Investigation of the electrocatalysed step polymerization of soluble poly(*N*-alkyl-3,6-carbazolylene)s

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Simultaneous g.p.c. and cyclic voltammetry measurements were carried out in the course of the electrocatalysed polymerization of various 3,6-dibromo(*N*-alkylcarbazole)s. The evolution of the molar mass population distribution as a function of the electrolysis time reveals a step polymerization process, while showing a termination of the chain growth due to the occurrence of monobrominated species. The consumption of the catalytic species corresponds in a first step to an increase in the chain length, while after given periods there is no more chain growth related to the continuous consumption of the catalytic precursor. The study of the effect of the initial [monomer]/[catalyst] ratio on the molar mass population evolution indicates that the coupling of Ni(0)-activated species is responsible for the chain growth.

(Keywords: electrocatalysis; step polymerization; poly(*N*-alkylcarbazole)s)

INTRODUCTION

Interest in electroactive polymers has increased tremendously during the last decade owing to their potential applications; since the report of the synthesis and doping of polyacetylene by Shirakawa *et al.*[1-3], a large amount of research has been carried out and reported[4].

In addition to polyacetylene, various structures have been investigated, among which polythiophene, polyaniline, polypyrrole and poly(*p*-phenylene) were found to be conducting after adequate doping. However, owing to their conjugated structures these materials were intractable, limiting both the potential applications and their characterizations.

It is well known that the attachment of substituents to conjugated polymer chains increases their processability[5]. A major advance in the processability of conducting polymers has been achieved with the incorporation of long and flexible substituents which, owing to their interactions with the solvents, allow the solubilization of these materials. This approach has been used successfully to produce soluble poly(3-alkylthiophene)s[6-9], poly(2,5-dimethoxy-1,4-phenylene)[10] or poly(2,5-dialkyl-1,4-phenylene)s[11-13]. Incorporation of bulky side groups, while enhancing the solubility, induced twisting and distortion of the backbone units and generally resulted in a decrease in the conjugation of the substituted polymers and their conductivity.

We have studied the synthesis of poly(*p*-phenylene)[14,15]. In order to obtain soluble materials, while avoiding the reduction of the electroactive properties induced by the introduction of bulky side groups, we used planar substituted biphenylic structures such as *N*-alkylcarbazoles. Solubility of these materials was induced by the presence of alkyl substituents on the nitrogen which have no effect on the planarity of adjacent phenylenes owing to the fused rings.

Poly(*N*-alkyl-3,6-carbazolylene)s were found to be soluble in organic solvents while exhibiting interesting electronic and electrochromic properties[16-19]. We recently[20] reported preliminary results on the electrocatalysed polymerization of various 3,6-dibromo-*N*-alkylcarbazoles. We showed that coupling of the monomer and oligomers occurs through step polymerization. The coupling mechanism may proceed either by reaction of a Ni(0)-activated monomer with a monomer molecule or by the coupling of two activated monomers.

A knowledge of the nature of the coupling reaction is crucial to the understanding of this polymerization mechanism and is a prerequisite in the attempt to produce materials with tailored compositions and properties[21,22]. We report herein some of the investigations carried out to elucidate the type of coupling mechanism involved in the step polymerization of 3,6-dibromo-*N*-alkylcarbazole (butyl and octyl) and to study the factors controlling chain growth.

EXPERIMENTAL

The synthetic route used is derived from that set up in our laboratory for the synthesis of poly(*p*-phenylene)[14,15]. The synthesis of poly(*N*-alkyl-3,6-carbazolylene)s, with the alkyl chain being a butyl or an octyl, was carried out as described previously[17-19]. It involves the cathodic reduction of a complex of $NiBr_2$/2,2'-bipyridine ($NiBr_2$/Bipy) into a Ni(0)-based catalytic system which, in the presence of 3,6-dibromo-*N*-butylcarbazole or 3,6-dibromo-*N*-octylcarbazole, leads to the formation of

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the corresponding polymer through a dehalogenative coupling process. The synthesis and purification of the various monomers and reagents were carried out as described previously[17–19,23]. The electrosynthesis was carried out in a three-compartment electrochemical cell, with a mercury cathode and a magnesium rod as anode. The potentials were referenced to a saturated calomel electrode (SCE). The electrochemical studies were performed with a Solea-Tacussel potentiostat (PJT 35-2).

In a typical experiment, 1 mmol of the catalytic precursor ($NiBr_2$/Bipy), x mmol of Bipy ($x=0$, 1 or 2) and y mmol of the monomer ($y=0.1$, 0.2, 1, 3 or 4) were added under argon to a solution of 30 mmol $LiBF_4$ in 100 ml *N,N*-dimethylacetamide (DMAc). The electroanalytical study of this solution, between −0.5 and −1.5 V/SCE, allows the determination of the reduction potential of the Ni(II) species to the active Ni(0) and was found to be −1.2 V/SCE. The cathode was polarized at a slightly higher potential, −1.3 V/SCE, in order to quantitatively reduce Ni(II) to Ni(0) and start the electrosynthesis. In the course of electrolysis, the applied potential was disconnected for a while and cyclic voltammetry was carried out with a second potentiostat (Solea-Tacussel, PRT 40-1X).

Concurrently to this cyclic voltammetry, aliquots of 10 ml of the solution were withdrawn at determined times. After being precipitated in acidified water and dried, the samples were analysed by g.p.c. (Waters apparatus) in tetrahydrofuran, calibrated with standard polystyrenes and with the chemically synthesized first terms of the carbazolic series (non-brominated, monobrominated and dibrominated monomers, dimers and tetramers)[23].

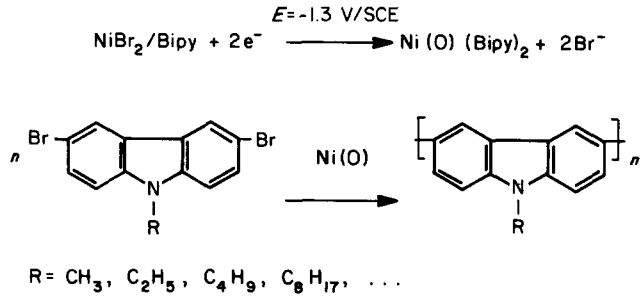

Figure 1 Electrosynthesis reaction scheme

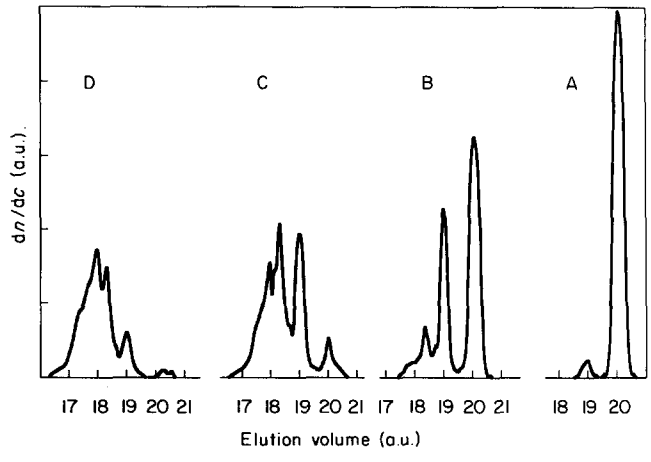

Figure 2 G.p.c. chromatograms of aliquots withdrawn at various reaction times: A, 15 min; B, 78 min; C, 140 min; D, 229 min

RESULTS AND DISCUSSION

General features

Poly(*N*-butyl-3,6-carbazolylene)s and poly(*N*-octyl-3,6-carbazolylene)s were synthesized according to the reaction scheme depicted in *Figure 1*. Exhaustive electrolysis of the catalytic precursor in the presence of different dibromo-*N*-alkylcarbazole yielded poly(*N*-alkyl-3,6-carbazolylene)s (PACz) which ranged from partially to completely soluble in common organic solvents, depending on the length of the *N*-substituted alkyl group. The molecular weight varied between 2000 and 3000 with a molar mass distribution, $M_w/M_n \approx 2$.

These polymers were obtained as neutral materials which, upon chemical doping with iodine, exhibited conductivities between 10^{-4} and 10^{-3} S cm^{-1}. The experimental details of the doping procedure and the conductivity measurements have been published previously[17–19].

The electroactivity of a thin film of PACz was investigated and revealed two anodic processes associated to two cathodic processes. Colour changes accompanied these redox processes: colourless to green ($+0.70\text{ V} < E < +0.90\text{ V}$) and green to blue ($+1.00\text{ V} < E < +1.30\text{ V}$). The effects of various parameters, such as the molecular weight, the film formation procedure or the length of *N*-substituted alkyl chain, on the electroactivity of these materials have been published elsewhere[19].

Spectroelectrochemical studies[24] performed on poly(*N*-butyl-3,6-carbazolylene) films disclose optical absorptions appearing at 850 nm for the green state and at 700 nm for the blue state. Such characteristics have been ascribed to the formation of radical cations (polarons) of carbazolic units during the first oxidation step followed by their oxidation to dications through the second step (blue species).

Study of the coupling process

Evolution of the molar mass population distribution of poly(*N*-butyl-3,6-carbazolylene) as a function of the electrolysis time was followed by g.p.c. (*Figure 2*). In the course of the electrosynthesis, the monomer concentration was found to decrease rapidly while dimer, trimer, tetramer and higher oligomers appeared consecutively. Analysis of mixtures of monomer and dimer of known composition allowed the determination of a chromatographic correction factor of 1.36 between these two species. The g.p.c. data were thus normalized and are represented in *Figure 3*.

The monomer concentration decreased to zero after about 2 h of reaction. Meanwhile dimer, trimer and tetramer appeared, their concentrations passing through a maximum. Afterwards, higher oligomers were detected, but owing to the lack of resolution of the g.p.c. technique for the highest terms, it was not possible to follow their evolution. From the features obtained, it was concluded that this was a step polymerization whose mechanism may involve two possible reaction pathways[20]. The first may proceed via the coupling of active sites [Ni(0)-activated monomer], whereas the second may involve the reaction between an activated site and the monomer (*Figure 4*). Details of the investigations carried out to elucidate the proposed reaction scheme have been reported previously by our group[17,20,25] and others[26–28].

In order to elucidate which path was followed, we investigated the effect of various parameters, among

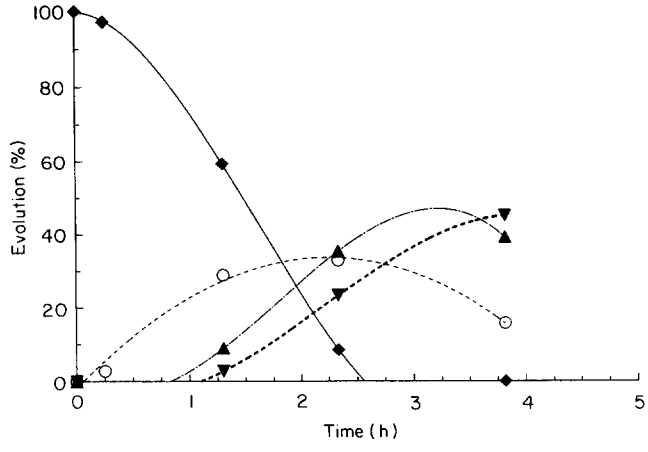

Figure 3 Evolution of the molar mass population distribution as a function of electrolysis time: ◆, monomer; ○, dimer; ▲, trimer; ▼, tetramer

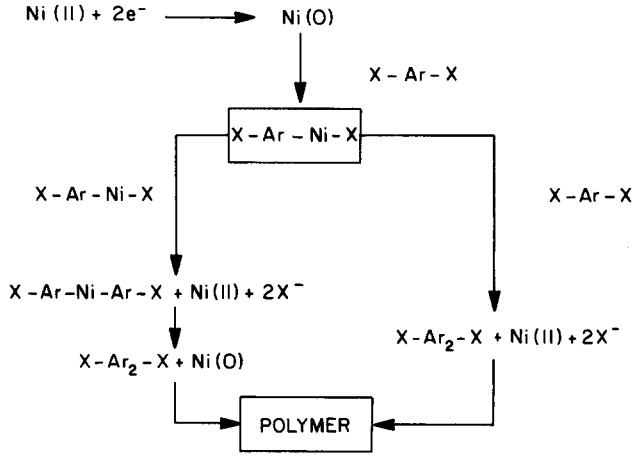

Figure 4 Proposed mechanisms of step polymerization

which was the initial ratio of the monomer to the catalytic precursor ([M]/[C]). By varying the relative concentration of Ni(II) in the system, it was possible to adjust the concentration of Ni(0)-activated monomer molecules compared to that of non-activated ones. We have shown recently[23,25] that the limiting reaction is the electrolysis of the Ni(II) to Ni(0), while the incorporation of the latter in a carbon–bromine bond occurs very rapidly, followed by the coupling process.

Evolution of the catalytic system during the electrolysis reaction was followed by cyclic voltammetry. The electroreduction of Ni(II) to Ni(0) (*Figure 5a*) showed a peak at −1.2 V/SCE associated with a reoxidation process at −1.00 V/SCE. During electrolysis, the intensity of this peak was found to decrease and to be directly proportional to the evolution of the Ni(II) concentration in the solution (*Figure 5b*).

Cyclic voltammetry measurements were performed during the electrolysis of the $NiBr_2$/Bipy complex in the absence of dihalo monomer. The evolution of the concentration of Ni(II) is shown in *Figure 6*. It was characterized by a roughly linear decrease as a function of electrolysis time. Experiments with [M]/[C] ratios of 0.1, 0.2, 1 and 4 were carried out, while keeping all other parameters constant. By following the molar mass population distribution and the concentration of the catalytic system, very distinct types of evolution were observed.

For [M]/[C] = 0.2, evolution of the Ni(II) concentration (*Figure 7a*), as given by cyclic voltammetry, showed that after a rapid decrease at the beginning of electrolysis, a plateau was reached which was followed by a very fast decrease in the Ni(II) concentration. The evolution of the molar mass distribution is shown in *Figure 7b*. The monomer concentration decreased very rapidly; meanwhile higher oligomers appeared (fraction B). After

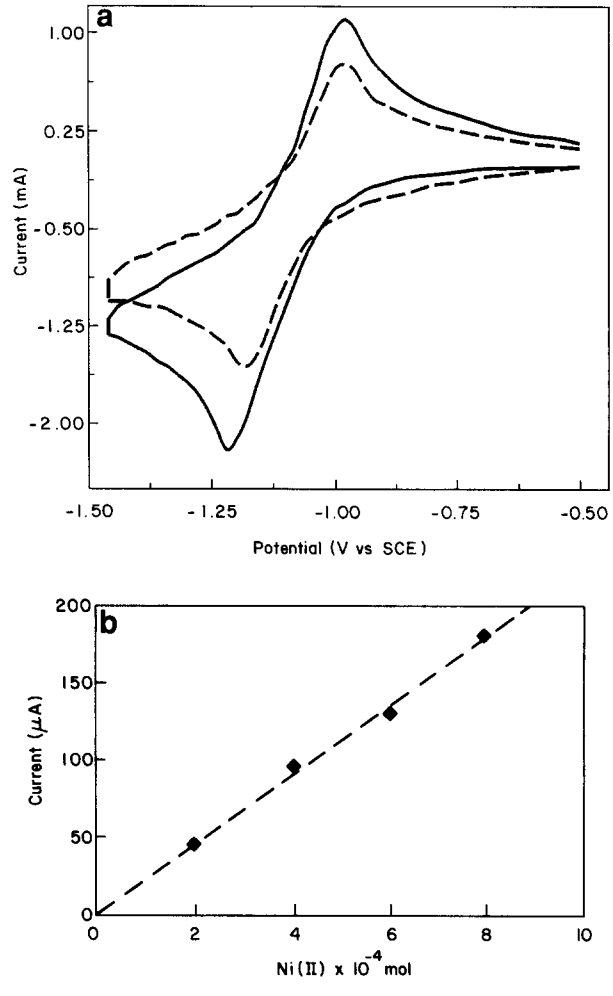

Figure 5 (a) Evolution of intensity of Ni(II) to Ni(0) electroreduction signal as a function of time: ——, before and – – –, after 15 min electrolysis. (b) Evolution of reduction peak intensity *versus* Ni(II) concentration

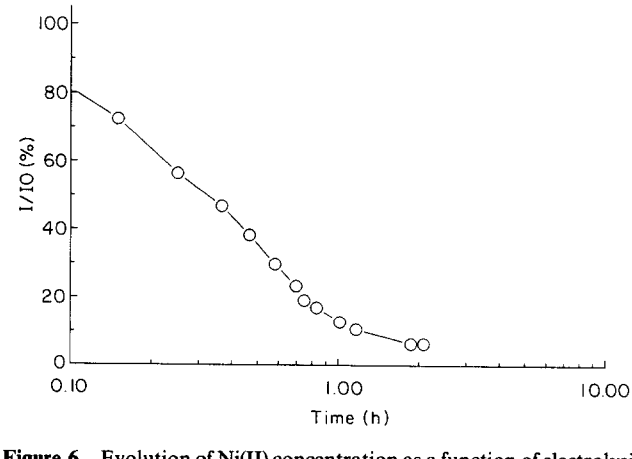

Figure 6 Evolution of Ni(II) concentration as a function of electrolysis time in the absence of dihalo monomers

1 h of electrolysis (fraction C), there was no more significant evolution of the mass population distribution except a decrease in the relative proportion of the polymer fraction, and the appearance of very short terms which could be attributed to the occurrence of debromination

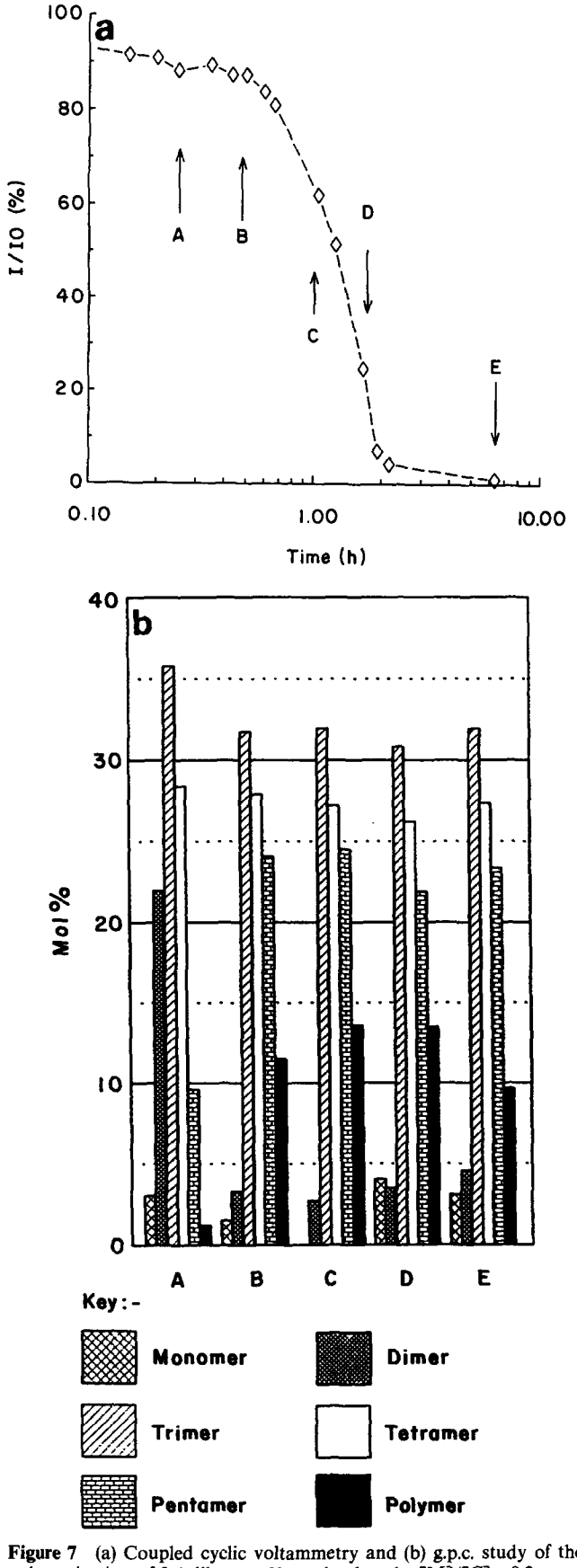

Figure 7 (a) Coupled cyclic voltammetry and (b) g.p.c. study of the polymerization of 3,6-dibromo-*N*-octylcarbazole; [M]/[C] = 0.2

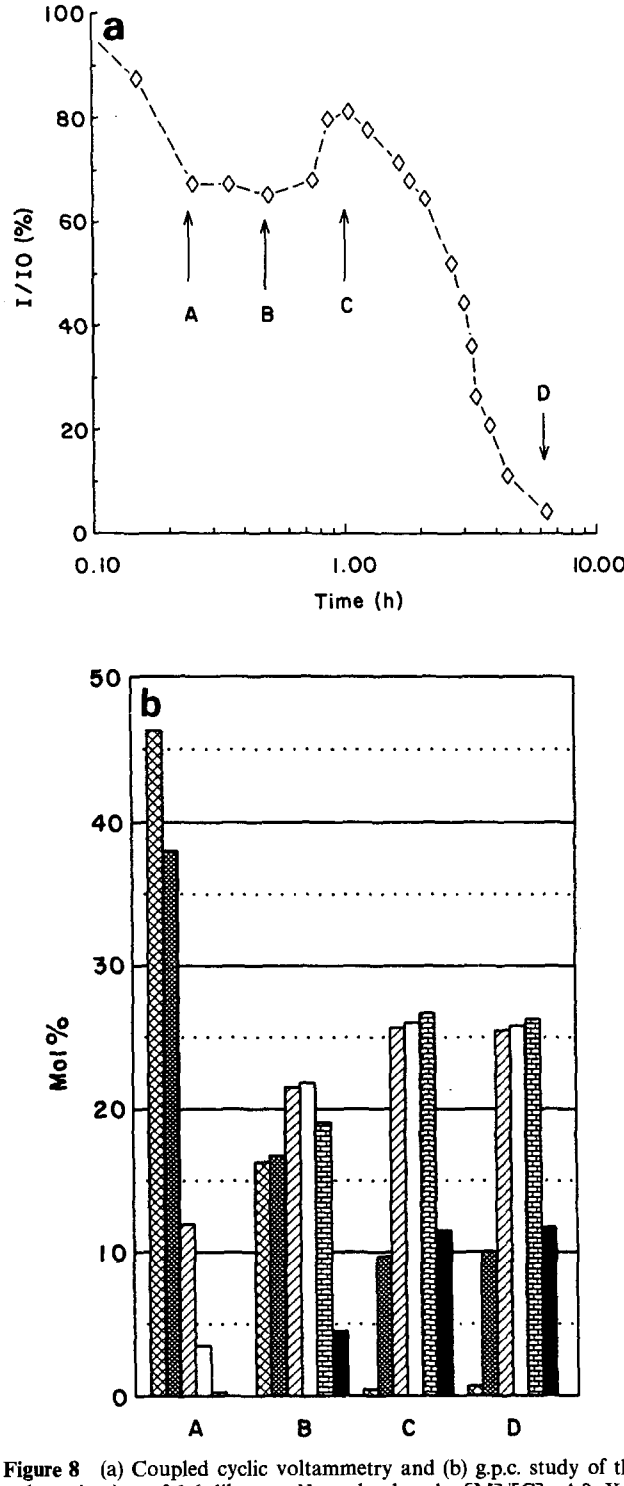

Figure 8 (a) Coupled cyclic voltammetry and (b) g.p.c. study of the polymerization of 3,6-dibromo-*N*-octylcarbazole; [M]/[C] = 1.0. Key as in *Figure 7*

reaction (see below for [M]/[C] = 1). In these conditions, i.e. low [M]/[C] ratio, the molecular weight was found to be around 10 000, which is one of the highest values we have ever reached with this polymerization method.

An increase in the ratio to [M]/[C] = 1 resulted in different behaviour of both the Ni(II) concentration (*Figure 8a*) and of the molar mass distribution in the course of electrolysis (*Figure 8b*). The Ni(II) concentration during the first 10 min of electrolysis decreases rapidly, then levels off for around 30 min. After 50 min of electrolysis, a sudden increase in the Ni(II) concentration is recorded, followed by another decrease. The molar mass distribution (*Figure 8b*) indicated that the monomer

consumption was slower in these conditions than in the previous ones ([M]/[C] = 0.2) and that the evolution of the relative concentration of the other species, dimer to polymer, also proceeded at a slower rate. Moreover, the maximum molecular weight reached was significantly lower than in the previous case (~3000 compared to ~10000).

The increase of the proportion of monomers to that of the active sites (Ni(0)-activated monomers) resulted in a slower evolution of the molar mass population distribution and a lower molecular weight product.

The appearance of a maximum in the Ni(II) concentration, after around 1 h of electrolysis, corresponded to the maximum evolution of the molar mass distribution (no difference between fractions C and D) with the exception of the detection of a small amount of very short terms. This increase of Ni(II) concentration after a given period of electrolysis may be associated with its massive release due to the coupling process and the drastic decrease of its reinsertion in carbon–bromine bonds. This decrease of the reinsertion process may be due to the occurrence of debromination reaction in the course of electrolysis, which results in the diminution of available carbon–bromine bonds. Indeed, this feature is supported by the elemental analyses, which indicate that the bromine content of the polymer is generally lower than expected for a material of the same molecular weight in which no debromination had occurred. Moreover, debrominated and monobrominated monomers have already been detected by g.p.c. in various samples.

For [M]/[C] = 4, the monomer consumption is much slower than in the above two cases and a significant amount (more than 15% of the initial concentration) remained after several hours of exhaustive electrolysis (*Figure 9b*). After 1 h, the molar mass distribution does not change any more. Moreover, the formation of higher oligomers is much slower and their proportion is also much smaller than in the case of low [M]/[C] ratios.

The cyclic voltammetry measurements carried out in the course of the electrosynthesis (*Figure 9a*) showed that the concentration of Ni(II) decreased regularly as a function of time with a sharp change in the Ni(II) consumption rate after around 2 h. This last evolution of the Ni(II) concentration, which was not accompanied by a significant coupling process, may correspond to reduction of the Ni(II) to Ni(0). Indeed, the slope is very similar to that obtained in the electrolysis of the catalytic precursor in the absence of dihalo monomer (*Figure 6*).

From all the above studies, it appeared that in the course of electrolysis, the materials evolved in such a way that no more changes in the molar mass distribution occurred after variable periods of time, depending on the [M]/[C] ratio. On the other hand, the efficiency of the catalytic system remained unchanged during the electrosynthesis. In order to check this point, 4,4′-dibromobiphenyl was added to the reaction cell after an exhaustive electrolysis of 3,6-dibromo(*N*-butylcarbazole). Poly(*N*-butyl-3,6-carbazolylene) and poly(*p*-phenylene) were obtained, indicating that the catalytic system remained efficient after complete consumption of the first monomer.

These results suggest that the step polymerization mechanism proceeds through the coupling of Ni(0)-activated species (the reaction pathway on the left-hand side of *Figure 4*). When the relative proportion of Ni(0) species in the solution is large, there is a much

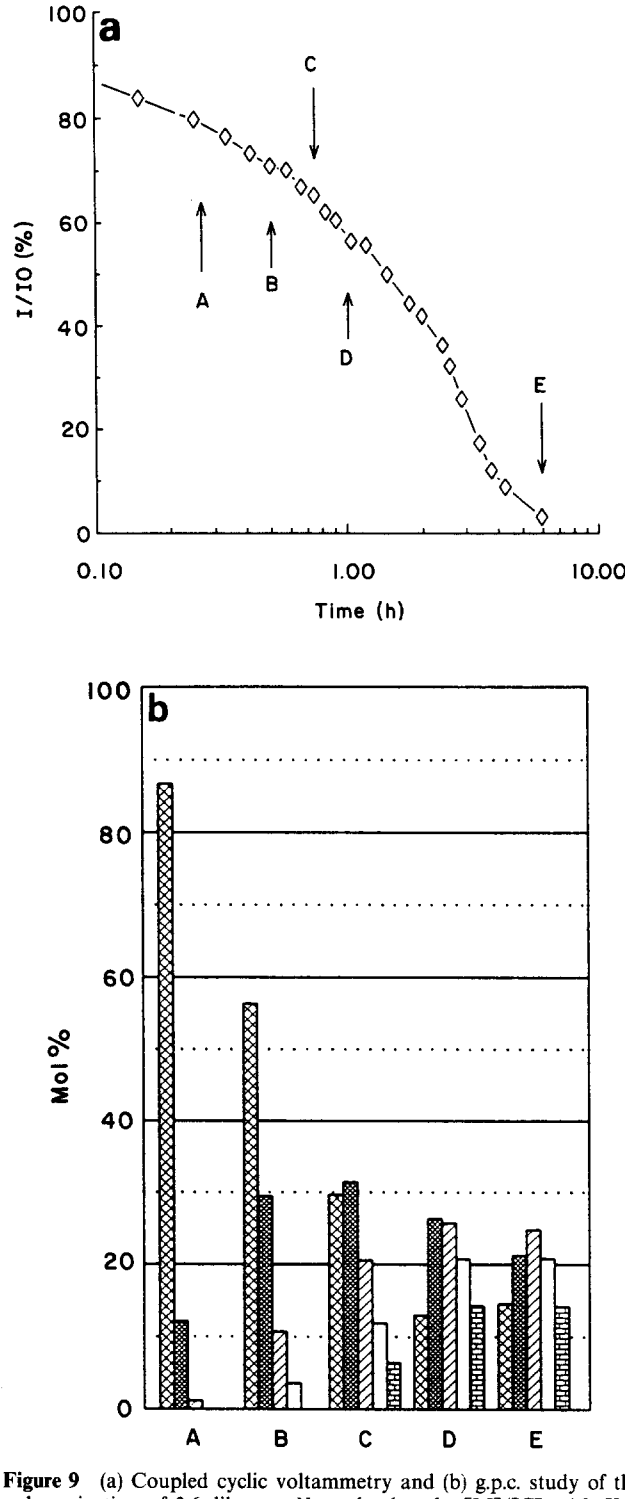

Figure 9 (a) Coupled cyclic voltammetry and (b) g.p.c. study of the polymerization of 3,6-dibromo-*N*-octylcarbazole; [M]/[C] = 4.0. Key as in *Figure 7*

greater amount of Ni(0)-activated species and the coupling of these species gives rise very rapidly to the higher oligomeric terms. However, in the case of higher [M]/[C] ratios, the proportion of Ni(0)-activated monomers is much lower, resulting in less rapid coupling. Shorter chains are thus obtained because significant dehalogenation reactions occur concurrently, which reduce the amount of available carbon–bromine bonds.

This coupling mechanism, involving the formation and coupling of Ni(0)-activated species, may also apply to the polymerization of dihalo monomers catalysed by chemically prepared zero-valent nickel complexes

(mixtures of bis(1,5-cyclooctadiene)nickel(0), $(Ni(cod)_2)$, and neutral ligand) as described recently by Yamamoto *et al.*[29].

CONCLUSION

The use of cyclic voltammetry coupled to g.p.c. measurements in the course of electrolysis was found to be very helpful in understanding the electrocatalysed step polymerization of various *N*-substituted dibromocarbazoles, giving insight to the coupling mechanism and the side reactions accompanying the polymerization. It is shown that the continuous formation of Ni(0)-activated species is essential to the chain growth, whereas debromination has a dramatic effect on it. The catalytic system is found to remain active even after exhaustive electrolysis.

A knowledge of the polymerization mechanism allows the determination of optimum conditions for copolymerization reactions in order to modulate the physical and electronic properties of electroactive materials. The synthesis and study of (phenylene–carbazolylene) copolymers will be the subject of a forthcoming paper.

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