Topological factors governing the HOMO–LUMO band gap of the density of states of periodic hydrocarbon polymer networks

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The band structures and density of states of 77 infintely large conjugated hydrocarbon polymer networks are calculated with HMO. A general rule for predicting whether the HOMO–LUMO band gap is zero or non-zero is proposed for an arbitrary hydrocarbon polymer network with periodic structure. The effects of bond alternation and of conjugate branching are discussed. Molecular design of high spin polymer networks is proposed.

1. Introduction

Since the magnitude of the HOMO–LUMO band gap (ΔE_g) of a conjugated polymer network is highly correlated with its conductive and other electronic properties, this problem has been extensively studied with a variety of methods from Hückel (HMO) to ab initio calculations [1–28]. Many of these calculations cannot overcome the arbitrariness in the choice of parameters and inevitably depend on the power of computers. Further, a number of factors have been believed to be crucial for the electronic structure of conjugated polymer networks [5]. However, the essential features of the π-electronic band structure can be rigorously formulated, and meaningful general rules are shown to be inferred from the results of the Hückel molecular orbital (HMO) method.

For example, Bochvar and Stankevich [1] pointed out that, when the monomer units are linked through only one bond, whether the energy band gap equals zero or not can be determined from the determinant $T(k) = H + B \exp(ik) + B^{\dagger} \exp(-ik)$, where H is the Hamiltonian of a monomer unit and B describes the interaction of this unit and its neighbors. They conclude that if $T(0)$ or $T(\pi)$ is zero, the corresponding

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polymer can be thought to be a potential conductor. Graovac et al. [3] extended this method and proposed an approach by which one can quickly discern a potential semiconductor from the structural formula of the network. They also pointed out [4] that a necessary condition for a system to have a zero energy gap is that the repeating benzenoid unit has a non-prime number of Kekulé valence structures.

Polansky and Tyutyulkov [2] wrote a comprehensive paper in which the mathematical conditions for the existence of forbidden zones and gaps within the band structure of infinitely large graphs can be derived. From numerical HMO calculations, Wennerström et al. pointed out the importance of the cyclic dimers of Hückel and Möbius types for the HOMO–LUMO band gap of conjugated polymers composed of repeating units linked by more than one bond [16,17]. They reported that their results of ΔE_g are qualitatively in agreement with those obtained by elaborate ab initio calculations. In a series of papers by Bonchev and Mekenyan [6–8], the relationship between ΔE_g and the Wiener index was examined for many polymers. They showed that the limiting values of ΔE_g toward infinitely lage polymers can be extrapolated by using this relationship.

Although so much research has been performed, a simple method has still not been found by which one can easily judge whether the energy band gap for an arbitrary hydrocarbon polymer is zero or not without recourse to tedious numerical calculations [24–28]. The present authors have clarified that the origin of the zero HOMO–LUMO band gap in certain classes of conjugated benzenoid polymer networks is due to the existence of non-bonding MO (NBMO) of their hypothetical cyclic monomer or dimer [18,19]. The fact that polynaphthalene has an abnormally narrow ΔE_g when calculated by the ab initio method [23] can quite easily be predicted by the existence of NBMOs in its cyclic monomer unit (vide infra). As a continuation of this work, mainly the topological dependency of the HOMO–LUMO band gap in the HMO scheme for infinitely large conjugated hydrocarbon networks is considered in this paper. The systems treated are those whose units are separated not only by one, but also more than two bonds. The units may not always be benzenoid. The effect of conjugate branching is also analyzed. A general but simple rule of discerning whether the ΔE_g of a system is zero or not is proposed.

2.   Method of calculation

A cyclic boundary condition is adopted for all the systems, since the global features of the electronic structures of infinitely large periodic networks are independent of the boundary condition [2,24,25,29]. For example, the HMOs of a cyclic polyacene (network No. 33 in chart 1) can be constructed from those of the parent butadiene units as shown in fig. 1, and as the limit of $N \rightarrow \infty$, the infinitely large polyacene can be described. The characteristic polynomial for this polymer is obtained as [18,19,30]
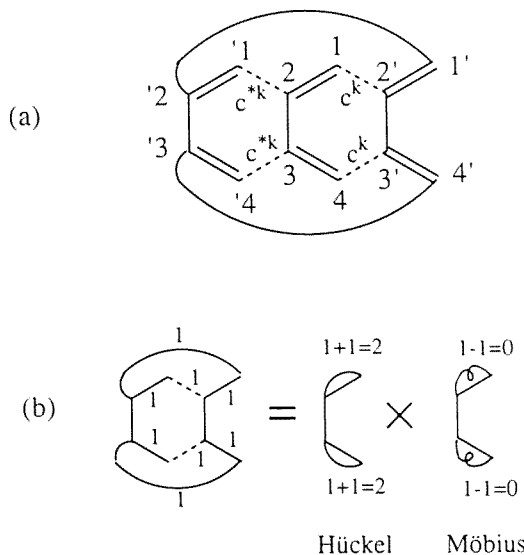
Fig. 1. (a) The polymer network of No. 33 composed of parent unit of butadiene. (b) The characteristic polynomial of the cyclic dimer which can be factored out into those of Hückel and Möbius cyclic (monomer) units. The numerals 1 and 2 are in units of β.

$$P_G(x) = \prod_{k=1}^{N} \begin{vmatrix} -x & 1+c^k & 0 & 0 \\ 1+c^{*k} & -x & 1 & 0 \\ 0 & 1 & -x & 1+c^{*k} \\ 0 & 0 & 1+c^k & -x \end{vmatrix}$$

$$= \prod_{k=1}^{N} f_{k\theta}(x). \tag{1}$$

$$f_{k\theta}(x) = x^4 - (5 + 4\cos\theta)x^2 + 4(1 + \cos k\theta)^2, \tag{2}$$

with $c^k = \exp(ik\theta)$, $c^{*k} = \exp(-ik\theta)$ and $k\theta = 2\pi k/N$ ($k = 1, 2, \ldots, N$).

The factor $f_{k\theta}(x)$ is the kth characteristic polynomial of the cyclic monomer unit. As $k\theta$ varies from 0 to π, the roots of $f_{k\theta}(x) = 0$ give the whole information on the electronic structure of the polymer, since the curves for $k\theta = \pi \sim 2\pi$ are symmetric with those for $k\theta = \pi \sim 0$. Namely, by plotting the roots $\{x_n\}$ of $f_{k\theta}(x) = 0$ along $k\theta$ from 0 to π as in fig. 2, one can obtain the band structure of the polymer. The lower and upper halves of the bands are, respectively, occupied and vacant, and
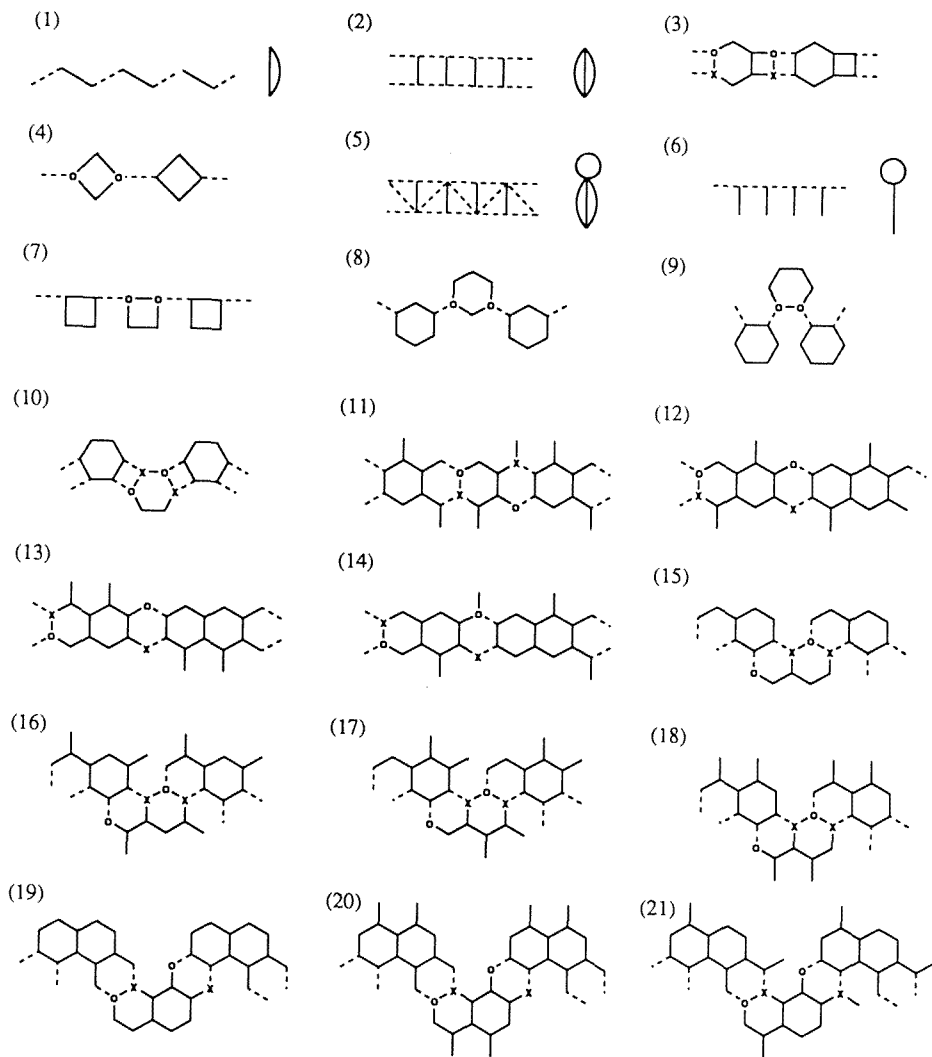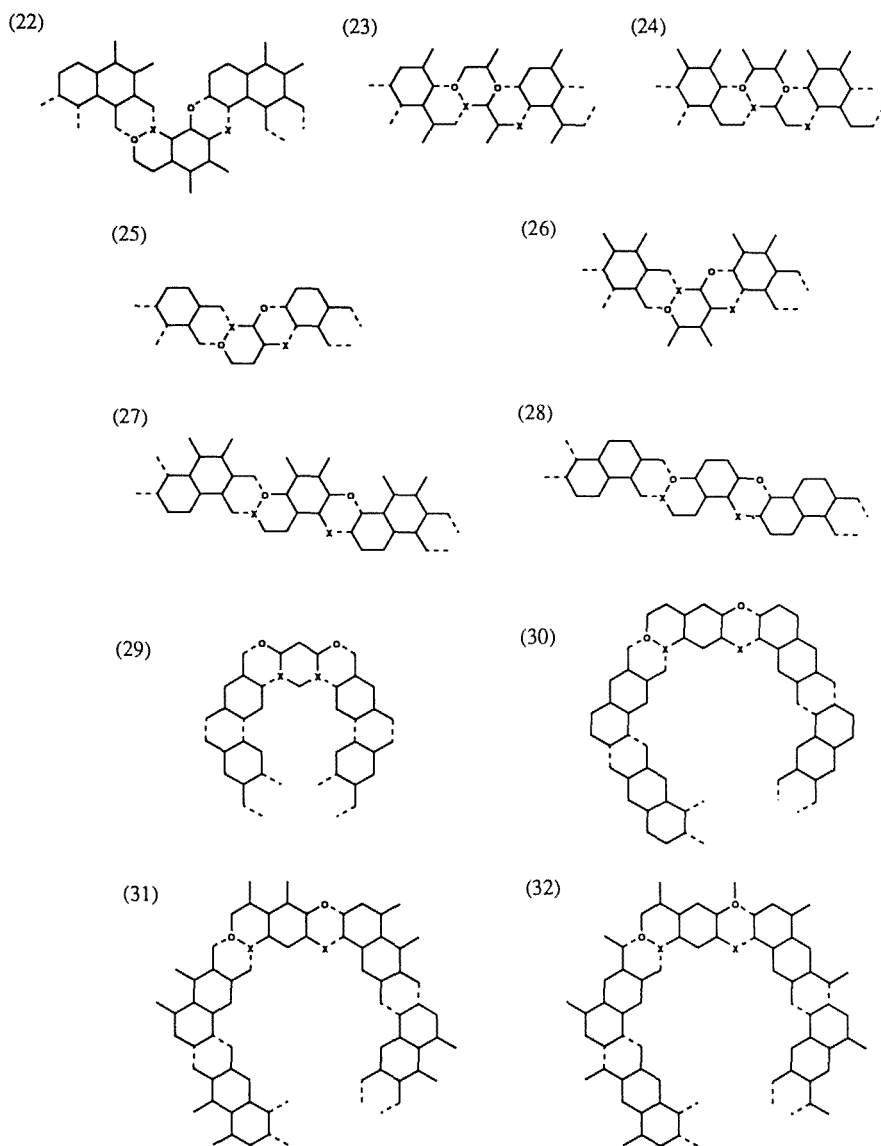
Chart 1 (continued)

(22)

(23)

(24)

(25)

(26)

(27)

(28)

(29)

(30)

(31)

(32)

Chart 1 (continued)

(33)

(34)

(35)

(33a)   (33b)

(34a)   (34b)

(35a)   (35b)

(36)

(37)

(41)

(36a)   (36b)

(37a)   (37b)

(41a)   (41b)

(38)

(38a)   (38b)

(39)

(40)

(42)
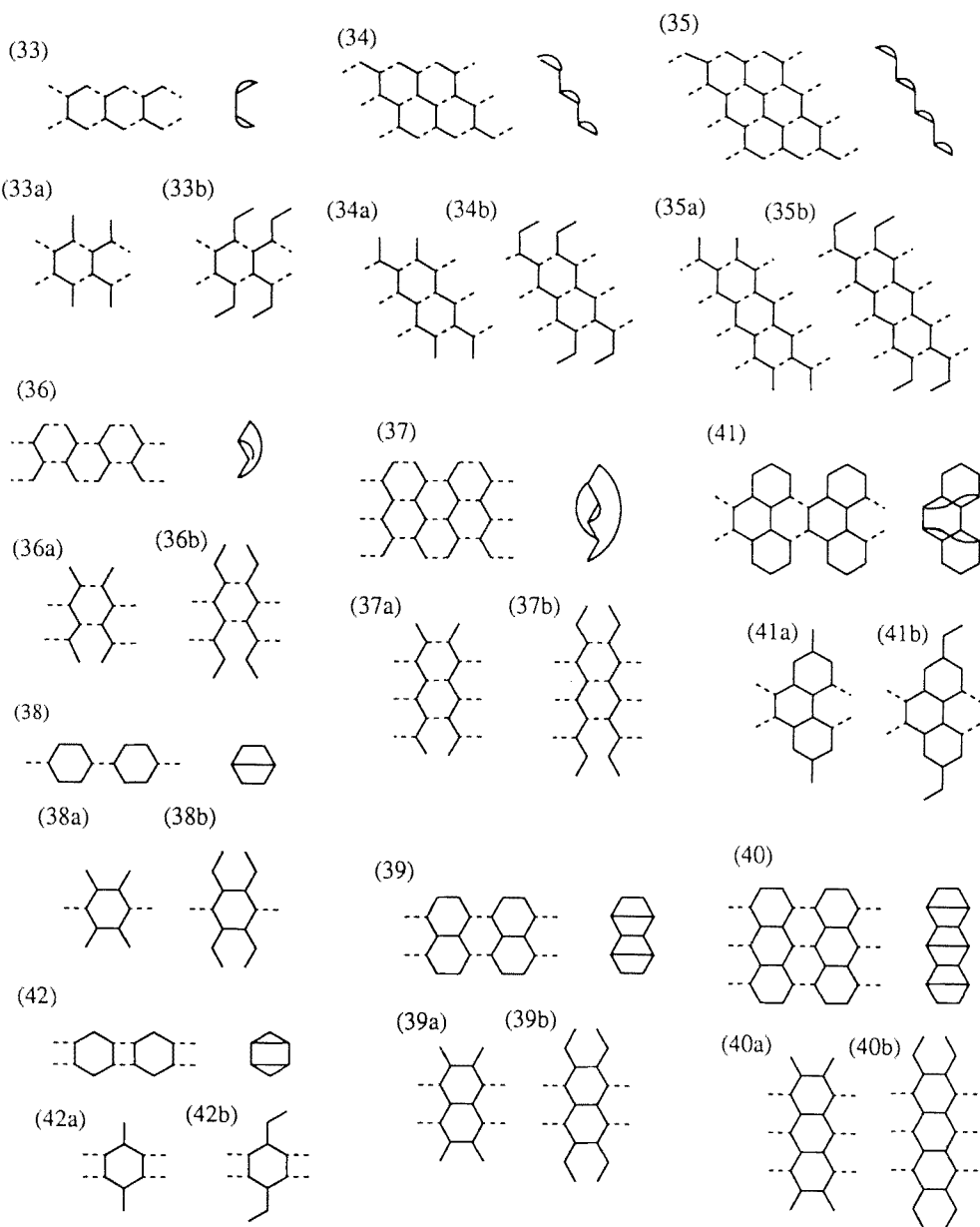
(39a)   (39b)

(40a)   (40b)
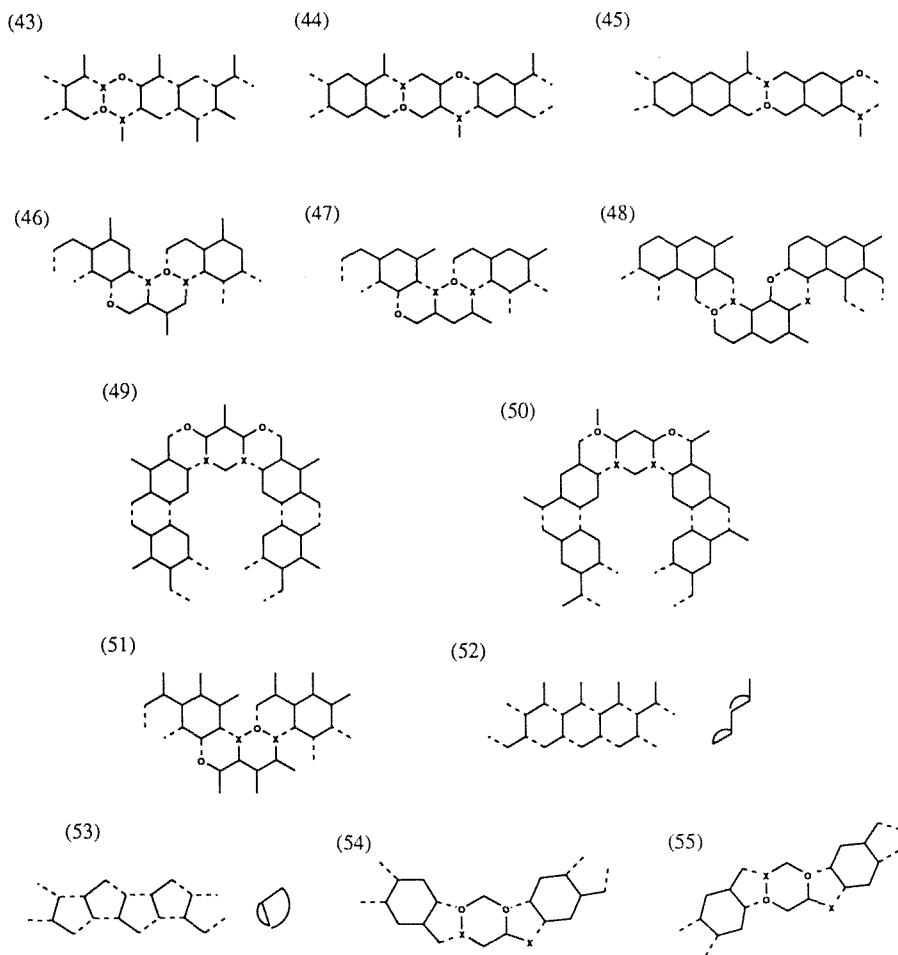
(42a)   (42b)

Chart 1 (continued)

Chart 1. Networks and cyclic units of the studied polymers. For those networks in which circles and crosses are drawn, the cyclic unit is obtained by drawing lines between the circles and between the crosses.

are called valence and conduction bands. The global features of the density of states of the polymer can be inferred from this diagram.

It can be seen from fig. 2 that the valence and conduction bands are linked together in the Brillouin zone in the case of polyacene. According to this HMO scheme, polyacene has a zero HOMO−LUMO band gap.[*] It has already been pointed out that $f_0(x)$ and $f_\pi(x)$, respectively, are nothing else but the characteristic polynomials of the cyclic monomer units of the Hückel and Möbius types as shown in fig. 1 [16−19].

[*]By introducing bond alternation, the HOMO−LUMO band gap opens but moderately [20].

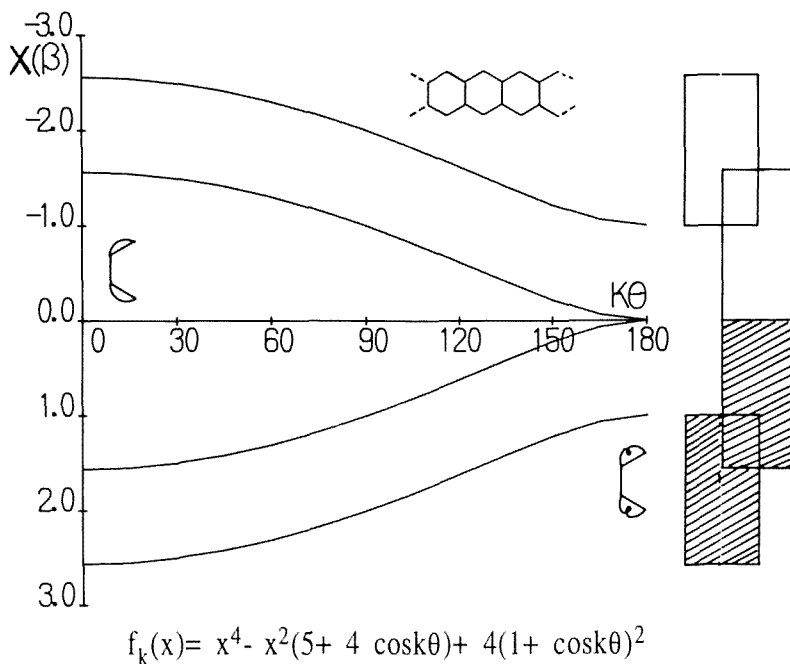$$f_k(x) = x^4 - x^2(5 + 4\cos k\theta) + 4(1 + \cos k\theta)^2$$

Fig. 2. S0 type band structure (No. 33) derived from E cyclic units, from which the profile of the density of states can be deduced. The energy levels at $k\theta = 0$ and π, respectively, are those of the Hückel and Möbius cyclic units. The hatched valence bands are in contact with the unhatched conduction bands.

In this study, the $f_{k\theta}(x)$ and the density of states of 77 periodic hydrocarbon polymer networks as shown in chart 1 were calculated, where the cyclic units of these polymers are also given. The parent units of all the polymers are either even (E, Nos. 1–42b) or odd (O, Nos. 43–55) alternants. Let us call these two types of polymer networks E- and O-parent polymers, depending on the parity of their parent units. Although most of the derived polymer networks are also alternant, networks 5, 53–55 are non-alternants. Bonchev et al. [6–8] studied the structures from Nos. 1 to 10 and 33 to 42, the latter group of which were selected to see the effect of conjugate branching, where the letters a and b, respectively, denote one and two for the length of branches.

3.   Patterns of density of states

The patterns of the band structures of the 77 polymer networks studied can be classified into five types, i.e. S0, S#, SN, A0, and A#, as shown in table 1. The first letter indicates the symmetry of the density of states (DS) with respect to the
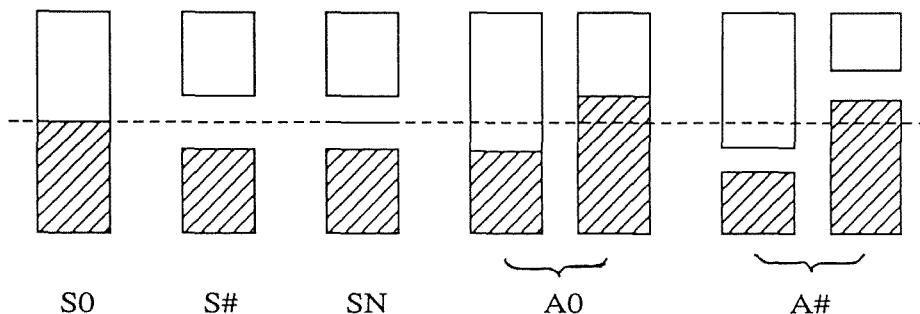
Table 1

Characteristic properties of the density of states of 77 polymer networks.

Network number	Type of parent unit	Real k root for $f_{k\theta}(0) = 0$	Pattern of cyclic unit[a]	Pattern type of DS
1–4	E	yes	E or O	S0
5	E	yes	E–O	A#[b]
6–32	E	no	E or O	S#[b]
$\left\{ \begin{array}{l} 33-41, \\ 42, 42b \end{array} \right\}$	E	$\left\{ \begin{array}{l} \text{yes} \\ \text{no} \end{array} \right.$	E or O / O	$\left. \begin{array}{l} \text{S0} \\ \text{S\#}^c \end{array} \right\}$
42a	E	NBMO	O	SN
43–50	O	yes	O	S0
51, 52	O	NBMO	O, E	SN
53–55	O	yes	E–O	A0

[a] E: even cycles, O: odd cycles, E–O: mixture of even and odd cycles.
[b] See table 2(a) for the magnitude of ΔE_g.
[c] See table 2(b) for the magnitude of ΔE_g. See also table 3.

SO   S#   SN   A0   A#

line $x = 0$. Most of the studied polymer networks are symmetric (S), while only Nos. 5, 53–55 are asymmetric (A). The second letter gives the HOMO–LUMO band gap information, i.e. 0 for zero and # for non-zero ΔE_g (see table 2(a), 2(b)). Networks Nos. 42a, 51 and 52 have highly degenerate NBMO levels between the symmetric HOMO–LUMO band gap, and are designated by SN. The only A#-type network, No. 5, is rather unrealistic, but it is a good example for showing the complexity of the correlation between the topological structure of the network and the magnitude of the ΔE_g.

Twenty-seven networks (S0 and A0) were found to have zero ΔE_g, namely, Nos. 1–4, 43–50, 53–55, and twelve networks from Nos. 33–42b (see table 3). All of them are found to have real root(s) for $f_{k\theta}(0) = 0$, which can be verified from the appendix. However, it should be noticed that this is not a sufficient condition

Table 2(a)

The values of the non-zero HOMO–LUMO band gap for polymers Nos. 5–32.

Polymer number[a]	Number of C atoms in parent unit	$\text{Min}\{|f_{k\theta}(0)|\}$	ΔE_g (in β)
5	2	0	0.800
6	2	1	0.828
7	4	1	0.764
8	6	4	1.640
9	6	1	0.890
10	6	1	1.236
11	10	1	0.165
12	14	1	0.211
13	14	1	0.102
14	14	4	0.324
15	8	5	0.890
16	10	1	0.323
17	10	4	0.784
18	10	1	0.259
19	12	12	0.600
20	14	1	0.188
21	14	1	0.143
22	14	9	0.652
23	10	1	0.253
24	10	1	0.619
25	8	4	0.695
26	10	1	0.548
27	12	4	0.621
28	14	4	0.568
29	8	4	1.159
30	12	9	0.821
31	14	1	0.132
32	14	4	0.341

[a]See chart 1.

for ΔE_g to be zero. Network No. 5 belongs to the A# type, although $f_{k\theta}(0) = 0$ is satisfied at $k\theta = 2\pi/3$.

If isomeric networks with non-zero ΔE_g are compared, the ordering of ΔE_g values can be roughly estimated from the values of $f_{k\theta}(0)$, except for special cases. The smallest $|f_{k\theta}(0)|$ value is given in table 2, together with the number of carbon atoms in the parent unit. As seen in table 3, several interesting features were found in Nos. 33–42b on the effect of the conjugate branching.

Table 2(b)

The values of the non-zero HOMO–LUMO band gap for polymers Nos. 33–41[a]

Polymer number[b]	Number of C atoms in parent unit	Min{ $\|f_{k\theta}(0)\|$ }	ΔE_g (in β)
33a	6	1	0.388
34a	8	1	0.190
35a	10	1	0.094
36	4	1	0.764
36b	8	1	0.430
37	6	1	0.494
37a	8	1	0.469
37b	10	1	0.369
38	6	1	0.828
38a	10	1	0.508
38b	14	1	0.548
39a	14	1	0.493
40	14	1	0.469
40b	22	1	0.323
41	14	16	0.622
41a	16	1	0.151
41b	18	16	0.622

[a] Other polymers have zero ΔE_g.
[b] See chart 1.

Table 3

Effect of branching on the relation between the root of $f_{k\theta}(0) = 0$ and ΔE_g.

No.[a]	Parent polymer		a-polymer		b-polymer	
	real k root[b]	type (ΔE_g)[c]	real k root	type (ΔE_g)	real k root	type (ΔE_g)
33	π	S0	no	S# (0.388)	π	S0
34	π	S0	no	S# (0.190)	π	S0
35	π	S0	no	S# (0.094)	π	S0
36	no	S# (0.764)	π	S0	no	S# (0.430)
37	no	S# (0.494)	no	S# (0.469)	no	S# (0.369)
38	no	S# (0.828)	no	S# (0.508)	no	S# (0.548)
39	0	S0	no	S# (0.493)	0	S0
40	no	S# (0.469)	0	S0	no	S# (0.323)
41	no	S# (0.622)	no	S# (0.151)	no	S# (0.622)
42	0	S0	NBMO	SN	0	S0

[a] See chart 1.
[b] Value of $k\theta$ for $f_{k\theta}(0) = 0$.
[c] See table 1.

All the O-parent polymers studied have either a NBMO (SN) or zero HOMO–LUMO gap (S0 or A0). As seen in the appendix, their $f_{k\theta}(0)$ is either zero or can be zero for $k\theta = \pi/2$. Among them, only Nos. 51 and 52 have highly degenerate NBMOs. Analysis of these special kinds of polymer networks is helpful for designing ferromagnetic polymers. With these interesting problems in mind, we discuss the topological dependency of the various features of conjugate hydrocarbon polymer networks.

4.   Symmetrical property of the band structure

Although all the studied parent units are alternant, some of the cyclic monomer units are non-alternant by joining pairs of atoms of the same group (starred or unstarred) in the parent unit. For example, both the parent units of polymers Nos. 4 and 55 are alternant, while their cyclic units are non-alternant, as shown in fig. 3.

Fig. 3.   Three types of cyclic units. E and O refer, respectively, to even-numbered and odd-numbered cyclic units.

However, No. 4 belongs to the S0 type, while No. 55 belongs to A0. The π-electronic energy levels of alternant hydrocarbon molecules have been known to obey the pairing theorem [31], but under what condition does the DS of a non-alternant polymer network become symmetric or asymmetric with respect to the line $x = 0$?

Suppose that there are m starred and $n - m$ unstarred carbon atoms in an alternant parent unit ($2m \geq n$). Its secular determinant can be written as

$$\begin{array}{cc} \overbrace{\text{starred}} & \overbrace{\text{unstarred}} \\ <----m----> & <---n-m---> \end{array}$$

$$\begin{vmatrix} \alpha-\varepsilon & 0 & & \\ & \ddots & & \mathcal{B} \\ 0 & \alpha-\varepsilon & & \\ \hline & & \alpha-\varepsilon & 0 \\ & \tilde{\mathcal{B}} & & \ddots \\ & & 0 & \alpha-\varepsilon \end{vmatrix} = 0. \qquad (4)$$

The symbol $\mathcal{B}$ in the upper-right $(m \times (n-m))$ block and $\tilde{\mathcal{B}}$ in the lower-left $((n-m) \times m)$ block of the determinant indicate that the elements corresponding to the bonded atom pair are β and zero otherwise. Next, let us consider what happens when we construct a cyclic unit from this graph. If the cyclic unit is also alternant, namely, a pair of starred and unstarred atoms are joined, then the c^k and c^{*k} terms appear in the off-diagonal blocks corresponding to the new bond to form a cyclic unit. For example, for the No. 33 polymer (polyacene), the secular determinant of the parent unit is

$$\begin{vmatrix} -x & 0 & 1 & 0 \\ 0 & -x & 1 & 1 \\ 1 & 1 & -x & 0 \\ 0 & 1 & 0 & -x \end{vmatrix}, \qquad (5)$$

where $-x = (\alpha - \varepsilon)/\beta$ (see fig. 3 for numbering of atoms). For the cyclic unit, the determinant becomes

$$f_{k\theta}(x) = \begin{vmatrix} -x & 0 & 1+c^k & 0 \\ 0 & -x & 1 & 1+c^{*k} \\ 1+c^{*k} & 1 & -x & 0 \\ 0 & 1+c^k & 0 & -x \end{vmatrix}, \qquad (6)$$

which turns out to be identical to eq. (1).

By a simple manipulation of this matrix, we can obtain the relation $(-1)^n f_{k\theta}(-x) = f_{k\theta}(x)$, which also immediately follows from interchanging the starred and unstarred atoms in the network. This means that the density of states of the system whose cyclic unit is alternant surely obeys the pairing theorem [26]. In this case, the cyclic unit has only even-membered rings, as in fig. 3. Let us simply call this type of cyclic unit an E cyclic unit.

There are two cases where an alternant parent unit forms a non-alternant cyclic unit, namely (i) by joining one or more pairs of atoms of the same (starred or unstarred) group, and (ii) by joining atoms not only of the same group but also of different groups. The cyclic units of these two cases may be called O and E–O cyclic units, respectively.

In the former case, the c^k and c^{*k} terms must appear in the diagonal blocks. The c^k and c^{*k} terms in $f(-x)$ have the opposite signs from those of $f(x)$ after the above-mentioned transformation. As a simple example, the No. 4 polymer may help us understand this situation. According to the numbering scheme of fig. 3, the determinant of the cyclic unit becomes

$$f_{k\theta}(x) = \begin{vmatrix} -x & 0 & 1 & 1 \\ 0 & -x & 1 & 1 \\ 1 & 1 & -x & c^k \\ 1 & 1 & c^{*k} & -x \end{vmatrix} . \tag{7}$$

By noting that $-c^k = c^{*(\pi/\theta - k)}$, one can obtain the following relation: $(-1)^n f_{k\theta}(-x) = f_{\pi - k\theta}(x)$ [26]. This implies that the $k\theta - x$ curves must be symmetric with respect to the point $(k\theta = \pi/2, x = 0)$, and consequently the DS is symmetric with respect to the $x = 0$ axis, as shown in fig. 4 for the No. 4 polymer.
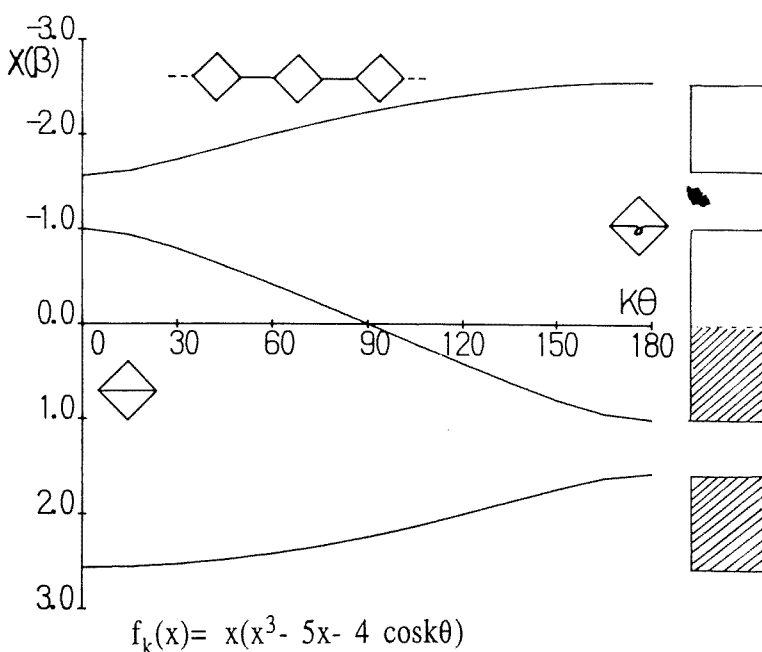

$$f_k(x) = x(x^3 - 5x - 4\cos k\theta)$$

Fig. 4. S0-type band structure (No. 4) derived from the O cyclic unit. Since the bands are symmetric with respect to the center point, the DS becomes symmetric with respect to the line $x = 0$.

In the second case, namely for an E–O cyclic unit, since the symmetrical structure is lost in the matrix, a simple relation no longer exists between $f_{k\theta}(x)$ and $f_{k\theta}(-x)$. Thus, the band structure becomes asymmetric, as shown in fig. 5, for the
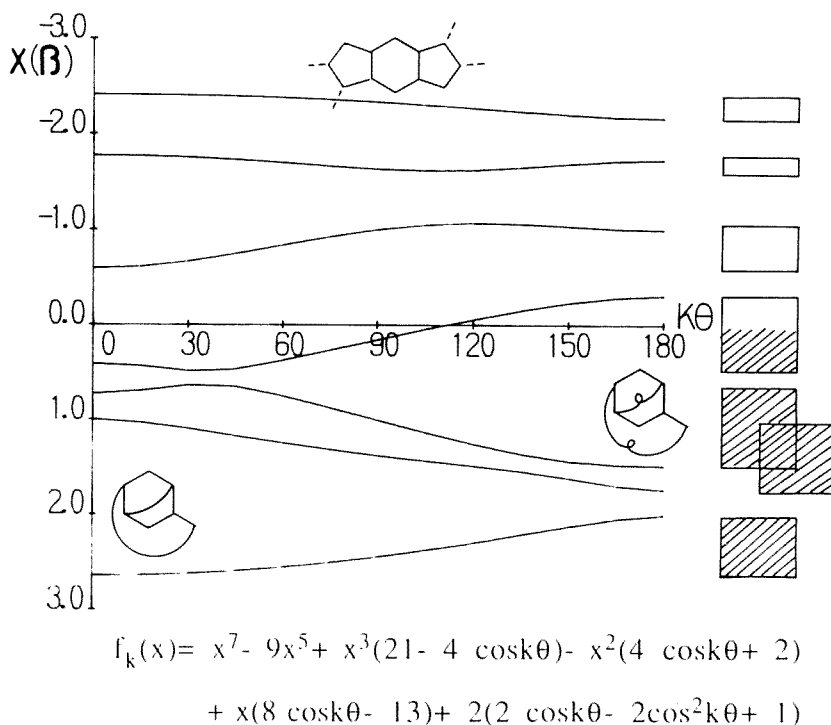

$$f_k(x) = x^7 - 9x^5 + x^3(21 - 4\cos k\theta) - x^2(4\cos k\theta + 2)$$

$$+ x(8\cos k\theta - 13) + 2(2\cos k\theta - 2\cos^2 k\theta + 1)$$

Fig. 5. A0 type band structure (No. 55) derived from the E–O cyclic unit.

No. 55 polymer. Among the polymers studied, only Nos. 5 and 53–55 have E–O cyclic units, and their DSs belong either to the A# or A0 type. Figure 3 illustrates how these types of cyclic units differ from each other.

Thus, one can say that if the cyclic unit is constructed from an alternant parent unit either by joining between the same type of atoms, or between different type atoms, the polymer becomes alternant and the DS is symmetric with respect to the $x = 0$ axis. If the number of the carbon atoms in the unit is even, then the number of the bands will be even, and the highest occupied band becomes the valence band. Then the HOMO–LUMO band gap corresponds to the gap between the two bands facing the $x = 0$ axis. In this case, the necessary condition for zero band gap is that these two bands merge together, namely, $k\theta$ has real roots for $f_{k\theta}(0) = 0$ in the range of $0 \leq k\theta \leq \pi$, as already pointed out.

For an O-polymer, the number of bands N_c must be odd, nN_c electrons occupy $N_c/2$ bands, and the central band must be half occupied, as shown in fig. 6 for the

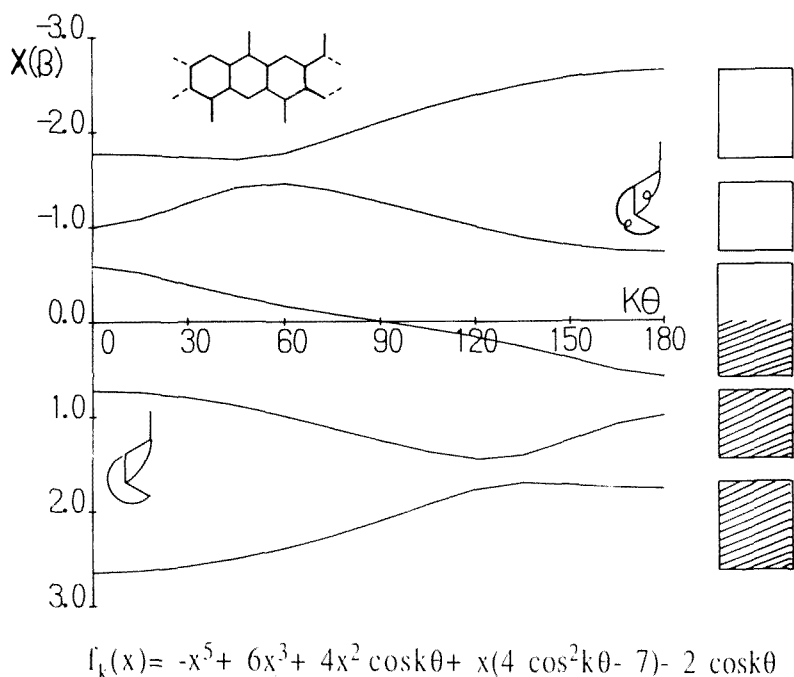$$f_k(x) = -x^5 + 6x^3 + 4x^2 \cos k\theta + x(4 \cos^2 k\theta - 7) - 2 \cos k\theta$$

Fig. 6. Band structure and cyclic unit of network No. 43.

No. 43 polymer. In this case, the kq root for $f_{k\theta}(0) = 0$ is $\pi/2$, and the band gap does not exist.

Although polymers composed of non-alternant units were not treated here, their DS is predicted to be asymmetric with respect to the $x = 0$ axis, since the energy levels do not obey the pairing theorem. If the number of carbon atoms in the parent unit is odd, N_c is also odd and and we can expect that the polymer has a partially occupied band as well as in the case of O-polymers with an E–O cyclic unit, i.e. Nos. 54 and 55 (fig. 5) polymers. When N_c is even, things become a little more complicated. Since no symmetry is expected in the $k\theta$–x curves and DS, a general rule for predicting the zero ΔE_g cannot be found.

5.   High spin polymer networks

Of course, one has to be cautious because of the possibility of a breakdown of the HMO scheme when degeneracy occurs at the Fermi level. Thus, the following discussion might be taken as a formal one. However, it is still meaningful in the mathematical analysis of the topological effect on the distribution of eigenvalues in conjugate polymer networks. Among the polymers studied, only three (Nos. 42a, 51, and 52) have highly degenerate NBMOs and are expected to have a ferromagnetic
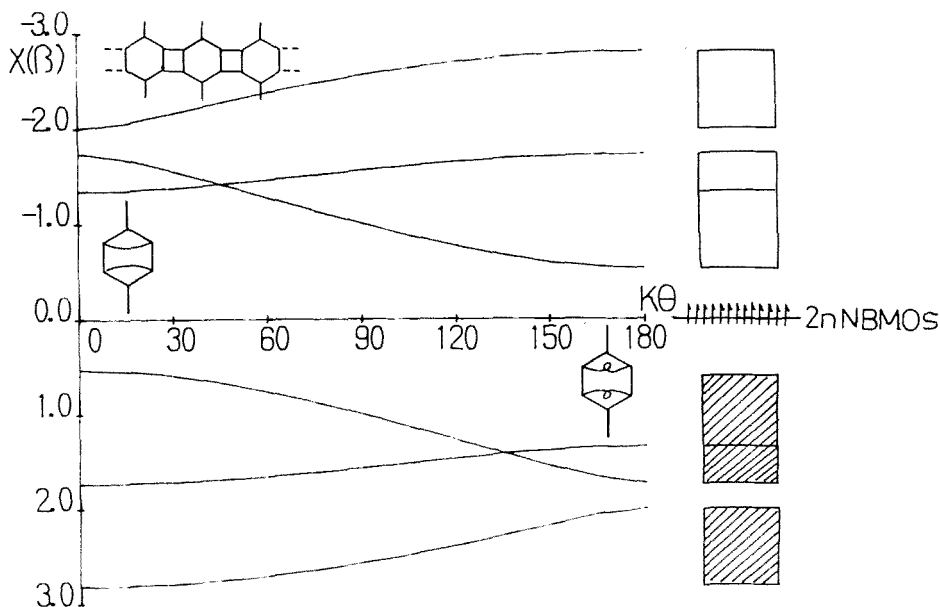
$$f_k(x)= x^2(x^6- 10x^4- 4x^3 \cos k\theta+ 25x^2+ 12x \cos k\theta- 16 + 4 \cos^2 k\theta)$$
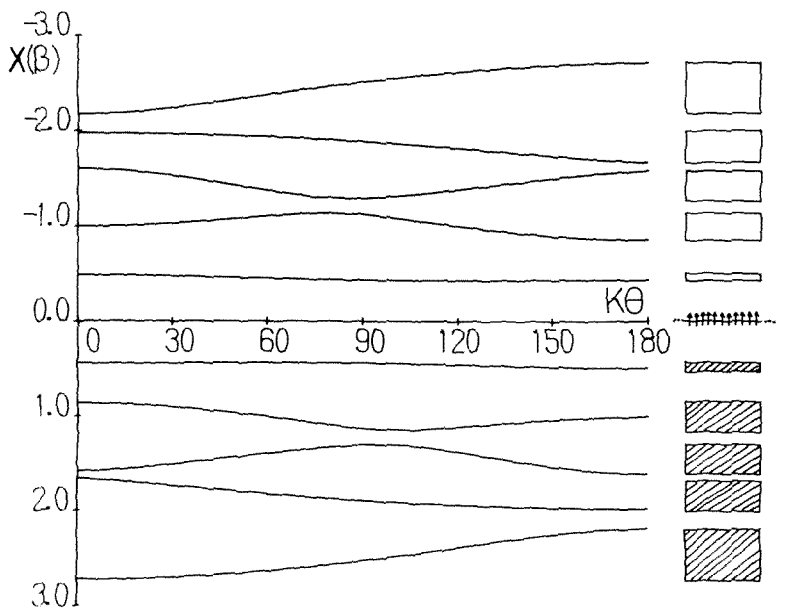
Fig. 7. Band structure and cyclic unit of network No. 42a.

property [32–38]. If the explicit expression of $f_{k\theta}(x)$ is known as in the appendix, one can unambiguously predict this property. Since Nos. 42a (fig. 7) and 51 (fig. 8) have an O cyclic unit and No. 52 has an E cyclic unit, their DSs are symmetric. Further, since the factored-out polynomial $[f_{k\theta}(x)/x^n]_{x=0}$ ($n = 2$ for No. 42a, $n = 1$ for Nos. 51 and 52) has no real $k\theta$ root, the DS has non-zero ΔE_g above and below the highly degenerate NBMOs.

That these three polymers have NBMOs can quite easily be deduced from the existence of an NBMO in their cyclic units as
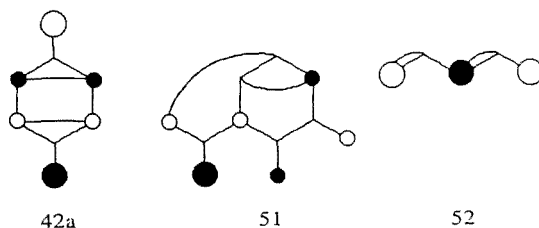
A little practice in drawing NBMO wavefunctions is very helpful for this type of analysis.

$$f_k(x) = x \,[x^{10} - 13x^8 - 2x^7 \cos k\theta + 56x^6 + 10x^5 \cos k\theta$$

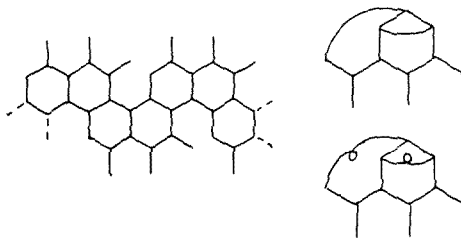$$- 97x^4 - 14x^3 \cos k\theta - x^2(4 \cos^2 k\theta - 64) + 4x \cos k\theta - 9]$$

Fig. 8. Band structure and cyclic unit of network No. 51.
The Hückel and Möbius cyclic units are also drawn.

A very special case we have found is the No. 42a polymer. It has $2n$ degenerate NBMOs occupied by $2n$ π-electrons with the same spin orientation in the ground state, as can be seen from fig. 7. In its characteristic polynomial, two zero x roots can be factored out. Hence, we can discern this kind of polymer fully from the characteristic polynomial $f_{k\theta}(x)$.

As pointed out in section 3, if the cyclic unit of an O parent unit is still alternant, the polymer will have n degenerate levels occupied by n π-electrons with the same spin orientation. This enables us to design polymer networks with high spin.
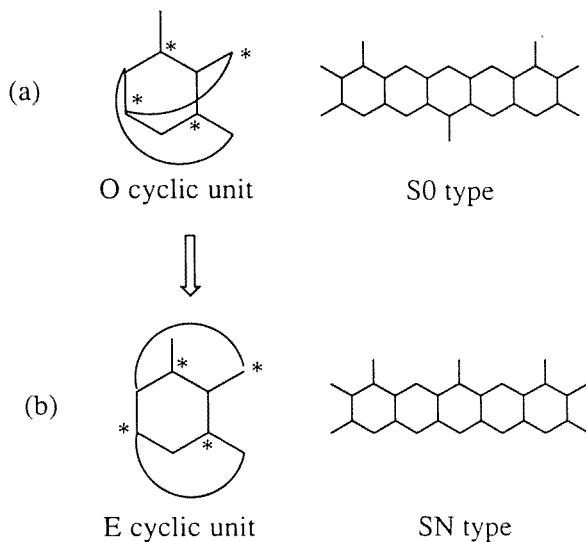
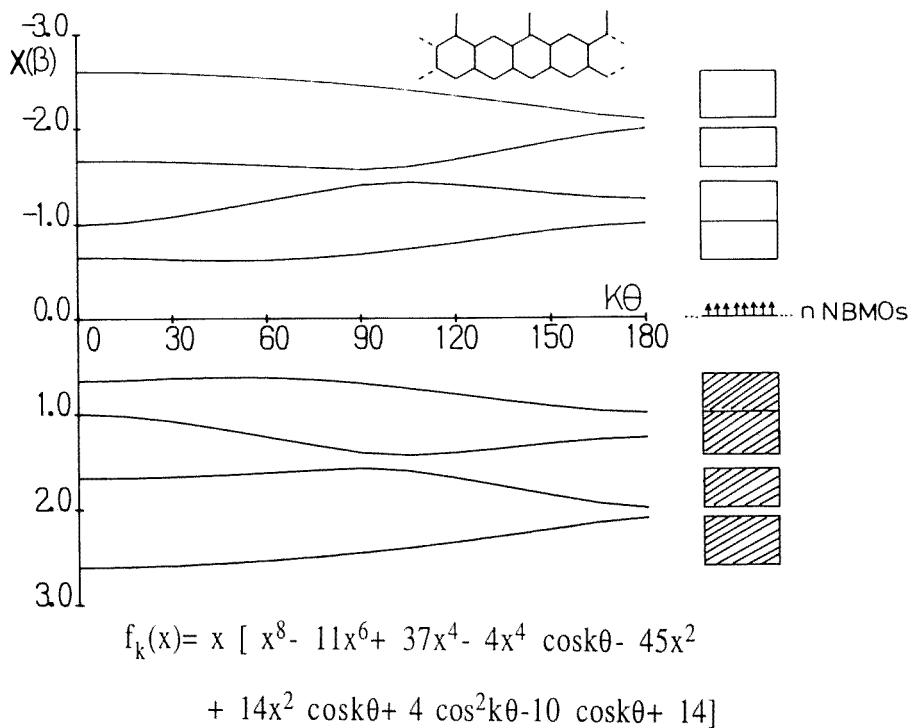Fig. 9. Construction of a new polymer network (b) by interchanging two key bonds in the cyclic unit (a).

$$f_k(x)= x \, [\, x^8 - 11x^6 + 37x^4 - 4x^4 \, \cos k\theta - 45x^2$$

$$+ \, 14x^2 \, \cos k\theta + 4 \, \cos^2 k\theta - 10 \, \cos k\theta + 14]$$

Fig. 10. The $f_{k\theta}(x)$ and band structure of the network derived by interchanging the mode of cyclization in No. 44 (see fig. 9).

For example, consider No. 44 polymer with zero ΔE_g (S0 type), whose cyclic unit is non-alternant (O cyclic) as shown in fig. 9(a). If we interchange the joint sites of the parent unit to change the cyclic unit into E cyclic as in fig. 9(b), a new polymer with high spin (SN type) can be obtained. Its $f_{k\theta}(x)$ equation and the band structure are shown in fig. 10. Similarly, from the O-polymers Nos. 43–50, which are all O cyclic and of S0 type, we can construct high spin polymers by interchanging the mode of cyclization, as exemplified in fig. 9.

6.   The effect of conjugate branching

The effect of conjugate branching for the ΔE_g value of DS is seen in table 3. All the polymers Nos. 33–42b are of either S0 or S# type, except for SN-type No. 42a. If the parent polymer is S0, the b-polymer (with ethylenic branching) is also S0, while the a-polymer (with methylenic branching) is S#. If the parent polymer is S#, the b-polymer is also S# with a slightly smaller ΔE_g value. On the other hand, the a-polymer is either S# or S0.

That the b-polymer has the same tendency toward the HOMO–LUMO band gap can quite easily be expected from the Kekulé structures. Ethylenic branching gives no essential change in the Kekulé structure, while methylenic branching usually destroys the pattern of the resonance structure as follows:

36   36a   36b
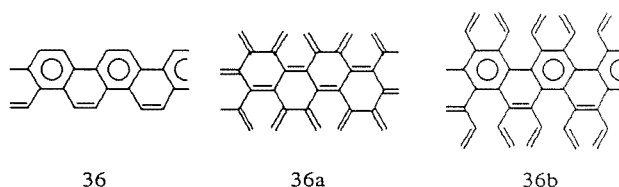
Thus, the methylenic branching opens up the zero ΔE_g of the parent polymer in each family of Nos. 33, 34, 35, and 39, and closed the non-zero ΔE_g in Nos. 36 and 40. Bonchev et al. [8] also pointed out these tendencies. However, this simple explanation does not apply to the families of polymers Nos. 37, 38 and 41.

It is to be noted here that by simply checking if the cyclic unit has NBMO, we can pick out the networks with zero ΔE_g from all the families of Nos. 33–42. As illustrated in figs. 11(a) and 11(b), the secret comes from the three-step periodicity of NBMO patterns in the series of polyomino graphs which correspond to the cyclic units of these polybensenoid networks [19].

Namely, from figs. 11(a) and 11(b), one can see that among the series of polyomino graphs, only those composed of $3n + 1$ ($n = 0, 1, 2, \ldots$) squares have NBMOs [19,25,27,28,39]. These polyomino graphs just represent the cyclic units of two families of polybenzenoid networks Nos. 1, 36, 37, . . . and Nos. 38, 39, 40, ... The DS of S0 type repeats in every third member for each family. Further,
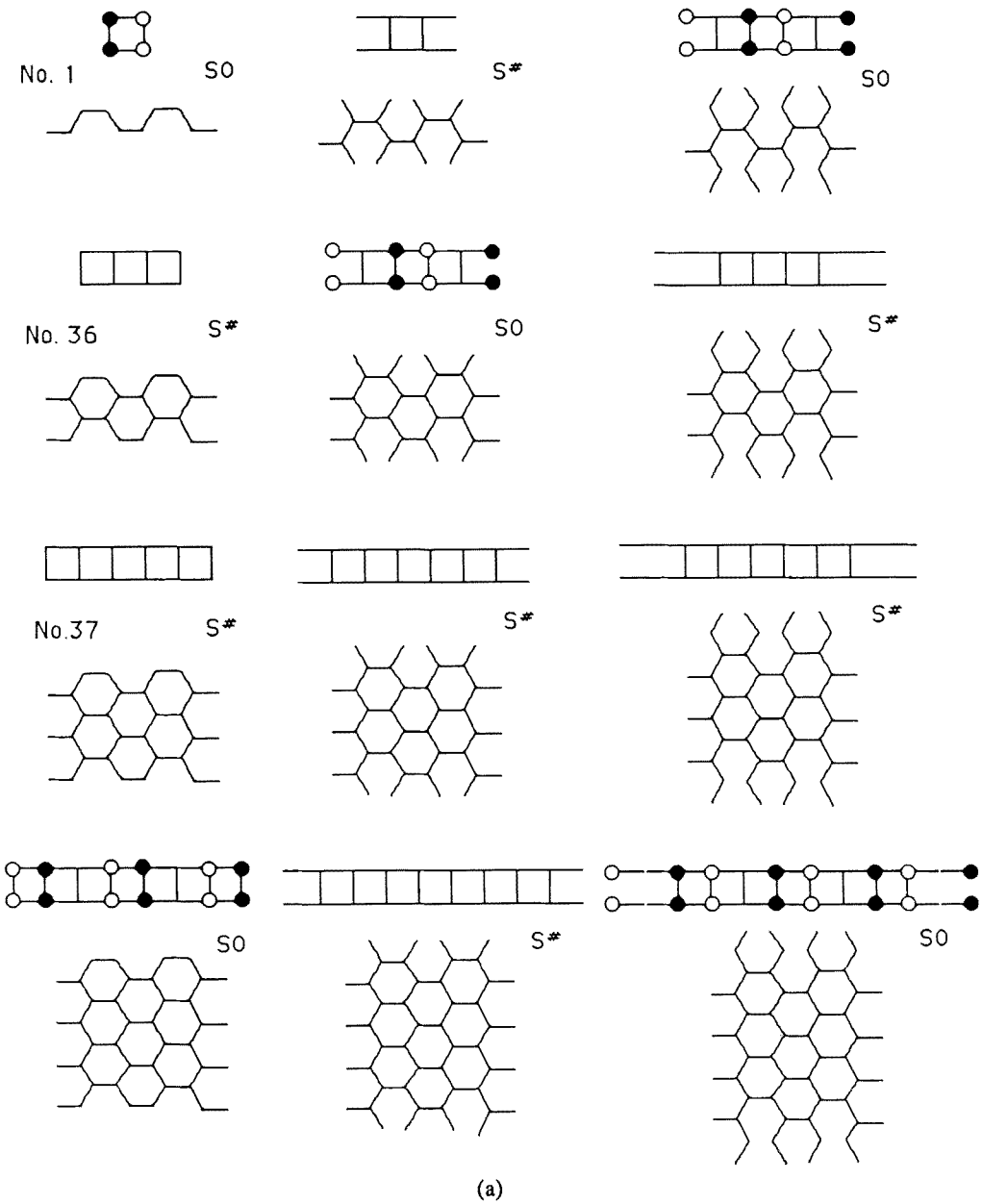
(a)

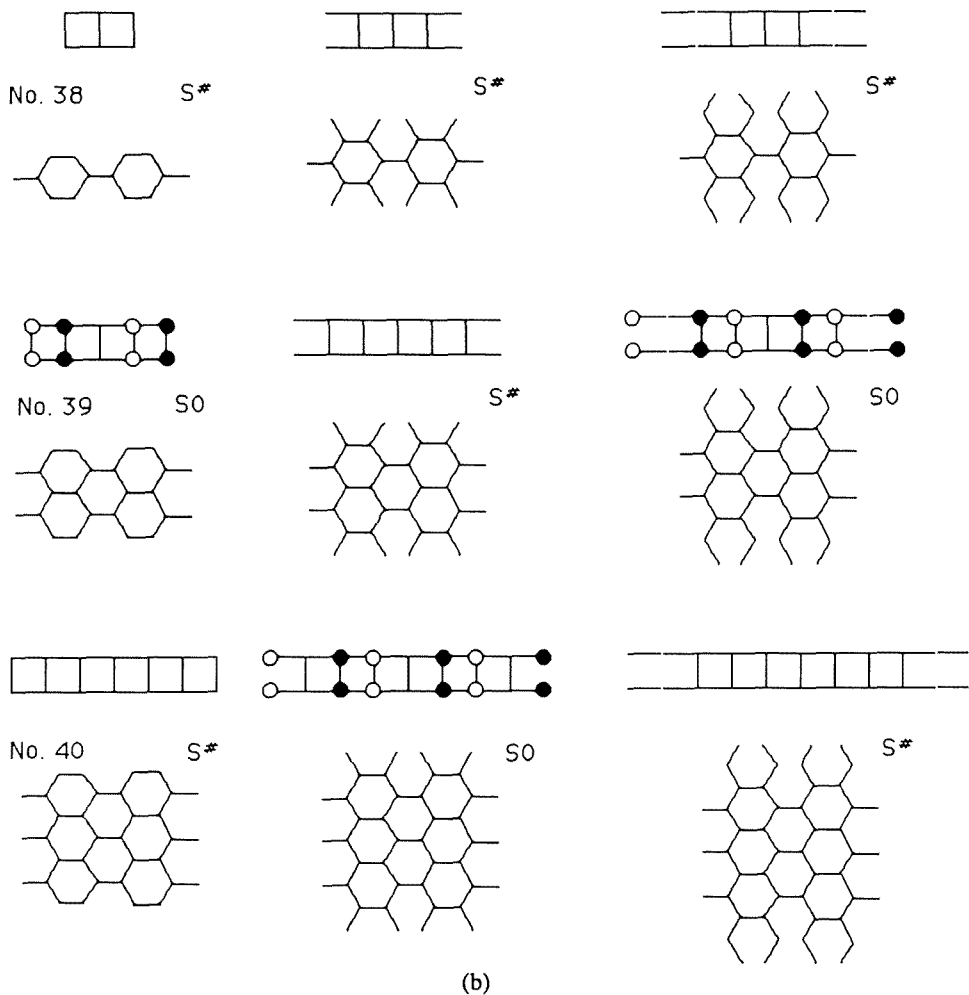Fig. 11. See following page for caption.

Fig. 11. The polymer networks and cyclic units of the series of graphs, (a) Nos. 1, 36, 37, and (b) Nos. 38–40. One of the two (degenerate) NBMOs is also drawn for the case where the cyclic unit has NBMOs. Compare the periodicity of the NBMO appearance with table 3.

every third member beginning from Nos. 1 and 39 within each family is shown to have DS of S0 type, while all the remaining networks have S# type DS.

Also for polymers with conjugate branching, only those networks whose cyclic unit (branched polyomino) have zero ΔE_g (S0 type) have NBMOs. Those branched polyominoes with NBMOs also appear as every third member within each family, as in figs. 11(a), 11(b). As a result, the following three trios (37, 37a, 37b), (38, 38a, 38b) and (41, 41a, 41b) all have non-zero ΔE_g (S# type).

Thus, by this theory we can clearly explain why the polynaphthalene network has an extraordinary narrow ΔE_g value among the family of networks Nos. 1, 38−40 according to more elaborate calculations [23].

If the absolute magnitudes of ΔE_g for these interesting polymer networks are to be discussed, we have to consider many other factors, including bond-alternation, skeletal σ-electrons, electronic repulsion, inter-polymer interaction, etc. [5]. Fortunately, however, the electronic structures of our systems, mainly of polybenzenoid networks, are shown to be reproduced quite well even in the simplest Hückel approximation [9]. In the worst case, where bond alternation is not intrinsicly negligible as in the case of poly-*p*-phenylene (No. 38), introduction of just a bond-alternation parameter is shown to improve quantitatively the profile of DS [40]. Refer also to the discussion in ref. [20], where the effect of bond alternation is extensively analyzed especially for the networks Nos. 1, 33 and 36 in the framework of HMO.

7.   Conclusion

From the previous discussions, we can summarize all the features of topologically possible conjugated hydrocarbon networks composed of alternant parent units, as shown in table 4, which explains that the profile of the band structure can be fully realized from the knowledge of the network topology and the characteristic polynomial $f_{k\theta}(x) = 0$.

Table 4

General rules for predicting the pattern of the density of states of conjugate polymer networks.

Cyclic unit	Root of $f_{k\theta}(0) = 0$	Parent unit	
		E-polymer even C atoms	O-polymer odd C atoms
E cyclic * — o even-membered ring	real k root	S0	S0
	no real k root	S#	S# or ?
O cyclic * — * o — o odd-membered ring	NBMO	SN	SN
E–O cyclic * — o * — * o — o even- and odd-membered rings	real k root	A# or A0	A0 or ?

Namely, as long as the cyclic unit is either E cyclic or O cyclic, its DS is symmetric and the pattern (S0, S#, and SN) of DS near the Fermi level can be predicted from the k root of $f_{k\theta}(x) = 0$ irrespective of the parity of the parent unit.

However, if the cyclic unit has both even and odd cycles, DS becomes asymmetric and a simple classification of prediction of the pattern can no longer be made. Nevertheless, with the knowledge obtained in this research we can design many conjugate polymers of potentially interesting electronic properties.

Appendix

The characteristic polynomials of the cyclic unit for all the polymers studied.

1:   $f_k(x) = x^2 - 2(1 + \cos k\theta)$,

2:   $f_k(x) = x^2 - 4x \cos k\theta - (1 - 4 \cos^2 k\theta)$,

3:   $f_k(x) = x^8 - 11x^6 + x^4(31 - 4 \cos k\theta) - x^2(25 - 4 \cos k\theta) + 4 \cos^2 k\theta$,

4:   $f_k(x) = x(x^3 - 5x - 4 \cos k\theta)$,

5:   $f_k(x) = x^2 - 2x \cos k\theta - (1 + 2 \cos k\theta)^2$,

6:   $f_k(x) = x^2 - 2x \cos k\theta - 1$,

7:   $f_k(x) = x^4 - x^2(5 + 2 \cos k\theta) + 1$,

8:   $f_k(x) = x^6 - 7x^4 - 2x^3 \cos k\theta + 11x^2 + 2x \cos k\theta - 4$,

9:   $f_k(x) = x^6 - x^4(7 + 2 \cos k\theta) + x^2(12 + 6 \cos k\theta) - (5 + 4 \cos k\theta)$

10: $f_k(x) = x^6 - 8x^4 - 4x^3 \cos k\theta + 12x^2 + 4x \cos k\theta - (1 + 4 \cos^2 k\theta)$,

11: $f_x(x) = x^{10} - 12x^8 + 46x^6 - 8x^5 \cos k\theta - 68x^4 + 24x^3 \cos k\theta + 4x^2(8 - \cos^2 k\theta)$
$\quad - 10x \cos k\theta - 1$,

12: $f_x(x) = x^{14} - 17x^{12} + 108x^{10} - x^8(326 + 4 \cos k\theta) + x^6(490 + 16 \cos k\theta)$
$\quad - x^4(345 + 16 \cos k\theta) + x^2(90 + 4 \cos^2 k\theta) - (5 - 4 \cos k\theta)$,

13: $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 326x^8 - 12x^7 \cos k\theta + 489x^6 + 56x^5 \cos k\theta$
$\quad - 339x^4 - 68x^3 \cos k\theta + x^2(81 - 4 \cos^2 k\theta) + 16x \cos k\theta - 1$,

14: $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 326x^8 - 12x^7 \cos k\theta + 490x^6 + 56x^5 \cos k\theta$
$\quad - 345x^4 - 66x^3 \cos k\theta + x^2(89 - 4 \cos^2 k\theta) + 14x \cos k\theta - 4$,

15: $f_k(x) = x^8 - 10x^6 - 2x^5 \cos k\theta + 29x^4 + 4x^3 \cos k\theta - 29x^2 + (9 - 4 \cos^2 k\theta)$,

16: $f_k(x) = x^{10} - 12x^8 - 2x^7 \cos k\theta + 46x^6 + 8x^5 \cos k\theta - 67x^4 - 8x^3 \cos k\theta$
$\quad + x^2(33 - 4 \cos^2 k\theta) + 2x \cos k\theta - 1$,

17: $f_k(x) = x^{10} - 12x^8 - 2x^7 \cos k\theta + 46x^6 + 8x^5 \cos k\theta - 68x^4 - 8x^3 \cos k\theta$
$\quad + x^2(37 - 4 \cos^2 k\theta) + 2x \cos k\theta - 4$,

18 : $f_k(x) = x^{10} - 12x^8 - 2x^7 \cos k\theta + 46x^6 + 8x^5 \cos k\theta - 67x^4 - 6x^3 \cos k\theta$
$+ x^2(33 - 4\cos^2 k\theta) - 4x \cos k\theta - 1,$

19 : $f_k(x) = x^{12} - 15x^{10} + 81x^8 - 4x^7 \cos k\theta - 199x^6 + 20x^5 \cos k\theta$
$+ 228x^4 - 32x^3 \cos k\theta - 108x^2 + 16x \cos k\theta + (16 - 4\cos^2 k\theta),$

20 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 4x^9 \cos k\theta - 326x^8 + 28x^7 \cos k\theta + 486x^6$
$- 64x^5 \cos k\theta - 328x^4 + 44x^3 \cos k\theta + x^2(73 - 4\cos^2 k\theta) + 4x \cos k\theta - 1,$

21 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 4x^9 \cos k\theta - 327x^8 + 26x^7 \cos k\theta + 494x^6$
$- 56x^5 \cos k\theta - 349x^4 + 44x^3 \cos k\theta + x^2(92 - 4\cos^2 k\theta) - 8x \cos k\theta - 1,$

22 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 4x^9 \cos k\theta - 327x^8 + 28x^7 \cos k\theta + 496x^6$
$- 66x^5 \cos k\theta - 359x^4 + 56x^3 \cos k\theta + x^2(107 - 4\cos^2 k\theta) - 10x \cos k\theta - 9,$

23 : $f_k(x) = x^{10} - 12x^8 + x^6(46 - 6 \cos k\theta) + x^4(28 \cos k\theta - 68)$
$+ x^2(34 - 26 \cos k\theta + 4\cos^2 k\theta) - 1,$

24 : $f_k(x) = x^{10} - 12x^8 + x^6(46 - 6 \cos k\theta) + x^4(28 \cos k\theta - 69)$
$+ x^2(38 - 28 \cos k\theta + 4\cos^2 k\theta) - (5 - 4 \cos k\theta),$

25 : $f_k(x) = x^8 - 10x^6 + x^4(29 - 4 \cos k\theta) - x^2(29 - 8 \cos k\theta) + (8 - 4\cos^2 k\theta),$

26 : $f_k(x) = x^{10} - 12x^8 + x^6(46 - 4 \cos k\theta) - x^4(68 - 16 \cos k\theta) + 45$
$+ x^2(37 - 16 \cos k\theta - 4\cos^2 k\theta) - (5 - 4 \cos k\theta),$

27 : $f_k(x) = x^{12} - 15x^{10} + 81x^8 - x^6(199 + 8 \cos k\theta) + x^4(229 + 36 \cos k\theta)$
$- x^2(112 + 48 \cos k\theta) + 4(4 + 4 \cos k\theta + \cos^2 k\theta),$

28 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - x^8(327 + 8 \cos k\theta) + x^6(496 + 48 \cos k\theta)$
$- x^4(362 + 88 \cos k\theta) + x^2(110 + 50 \cos k\theta + 4\cos^2 k\theta) - (10 + 6 \cos k\theta),$

29 : $f_k(x) = x^8 - 10x^6 - 2x^5 \cos k\theta + 29x^4 - 3x^3 \cos k\theta - 28x^2$
$- 4x \cos k\theta + 4(1 + \cos^2 k\theta),$

30 : $f_k(x) = x^{12} - 15x^{10} + 81x^8 - 2x^7 \cos k\theta - 198x^6 + 6x^5 \cos k\theta + 224x^4$
$- 6x^3 \cos k\theta - 102x^2 + 4x \cos k\theta + (9 + 4\cos^2 k\theta),$

31 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 2x^9 \cos k\theta - 326x^8 + 10x^7 \cos k\theta$
$+ 488x^6 - 20x^5 \cos k\theta - 336x^4 + 22x^3 \cos k\theta$
$+ x^2(78 + 4\cos^2 k\theta) - 10x \cos k\theta - 1,$

32 : $f_k(x) = x^{14} - 17x^{12} + 108x^{10} - 2x^9 \cos k\theta - 326x^8 + 10x^7 \cos k\theta + 489x^6$

$\qquad - 20x^5 \cos k\theta - 342x^4 + 22x^3 \cos k\theta + x^2(88 + 4\cos^2 k\theta) - 10x \cos k\theta - 4,$

33 : $f_k(x) = x^4 - x^2(5 + 4\cos k\theta) + 4(1 + \cos k\theta)^2,$

33a : $f_k(x) = x^6 - x^4(7 + 4\cos k\theta) + x^2(11 + 12\cos k\theta + 4\cos^2 k\theta) - 1,$

33b : $f_k(x) = x^8 - x^6(9 + 4\cos k\theta) + x^4(24 + 20\cos k\theta + 4\cos^2 k\theta)$

$\qquad - x^2(20 + 24\cos k\theta + 8\cos^2 k\theta) + 4(1 + \cos k\theta)^2,$

34 : $f_k(x) = x^6 - x^4(8 + 6\cos k\theta) + x^2(17 + 28\cos k\theta + 12\cos^2 k\theta) - 8(1 + \cos k\theta)^3,$

34a : $f_k(x) = x^8 - x^6(10 + 6\cos k\theta) + x^4(30 + 36\cos k\theta + 12\cos^2 k\theta)$

$\qquad - x^2(26 + 46\cos k\theta + 32\cos^2 k\theta + 8\cos^3 k\theta) + 1,$

34b : $f_k(x) = x^{10} - 6x^8(2 + \cos k\theta) + x^6(49 + 48\cos k\theta + 12\cos^2 k\theta)$

$\qquad - x^4(80 + 116\cos k\theta + 56\cos^2 k\theta + 8\cos^3 k\theta)$

$\qquad + x^2(48 + 96\cos k\theta + 68\cos^2 k\theta + 16\cos^3 k\theta) - 8(1 + \cos k\theta)^3,$

35 : $f_k(x) = x^8 - x^6(11 + 8\cos k\theta) + x^4(39 + 60\cos k\theta + 24\cos^2 k\theta)$

$\qquad - x^2(49 + 124\cos k\theta + 108\cos^2 k\theta + 32\cos^3 k\theta) + 16(1 + \cos k\theta)^4,$

35a : $f_k(x) = x^{10} - x^8(13 + 8\cos k\theta) + x^6(58 + 72\cos k\theta + 24\cos^2 k\theta)$

$\qquad - x^4(102 + 192\cos k\theta + 132\cos^2 k\theta + 32\cos^3 k\theta)$

$\qquad + x^2(57 + 144\cos k\theta + 156\cos^2 k\theta + 80\cos^3 k\theta + 16\cos^4 k\theta) - 1,$

35b : $f_k(x) = x^{12} - x^{10}(15 + 8\cos k\theta) + x^8(83 + 88\cos k\theta + 24\cos^2 k\theta)$

$\qquad - x^6(209 + 332\cos k\theta + 180\cos^2 k\theta + 32\cos^3 k\theta)$

$\qquad + x^4(240 + 516\cos k\theta + 420\cos^2 k\theta + 144\cos^3 k\theta + 16\cos^4 k\theta)$

$\qquad - x^2(112 + 320\cos k\theta + 356\cos^2 k\theta + 176\cos^3 k\theta + 32\cos^4 k\theta)$

$\qquad + 16(1 + \cos k\theta)^4,$

36 : $f_k(x) = x^4 - x^2(5 + 2\cos k\theta) + (5 - 4\cos^2 k\theta),$

36a : $f_k(x) = x^6 - x^4(7 + 2\cos k\theta) + x^2(12 + 4\cos k\theta - 4\cos^2 k\theta) - 2(1 + \cos k\theta),$

36b : $f_k(x) = x^8 - x^6(9 + 2\cos k\theta) + x^4(25 + 8\cos k\theta - 4\cos^2 k\theta)$

$\qquad - x^2(23 + 8\cos k\theta - 8\cos^2 k\theta) + (5 - 4\cos^2 k\theta),$

37 : $f_k(x) = x^6 - x^4(8 + 2\cos k\theta) + x^2(19 + 6\cos k\theta - 8\cos^2 k\theta)$

$\qquad - (13 + 8\cos k\theta - 12\cos^2 k\theta - 8\cos^3 k\theta),$

37a : $f_k(x) = x^8 - x^6(10 + 2\cos k\theta) + x^4(32 + 10\cos k\theta - 8\cos^2 k\theta)$

$\quad - x^2(34 + 14\cos k\theta - 20\cos^2 k\theta - 8\cos^3 k\theta) + (5 - 4\cos^2 k\theta),$

37b : $f_k(x) = x^{10} - x^8(12 + 2\cos k\theta) + x^6(51 + 14\cos k\theta - 8\cos^2 k\theta)$

$\quad - x^4(92 + 32\cos k\theta - 36\cos^2 k\theta - 8\cos^3 k\theta)$

$\quad + x^2(66 + 26\cos k\theta - 44\cos^2 k\theta - 16\cos^3 k\theta)$

$\quad - (13 + 8\cos k\theta - 12\cos^2 k\theta - 8\cos^3 k\theta),$

38 : $\quad f_k(x) = x^6 - 7x^4 + x^2(11 - 4\cos k\theta) - (5 - 4\cos k\theta),$

38a : $f_k(x) = x^{10} - 11x^8 + x^6(37 - 4\cos k\theta) - x^4(45 - 12\cos k\theta)$

$\quad + x^2(15 - 4\cos k\theta) - 1,$

38b : $f_k(x) = x^{14} - 15x^{12} + x^{10}(83 - 4\cos k\theta) - x^8(219 - 28\cos k\theta)$

$\quad + x^6(292 - 68\cos k\theta) - x^4(190 - 72\cos k\theta) + x^2(53 - 32\cos k\theta)$

$\quad - (5 - 4\cos k\theta),$

39 : $\quad f_k(x) = x^{10} - 13x^8 + 8x^6(7 - \cos k\theta) - 4x^4(25 - 12\cos k\theta)$

$\quad + 4x^2(19 - 18\cos k\theta + 3\cos^2 k\theta) - 4(5 - 8\cos k\theta + 3\cos^2 k\theta),$

39a : $f_k(x) = x^{14} - 17x^{12} + x^{10}(106 - 8\cos k\theta) - x^8(308 - 72\cos k\theta)$

$\quad + x^6(439 - 196\cos k\theta + 12\cos^2 k\theta) - x^4(287 - 192\cos k\theta$

$\quad + 28\cos^2 k\theta) + x^2(67 - 52\cos k\theta + 8\cos^2 k\theta) - (5 - 4\cos k\theta),$

39b : $f_k(x) = [x^{10} - 13x^8 + x^6(54 - 6\cos k\theta) - x^4(91 - 26\cos k\theta)$

$\quad + x^2(59 - 30\cos k\theta) - (10 - 6\cos k\theta)][x^8 - 8x^6$

$\quad + x^4(18 - 2\cos k\theta) - x^2(13 - 4\cos k\theta) + 2(1 - \cos k\theta)],$

40 : $\quad f_k(x) = (x^2 - 1)[x^8 - 12x^6 + x^4(42 - 8\cos k\theta) - x^2(52 - 32\cos k\theta)$

$\quad + (17 - 24\cos k\theta + 8\cos^2 k\theta)][x^4 - 6x^2 + (5 - 4\cos k\theta)],$

40a : $f_k(x) = [x^{10} - 14x^8 + x^6(63 - 8\cos k\theta) - x^4(111 - 44\cos k\theta)$

$\quad + x^2(71 - 50\cos k\theta + 8\cos^2 k\theta) - (10 - 6\cos k\theta)][x^8 - 9x^6$

$\quad + x^4(22 - 4\cos k\theta) - x^2(17 - 8\cos k\theta) + 2(1 - \cos k\theta)],$

40b : $f_k(x) = (x^2 - 1)[x^{10} - 15x^8 + x^6(75 - 8\cos k\theta) - x^4(152 - 52\cos k\theta)$

$\quad + x^2(115 - 82\cos k\theta + 8\cos^2 k\theta) - (17 - 24\cos k\theta + 8\cos^2 k\theta)]$

$\quad [x^{10} - 11x^8 + x^6(39 - 4\cos k\theta) - x^4(56 - 16\cos k\theta)$

$\quad + x^2(31 - 18\cos k\theta) - (5 - 4\cos k\theta)],$

41 : $f_k(x) = [x^7 - 2x^6 - 7x^5 + 12x^4 + x^3(13 - 2\cos k\theta) - 18x^2$

$- x(7 - 2\cos k\theta) + (6 + 2\cos k\theta)][x^7 + 2x^6 - 7x^5 - 12x^4$

$+ x^3(13 - 2\cos k\theta) + 18x^2 - x(7 - 2\cos k\theta) - (6 + 2\cos k\theta)],$

41a : $f_k(x) = [x^8 - 2x^7 - 8x^6 + 14x^5 + x^4(18 - 2\cos k\theta) - 26x^3$

$- x^2(12 - 4\cos k\theta) + x(12 + 2\cos k\theta) - 1][x^8 - 2x^7$

$- 8x^6 - 14x^5 + x^4(18 + 2\cos k\theta) + 26x^3 - x^2(12 + 4\cos k\theta)$

$- x(12 - 2\cos k\theta) - 1],$

41b : $f_k(x) = [x^9 - 2x^8 - 9x^7 + 16x^6 + x^5(25 - 2\cos k\theta) - 38x^4 - x^3(25 - 6\cos k\theta)$

$+ x^2(30 + 2\cos k\theta) + x(6 - 2\cos k\theta) - (6 + 2\cos k\theta)]$

$[x^9 + 2x^8 - 9x^7 - 16x^6 + x^5(25 - 2\cos k\theta) + 38x^4 - x^3(25 - 6\cos k\theta)$

$- x^2(30 + 2\cos k\theta) + x(6 - 2\cos k\theta) + (6 + 2\cos k\theta)],$

42 : $f_k(x) = x^6 - 8x^4 - 4x^3\cos k\theta + 12x^2 + 8x\cos k\theta - 4(1 - \cos^2 k\theta),$

42a : $f_k(x) = x^2[x^6 - 10x^4 - 4x^3\cos k\theta + 25x^2 + 12x\cos k\theta - 4(4 - \cos^2 k\theta)],$

42b : $f_k(x) = x^{10} - 12x^8 - 4x^7\cos k\theta + 44x^6 + 20x^5 - x^4(60 - 4\cos^2 k\theta)$

$- 24x^3\cos k\theta + x^2(28 - 8\cos^2 k\theta) + 8x\cos k\theta - 4(1 - \cos^2 k\theta),$

43 : $f_k(x) = x^5 - 6x^3 - 4x^2\cos k\theta + x(7 - 4\cos^2 k\theta) + 2\cos k\theta,$

44 : $f_k(x) = x^9 - 11x^7 + 37x^5 - 8x^4\cos k\theta - 45x^3 + 20x^2\cos k\theta$

$+ 2x(7 - 2\cos^2 k\theta) - 4\cos k\theta,$

45 : $f_k(x) = x^{13} - 16x^{11} + 94x^9 - 256x^7 - 12x^6\cos k\theta + 334x^5 + 50x^4\cos k\theta$

$- 188x^3 - 50x^2\cos k\theta + x(29 - 4\cos^2 k\theta) + 6\cos k\theta,$

46 : $f_k(x) = x^9 - 11x^7 - 2x^6\cos k\theta + 37x^5 + 6x^4\cos k\theta - 45x^3$

$- 2x^2\cos k\theta + x(18 - 4\cos^2 k\theta) - 2\cos k\theta,$

47 : $f_k(x) = x^9 - 11x^7 - 2x^6\cos k\theta + 37x^5 + 6x^4\cos k\theta - 45x^3$

$- 4x^2\cos k\theta + x(17 - 4\cos^2 k\theta) + 2\cos k\theta,$

48 : $f_k(x) = x^{13} - 16x^{11} + 94x^9 - 4x^8\cos k\theta - 257x^7 + 24x^6\cos k\theta$

$+ 338x^5 - 48x^4\cos k\theta - 194x^3 + 34x^2\cos k\theta + 4x(9 - \cos^2 k\theta)$

$- 4\cos k\theta,$

49 : $f_k(x) = x^9 - 11x^7 - 2x^6\cos k\theta + 37x^5 + 8x^4\cos k\theta - 45x^3$

$- 10x^2\cos k\theta + x(14 + 4\cos^2 k\theta) + 4\cos k\theta,$

50 : $f_k(x) = x^9 - 11x^7 - 2x^6 \cos k\theta + 37x^5 + 8x^4 \cos k\theta - 44x^3$

$\qquad - 8x^2 \cos k\theta + 4x(3 + \cos^2 k\theta) + 2 \cos k\theta,$

51 : $f_k(x) = x[x^{10} - 13x^8 - 2x^7 \cos k\theta + 56x^6 + 10x^5 \cos k\theta - 97x^4$

$\qquad - 14x^3 \cos k\theta + x^2(64 - 4\cos^2 k\theta) + 4x \cos k\theta - 9],$

52 : $f_k(x) = x[x^4 - x^2(6 + 4\cos k\theta) + (7 + 10\cos k\theta + 4\cos^2 k\theta)],$

53 : $f_k(x) = x^3 - x(4 + 2\cos k\theta) + (2 - 2\cos k\theta - 4\cos^2 k\theta),$

54 : $f_k(x) = x^7 - 9x^5 - 2x^4 \cos k\theta + x^3(21 - 2\cos k\theta) - x^2(2 - 6\cos k\theta)$

$\qquad - 4x(3 - \cos k\theta) - 4\cos k\theta(1 - \cos k\theta),$

55 : $f_k(x) = x^7 - 9x^5 + x^3(21 - 4\cos k\theta) - x^2(2 + 4\cos k\theta)$

$\qquad - x(13 - 8\cos k\theta) + 2(1 + 2\cos k\theta - 2\cos^2 k\theta),$

56 : $f_k(x) = x^{11} - 13x^9 + 59x^7 - 2x^6 - 114x^5 + x^4(12 - 4\cos k\theta) + x^3(94 - 4\cos k\theta)$

$\qquad - x^2(18 - 8\cos k\theta) - x(27 - 4\cos k\theta) + (8 - 4\cos k\theta)$

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