

## **Synthesis and characterization of poly (N-butyl-3,6-carbazolediyl)**

### **A new soluble electroactive material**

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#### Summary

Poly(N-butyl-3,6-carbazolediyl) was synthesized by electrochemical reduction of the NiBr<sub>2</sub>·2,2'-bipyridine/3,6 dibromo N-butylcarbazole system in N,N dimethylacetamide. The favorable interactions between solvent and butyl groups lead to the solubilization of the electroactive polymer in organic medium and allowed the determination of macromolecular and structural features by means of classical methods. From <sup>13</sup>C NMR investigations it was concluded to a  $\pi$  conjugation centered on the nitrogen atom of the carbazolic structure.

#### Introduction

During the last five years, one of the target in chemistry of electroactive polymers, has been the synthesis of soluble and processable materials (1).

Concerning polyaromatics, important results have been obtained in this field, by synthesizing soluble phenylenic based copolymers (2-3) and thiophenic homopolymers (4-5). Additional important aspects connected with the solubility of these materials deal with the determination of their macromolecular and structural features by means of classical physico-chemical methods. Such determinations are of a particular interest for a better understanding of the structure properties relationships as well as the synthesis of new structures with optimized properties.

Concerning polycarbazolic derivatives, we recently described a new polymerization route, proceeding by electro-reduction of dibromo-N-substituted carbazoles and leading to linear well-defined polymeric structures (6).

The present work is devoted to the electrosynthesis and the characterization of soluble poly (N-butyl-3,6-carbazolediyl).

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## Experimental

### Chemicals

3,6 dibromo N-butylcarbazole was synthesized according to the method previously described for the preparation of the N-ethyl derivative (6). Chromatography of the crude product on silica gel column using an ether-hexane mixture (10% in vol.) as eluent gave a white crystalline solid (mp = 74-75°C).

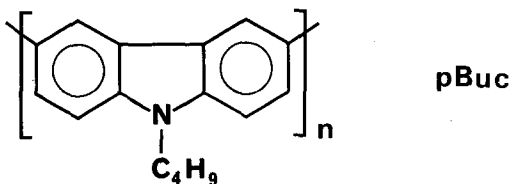
N,N dimethylacetamide (DMA) was distilled from calcium hydride. The supporting salt  $\text{LiBF}_4$  were vacuum dried overnight at 120°C. The catalytic precursor  $\text{NiBr}_2 \cdot 2,2'$  bipyridine ( $\text{NiBr}_2 \cdot \text{B}$ ) was prepared by adding 1.55 g (10 mmol.) of B to a solution of 2.7 g (10 mmol.) of  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  in 50 ml of ethanol. The resulting green suspension was filtered, washed with ethanol and dried under vacuum.

### Electrosyntheses

A three electrode cell with two compartments separated by a sintered glass disk was used for electrosyntheses. The potential applied to the working electrode (a mercury pool) was monitored by a Solea-Tacussel PJT 35-2 potentiostat. The counter electrode was a magnesium cylinder and the reference a saturated calomel electrode (SCE).

In a typical experiment 0.5 mmol. of the catalytic precursor  $\text{NiBr}_2 \cdot \text{B}$  and 5 mmol. of the monomer were added under argon, to a solution of 30 mmol of  $\text{LiBF}_4$  in 100 ml of DMA. The cathode was polarized at the working potential ( $E = -1,3 \text{ V/SCE}$ ). As the electrosynthesis starts the solution of  $\text{NiBr}_2 \cdot \text{B}$  turns instantaneously red so showing up the presence of C-Ni-Br active sites (6). The current intensity remained stable all along the electrosynthesis and finally decreased when complete conversion was reached.

The resulting solution was poured into aqueous sulfuric acid. The grey suspension of poly (N-butyl-3,6-carbazolediyl) (named pBuc) was separated by filtration, washed successively with water and methanol, then vacuum dried and weighted. Moreover, the direct titration of aqueous phase provided the bromine balance.



### Physico-chemical characterizations :

Molar masses determination was performed by GPC at 20°C, in tetrahydrofuran, with a Waters GPC apparatus calibrated with standard polystyrene samples.

$^{13}\text{C}$  NMR of polymers was performed with a Bruker 250 DS (62,5 MHz) and UV-Visible spectroscopy with a Varian DMS 100.

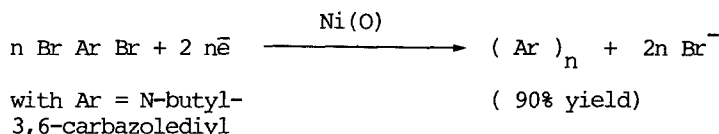
Elemental analysis indicated that the material composition was in agreement with the theoretical one.

$(C_{16}H_{15}N)_n$	Calculated : C% : 86,88; N% : 6,33 ; H% : 6,79
	Found : C% : 84,44; N% : 6,22 ; H% : 6,58
	Br%: 0,32

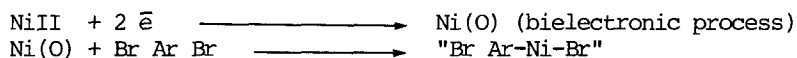
## Results and discussion

### Synthesis of poly (N-butyl-3,6-carbazolediyl) (pBuc)

The process used (see experimental part for details), involves the cathodic reduction of  $NiBr_2 \cdot 2,2'$ bipyridine complex ( $NiBr_2 \cdot B$ ) yielding Ni(0) based catalytic system which in presence of 3,6' dibromo N-butyl-carbazole, gives rise to the formation of pBuc according to the overall reaction scheme (6) :



Electrochemical behavior of the system is similar to the one described for the N-ethyl derivative (6). The Ni(0) complexes obtained by reduction of the catalytic precursor  $NiBr_2 \cdot B$ , is instantaneously inserted into a C-Br bond of the monomer, so yielding potentially active sites "C-Ni-Br" type as follows :



The propagation step would occur by condensation of the above species as it has been proposed for the 3,6 dibromo N-ethylcarbazole.

### Characterization of pBuc

#### Solubility and GPC :

The complete solubility of pBuc, at room temperature, in acceptor solvents (such as nitrobenzene, trichlorobenzene) as well as in donor ones (as tetrahydrofuran, dimethylacetamide) shows up the favorable polymer-solvent interactions induced by the butyl groups linked to nitrogen atoms of carbazolic units. Indeed, in the same experimental conditions, poly (N-ethyl-3,6-carbazolediyl) is only partially soluble in the above solvents (6).

This solubility allows the determination of molar masses by classical methods as GPC. Chromatograms obtained disclose a relatively narrow molar mass distribution ( $\bar{M}_w/\bar{M}_n \approx 2$ ) with  $\bar{M}_n$  values of  $\approx 3000$  corresponding to macromolecular chains constituted with  $\approx 15$  carbazolic units.

## UV-Visible :

The optical absorption spectrum of pBuc in THF solution or film (see Fig. 1) is characterized by a wide maximum centered at 300-310 nm and an absorption threshold corresponding, in these experimental conditions, to an interband transition of  $E \approx 3.4-3.2$  eV (360-390 nm). This energy value is close to the one obtain for films of poly-paraphenylene ( $E \approx 2.8-3$  eV) synthesized in similar conditions (7).

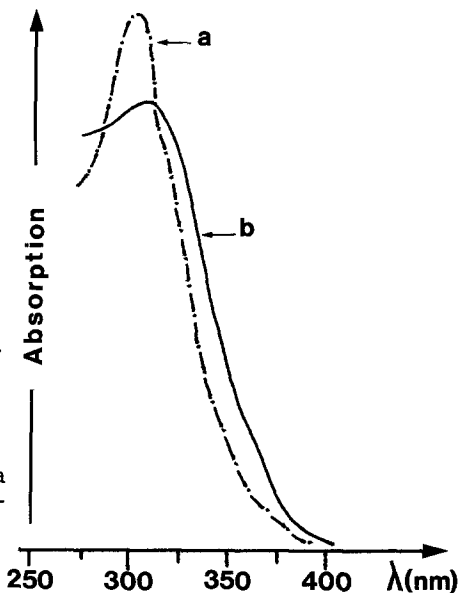


Fig. 1 : Optical absorption spectra of pBuc : (a) in THF solution ; (b) film

 $^{13}\text{C}$  NMR :

In order to simplify assignments of the different aromatic carbons of the carbazolic structure  $^{13}\text{C}$  NMR spectrum of pBuc (Fig. 2) has been compared to the one of a N-alkyl model of the constitutive units of the macromolecular chain the N-ethyl carbazole (dotted line in Fig 2).

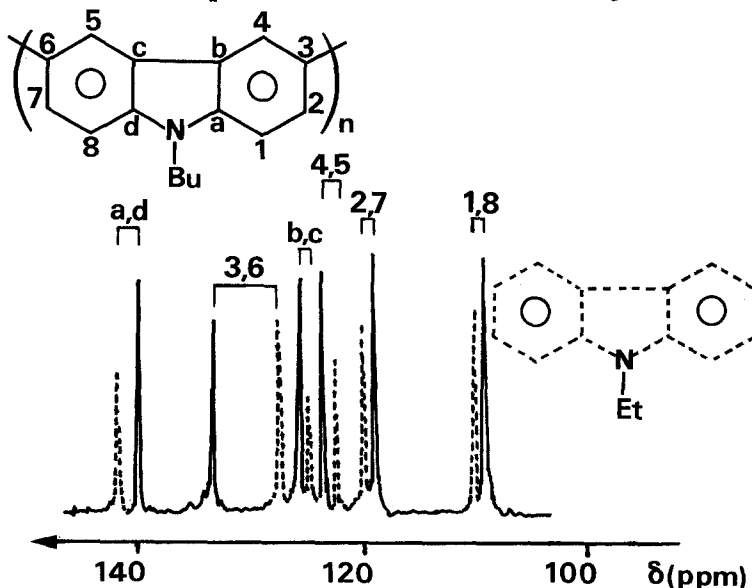


Fig. 2 :  $^{13}\text{C}$  NMR spectra of pBuc and N-ethyl carbazole (Aromatic region).

Comparison of these spectra allows assignments of the different peaks corresponding to the carbon resonances of the polymeric structure (results are mentioned in Table I). In particular, the 3,6 linkages can be unambiguously attributed to the signal at 133.4 ppm appearing 6 ppm downfield with respect to the corresponding carbons of the model compound.

The effect of the conjugation of  $\pi$  bonds along the carbazolic skeleton differently affects the whole carbon population; the shielding of the carbons 1,8;2,7; a,d indicating that a pyrrolic conjugation is more favored than a phenylenic one (see Table I  $\delta$  ppm of pBuc with respect to N-ethyl carbazole).

TABLE I

$^{13}\text{C}$  NMR assignments of pBuc and N-Ethylcarbazole as model compound of monomer unit (solvent :  $\text{CDCl}_3$ )

Aromatic region N° of the carbon atom	Chemical shift in ppm from TMS	
	pBuc	N-ethylcarbazole
a,d	140.1	141.8
3,6	133.4	127.2
b,c	125.5	124.7
4,5	123.8	122.0
2,7	118.9	120.4
1,8	109.0	110.1
Aliphatic region		
N-CH <sub>2</sub> -	42.9	38.8
N-CH <sub>2</sub> -CH <sub>2</sub> -	31.2	-
N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	20.5	-
N-(CH <sub>2</sub> ) <sub>n</sub> -CH <sub>3</sub>		
n = 1	-	14.8
n = 3	13.8	-

Chemical doping :

Exposed to iodine or bromine vapor, the polymer (in powder) gives rise to deep green material, stable exposed to air, and whose conductivity is situated in the semi-conducting range  $10^{-4} > \sigma > 10^{-1}$  ( $\text{S}\cdot\text{cm}^{-1}$ ).

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