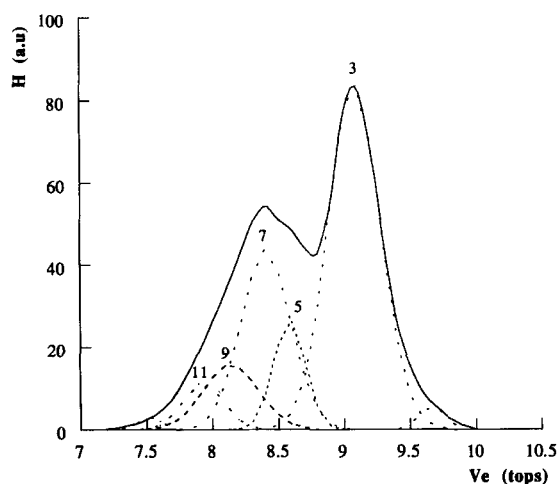
In the Knoevenagel condensation, side reactions such

(a)

$C_{sp3}-C \equiv N$

(b)

H
$\diagdown$
$C = O$
$\diagup$

(c)

$C_{sp2}-C \equiv N$

H
$\diagdown$
$C = O$
$\diagup$

H
$\diagdown$
$C = C$
$\diagup$ $\diagdown$

(d)

$C_{sp2}-C \equiv N$

H
$\diagdown$
$C = O$
$\diagup$

H
$\diagdown$
$C = C$
$\diagup$ $\diagdown$

4000 3500 3000 2500 2000 1500 1000 500

cm^{-1}

Figure 3 *FT*i.r. spectra of (a) monomer **4**; (b) monomer **5**; (c) insoluble fraction of copolymer **1**; (d) soluble fraction of copolymer **1**

Figure 4 S.e.c. chromatogram of a soluble fraction of copolymer **1**
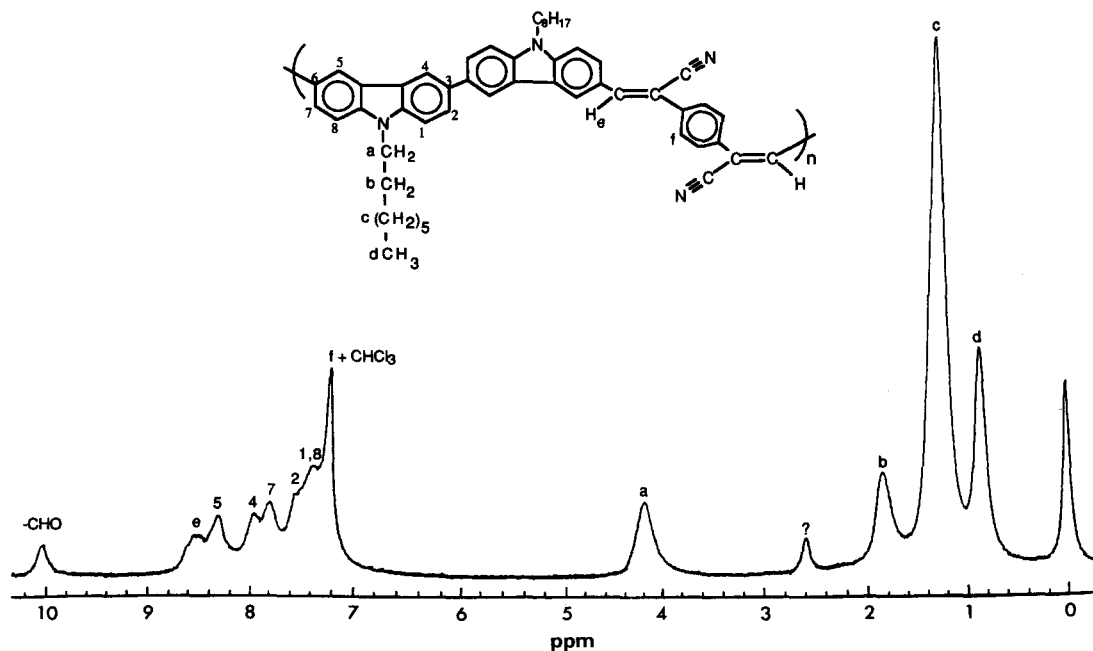
Figure 5 ^{1}H n.m.r. spectrum of the cooligomers in CDCl$_3$ (TMS as reference)

as Michael and Thorpe reactions have been postulated to explain the insolubility of polycyanoterephthalylidenes[12]. In the present case, we have found by distinct experiments that the dialdehyde, 4, allowed in contact with tetrabutylammonium hydroxide at 20°C did not react, whereas the diacetonitrile, 5, gave rise rapidly to the formation of a new species showing an i.r. absorption at 2143 cm^{-1} (probably a different cyano group). The same species was also formed in the course of polycondensation and has been identified in the unfractionated reaction mixture. However, no trace of this compound was found either in the i.r. spectrum of the washed insoluble fraction or in the n.m.r. spectrum of the aromatic region of the THF-soluble fraction. Though this compound has not been identified, it is clear that it is formed rapidly by reaction of the diacetonitrile, 5, with a base and is responsible for the non-quantitative polymer yields and the exclusive presence of aldehyde end groups. When the catalyst concentration is low, the side-reaction consuming 5 is favoured with respect to polycondensation, the overall polymer yield is lowered and the DP_n is smaller (as shown by the increasing proportion of soluble oligomers; *Table 1*). On the contrary, an increase of the temperature accelerates the Knoevenagel condensation more than the side-reaction and the overall polymer yield increases with a corresponding increase of the DP_n (lower proportion of oligomers).

It is noteworthy that side-reactions occurring onto the vinylene or the cyano groups (such as Michael or Thorpe additions, respectively) would lead to a methine linked to an aryl and a cyano group, but such a structure was not detected by i.r. or ^{1}H n.m.r. In the i.r. spectrum of the insoluble polymer, only one type of cyano group was observed at 2208 cm^{-1} (*Figure 3c*) and in the ^{1}H n.m.r. spectrum of the soluble fraction, no signal was found in the region between 6 and 7 ppm where the resonance of –CH(Ar)–C≡N is expected to be found.

Although crosslinking of the copolymers cannot be ruled out, the insolubility of copolymer 1 is probably due to the extreme rigidity of the macromolecular chains.
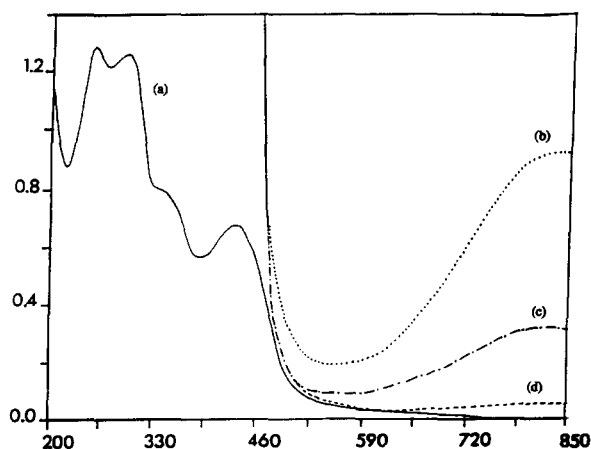

Figure 6 Absorbance spectra of copolymer 1: (a) in the neutral state; (b) 5 min after doping by NOBF$_4$; (c) 1 h; (d) 8 h

This copolymer appears to be much more rigid than poly(N-octyl-3,6-carbazolylene) since samples of homopolymer with $DP_n \sim 36$ were found to be wholly soluble in organic solvents[14]. Thus the increased stiffness of the chain should be attributed to the presence of the phenylene-bis-cyanovinylene units, and is probably due not only to the *para*-substituted phenyl ring, but also to the formation of an internal charge transfer complex between the electron-acceptor phenyl-bis-cyanovinylene units and the electron-donor carbazole units.

This assumption seems to be confirmed by the u.v.-visible spectra of the low-DP fraction in CHCl$_3$ solution and in cast-films (*Figure 6*). In both cases, an absorption band with a maximum at 420 nm was observed which is an unexpected long wavelength transition for a non-extended π-conjugation. The onset of absorption of the solid state corresponds to a bandgap value $E_g \sim 2.5$ eV. This value is much lower than that of poly(N-butyl-3,6-carbazolylene) ($E_g \sim 3.2$–3.4 eV)[15], but very similar to that of polycyanoterephthalylidenes of low molecular

weight ($E_g \sim 2.6\,eV$)[12]. Hence, it may be considered that a regular alternation of donor and acceptor group in the conjugated backbone lowers the bandgap according to the recent concept applied by Havinga *et al.*[16] to the synthesis of small-bandgap polycroconaines and polysquaraines.

Properties

D.s.c. analysis of the copolymer disclosed the presence of a glass transition at 85°C for the soluble fraction. This T_g value is higher than that found for poly(*N*-octyl-3,6-carbazolylene)[17] with close DP_n (for $DP_n = 7$, $T_g = 60°C$). This difference may be ascribed to the effect of the dipole developed in **1**, between the donor carbazole units and the acceptor phenyl-bis-cyanovinylene moieties, leading to an increase of the stiffness of the macromolecular chains and consequently to an increase of the T_g value. No melting point or other thermal transition was observed in the range $-10°C/+300°C$. Within the same temperature range, the insoluble polymer exhibited a flat temperature profile. The infusibility of the high molar mass polymer suggests either crosslinking or decomposition before melting. However, thermogravimetric analyses indicated that the copolymer was fairly resistant to thermal degradation. The 2% weight loss temperature is 450°C under nitrogen and 370°C under air (heating rate $10°\,min^{-1}$).

Iodine and iron trichloride have been shown to be effective oxidants for bicarbazyle and poly-carbazolylenes[7,15,18]. They were also tested in the case of copolymer **1**. Upon exposure to iodine vapour, neither a film nor a powder were oxidized. All attempts to oxidize the soluble low-*DP* material by I_2 or $FeCl_3$ in $CHCl_3$ solution were also negative.

However, oxidation of **1** was effective by adding nitrosonium tetrafluoroborate (NOBF$_4$) to a solution of oligomers in nitrobenzene. Instantaneously, the orange-red solution turned dark green, the characteristic colour of the bicarbazyl radical-cations[19]. As shown in *Figure 6*, the spectrum of the doped copolymer exhibits a broad absorption with a maximum centred at 830 nm, a wavelength close to that observed for the radical-cations of the carbazole dyads constitutive of poly(*N*-butyl-3,6-carbazolylene)[20]. However, under the conditions used in this study, the doped state of **1** was found to be unstable and a rapid decrease of the signal was observed (*Figure 6*). After 8 h, dedoping was complete and the sample could not be doped again by addition of an extra aliquot of NOBF$_4$, indicating that an irreversible modification of the chemical structure had occurred.

It is worth noting that a strong oxidizing agent such as NOBF$_4$ with a high redox potential value ($E_{ox} = 1.27\,V$ vs saturated calomel electrode[21]) is required to dope copolymer **1**. Iodine ($E_{ox} = 0.3\,V$) and FeCl$_3$ ($E_{ox} = 0.53\,V$) are not able to oxidize **1**, but are effective in the case of a carbazolic structure 3,6-substituted by electron-withdrawing groups as extensively described by Ambrose[19]. It has been shown that substituting the 3–6 positions of the carbazole nucleus by electron-acceptor substituents makes the carbazole less oxidizable and leads to an anodic shift of the oxidation potential and a decrease of the radical-cation stability in the oxidized state. Hence, in the present case, substitution of the bicarbazolylene unit by phenylene-bis-cyano-vinylene groups is expected to produce a similar effect. This was confirmed by studying the cyclic voltammetry
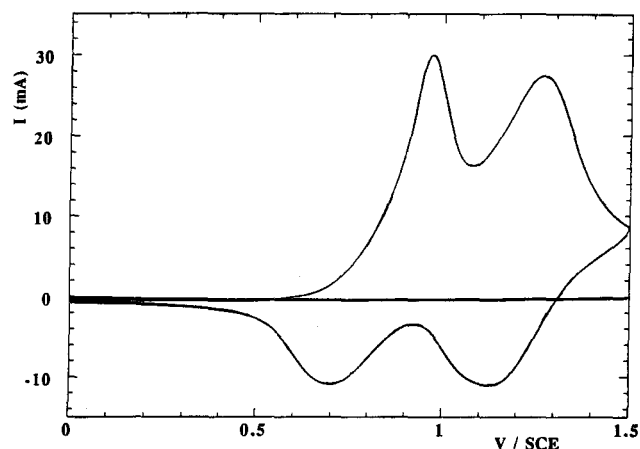

Figure 7 Cyclic voltammetric curve of copolymer **1** (solution-cast film onto ITO glass)

(c.v.) of copolymer films cast from solution onto glassy carbon and ITO glass electrodes (a typical c.v. is shown on *Figure 7*). The red-coloured polymer films turn successively to green and blue upon anodic oxidation. These colour changes are associated with two oxidation peaks at 0.95 and 1.35 V, respectively. The two anodic waves were ascribed to the formation of the radical cation of the bicarbazolylene unit for the first oxidation step (0.95 V) followed by its oxidation into dication through the second step (1.35 V). As expected, the two oxidation peaks of **1** are 0.1–0.2 V more anodic than that observed for the carbazolic dyads of the poly(*N*-butyl-3,6-carbazolylene) under the same experimental conditions (0.85 V; 1.15 V/SCE, respectively)[20]. Moreover, the electronic effect of the phenylene-cyanovinylene withdrawing substituents shows up in the instability of the doped state. Indeed, successive CV performed between 0 and 1 V demonstrated a dramatic decrease in the observed signals which were found to completely disappear after a few cycles. By contrast, poly(*N*-alkylcarbazolylene) radical-cations display relatively good stability (C. Chevrot and A. Siove, unpublished results).

CONCLUSION

The Knoevenagel condensation has been applied to the synthesis of ([bicarbazolylene]-*alt*-[phenylene-bis(cyano-vinylene)]) copolymers. These materials were mostly insoluble in organic solvents. However, depending on the experimental conditions, a small amount of soluble oligomers could be obtained. The relative proportion of these increases when the conditions are mild (low base concentration, moderate temperature), but the yield decreases simultaneously (because of side-reactions consuming the dinitrile) which results in a decrease of the DP_n and the exclusive formation of aldehyde end groups. A complete conversion is obtained only at high temperature with a high catalyst concentration. In these conditions, the polymer is entirely insoluble and has a DP_n larger than 40 ($M_n > 14\,500$).

The insolubility of the polymer is attributed to the rigidity of the main chain which is probably much larger than in the case of poly(*N*-alkylcarbazole)s. The alternation of electron–donor carbazolylene units and the electron-withdrawing phenylene-cyanovinylene entities may explain the rigidity of the macromolecular chains.

Moreover, the regular alternation of donor–acceptor moieties is thought to be involved in lowering the bandgap of the soluble oligomers and in decreasing the stability of the bicarbazolylium radical-cations in the doped state. Lastly, materials were fairly resistant to thermal degradation up to 450°C.

REFERENCES

1. Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L. and Holmes, A. B., *Nature*, 1990, **347**, 539.
2. Braun, D. and Heeger, A. J., *Appl. Phys. Lett.*, 1991, **58**, 1982.
3. Doi, S., Kuwara, M., Noguchi, T. and Ohnishi, T., *Synth. Met.*, 1993, **55–57**, 4174.
4. Ohmori, Y., Uchida, M., Muro, K. and Yoshino, K., *Jap. J. Appl. Phys.*, 1991, **30**, L 1938.
5. Yang, Z., Sokolik, I. and Karasz, F., *Macromolecules*, 1993, **26**, 1188.
6. Zhang, C., von Seggern, H., Pakbaz, K., Kraabel, B., Schmidt, H. W. and Heeger, A. J., *Synth. Met.*, 1994, **62**, 35.
7. Siove, A., David, R., Adès, D., Roux, C. and Leclerc, M., *J. Chim. Phys.*, 1995, **92**, 787.
8. Romero, D. B., Schaer, M., Leclerc, M., Adès, D., Siove, A. and Zuppiroli, L., *Synth. Met.*, in press.
9. Greenham, N. C., Moratti, S. C., Bradley, D. D. C., Friend, R. H. and Holmes, A. B., *Nature*, 1993, **365**, 628.
10. Pielichowski, J., Popielarz, R. and Chrzaszed, R., *J. Polym. Sci., Polym. Lett. Ed.*, 1985, **23**, 387.
11. Bruck, P., *J. Org. Chem.*, 1970, **35**, 2222.
12. Lenz, R. W. and Handlovitis, C. E., *J. Org. Chem.*, 1960, **25**, 813.
13. Hörhold, H. H., *Z. Chem.*, 1972, **12**, 41.
14. Siove, A., Aboulkassim, A., Faïd, K. and Adès, D., *Polym. Int.*, 1995, **37**, 171.
15. Ngbilo, E., Adès, D., Chevrot, C. and Siove, A., *Polym. Bull.*, 1990, **24**, 17.
16. Havinga, E. E., Ten Hoeve, W. and Wynberg, H., *Polym. Bull.*, 1992, **29**, 119.
17. Siove, A. and Belorgey, G., *Polym. Bull.*, 1993, **31**, 105.
18. Jenekhe, S. A., Wellinghoff, S. T. and Reed, J. F., *Mol. Cryst. Liq. Cryst.*, 1984, **105**, 175.
19. Ambrose, J. F., Carpenter, L. L. and Nelson, R. F., *J. Electrochem. Soc.*, 1975, **122**, 876.
20. Pelous, Y., Froyer, G., Adès, D., Chevrot, C. and Siove, A., *Polym. Commun.*, 1990, **31**, 341.
21. Bontempelli, G., Mazzochin, G. A. and Magno, F., *J. Electroanal. Chem.*, 1974, **55**, 91.