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Electropolymerization of Cyanogen in the Presence of a Heterocyclic Anion

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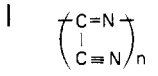
ABSTRACT: Cyanogen is electropolymerized by using salts of the heterocyclic anion $C_7N_7^-$ as the electrolyte in order to understand the nature of the polymerization process in more detail. Even though such preparations give low molecular weights between 400 and 900, the polymer still has fiber-forming properties and can be converted to carbon fibers. It is estimated from ^1H NMR and calorimetric measurements that one heterocyclic anion per 40 cyanogen monomers is incorporated as either a chain end or within the chain and that the alkylammonium cation serves as a closely bound gegenion.

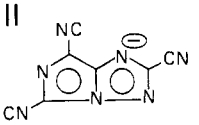
Introduction

We have recently reported the preparation of poly(cyanogen) (PCN) (I) via the electropolymerization of

I



II



cyanogen (ethanedinitrile, C_2N_2) in acetonitrile containing an electrolyte such as tetraethylammonium tetrafluoroborate.[1,2] Spectroscopic data indicated that the reaction proceeds via the initial formation of a heterocyclic anion, $C_7N_7^-$ (II) (1*H*-imidazo[1,5-*b*]-*s*-triazole-2,5,7-tricarbonitrile), from the reaction of C_2N_2 with CN^- produced at the cathode by a one-electron reduction. A small amount of $C_7N_7^-$ or dimeric forms derived therefrom could possibly be incorporated in the polymer, but no assessment of the amount could be made via NMR, infrared, or UV-visible spectroscopy. The spectral characteristics of the black polymers have been presented earlier.[1]

In order to further understand this problem, it was decided to utilize $Et_4N^+C_7N_7^-$ as the electrolyte to maximize the likelihood that incorporation of derived structures occurs. ^1H NMR allows the assessment of the tetraethylammonium moieties in the polymer, whereas differential scanning calorimetric studies (DSC) indicate an exothermic peak always occurs when the heterocyclic anion is heated to about 630–640 K. By employing these methods, it is possible to determine the extent of incorporation of $C_7N_7^-$ into PCN.

PCN prepared in this way was found to have lower molecular weight than that prepared with conventional electrolytes. In spite of the molecular weight being only 400–900, the polymer still has film- and fiber-forming properties and can be converted to carbon fibers.

Experimental Procedures

The preparation of $Et_4NC_7N_7$, $Me_4C_7N_7$, and HC_7N_7 followed the procedure of Wiley et al.[3] Acetonitrile (U.V. grade, Burdick & Jackson Laboratories) was distilled over CaH_2 in an inert atmosphere and stored under high-purity nitrogen. Cyanogen gas (minimum purity 99%) from Matheson Gas Products contained, by analysis, 5 ppm O_2, 23 ppm N_2, and 50 ppm H_2O. It was purified by passing it through a scrubbing train that consisted of a silver nitrate bubbler (to remove hydrogen cyanide), a calcium chloride tower, a sodium hydroxide tower (to remove carbon dioxide), and a phosphorus pentoxide tower to remove traces of water. A typical polymerization was performed as follows. Polymerizations were initiated electrochemically in cells that consisted of two circular glassy carbon electrodes 2.5 cm in diameter and 1 cm apart. The total volume of the cell was about 100 mL. The experiments were conducted under conditions of constant voltage with a dc power supply (Hewlett-Packard 611A). Typically, the voltage was held between 5 and 15 V (at an initial current of 50–80 mA) for 72 h. Cyanogen was bubbled through dry acetonitrile containing about 0.02 M electrolyte. The cyanogen concentration was determined to be 1.2 M by potentiometric titration. For this determination, a 1-mL aliquot was added to 30 mL of 0.1 M KOH solution, cyanogen was disproportionated into CN^- and CNO^-, and a titration was performed with a stock silver nitrate solution employing a silver electrode (Orion Model 701A digital pH/mv meter) to detect the end point.

Polymer formed both at the anode and in solution. In the early stages of polymerization, the polymer formed a coherent thin film on the carbon electrode, which started to flake and peel off as the reaction proceeded further. The solution polymeric product was precipitated by pouring the solution into a 1:2 mixture of CH_3CN and ethyl ether, kept dry inside a glovebox, giving a black solid. The unreacted electrolyte dissolves in the CH_3CN/ether (1:2) mixture. The yield of the polymer is typically approximately 75% based on the $(CN)_2$ used. The crude polymeric products were submitted for elemental analysis and molecular weight

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Table I
Electropolymerization of 1.2 M Cyanogen in Acetonitrile Using Glassy Carbon Electrodes at 25 °C

sample	electrolyte[a]	voltage,[b] V	current, mA initial	current, mA final	polymer av MW
PCN 1	$Et_4NC_7N_7$	9	50	1.0	901
PCN 2	$Et_4NC_7N_7$	5	46.2	1.0	400
PCN 3	$Et_4NC_7N_7$	15	84.0	2.9	885
PCN 4	$Me_4NC_7N_7$	5	35.8	0.4	503
PCN 5	HC_7N_7	9	20.0	0.3	513

[a] 0.02 M. [b] Direct current.

Table II
Analytical Data on Poly(cyanogen) Prepared by Electropolymerization at 25 °C in Acetonitrile

sample	C, %	N, %	H, %	O, %	C/N
PCN 1	48.97	45.94	2.65	2.13	1.24
PCN 2	50.51	44.22	3.19	2.08	1.30
PCN 3	47.93	46.13	2.54	3.33	1.21
PCN 4	48.03	47.95	2.19	2.09	1.17
PCN 5	45.83	44.88	2.22	6.50	1.19

Table III
Enthalpic (ΔH) Values for the Polymeric Products and $Et_4NC_7N_7$ Determined by DSC

sample	MW	ΔH, cal/g	ΔH, kcal/mol	ratio $C_7N_7^-$:PCN
$Et_4NC_7N_7$	312	−81.48	−25.4	
PCN 1	901	−12.07	−10.9	0.42:1
PCN 2	400	−54.48	−21.8	0.85:1
PCN 3	885	−10.8	−8.85	0.35:1

determination by vapor pressure osmometry (Galbraith Laboratories, Inc.). As shown in Table I, molecular weights from 400 to 900 were achieved. A small amount of oxidation was encountered, even though precautions were taken to exclude O_2 and H_2O during the preparation and workup of the polymer. Table II shows typical analytical data and C/N ratios, which show the same type of deviations discussed in our earlier work.[1,2]

Thermogravimetric and DSC analyses were performed on a Perkin-Elmer TGA-2 and DSC-2C, respectively. ^1H NMR spectra were taken on a Perkin-Elmer R32 spectrometer, and infrared spectra were recorded on a Nicolet 20SX FTIR. Pyrolysis of PCN fibers was performed in evacuated quartz tubes or in ceramic boats in inert atmosphere.

Results

DSC experiments on PCN containing $C_7N_7^-$ show a broad exothermic peak with a minimum at 630 K, corresponding to a reaction with an enthalpy of −10 kcal/mol, as is shown in Figure 1. When a similar analysis was performed on $Et_4N^+C_7N_7^-$ (Figure 2), the same broad exothermic peak was observed at 640 K with an enthalpy of −25.4 kcal/mol. These enthalpic values of several different samples of PCN are presented in Table III. The number of heterocyclic anions per polymer chain was then estimated from these enthalpies; a value of one anion per 1–3 polymer chains (Table III) was obtained.

Because the cation Et_4N^+ can bind to anionic sites, integrating the area under the curve of a ^1H NMR spectrum can be used to determine the sum of any heterocyclic anions as well as any cations serving as end groups capping the polymer chain. A calibration curve showing that intensity of the ^1H NMR signal is linear in Et_4N^+ concentration was determined by using the pure salt $Et_4N^+C_7N_7^-$.

The estimates by these two methodologies are compared in Table IV and are reasonably consistent. It also appears that the amount of anion incorporated into the polymer decreases as the voltage of the electropolymerization increases.

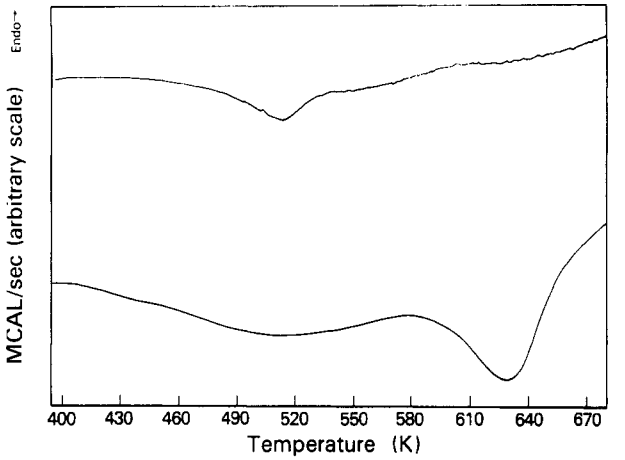


Figure 1. DSC curve for PCN (upper curve) MW 986, PCN-($C_7N_7^-$) (lower curve) MW 901. Enthalpy associated with $C_7N_7^-$ moieties (−10.8 Kcal/mol) estimated from the exotherm at 629 K. Scan rate for both samples 40 °C/min.

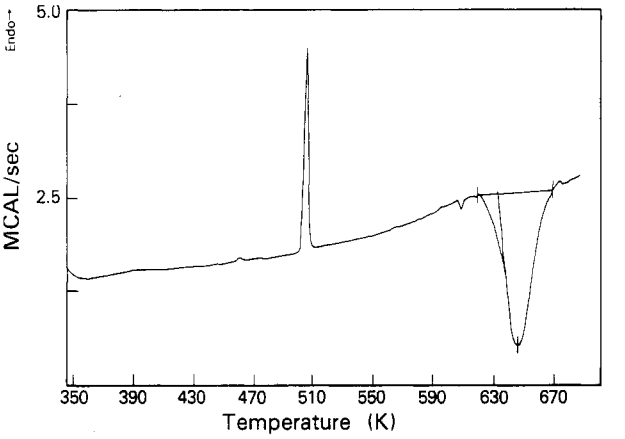


Figure 2. DSC curve for $Et_4N^+C_7N_7^-$ heated at 40 °C/min in nitrogen. Sample weight 0.81 mg and enthalpy −81.5 cal/g for exotherm with onset at 630 K.

Table IV
Comparison of the $C_7N_7^-$:PCN Ratio Estimated from DSC and ^1H NMR

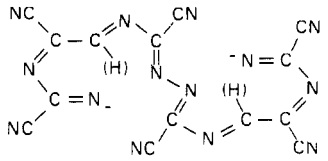
sample	MW	electropolymerization voltage, V	ratio from DSC	ratio from ^1H NMR
PCN 1	901	9	0.4:1	0.4:1
PCN 2	400	5	0.8:1	0.6:1; 0.7:1
PCN 3	895	15	0.4:1	0.4:1
PCN 4	503	5	0.5:1	

A thermogravimetric analysis on PCN($C_7N_7^-$) shows that the polymer undergoes a weight loss of 80% when heated to 1000 °C in nitrogen, higher than that observed for PCN prepared with a conventional electrolyte. This effect is probably due to the large molecular weight differences in the two preparations.

Heat treatment of the polymer was conducted in fiber form. The preparation of fiber from PCN($C_7N_7^-$) followed the same procedure already described for conventional PCN[2], except that 45–48% by weight of polymer was used in tetrahydrofuran or dimethylformamide as the "spinning" solution. Both their conductivities[1,2] and mechanical properties[4] were similar to those observed on conventional PCN.[1]

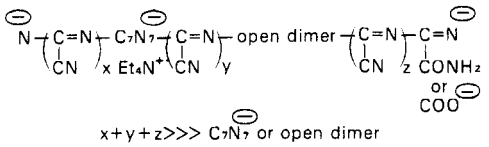
Discussion

The incorporation of $C_7N_7^-$ into PCN can be visualized as occurring in several ways. In our earlier work,[1,2] we speculated about an open dimeric form of this anion (III)[5]



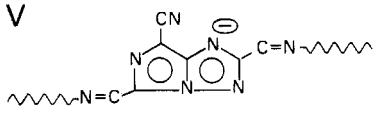
III

IV

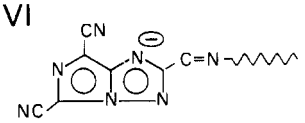


which could be formed at the anode by oxidation of $C_7N_7^-$, leading to occasional carbon–carbon and nitrogen–nitrogen links in the backbone. Our view of the "real" polymer is shown in IV. $C_7N_7^-$ anion that is not dimerized can be incorporated at a chain end or within the chain in two forms (V and VI).

V



VI



The results of DSC and ^1H NMR studies suggest that the concentrations of $C_7N_7^-$ related species and Et_4N^+ in the polymer are essentially the same and that there is approximately one $C_7N_7^-$ anion per 40 C_2N_2 units. It is the incorporation of tetraalkylammonium groups that explains the C/N ratios being greater than 1:1 as well as the hydrogen content (~2%) of PCN. Adventitious protons are undoubtedly also responsible for chain termination.

Using HC_7N_7 as an electrolyte instead of the tetraethylammonium salt leads to the molecular weight decreasing by a factor of 2. It has been noted by Sato et al.[6] in studies of electropolymerization of acrylonitrile that polymerization rate and molecular weight increase with increasing size of the alkylammonium ion in the supporting electrolyte.

The fact that a polymer of such low molecular weight still forms fibers implies that dipole–dipole interactions between —C≡N groups on neighboring chains are important in giving this interesting new polymer cooperative properties.

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Mesoionic Polymerization. Poly(oxyvinylene) Lactams from *N*-(Chloroacetyl) Lactams through an Isomunchnone Intermediate

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ABSTRACT: The polymerization of *N*-(chloroacetyl) lactams to yield poly(oxyvinylene) lactams is described. Evidence for the polymer structure includes spectral characterization by IR, ^1H NMR, and ^{13}C NMR, and degradation behavior. Polymerization was found to occur for 2-haloacyl-substituted lactams only and not for 3- or 4-haloacyl derivatives. *N*-(Chloroacetyl) lactams of ring size six, seven, and eight were found to polymerize spontaneously at ambient temperature and at higher temperatures. The five-membered lactam failed to polymerize under any conditions. Polymers synthesized from *N*-(chloroacetyl)caprolactam exhibited inherent viscosities in the range 0.03–0.07 dL/g and were soluble in a wide variety of organic solvents, including ketones, aromatics, lower alcohols, tetrahydrofuran, and dimethyl sulfoxide. The polymerization mechanism postulated involves formation of a mesoionic 1,3-oxazolium-4-oxide or "isomunchnone" intermediate. Polymer is formed by sequential Michael addition and ring opening of this species. Support for the isomunchnone intermediate involved trapping with dimethyl acetylenedicarboxylate. The initial 1,3-dipolar cycloaddition product rearranged to a pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[*a*]pyridin-2-one.

Introduction

The variety of polymerization mechanisms that have so far been demonstrated include almost all those that can be imagined. Neutral, radical, cationic, anionic, complexed, and zwitterionic intermediates have been postulated or demonstrated for a range of chain-growth and step-growth systems. We report in this paper what we believe to be the first polymerization in which a *mesoionic* intermediate is involved.

A mesoionic compound is usually a heterocyclic species for which an unusual bonding structure can be drawn that possesses formal charge separation. "Sydnones" (1) are considered to be one of the first families of mesoionic compounds to be discovered.[1] Following the serendipitous

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