

Electrosynthesis of Electrically Conducting Polyanthracene

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Abstract

Electrosynthesis of polyanthracene was carried out in acetone containing $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as a supporting electrolyte. The Silver like coating of polyanthracene was found to be deposited on the anode surface. The electrical conductivity of the polymer was found to be low $\approx 10^{-3} \text{ S cm}^{-1}$, which lies in the range of semiconductor. Cyclic Voltammograms shows that the formation of polyanthracene was not properly reversible but irreversible. The mechanism of the polymerization was elucidated.

Keywords: Electrosynthesis, Polyanthracene, Mechanism.

Original Research Article

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INTRODUCTION

Polyanthracene is a π -conjugated polymer with unique properties making it a promising material for various advanced applications. Polyanthracene has high thermal stability and enhanced photo-reactivity composed to its monomeric form which makes it photo responsive material. Hence, it is used as organic semiconductors and Organic Light Emitting Diodes (OLEDs) [1, 2]. It may also be used in chemical and biomedical applications such as controlled drug release, bio-sensing, tissue engineering and self-healing materials [3-5]. Several methods can be employed for the synthesis of polyanthracene which include chemical, photochemical or electrochemical [2,6] but electrochemical method is an elegant way because it can be controlled at will and this method is environment friendly [7-8] as it does not rely on toxic chemical oxidants, thereby aligns with the principle of green chemistry. The polymer films produced are generally of high purity as external chemical oxidants and polymerization initiators are avoided in this method.

EXPERIMENTAL

Materials

Acetone is purified by fractional distillation. Borontrifluoride etherate, $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ and anthracene were of analytical grade and used without further purification.

Polymerization Method

Under constant current electrolysis, polymerization was carried out in a simple one compartment glass cell that could accommodate two platinum electrodes of the area $2.5 \times 1.7 \text{ cm}^2$. The cell was charged with known amounts of monomer, solvent and supporting electrolyte. Then the cell was thermostated at 30°C and subjected to electrolysis at constant current. The electrolysis was terminated at a known time and the anode was coated with silvery brown-black polymer. The polymer film deposited was highly brittle and loosely attached to the electrode surface. The electrical conductivity was measured by two probe method. PalmSen's cyclic voltammeter, Netherland was used to record the cyclic voltammograms in a single compartment three electrodes cell under N_2

atmosphere. The working electrode was a platinum microelectrode, the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode.

Results and Discussion

The Polymerization of anthracene was

investigated in its solution in acetone using $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as a supporting electrolyte to obtain polyanthracene. Polymers were obtained as silver brown deposition on anode. The yield and electrical conductivity of the resulting polymers were determined. The polymer yield increases with the increase in the time of electrolysis at different current as shown in Figure 1.

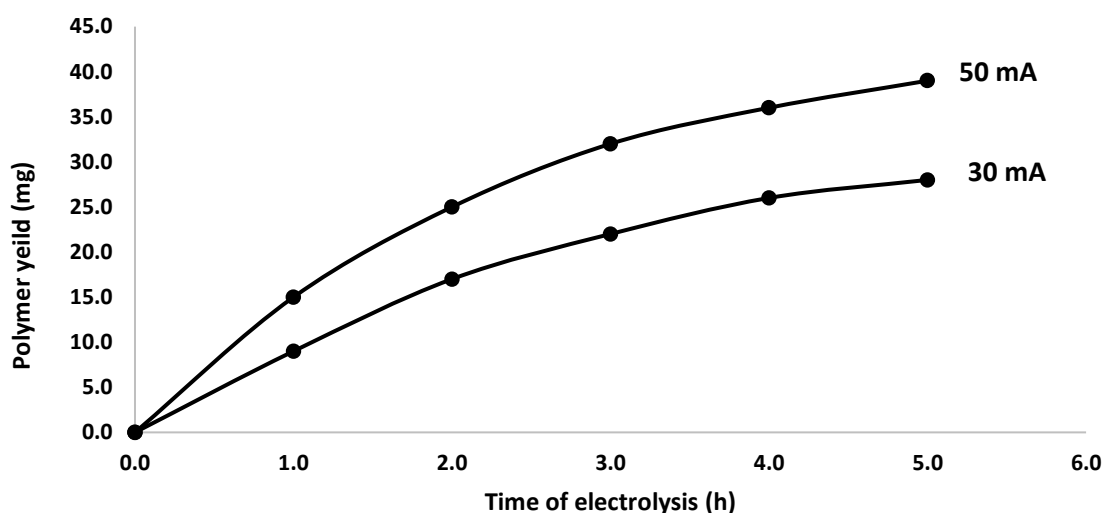


Figure 1. Time conversion curves for the anodic polymerization of anthracene (0.112 mol L^{-1}) at different current levels in acetone containing $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (1.3 mol L^{-1}).

The variation of electrical conductance with the

time of electrolysis is shown in Figure 2, which indicates that the conductivity of the polymer obtained was considerably low ($\approx 10^{-3} \text{ S cm}^{-1}$) and shows that the polymer actually lies in the range of semiconductor.

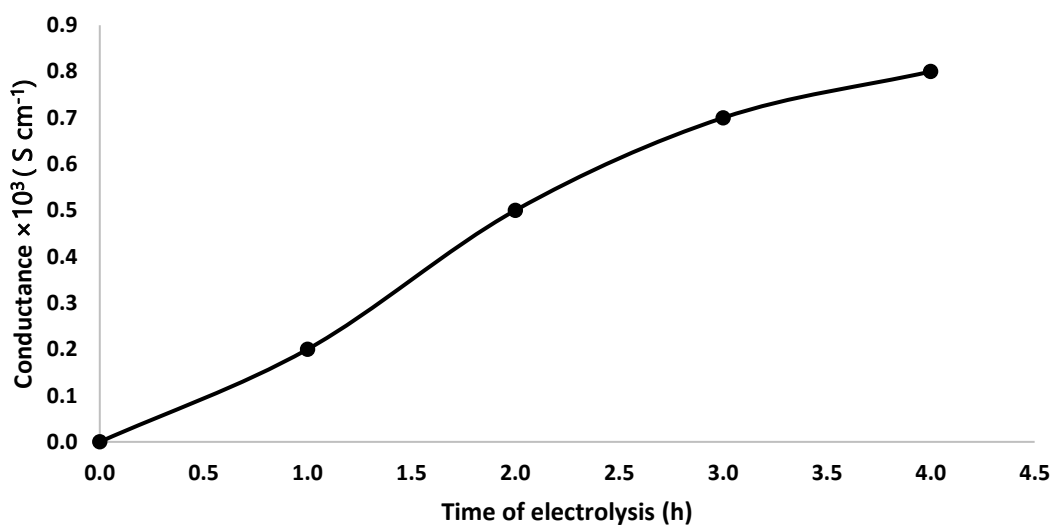


Figure 2. Variation of conductance with the time of electrolysis; current = 50 mA; $[C_{10}H_{14}] = 0.122 \text{ mol L}^{-1}$ and $[BF_3O(C_2H_5)_2] = 1.3 \text{ mol L}^{-1}$.

The electrical conductivity of the polymer, polyanthracene, increased with the increase in electrolysis time which may be due to the greater number of doping, which increased the number of defects, polaron, bipolaron and solitron. Figure 3 shows the cyclic voltammograms (CVs) during the electrosynthesis of polyanthracene in acetone with $BF_3O(C_2H_5)_2$ as a supporting electrolyte and the multiple overlapping curves suggested that the experiment was run for multiple cycles. The rising current in the positive potential region, around +0.925 V indicated the oxidation of the anthracene monomer. The oxidation leads to the formation of radical cation

and it is the initial step of polymerization. The subsequent current plateaus and overall change in the shape of the voltammograms over multiple cycles suggest the formation of polymer film on the surface of the electrode. The current response changed with the growth of polymer film, in comparison to the initial cycle. Unlike the polyaniline and poly(p-phenylene) systems [10-11], the reduction peaks were absent in the reverse scan which showed that the process was irreversible and oxidized species immediately reacted to form the polymer film rather than reduced back to the monomer. The gradual shifting of the curves slightly upwards showed that the conducting polymer film was growing on the electrode surface which increased the electroactive area and thereby current also rose.

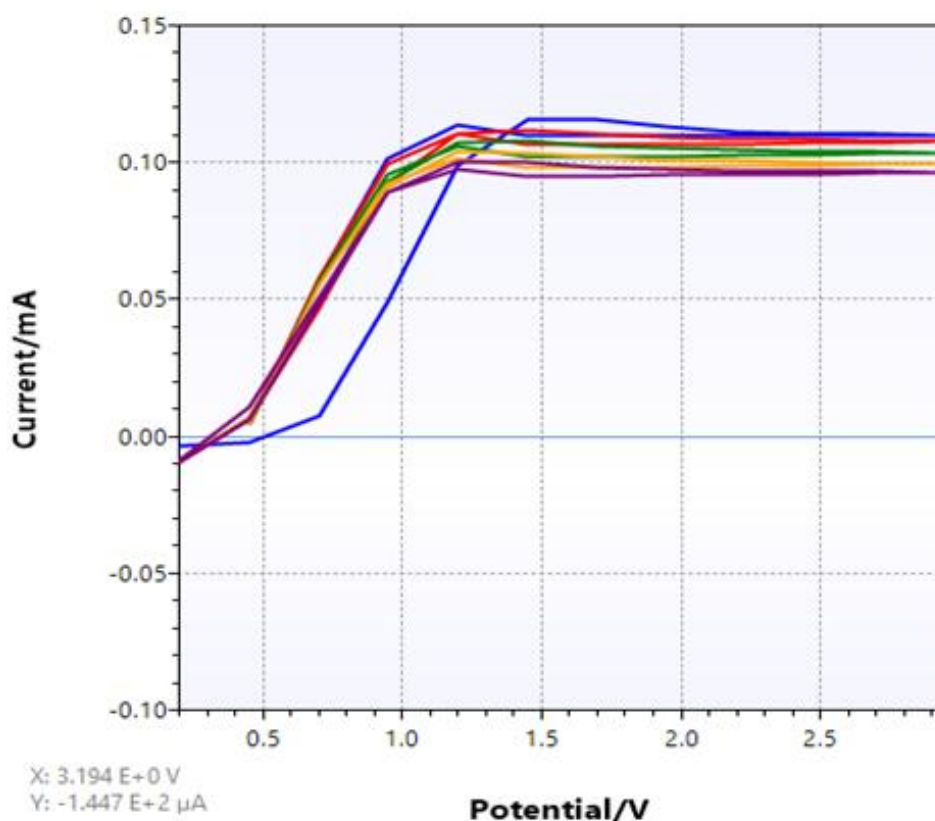
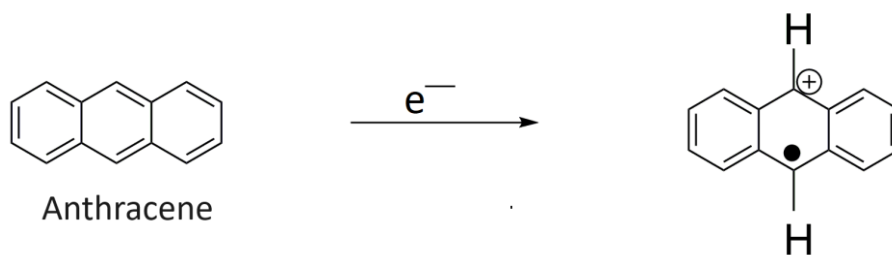


Figure 3. Cyclic voltammograms of the solution of anthracene (0.112 mol L^{-1}) and $BF_3O(C_2H_5)_2$ (1.3 mol L^{-1}) in acetone.

Mechanism

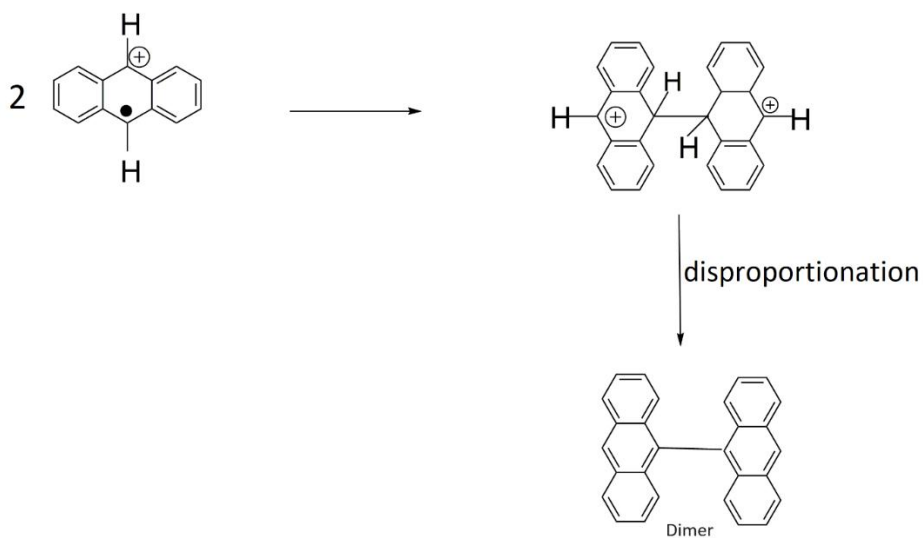
The mechanism of polyanthracene

formation is typically through oxidative coupling as mentioned earlier [9-10]. The anthracene monomer is oxidized to form a radical cation. Due to the higher electron density and lower aromaticity, the unpaired electron and positive charges are preferentially located at C9 and C10 positions.



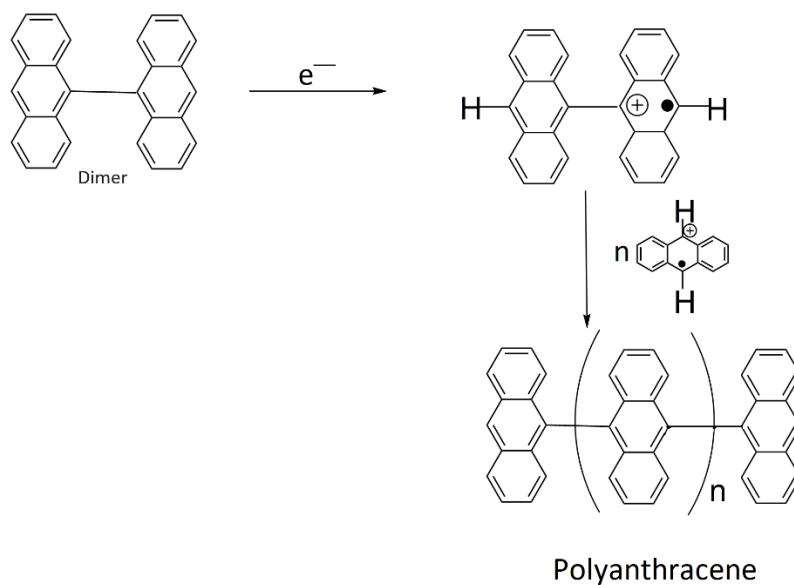
These cations undergo a rapid coupling reaction to form a dimeric dication. Due to high unstability and non-aromaticity, it restores the

stability and aromaticity by losing two protons (H^+) from C 9 and C10 positions. This creates a stable dimer.



In this similar manner the dimer is again oxidized and repeats the same cycles to undergo the

continuous chain growth, producing polyanthracene.



CONCLUSION

This method to synthesize polyanthracene is easy and environment friendly. The yield and conductivity may further be increased by changing the solvent or supporting electrolyte.

Acknowledgement

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