

The Synthesis and Properties of Several Polypropargylpyridinium and Polypropargylbipyridinium Polyelectrolytes and their Simple and Complex Tetracyanoquinodimethane Ion-Radical Salts. I. Electrophysical Properties

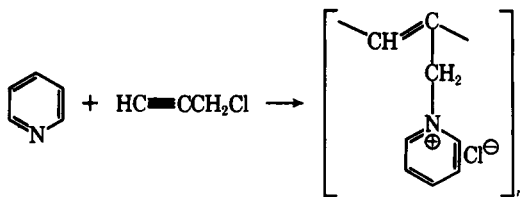
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Synopsis

Poly(propargylpyridinium chloride), poly(propargyl-4-vinylpyridinium chloride), poly(propargyl-2,2-bipyridinium chloride), poly(propargyl-1-methyl-2,2-bipyridinium methylsulfate chloride), poly(N-ethyl-vinylpyridinium bromide), and poly(propargyl-2-hydroxyquinolium chloride) were synthesized and a number of simple and complex tetracyanoquinodimethane ion-radical polyelectrolytes were prepared from them. An attempt was made to understand how the molecular structure of these compounds manifests itself in their observed electrophysical properties. Our results show increased electroconductivity in cases of simple and complex ion-radical polyelectrolytes where the conjugated bond polymer "backbone" is in close proximity to dipyrindyl polarizing side groups.

INTRODUCTION

As seen from the literature,¹⁻¹¹ it has already been shown that many organic and polyelectrolyte tetracyanoquinodimethane TCNQ ion-radical derivatives have good semiconductor properties.¹² Having this in mind, we synthesized poly(propargylpyridinium chloride) (PPC), poly(propargyl-4-vinylpyridinium chloride) (PPVC), poly(propargyl-2,2-bipyridinium chloride) (PPBC), poly(propargyl-1-methyl-2,2-bipyridinium methylsulfate chloride) (PMBMC), poly(N-ethylvinylpyridinium bromide) (PEVPB), and poly(propargyl-2-hydroxyquinolium chloride) (PHQC) by the spontaneous polymerization of propargyl chloride with the corresponding pyridine, bipyridine, or quinoline bases e.g.,



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Simple TCNQ polyelectrolytes were prepared from the polypropargylpyridinium, polypropargylbipyridinium, and polypropargylquinolinium polymer salts, RB^+X^- , where R is polypropargyl, B^+ is a quarternary nitrogenous base cation, and X is a chloride or bromide anion, by metathesis with the lithium salt LiTCNQ, of the anion radical of TCNQ, and the complex polymer salts by incorporation of neutral TCNQ into the simple polyelectrolyte TCNQ derivatives.

A study of the electrophysical properties of these compounds was made and it was found that the complex polymer TCNQ anion radical derivatives exhibit the highest electroconductivity and that a polyconjugated bond system in some cases enhances the electroconductivity of complex and single polymer TCNQ anion radical derivatives.

EXPERIMENTAL

Synthesis of Poly(propargylpyridinium Chloride)

One ml pyridine, 1.1 ml propargyl chloride, and 2 ml methanol were injected from syringes into a glass ampoule. Argon passing through a thin glass capillary bubbled through the liquid mixture 15 min, displacing the air in the ampoule. Afterward, the ampoule was sealed and heated in a thermostat for 15 hr at 70°C. The ampoule was then opened and the contents poured into a beaker containing 50 ml ether. The dark-brown precipitate was separated by a centrifuge and dried in a vacuum heating closet (10^{-2} mm, 100°C) for 10 hr. The product was hygroscopic and had to be kept in a desiccator with potassium hydroxide.

ANAL. Calcd. for C_8H_8NCl : C, 62.6%, H, 5.28%; N, 11.15%; Cl, 20.2%. Found: C 62.5%, H 5.20%, N 11.60%, Cl 20.7%

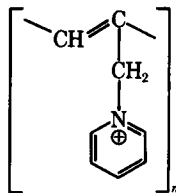
The other polyelectrolytes were prepared similarly; PPVC from poly(4-vinylpyridine) and propargyl chloride,¹³ PPBC from 2,2-dipyridyl and propargyl chloride, PMBMC from PPBC by quarternizing the second dipyridyl nitrogen with an excess of dimethyl sulfate in dimethyl sulfoxide solution, PEVPB from 4-vinylpyridine and ethyl bromide,¹⁴ and PHQC from 2-hydroxyquinoline and propargyl chloride.

The molecular weights of PPC, PPBC, and PMBMC were found to be about 2000. They dissolve in water and organic solvents. Both in solution and in powder form these salts display an EPR singlet.

PPVC is crosslinked and insoluble. The PEVPB obtained had a molecular weight of 100,000.

Synthesis of $(PPC)_n^+TCNQ_n^-TCNQ_n^0$

The symbol $(PPC)_n^+$ here signifies the polypropargylpyridinium polycation



Dissolve 0.06 g poly(propargylpyridinium chloride) in 20 ml distilled water. In another beaker dissolve 0.1 g LiTCNQ (a 22% excess) in 20 ml water. Slowly, drop by drop, add the second solution to the first while constantly mixing. Five minutes after the solutions have been mixed together, separate the precipitate with a centrifuge. The mother liquor is colorless. The precipitate should be washed several times with water and recentrifuged and then dried in a vacuum heating closet at 80°C and 10⁻² mm for 6 hr.

Identification by elemental analysis gave unsatisfactory results and, since the polyelectrolyte was amorphous, it was not possible to crystallize it. However, since the mother liquor was colorless after centrifugation (PPC is a dark-brown solution and LiTCNQ is a dark-purple solution), the authors postulated that all the TCNQ added was integrated into the composition of the complex ion-radical polymer salts and the excess (22%) TCNQ disproportionated to neutral TCNQ. This postulation is supported by ultraviolet spectral data of the obtained TCNQ adsorption at 420 m μ , 740 m μ , and 840 m μ as well as the adsorption of neutral TCNQ at 395 m μ .

(PHQC)_n⁺TCNQ_n⁻TCNQ_m⁰, (PMBMC)_n⁺TCNQ_n⁻TCNQ_m⁰, and (PEVPB)_n⁺TCNQ_nTCNQ_m⁰ were prepared similarly.

All the complex quarternary polymer ion-radical tetracyanoquinodimethane derivatives were insoluble in acetone and dissolved in polar solvents. As a powder they display an EPR singlet which breaks up into 45 lines in dimethyl sulfoxide solution. In the presence of oxygen the 45 EPR lines do not appear in the sample solutions; instead, only a singlet can be detected.

Synthesis of (PPC)_n⁺TCNQ_n⁻

(PPC)_n⁺TCNQ_n⁻TCNQ_m⁰ is placed in an extracting vessel and the neutral TCNQ extracted with benzene for 10 hr after the extract benzene reflux solution becomes colorless. The resulting product is then dried in a vacuum heating closet at 80°C and 10⁻² mm.

(PMBMC)_n⁺TCNQ_n⁻ and (PEVPB)_n⁺TCNQ_n⁻ were prepared similarly. The ultraviolet adsorption band of 395 m μ characteristic of neutral TCNQ does not appear in the derivatives prepared in this way. These polymer salts dissolve in dimethylsulphoxide. X-ray diffraction patterns of (PPC)_n⁺TCNQ_n⁻ and (PEVPB)_n⁺TCNQ_n⁻ show diffuse rings typical of amorphous polymers.

Measurements

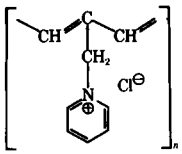
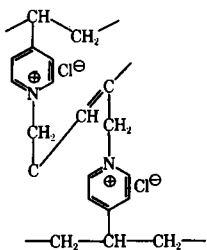
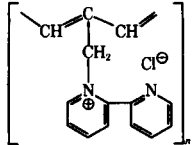
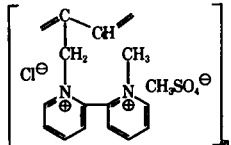
EPR measurements were carried out on a "Joel." The specific resistivity of pressed powder samples was measured between two electrodes in a 10⁻² mm vacuum at pressures of 1000 kg/cm². The activation energies were determined in a 20–120°C temperature range from the equation

$$\rho = \rho_0 \exp \left(\frac{-\Delta E}{2KT} \right).$$

RESULTS AND DISCUSSION

The electrophysical properties of the polypropargylpyridinium and polypropargylbipyridinium polyelectrolytes are given in Table I. It is interesting to

TABLE I
Electrophysical Properties of Polypropargylpyridinium, Polypropargyl-
(4-vinylpyridinium), and Polypropargylbipyridinium Polyelectrolytes

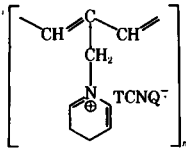
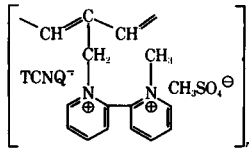
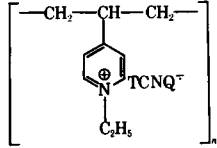
Poly-electrolyte	Formula	Specific resistivity at 20°C, ohm cm	E , eV	ESR, spin/g
PPC		6×10^{10}	2.05	4.8×10^{16}
PPVC		6×10^{10}	2.53	
PPBC		2.6×10^{10}		
PMBMC		1.3×10^{11}	2.18	

note here that the electroconductivities of PPC and crosslinked PPVC are identical. Apparently, the molecular weight of the organic semiconductor does not play a determining role.

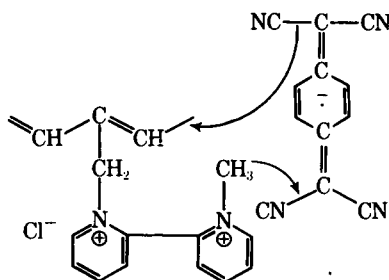
The specific resistivities and activation energies of the simple ion-radical TCNQ derivatives are given in Table II. The electroconductivity of $(\text{PPC})_n^+ \text{TCNQ}_n^-$ and $(\text{PEVPB})_n^+ \text{TCNQ}_n^-$ are of the magnitude of 10^{-12} to 10^{-13} ohm $^{-1}$ cm $^{-1}$ ($\sigma = 1/\rho$) which is typical of poor semiconductors. In the case of $(\text{PPC})_n^+ \text{TCNQ}_n^-$ and $(\text{PEVPB})_n^+ \text{TCNQ}_n^-$ it would seem that the presence of a conjugated bond system by itself does not influence the electroconductivity of simple TCNQ polyelectrolytes. Perhaps here the induction effect of the methylene group weakens the joint interaction between the conjugated bond system and the TCNQ anion radical.

However, the increased electroconductivity of $(\text{PMBMC})_n^+ \text{TCNQ}_n^-$ suggests such interaction between the conjugated bond system and the dipyrindyl ring. Perhaps this takes place in $(\text{PMBMC})_n^+ \text{TCNQ}_n^-$ because the methyl group alkylated into the dipyrindyl ring shortens the distance between the poly-

TABLE II
Electrical Properties of Simple Polypropargylpyridinium, Polypropargylbipyridinium, and Poly(4-vinylpyridinium) Ion-Radical TCNQ Salts

Name symbol	Formula	Specific resistivity, at 20°C, ohm cm	E , eV
$(\text{PPC})_n^+ \text{TCNQ}_n^-$		6.0×10^{11}	0.83
$(\text{PMBMC})_n^+ \text{TCNQ}_n^-$		1.3×10^6	0.507
$(\text{PEVPB})_n^+ \text{TCNQ}_n^-$		6.0×10^{12}	1.91

mer backbone and the polarizing side groups, thereby counterbalancing the effect of the methylene group. This effect does not appear in the initial PMBMC whose electroconductivity is less than that of PPBC. Therefore, it is quite possible the anion-radical TCNQ serves as a "bridge" between the conjugated bond "backbone" and the dipyridyl side group. The very strong electron affinity of the TCNQ anion radical could surpass the opposing positive charges of the two quarternized nitrogen atoms which would tend to retain electron density. This effect can be illustrated by the following scheme:



The plane of the TCNQ molecule would have to be different (but parallel) to that of the polyelectrolyte for a geometric fit. The presence of neutral TCNQ in the complex ion-radical polymer salts brings about a marked increase in the electroconductivity, as seen in Table III. The specific resistivities here are in the range 10^2 to 10^9 ohm cm. $(\text{PMBMC})_n^+ \text{TCNQ}_n^- \cdot \text{TCNQ}_m^0$ has the greatest electroconductivity of the complex ion-radical polymer salts. Again, as in the case of $(\text{PMBMC})_n^+ \text{TCNQ}_n^-$, this may be due to the close proximity of the methyl group alkylated into the dipyridyl ring to the conjugated bond system.

TABLE III

Electrophysical Properties of Complex Polypropargylpyridinium, Polypropargylquinolium, Polypropargylbipyridinium, and Poly(4-vinylpyridinium) Ion-Radical TCNQ Salts

Name symbol	Formula	TCNQ excess m/n	Specific resis- tivity at 20°C, ohm cm	EPR, spin/g
$(\text{PPC})_n^+ \text{TCNQ}_n^- \text{TCNQ}_m^0$		0.22	1.2×10^4	3.8×10^{20}
$(\text{PHQC})_n^+ \text{TCNQ}_n^- \text{TCNQ}_m^0$		0.11	5.2×10^4	4.9×10^{19}
$(\text{PMBMC})_n^+ \text{TCNQ}_n^- \text{TCNQ}_m^0$		0.20	9.5×10^1	
$(\text{PEVPB})_n^+ \text{TCNQ}_n^- \text{TCNQ}_m^0$		0.11	8.2×10^8	

Nomenclature

- K Boltzmann constant
 T absolute temperature
 ΔE activation energy of specific resistivity

Subscripts

- n number of repeating units in the polymer chain
 m number of neutral TCNQ molecules in the polymer chain
 \cdot anion radical
 0 neutral molecule

Greek Symbols

- $m\mu$ millimicron
 ρ specific resistivity
 σ electroconductivity

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