

On the Polymerization of Acetylenic Derivatives XXIV. Some Structural Peculiarities of Poly(α -ethynylnaphthalene)

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ABSTRACT: The present paper deals with the study of conjugated chains of a *trans-cisoidal* poly(α -ethynylnaphthalene), (α -EN), obtained by bulk polymerization of α -EN with $(\text{PPh}_3)_2 \cdot \text{NiBr}_2$. Based on the results obtained from electronic spectra and electrical conductivity measurements, using the fractions with molecular weight between 3732 and 528, a polymer structure built up from interrupted conjugated blocks is proposed. It is assumed that this interruption of the electronic conjugation system has structural reasons *i.e.*, it is given by the rotation of parts of the polymer chain around some C—C single bonds, thus hindering the complete overlapping of certain π orbitals. These conjugated blocks have 3—4 conjugated or partial conjugated monomeric units. This structure could explain the low values of electrical conductivity as well as the paramagnetic centers of polyacetylenes with aromatic substituents.

KEY WORDS α -Ethynylnaphthalene / *Trans-Cisoidal* / Conjugated Block / Electrical Conductivity / Electronic Spectra / Paramagnetic Center / Partial Conjugation /

Taking into account the effective interaction energy (for Little's four-carbon unit) calculated¹ for ethynylnaphthalene (-2.1 eV), and using a value included among the energy values required by Little for a macromolecular superconductor,² we proposed to study the structures and properties of poly(α -ethynylnaphthalene)^{3,4} and poly(β -ethynylnaphthalene).⁵

First of all, the question arises if it is possible for a head-to-head (or tail-to-tail) structure for poly(ethynylnaphthalene) to obey the structure conditions required by Little's theory. The reduced probability to get such a structure by the polymerization of aromatic acetylenes⁶ does not justify the unsatisfactory electrical properties of the polymers, since the value of the effective interaction energy, calculated for the two-carbon unit, is 0.252 eV.¹ This value is also included within the limits required by Little's theory for an organic superconductor.

However, the electrical properties of the semi-conducting^{3,4} and superconducting polymers^{7,8} synthesized did not fulfill our hopes.

EXPERIMENTAL

Materials

α -Ethynylnaphthalene (α -EN), was synthesised by Leroy's method⁹ from α -acetylnaphthalene (α -AN) by chlorination and subsequent dehydrochlorination. Characteristic of the IR spectrum of α -EN are the 2190 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$) and 3380 cm^{-1} ($\nu_{\text{C}-\text{H}}$) bands (Figure 1). The NMR spectrum of α -EN exhibits at 3.35 ppm the resonance of ethynylic proton and at 7.05—7.80 and 8.15—8.40 ppm the peaks of aromatic protons (Figure 2).

$\text{NiBr}_2 \cdot (\text{PPh}_3)_2$ was synthesized by Venanzi's method.¹⁰ Poly(α -ethynylnaphthalene) was obtained by bulk polymerization of α -EN with 5-% $\text{NiBr}_2 \cdot (\text{PPh}_3)_2$ at 140°C and was purified by reprecipitation four times from benzene by the addition of methanol.⁴ The IR spectrum of poly(α -ethynylnaphthalene) synthesized by this method is characteristic of a *trans*-configuration (Figure 1). The IR spectrum of a *cis*-configuration presents the *cis* C—H out-of-plane deformation at 700 cm^{-1} .⁴ According to NMR studies of *trans-cisoidal* (three monomer units

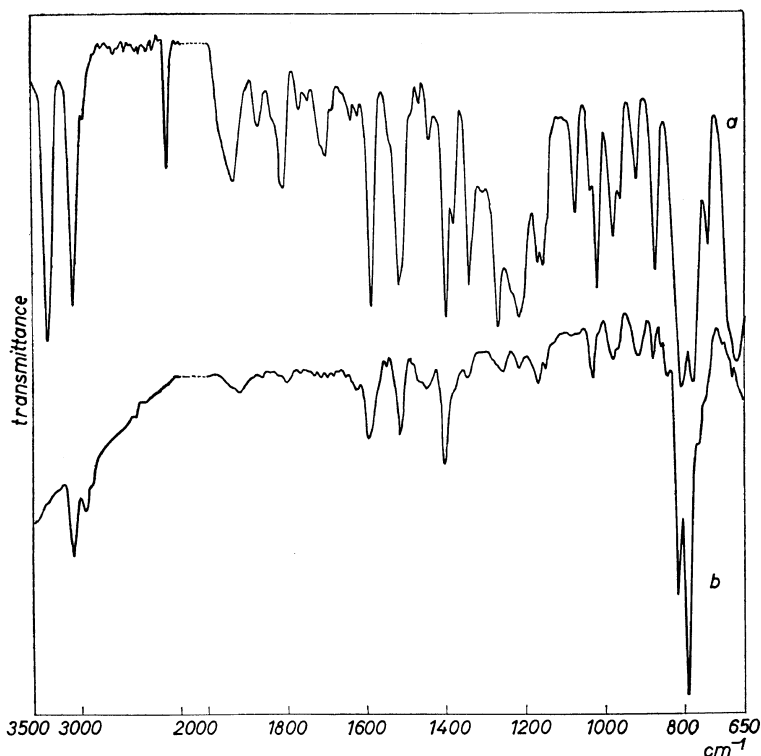


Figure 1. IR spectra of (a) α -ethynylnaphthalene, (b) poly(α -ethynylnaphthalene); (KBr pellets).

on screw) and *trans-transoidal* (twelve monomer units on screw) structural models only a *trans-cisoidal* structure has to have all protons in the same field. In the case of a *trans-transoidal* structure, one proton must be shifted to lower values of σ . According to these findings poly(α -ethynylnaphthalene) obtained by polymerization of (α -EN) with $\text{NiBr}_2 \cdot (\text{PPh}_3)_2$ should have a *trans-cisoidal* structure, because only this conformation gives an NMR spectrum such as that shown in Figure 2.

This polymer was fractionated by successive precipitations with methanol from benzene solutions.

Polymer Characterization

The average molecular weights were determined in benzene solutions by the cryoscopic method, using two thermistors as the sensing elements.

Electrical conductivity and electron paramagnetic resonance spectra were obtained as in reference.⁴

Electronic spectra were recorded on a UNICAM SP-800 spectrophotometer using dioxane solutions for the ultraviolet range (M/5000) and benzene solutions (M/500) for the visible region. The softening intervals were read on a Boetius instrument. Nuclear magnetic resonance spectra were obtained on a JEOL 60-MHz NMR device, using CCl_4 as a solvent, and infrared spectra were run on a UNICAM SP-200 recording spectrophotometer (KBr pellets).

RESULTS AND DISCUSSION

Our previous papers on the synthesis of some poly(arylacetylenes):³⁻⁵ poly(phenylacetylene), poly(α -ethynylnaphthalene), poly(β -ethynylnaphthalene), and poly(9-ethynylantracene), pointed out the following possible polymer structures: *trans-cisoidal*, *cis-transoidal*, and *cis-cisoidal*.

The atomic models for these structures exclude the coplanarity of the backbone for steric

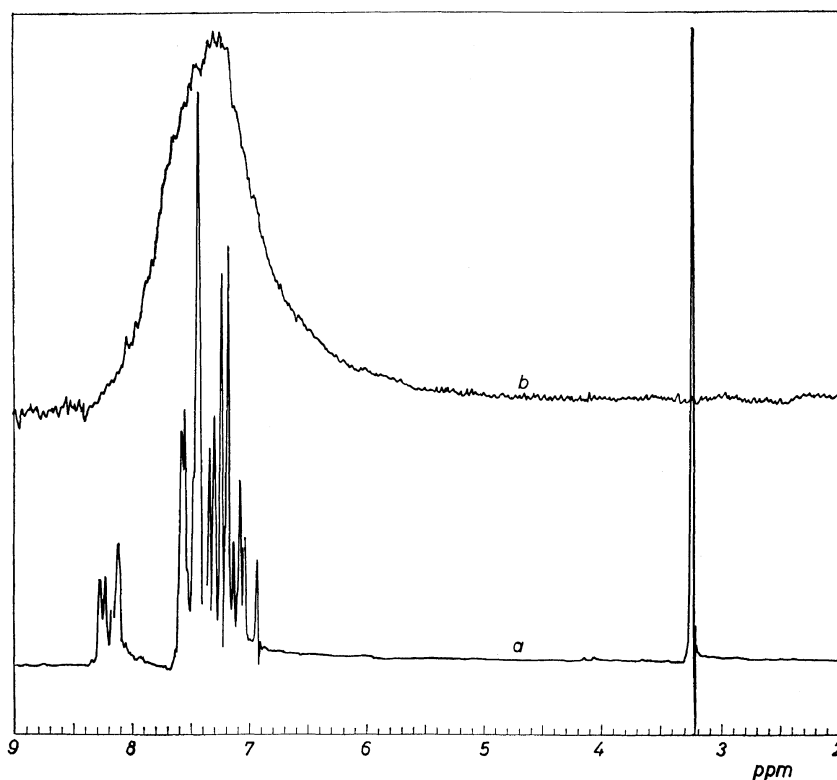


Figure 2. NMR spectra of (a) α -ethylnaphthalene, (b) poly(α -ethylnaphthalene); (CCl_4 solutions).

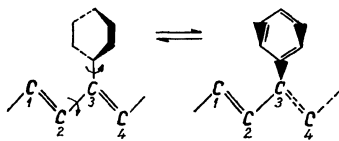


Figure 3. The possible rotation motions in an aromatic monosubstituted polyacetylene.

reasons. In order to build the above geometrical isomers, two rotational motions are required (Figure 3): *i.e.*, a rotation of the chain around a formal single bond C—C (which breaks the π electrons delocalization at that point), and a rotation of the aromatic substituent which breaks the delocalization between the backbone plane and that of the substituent.

Thus one may consider that each double bond can exist in two extreme states: the first one when two adjacent double bonds are coplanar but not in the same plane with the aromatic ring, and the second one when these double

bonds are not coplanar, but one of them is coplanar with the aromatic ring.

All isomers can exist only as helicoidal structures, except for the *cis-cisoidal* one which has a perfect 3/1 helix (*i.e.* having trimers on the screw). The *cis-cisoidal* structure is highly crystalline and insoluble.^{4,5}

The *cis-transoidal* structure isomerizes to a *cis-cisoidal* one under the conditions which facilitate the motion and rotation of chain segments (*e.g.*, in solution). Only the *trans-cisoidal* structure is soluble, stable, and fractionable.

The electronic spectra of all the poly(α -EN) fractions have the same linear shape, characterized by a continuous absorption from the ultraviolet into the visible region, with a maximum at $286 \text{ m}\mu$, (Figures 4, 5). The Intensity absorption in the visible region is the same for all poly(α -EN) fractions (Figure 5). The extremum at $286 \text{ m}\mu$ does not depend on the molecular weight or on the polymer synthesis method,⁴ and we assigned it to the naphthalene

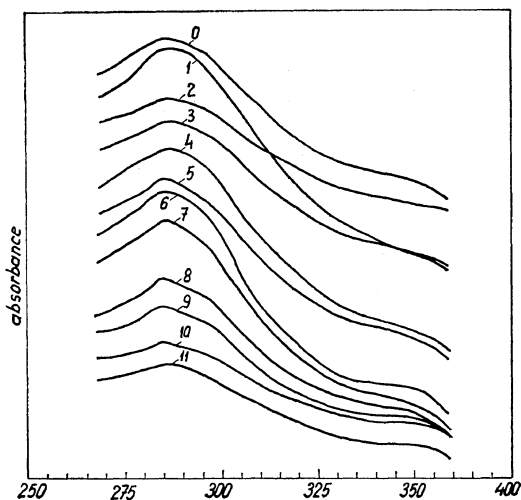


Figure 4. UV spectra of poly(α -ethylnaphthalene). The spectra numbers correspond to the polymer numbers in Table I.

chromophore (Figure 4). At the same time the continuous absorption in the visible region can be assigned to the conjugated double bonds in the chain.

It can be concluded that under the synthesis conditions used the number of effectively conjugated double bonds does not increase with the polymerization degree of poly(α -EN). Thus, they remain constant and are lower than the polymerization degree. The fact that, starting with the fraction whose polymerization degree

is 3–4, the visible absorption value remains the same, can lead to an argument that the number of effectively conjugated double bonds, irrespective of the polymerization degree, does not exceed the value 3 or 4. As most of the single bonds do not break the delocalization completely, the π orbitals can be partially overlapped on a length of 3–4 mers, leading to partial conjugation.¹¹ From the literature data, the rotation angle about a single bond has been estimated to be between 20 and 50 degrees.¹²

From the thermodynamic point of view, the various rotational conformations adopted by poly(α -EN) lead to the loss of delocalization and, consequently, to the increase of the free energy of the system, increasing the energetic and entropic factors. On the other hand, the conjugation loss may allow a bulky substituent to adopt a conformation of a greater conjugation, which leads finally to an appreciable decrease of the energetic factor. Thus, the loss of conjugation of the backbone may be balanced by the conjugation with the aromatic substituent.

Consequently, the thermodynamic reasons explain the small probability of obtaining polyacetylene with aromatic substituents having a high degree of π electron delocalization.

Taking into consideration the fact that electrical conductivity measurements made on pellets have poor reproducibility, we can admit that the slight differences between the electrical conduc-

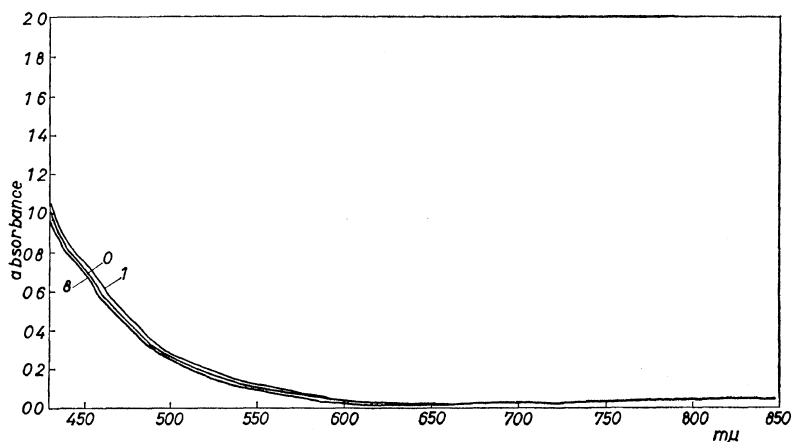


Figure 5. Visible spectra of poly(α -ethylnaphthalene). The spectra numbers correspond to the polymer numbers in Table I.

Table I. Electrophysical properties of poly(α -ethynyl-naphthalene)

No.	\bar{M}_n	$\sigma_{20^\circ\text{C}}$, $\text{ohm}^{-1}\text{cm}^{-1}$	E^a , eV	Unpaired spins/gram	λ_{max} , $\mu\mu$	Number of unpaired spins/conjugated block (three conjugated double bonds)	Softening temp, $^\circ\text{C}$
0 ^a	923	3.00×10^{-17}	0.52	1.80×10^{18}	285—88	1.36×10^{-3}	220—222
1	3732	1.13×10^{-17}	0.90	0.66×10^{18}	287—88	0.50×10^{-3}	260—263
2	2415	6.84×10^{-17}	0.25	1.32×10^{18}	287	0.99×10^{-3}	235—237
3	1437	2.24×10^{-16}	0.41	3.43×10^{18}	287	2.59×10^{-3}	225—228
4	1038	2.30×10^{-16}	0.41	1.86×10^{18}	287	1.41×10^{-3}	218—220
5	888	1.87×10^{-16}	0.50	1.88×10^{18}	286	1.42×10^{-3}	215—220
6	768	1.40×10^{-17}	0.82	2.29×10^{18}	286	1.73×10^{-3}	210—212
7	652	1.02×10^{-18}	0.90	1.92×10^{18}	286	1.45×10^{-3}	195—198
8	528	1.68×10^{-16}	0.71	0.96×10^{18}	286	0.73×10^{-3}	173—175

^a Unfractionated polymer.

tivities at 20°C obtained for the poly(α -EN) fractions are within the range of experimental errors (Table I). The same considerations can be made for the unpaired spin concentrations.

The low values (practically constant) of the electrical conductivities obtained for all poly(α -EN) fractions confirm the above mentioned assumption about the partially conjugated backbone microstructure.

From the point of view of magnetic behavior, the discontinuous character of the polyenic chains' conjugation generates structural defects whose unpaired π bonds can explain the appearance of paramagnetic signals (13—19).

In conclusion, the magnetic and electrical properties of acetylenic polymers must be correlated with the length of the conjugated blocks. For example, in the case of poly(phenylacetylene), the spin concentration does not depend on the molecular weight of the polymers but on their conformation, which determines the size of the conjugated blocks.^{14,16}

REFERENCES

- R. H. Wiley, A. M. Sapse, and J. Y. Lee, *J. Macromol. Sci.-Chem.*, **A4**(1), 203 (1970).
- W. A. Little, *Phys. Rev.*, **156**, 396 (1967); *ibid.*, **134**, 1416 (1964); *J. Polym. Sci., Part C*, **29**, 17 (1970).
- Cr. Simionescu, Sv. Dumitrescu, I. Negulescu, V. Percec, M. Grigoraş, I. Diaconu, M. Leancă, and L. Goraş, *Vysokomol. Soedin., Ser. A*, **4**, 790 (1974).
- Cr. Simionescu, Sv. Dumitrescu, V. Percec, I. Negulescu, and I. Diaconu, *J. Polym. Sci., Symposia*, **42**, 201 (1973).
- Cr. Simionescu, Sv. Dumitrescu, and V. Percec, *Polymer J.*, **8**, 139 (1976).
- A. A. Berlin, *Vysokomol. Soedin., Ser. A*, **13**, 206 (1971).
- J. H. Hodkin and J. Heller, *J. Polym. Sci., Part C*, **29**, 37 (1970).
- G. F. D'Alenio, M. Rahman, C. F. Rhodes, and J. Huang, *J. Macromol. Sci.-Chem.*, **A6**(1), 51 (1972).
- M. J. A. Leroy, *Bull. Soc. Chim. Fr.*, **6**, 385 (1891).
- L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).
- P. M. Duncan and W. G. Forbes, *Polymer Preprint*, 1035 (1966).
- A. A. Berlin, *J. Polym. Sci., Part C*, **29**, 187 (1970).
- P. Ehrlich, R. J. Kern, E. D. Pierron, and T. Provder, *J. Polym. Sci., Part B*, **5**, 911 (1967).
- P. Ehrlich, *J. Macromol. Sci.-Phys.*, **B2**(2), 153 (1968).
- A. A. Berlin, *J. Macromol. Sci.-Chem.*, **A5**(7), 1187 (1971).
- G. M. Holob, P. Ehrlich, and R. D. Allendoerfer, *Macromolecules*, **5**, 569 (1972).
- J. A. Pople, and S. H. Walmsley, *Mol. Phys.*, **5**, 15 (1962).
- R. H. Baughman, G. J. Exarhos, and W. M. Risen, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2189 (1974).
- P. Ehrlich, E. C. Mertzluft, and R. D. Allendoerfer, *J. Polym. Sci., Polym. Letters Ed.*, **12**, 125 (1974).