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Wiener Index in Random Polyphenyl Chains[1]

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Abstract

The Wiener index of a connected graph is the sum of the distances between all pairs of vertices of the graph. In this paper, we obtain a simple exact formula for the expected value of the Wiener index of a random polyphenyl chain.

1 Introduction

A kind of macrocyclic aromatic hydrocarbons called polyphenyls and their derivatives attracted the attention of chemists for many years [1–3]. The derivatives of polyphenyls are very often seen chemicals, which can be used in organic synthesis, drug synthesis, heat exchanger, etc. Biphenyl compounds also have extensive industrial applications. For example, 4,4-bis (chloromethyl) biphenyl can be used for the synthesis of brightening agents. Especially, polychlorinated biphenyls (PCBs) can be applied in print and dyeing extensively [4, 5]. On the other side, PCBs are dangerous organic pollutants, which lead to global pollution.

The Wiener index of a connected graph is the sum of the distances between all pairs of vertices of the graph. It was first reported by Wiener [6] in the study of paraffin boiling points. In the second half of the 20th century, the Wiener index was found to be correlated to many physico-chemical properties and to have pharmacologic applications. [7] characterize the polyphenyl chains with minimum and maximum Wiener indices among all polyphenyl chains with n hexagons, and tree-like polyphenyl systems with maximum

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Wiener index. I. Gutman [8–10] studied the perfect matchings and Wiener index about random benzenoid chains in 1990s. In this paper, we obtain a simple exact formula for the expected value of the Wiener index of a random polyphenyl chain. Furthermore its asymptotic behavior is also considered.

2 Preliminaries

Let G be a graph with vertex set $\{v_1, v_2, \cdots, v_n\}$. The distance $d(v_r, v_s)$ between v_r and v_s in G is the length, or number of edges, of a shortest path in G that connects v_r and v_s. Under this definition $d(v_r, v_r) = 0$. The Wiener number of G is then defined by

$$W(G) = \sum_{r<s} d(v_r, v_s) = \frac{1}{2}\sum_{r=1}^{n}\sum_{s=1}^{n} d(v_r, v_s) = \frac{1}{2}\sum_{r=1}^{n} d(v_r|G)$$

where $d(v_r|G)$ is the Wiener number of vertex v_r in G, defined by

$$d(v_r|G) = \sum_{s=1}^{n} d(v_r, v_s)$$

The molecular graphs (or more precisely, the graphs representing the carbon-atoms) of polyphenyls are called the polyphenyl system. If each vertex of the polyphenyl system lies in a hexagon and the graph obtained by contracting every hexagon into a vertex in the polyphenyl system is a path, we say that it is a polyphenyl chain. Fig. 1 show the unique plyphenyl chains for $n = 1, 2$ and all the polyphenyl chains for $n = 3, 4$.

More generally, a polyphenyl chain PPC_n with n hexagons can be regarded as a polyphenyl chain PPC_{n-1} with $n-1$ hexagons to which a new terminal hexagon has been adjoined by an edge (see Fig. 2).

But for $n \geq 3$, the terminal hexagon can be attached in three ways, which results in the local arrangements we describe as PPC_{n+1}^1, PPC_{n+1}^2, PPC_{n+1}^3 (see Fig. 3).

A random polyphenyl chain $PPC(n, p_1, p_2)$ with n hexagons is a polyphenyl chain obtained by stepwise addition of terminal hexagons. At each step k $(= 3, 4, \ldots, n)$ a random selection is made from one of the three possible constructions: (1) $PPC_{k-1} \to PPC_k^1$, with probability p_1, (2) $PPC_{k-1} \to PPC_k^2$, with probability p_2, (2) $PPC_{k-1} \to PPC_k^3$, with probability $1 - p_1 - p_2$. We assume that the probabilities p_1 and p_2 are constants, invariant to the step parameter k. That is, the process described is a zeroth-order Markov Process. For $PPC(n, p_1, p_2)$, the Wiener number is a random variable. In this paper, we obtain a simple exact formula of its expected value $E(W(PPC(n, p_1, p_2)))$.

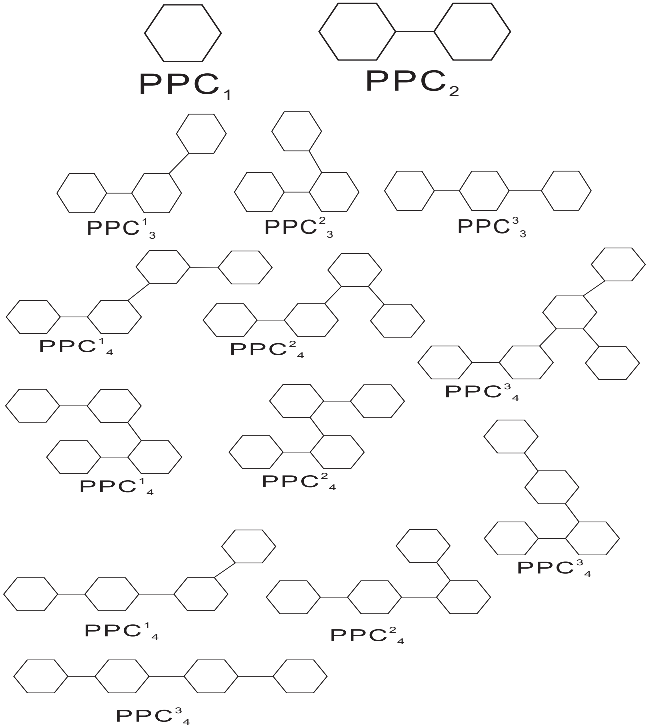

Figure 1: Polyphenyl chain

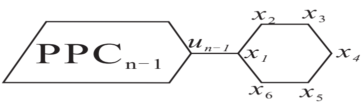

Figure 2: A polyphenyl chain PPC_n with n hexagons

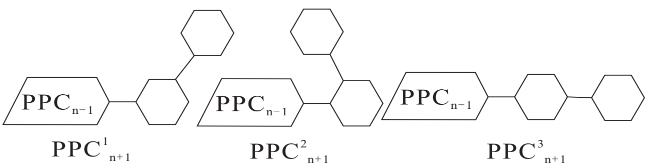

Figure 3: The three types of local arrangements in polyphenyl chains

3 Main result

Theorem 1 *For $n \geq 1$, we have*

$$E(W(PPC(n, p_1, p_2))) = (24 - 6p_1 - 12p_2)n^3 + (18p_1 + 36p_2)n^2 + (3 - 12p_1 - 24p_2)n$$

Proof: As described above, the plyphenyl chain PPC$_n$ is obtained by attaching PPC$_{n-1}$ a new terminal hexagon by an edge (see Fig. 2). Suppose the terminal hexagon spans by vertices $x_1, x_2, \cdots, x_6$, and the new edge is $u_{n-1}x_1$ (see Fig. 2). Note that:

1. For any $v \in PPC_{n-1}$, $d(x_k, v) = d(u_{n-1}, v) + k$, $(k = 1, 2, 3, 4)$,
   $d(x_5, v) = d(u_{n-1}, v) + 3$, $d(x_6, v) = d(u_{n-1}, v) + 2$;

2. PPC_{n-1} has $6(n-1)$ vertices;

3. $\sum_{i=1}^{6} d(x_k, x_i) = 9$, $\forall k \in \{1, 2, 3, 4, 5, 6\}$.

So we have:

$$d(x_1|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 1 \times 6(n-1) + 9 \tag{1a}$$

$$d(x_2|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 2 \times 6(n-1) + 9 \tag{1b}$$

$$d(x_3|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 3 \times 6(n-1) + 9 \tag{1c}$$

$$d(x_4|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 4 \times 6(n-1) + 9 \tag{1d}$$

$$d(x_5|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 3 \times 6(n-1) + 9 \tag{1e}$$

$$d(x_6|PPC_n) = d(u_{n-1}|PPC_{n-1}) + 2 \times 6(n-1) + 9 \tag{1f}$$

and

$$W(PPC_n) = W(PPC_{n-1}) + 6d(u_{n-1}|PPC_{n-1}) + 90n - 36 - \frac{1}{2}\sum_{i=1}^{6}\sum_{j=1}^{6} d(v_i, v_j)$$

Then

$$W(PPC_{n+1}) = W(PPC_n) + 6d(u_n|PPC_n) + 90n + 27 \tag{2}$$

For a random polyphenyl chain $PPC(n, p_1, p_2)$, the distance number $d(u_n|PPC(n, p_1, p_2))$ is a random variable and we denote its expected value by

$$U_n = E(d(u_n|PPC(n, p_1, p_2)))$$

There are three cases to consider:

case 1. $PPC_n \rightarrow PPC^1_{n+1}$. In this case, u_n coincides with the vertex labeled x_3 or x_5. Consequently, $d(u_n|PPCn)$ is given by eq. $(1c)$ or $(1e)$.

case 2. $PPC_n \rightarrow PPC^2_{n+1}$. In this case, u_n coincides with the vertex labeled x_2 or x_6. Consequently, $d(u_n|PPCn)$ is given by eq. $(1b)$ or $(1f)$.

case 3. $PPC_n \rightarrow PPC^3_{n+1}$. In this case, u_n coincides with the vertex labeled x_4. Consequently, $d(u_n|PPCn)$ is given by eq. $(1d)$.

Since the above three cases occur in random polyphenyl chains with probabilities p_1, p_2 and $1 - p_1 - p_2$, we immediately obtaine

$$\begin{aligned}U_n =& p_1[d(u_n|PPC(n-1, p_1, p_2)) + 3 \times 6(n-1) + 9] \\ &+ p_2[d(u_n|PPC(n-1, p_1, p_2)) + 2 \times 6(n-1) + 9] \\ &+ (1 - p_1 - p_2)[d(u_n|PPC(n-1, p_1, p_2)) + 4 \times 6(n-1) + 9]\end{aligned}$$

By applying the expectation operator to the above equation, and noting that $E(U_n) = U_n$, we obtain

$$U_n = p_1(U_{n-1} + 18n - 9) + p_2(U_{n-1} + 12n - 3) + (1 - p_1 - p_2)(U_{n-1} + 24n - 15)$$

It is easily transformed into:

$$U_n = U_{n-1} + (24 - 6p_1 - 12p_2)n + 6p_1 + 12p_2 - 15$$

The boundary condition is

$$U_1 = E(d(u_1|PPC(1, p_1, p_2))) = 1 + 1 + 2 + 2 + 3 = 9$$

Using the above recurrence relation and the boundary condition, we have

$$U_n = (12 - 3p_1 - 6p_2)n^2 + (3p_1 + 6p_2 - 3)n \tag{3}$$

A recurrence relation for the expected value of the Wiener number of a random polyphenyl chain can be obtained from eq. (2) by using $PPC(k, p_1, p_2)$ in place of PPC_k $(k = n, n+1)$ and by using the expectation operator. and using eq. (3) we obtain

$$\begin{aligned}E(W(PPC(n, p_1, p_2))) =& E(W(PPC(n-1, p_1, p_2))) + 6U_n + 90n + 27 \\ =& E(W(PPC(n-1, p_1, p_2))) + 6[(12 - 3p_1 - 6p_2)n^2 \\ &+ (3p_1 + 6p_2 - 3)n] + 90n + 27\end{aligned}$$

The boundary condition is

$$E(W(PPC(1,p_1,p_2))) = 27$$

Using the above recurrence relation and the boundary condition, we have

$$E(W(PPC(n,p_1,p_2))) = (24-6p_1-12p_2)n^3 + (18p_1+36p_2)n^2 + (3-12p_1-24p_2)n$$

$\square$

At the end of this paper, we point out that

$$E(W(PPC(n,p_1,p_2))) \sim (24-6p_1-12p_2)n^3$$

That is $E(W(PPC(n,p_1,p_2)))$ is asymptotic to a cubic in n as $n \to \infty$

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