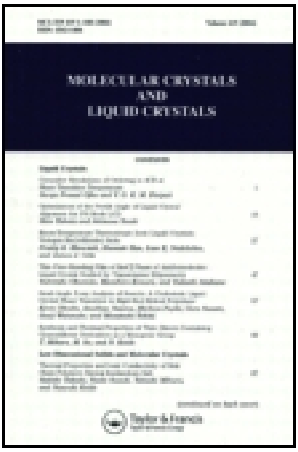

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Topological Spin Polarization and a VB Picture of Infinite Model Systems for Organic Polymer Magnets in Terms of Electronic Band Calculations

Takejl Takui [a] , Yoshio Teki [b] , Kazunobu Sato [a] & Koichi Itoh [b]

[a] Department of Chemistry, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Material Science, Faculty of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

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TOPOLOGICAL SPIN POLARIZATION AND A VB PICTURE OF INFINITE MODEL SYSTEMS FOR ORGANIC POLYMER MAGNETS IN TERMS OF ELECTRONIC BAND CALCULATIONS

TAKEJI TAKUI,[1] YOSHIO TEKI,[2] KAZUNOBU SATO,[1] and KOICHI ITOH[2]
[1]Department of Chemistry and [2]Department of Material Science, Faculty of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Absract This paper deals with a polymer version of the topological π-spin polarization interrelated to the topological superdegeneracy of crystal orbitals of infinite or extended polymeric spin systems and also with a VB picture of their spin structure in terms of simple electronic band calculations. We stress that the theoretical models (traveling wave approach) introduced predict essential features of magnetic properties of polymeric systems which yield crucial aspects for their materials design. The model calculation has also been made for various types of inter-polymer interactions in order to understand the topological spin polarization of higher-dimensional infinite or extended polymeric spin systems and the topological nature of inter-polymer contacts (inter-polymer connectedness). The results have shown that the connectedness gives rise to the prominent modulation of band structures and π spin polarizations which is highly dependent on the topology of the contacts. Thus, the results serve for molecular designs for novel intriguing organic magnetic systems such as multifunctionality molecular magnetic materials. The VB representation in the k space has disclosed such a physical picture for the infinite spin system that can not be expected from the simple or intuitive extension obtained for a finite system. Naturally, in the VB picture the contributing weight of a particular spin structure undergoes fluctuation in the k space as the physical consequence of the intersegment interaction in the infinite system.

INTRODUCTION

Organic molecular based magnetism (abbreviated to organic magnetism)[1,2] has attracted widely increasing interest from both the pure and applied sciences for the last decade.[3-6] This is partly due to the rich variety of novel physical phenomena and properties which synthetic organomagnetic materials are expected to exhibit both macro- and meso-scopically and due to their underlying potential applications as future technology in materials sciences.[7,8]

A rapid development of this research field crucially owes the fact that the study of organic magnetism has conveyed important conceptual advances in chemistry and physics. Purely organic magnetism, defined typically as ferromagnetism originating in purely organic building spin systems composed of only light atoms such as C,H, N, O, and S, is apparently a controversial issue simply because organic substances are intrinsically diamagnetic. The search for organic magnetic materials, however, is not only the focus of the contemporary topics in materials science but also an important issue of the interplay between theory and experiment in physics and rapidly developing spin chemistry.[1-6]

Naturally, organic magnetism appearing in various forms of macroscopic scale involves cooperative phenomena and phase transitions which are inherently related to infinite or macroscopically extended length of coherence in magnetic interactions of organic materials. In view of polymeric organic magnetic materials, it should be emphasized that the first conceptual advance in the research field of organic magnetism was made in the context of a proposal of hypothetical one- or two-dimensional organic polymer ferromagnets and super high-spin polymers with extremely large spins (assemblages of a great number of exchange-coupled spins), as shown in Figure 1.[1a-c]

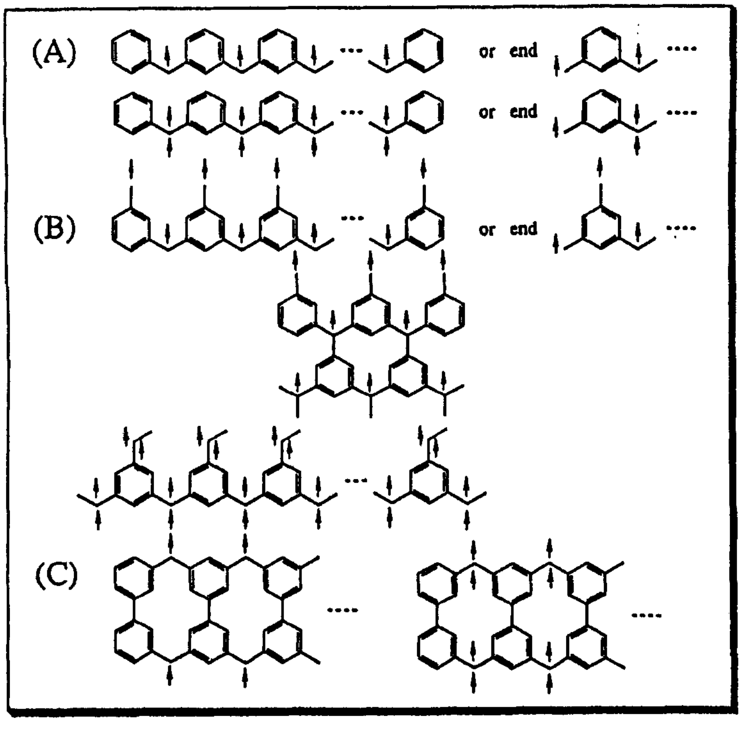

FIGURE 1 Through-bond superparamagnetic and ferromagnetic hydrocarbon-based polymers proposed at early times in terms of the robust spin polarization.[1a-c] It was shown later on that the polymers (C) were not the case.[1d,f]

The first documented through-bond approach[15] to organic ferromagnetism appeared at early times exploited the topological nature of the symmetry of π-conjugated electron network in organic molecules, which renders the degeneracy of singly occupied π-nonbonding MOs unlimited (the topological degeneracy of the nonbonding MOs associated with topological robust π-spin polarization as an underlying mechanism of organic ferromagnetic states).[1a-c] In contrast, the degree of the orbital degeneracy stemming from group-theoretical symmetry argument is limited. The very viewpoint of the topological symmetry disclosed the possible occurrence of organic polymer superpara- and ferro-magnets, followed by conceptual advances particularly in spin chemistry. It is important to realize that the through-bond approach is based on the topological nature of the through-bond linkage modes of π-conjugated spin systems.

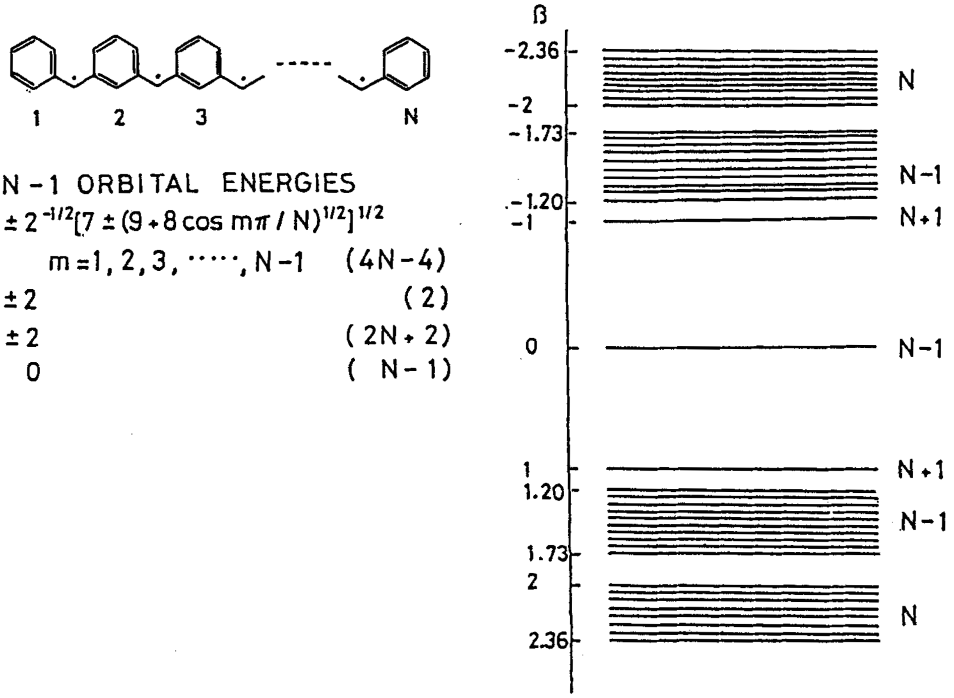

FIGURE 2 The first documented band-structure calculation for a *m*-benzyl-based polymeric spin system.[1a,c] An analytical solution in terms of Hückel Hamiltonian is given. The NBMO band at zero energy is superdegenerate.

Figure 2 shows the first documented band-structure calculation revealing the possible occurrence of ferromagnetic ground states for purely organic polymeric spin systems.[1a,c] The particular topology of π-conjugated electron network in alternant hydrocarbon-based polymeric systems, i.e., *meta*- or *1-,3-,5-*connectivity gives rise to the superdegeneracy[14b] of half-filled NBMOs in their ground state as depicted for a *m*-benzyl radical-based one-dimensional magnetic polymer in Figure 2. This symmetry requirement is closely related to topologically controlled robust dynamic spin polarization of the systems at hand (topological π-spin polarization approach). The argument for this can be rationalized by a DODS-based picture with electron repulsion taken into account. The argument exactly corresponds to an MO description of molecular Hund's rule. It was a logical consequence that this approach predicted the occurrence of super high-spin macromolecules having extremely large spins or polymeric superpara- and ferro-magnetic polymers as shown in Figure 1.

The use of topological symmetry in obtaining organic high-spin ground states for finite systems and ferromagnetic states for infinite systems gives a completely different answer to the degree of orbital degeneracy in organic molecular systems. In this context, π-topological based organic magnetism has not been any analogues to atomic based magnetism nor molecule-based magnetism via through-space approaches.[15] The low symmetry intrinsic to organic molecules is the essential reason why ground-state high-spin multiplicities exceeding triplet had never appeared from organic substances until the first organic high-spin quintet molecule was detected in 1967[23] whose molecular design was exactly made by the use of the topological symmetry argument. The concept has frequently been utilized as general guiding principle for molecular designing of organic magnetic materials and experimentally tested.[3-6] Until recently, efforts from both experimental and theoretical sides have been made to control spin alignment in organic molecules and to understand underlying mechanisms, particularly electronic spin structures of open-shell systems in the ground and low-lying excited states.[1-6,9-14] All issues of organic magnetism constitute current spin chemistry and the focus of contemporary topics in science.

Recent conceptual advances related to organic finite systems[1-6] have no doubt taken their crucial part in particular aspects of the development of the research fields. Nevertheless, conceptual advances focusing on infinite or extended organic polymeric spin systems have not been made much so far.[1a-e,13,14,26] The understanding inherent in the infinite spin systems serves the purposes of materials challenges and molecular designs for novel organic intriguing magnetic materials. In this work, particular importance has been given to the exposition of the fundamental bases of polymeric organic magnetism (through-bond approach) such as molecular designs by utilizing the topological superdegeneracy of traveling wave orbitals (crystal orbitals), the dimensionality in spin structure, and the topology of inter-polymer contacts (inter-polymer connectedness) in terms of electronic band-struc ture calculations based on traveling wave approach (crystal orbital approach). This work also describes the first attempt to expound organic infinite polymeric open-shell systems in terms of VB approach. The VB picture has been obtained from the band-structure calculations.

BAND STRUCTURES OF ONE- AND TWO-DIMENSIONAL POLYMERIC MAGNETIC SYSTEMS WITH TOPOLOGICALLY CONTROLLED SPIN POLARIZATION

Traveling Wave/Crystal Orbital Approach

Since the first documented band-structure treatment[1a,c] theoretical studies of the possible occurrence of band structures from organic magnetic polymers or extended spin systems have been made in various levels of approximation.[1e,13,14,26] The first treatment, which proved the unlimitation of the degree of π-topological orbital degeneracy for a one-dimensional ferromagnetic polymer, had appeared at earlier times before crystal orbital approach was established in polymer chemistry. We stress that in some aspects of electronic spin structures of organic polymeric systems simple and intuitive extensions obtained from a finite system to its infinite polymeric system do not work. We also stress that the theoretical model introduced in this section predicts essential general features of magnetic properties of the polymeric spin system which yield crucial aspects for its molecular designing, despite the fact that simplified theoretical models only represent coarse qualitative features of physical properties. Due care and attention are required when the present method applies to non-alternant hydrocarbon-based polymeric spin systems in order to predict their potentiality as novel magnetic functionality materials. Introduction of hetero-atomic spin sites can be mostly treated as a trivial extension. The model introduced in this section is the simplest possible version for band-structure calculations of organic magnetic polymers and their inter-polymer interaction. The model is called traveling wave or crystal orbital approach. In the following, we first describe the model briefly. Next, to illustrate the general features of the band structures we consider typical one-dimensional polymeric spin systems. Finally, to foresee underlying features of band structures due to inter-polymer interactions taking place in higher dimensional magnetic polymeric systems we advance the traveling wave approach to quasi two-dimensional magnetic polymeric systems.

We now consider the simplest version of the traveling wave approach.[27] A Hamiltonian for infinite or extended polymeric systems is defined as

$$H = (-1/2)\Delta + V(r) \qquad (1)$$

where the terms in atomic energy units have usual meanings and the potential term V(r) undergoes translation symmetry, i.e.,

$$V(r) = V(r+R_l) \qquad (l = 1,2,\cdots,N). \tag{2}$$

This symmetry requirement is the physical consequence of the assumption that a polymeric system under study is characterized by an N-segment structure, where l denotes the numbering of the segment. The solution for one-electron Schrödinger equation is given as

$$\hat{H}\Psi(r) = E\Psi(r). \tag{3}$$

We assume that the wave function $\Psi(r)$ of the system undergoes the Born-von Kármán's periodic boundary condition satisfying

$$\Psi(r+R_N) = \Psi(r), \tag{4}$$

which corresponds to the physical property of the N-segment structure. The molecular orbital wavefunction $\Psi(r)$ of the polymeric system is approximated to be comprised of the linear combination of ϕ_m (m = 1,2,....) orbitals describing each segment l, i.e.,

$$\Psi_m(r) = \sum_{l=1}^{N} C_{m,l}\, \Phi_m(r-R_l), \tag{5}$$

Coefficients $C_{m,l}$ can be evaluated in terms of traveling wave solutions, defining $C_l=Ce^{ikl}$ for one dimension and requiring repetition of the values for the coefficients satisfying the periodic condition $C_{l+N}=C_l$ or $e^{i(l+N)k} = e^{ilk}$ (l = 1,2,...., N), which implies

$$Nk = 2\pi j \qquad (j = 0,\pm1,\pm2,.......). \tag{6}$$

We obtain for the molecular orbitals of the polymeric system

$$\Psi_{m,j}(r) = (1/\sqrt{N}) \sum_{l=1}^{N} e^{i(2\pi j/N)l}\Phi_m(r-R_l). \tag{7}$$

The above definition for C_l is readily extended to three dimensional systems by the use of three basis vectors as $C_l = e^{ik\cdot l}$ and $R_l = l_1a_1 + l_2a_2 + l_3a_3$ (l_i = 1,2,...). For the orbital $\{\Phi_m(r-R_l)\}$, we assume

$$<\phi_m(r-R_l)\,|\,\phi_m(r-R_{l'})>=\delta_{ll'}, \qquad (8)$$

ensuring the normalization of $\Psi_{m,j}(r)$. In addition, the nearest-neighbor segment interaction and intra-segment interaction taken into account, matrix elements of H are non-vanishing only for l=l', l=l'±1. Within the framework of this assumption,

$$\begin{aligned}<\Psi_{m,j}|\hat{H}|\Psi_{m,j}> &= (1/N)\sum_{l=1}^{N}\{<\phi_m(r-R_l)|\hat{H}|\phi_m(r-R_l)> \\ &\quad +e^{-ik}<\phi_m(r-R_l)|\hat{H}|\phi_m(r-R_{l-1})> \\ &\quad +e^{+ik}<\phi_m(r-R_l|\hat{H}|\phi_m(r-R_{l+1})|\} \qquad (9) \\ &= <\phi_m(r-R_l)|\hat{H}|\phi_m(r-R_l)|> \\ &\quad +e^{-ik}<\phi_m(r-R_l)|\hat{H}|\phi_m(r-R_{l-1})> \\ &\quad +e^{+ik}<\phi_m(r-R_l)|\hat{H}|\phi_m(r-R_{l+1})> \qquad (10)\end{aligned}$$

where k is given by Equation (6). Equation (10) is obtained since the matrix elements of { } in Equation (9) are independent of the segment number l. For simplicity setting up the orbital for the segment in terms of the LCAO approximation and solving the usual secular equations by means of Rayleigh and Ritz linear variation method, traveling wave (crystal orbital) energies and coefficients of the LCAOs of $\phi_m(r-R_l)$ can be evaluated as traveling wave solutions, which correspond to a description of a mobile electron with non-zero linear momentum in the periodic "lattice" comprised of the N-segment structure. This can be verified by computing the expectation value $< \phi_m(r-R_l|p|\phi_m(r-R_l)$ for linear momentum p. The expectation value varies to zero continuously, depending on the k value, i.e., integral j in Equation (6).

We stress that the above traveling wave approach applies to a simplified version dealing with $\phi_m(r-R_l)$, which is able to illustrate general features of infinite organic magnetic systems in contrast to finite ones. The approach here aims to derive band structures of the infinite polymeric spin systems governed by the topological nature of spin polarization, specifying microscopic descriptions of segments and inter-polymer interactions (the topology of inter-polymer contracts).

One-Dimensional Infinite or Extended Polymeric Spin Systems

For simplicity we consider a one-dimensional magnetic system which has been proposed by Ovchinnikov[1e] as a model for through-bond approach, as shown in Figure 3. X denotes the side-chain 1/2-spin site, where X is assumed either a single atom or a molecular frame with more or less π-conjugated electron network. In the following first let us consider a three-homo-site system, i.e., X=C. In Figure

3 the carbon site is numbered and L(=l) denotes the segment number. For simplicity we neglect the bond alternation of the system. The possible occurrence of the bond alternation and its influence can be readily taken into account. The secular equation problem here is given as

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1+\exp(+ik) \\ 0 & 1+\exp(-ik) & x \end{vmatrix} = 0, \qquad (11)$$

where $k=2\pi j/N$ (j = 1,2,....,N) and N stands for the total number of the segments.

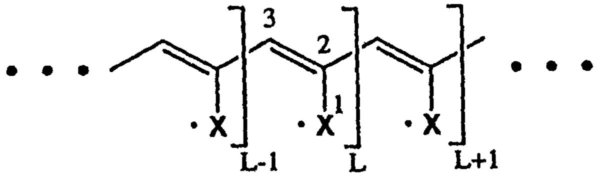

FIGURE 3 Segment structure of a simplified model for one-dimensional magnetic polymers. The carbon sites and one 1/2-spin sites (X) are denoted by figures. L(=l) designates the segment number. The site X can comprise an inner structure.

The crystal orbital (the traveling wave with a band index i) energy E_i is given by $E_i=\alpha+x_i(-\beta)$ (i = 1,2,3) and the probability amplitude coefficients $C_{i,r}$ (r = 1,2,3) of the i-th crystal orbital are generally complex because the approach is based on the non-zero expectation value for the linear momentum of the system. The traveling

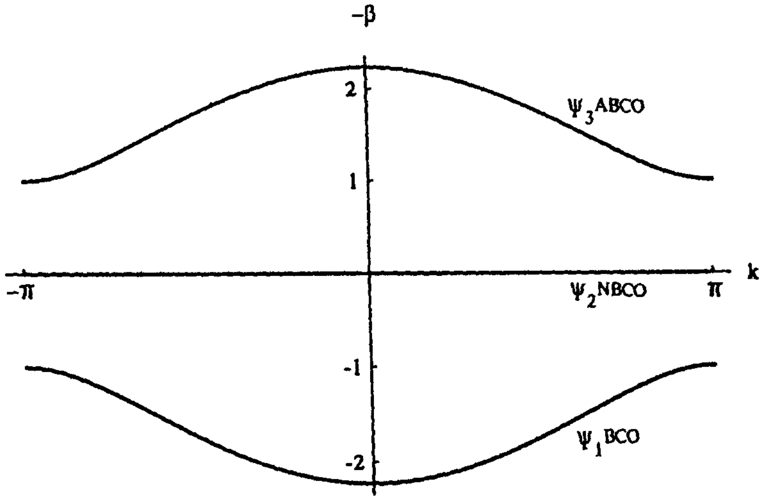

FIGURE 4 Band structure of the 1D polymeric spin system calculated by the traveling wave (crystal orbital) approach. No bond alternation is assumed.

wave solution is analytically soluble and the obtained band structure and probability amplitude $|C_{i,r}|^2$ corresponding to the crystal orbital pattern with an i band index are given as a function of a one-dimensional wavevector k, i.e., in the k-space. The density of the traveling wave state can be also obtained, but not given here. The band indexes 1, 2, and 3 correspond to the bonding, nonbonding, and antibonding orbital in terms of molecular orbital theory, respectively. The traveling wave solution for the one-dimensional system studied here is schematically shown in Figure 4 for the band structure and Figure 5 for the probability amplitude $|C_{i,r}|^2$, respectively.

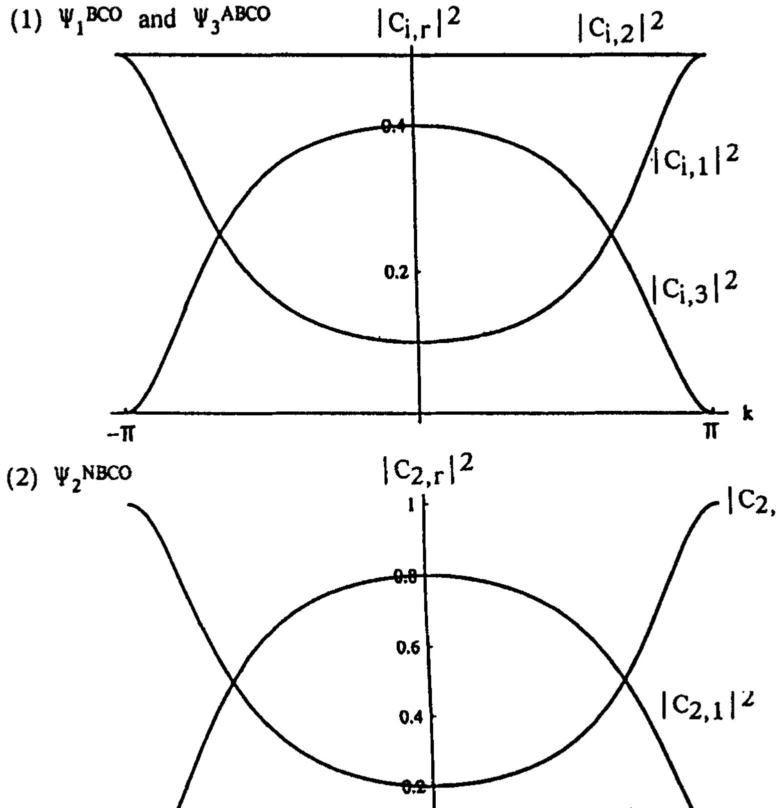

FIGURE 5 Probability amplitudes of the bonding (band index 1), antibonding (band index 3), and nonbonding (band index 2) traveling waves (crystal orbitals). $C_{i,r}$ stands for the amplitude coefficient of the r site in the i band.

3N π-electrons each of which belongs to each 2pπ atomic orbital of the carbon site (l,r) of the system occupy these two low-lying bands in the ground state of the system. The 2N electrons can be accommodated antiferromagnetically pairwise in the bonding band (bonding crysatl orbital: BCO) and the remaining N electrons in the N-fold superdegenerate nonbonding band (NBCO) at zero energy. Delocalized nature is one of the salient features of this topologically superdegenerate π-nonbonding band in the infinite system. At zero absolute temperature the system is expected to undergo being ferromagnetic. All the N electrons energetically favor spin parallel alignment in the N-fold superdegenerate zero-energy band characterized by zero bandwidth if the sizable or robust spin polarization of the system is fulfilled. The underlying mechanism for this spin alignment is termed as topologically controlled spin polarization in organic polymeric spin systems. The basic idea behind the mechanism is closely related to the topological dynamic spin polarization for organic high-spin molecules as finite systems. The mechanism is an infinite version of the topological dynamic spin polarization. Nevertheless, it should be emphasized that it is not necessarily a simple extension from the dynamic spin polarization for finite systems, when we interpret spin structures of the polymeric spin system in order to predict magnetic properties of the system in terms of microscopic descriptions. Physical properties unpredictable straightforwardly from finite systems naturally originate in inter-segment interactions introduced in the traveling wave approach. For higher-dimensional infinite systems, additional inter-polymer interactions are responsible for the unpredictable properties.

The salient features inherent in polymeric spin systems have already appeared in Figure 5. The probability amplitudes of the traveling wave in the k-space vary, particularly $|C_{i,3}|^2$ (band index i=1,3) at the carbon site 3 of the bonding and antibonding bands and $|C_{2,1}|^2$ at the site 1 of the nonbonding band, are vanishing at $j= \pm N/2$ ($\cos k = -1$), where the corresponding state density becomes extremely large. The amplitude $|C_{2,2}|^2$ is vanishing because no electron correlation is considered. It turns out that within the framework of the present simplified treatment the π spin densities ρ_1 and ρ_2 on the carbon sites 1 and 2, respectively, vanish at the same point even if electron correlation is taken into account as shown in Figure 6. The results show that the spin characteristic of the hydrocarbon-based polymeric model in Figure 3 cannot be simply attributed to the side-chain 1/2-spin type, but a spin characteristic of whole one 1/2-spin on the backbone chain type features in the infinite system. Figure 6 clearly illustrates the underlying nature of polymeric magnetic systems which cannot be predicted from intuitive considerations of finite magnetic molecules. The behavior of the spin density distribution of polymeric spin systems with extended π-conjugation becomes much more complicated, featuring in the organic magnetic polymer systems. This complication arises from the topological nature of intra- and inter-polymer interactions in higher-dimensional structure

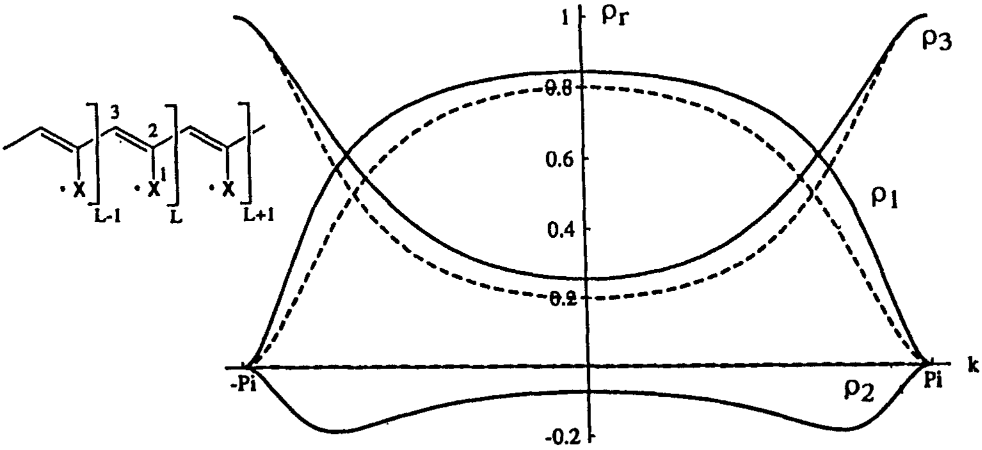

FIGURE 6 k-Space representation of the π spin density ρ_r (r=1,2,3) on the carbon site r of the 1D polymeric spin system (see Figure 3). Solid and broken curves denote the calculated π spin densities with and without electron correlation, respectively.

and will be illustrated later.

Let us briefly summarize the systems where the X spin site is hetero-atomic or comprises an inner segment structure with more or less spin polarization such as various pheoxyl radicals and phenyl nitroxides. Band-structure calculations in terms of the traveling wave approach predict as follows. If the systems are characterized by rather weak spin polarization and their spin site is hetero-atomic, their nonbonding band is expected to undergo stabilization below zero energy, but antiferromagnetic spin alignments in the k= ±π region hamper the ferromagnetic property of the systems. In some cases with topologically controlled but weak spin polarization the systems only show paramagnetism since inter-polymer antiferromagnetic contacts dominate intra-polymer ferromagnetic spin alignments. On the other hand, some interesting hetero-atomic effects feature in the relative order of bonding and nonbonding bands. The hetero-atomic effect appears in diminishing their band energy gaps between the NBCO and the nearby BCO, predicting modulations of thermal and optical properties of magnetic polymer systems. Systematic studies in this direction of the research on the experimental sides will be required.

Next, in terms of the traveling wave approach we consider a series of polymeric model spin systems for the through-bond approach whose spin alignment of their high-spin oligomers and molecules have been extensively studied for more than the last two decades. Figure 7(a) illustrates the calculated band structure of the first model ferromagnetic polymer(see Figure 2) whose segment is comprised of *m*-benzyl

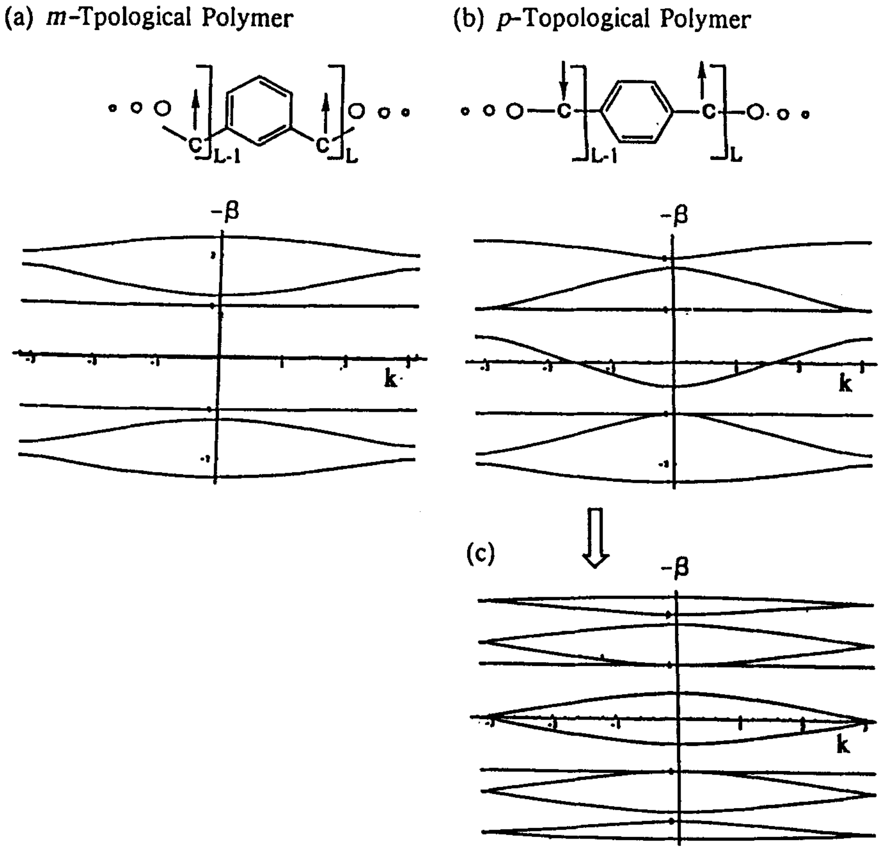

FIGURE 7 Band structures of quasi-1D π-topological magnetic polymers (a) and (b) with the m- and p-benzyl segment, respectively. (a)The first documented model ferromagnetic polymeric system. (c)The p-topological polymer (b) undergoes Piels-type destabilization via the dimerization of the segment.

radical. Figure 7(b) shows the band structure of a p-topological isomer of the m-topological model polymer in Figure 7(a). Figures 7(a) and 7(b) clearly illustrate a marked difference in the nonbonding band structure appearing at and around zero energy. The m-topological polymer constitutes the N-fold superdegenerate nonbonding band with an infinitely thin bandwidth and its delocalized nature, which guarantees robust positive spin-exchange interactions in the half-filled NBCO. In contrast, the p-topological polymer gives rise to the non-degenerate nonbonding crystal orbital band with a large bandwidth. Each nonbonding band is the highest occupied one which accommodates N π-electrons in the ground state of the topological polymer. It turns out that the ferromagnetic ground state is expected to occur for the one-dimensional *m*-topological polymer at infinitely zero temperature while the antiferromagnetic state for the *p*-topological one. Thus, the *m*-topological polymer is a candidate for superparamagnets. The possible occurrence of spin wave states for the *m*-topological polymer has been discussed in terms of the Kondo-Hubbard model Hamiltonian approach.[14] The above contrast arises from the topological nature of π-electron network in the infinite system. This contrast becomes further enhanced if bond alternation is taken into account, as shown in Figure 7(c). The bond alternation undergoes the dimerization of the segment for the *p*-topological polymer, giving rise to Peierls-type destabilization of the *p*-topological polymer and leading to the diamagnetic ground state. Such destabilization will not occur for the *m*-topological polymer.

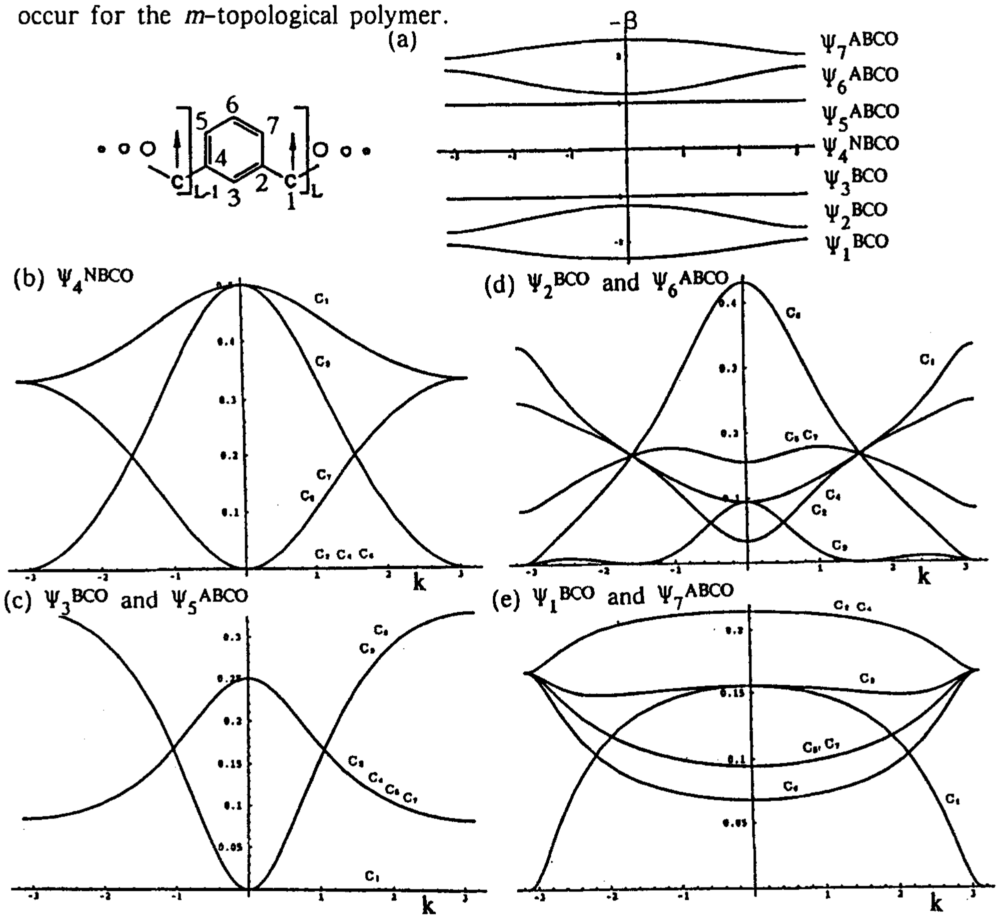

FIGURE 8 Spin density and probability amplitude coefficient at the carbon site r, $|C_{i,r}|^2$ of the crystal band i of the *m*-benzyl-based ferromagnetic model polymer. (a) Band structure. (b) Spin densities, $|C_{4,r}|^2$ of the NBCO. No electron correlation is considered.

Figure 8(c)-(e) and 8(b) depicts the probability amplitude coefficients $|C_{i,r}|^2$ describing their traveling wave pattern and the π-spin density distribution on the carbon sites of the *m*-topological polymer in the k-space, respectively, showing that the similar features mentioned above for the three-carbon-site model appear and that a simple extension of the dynamic spin polarization does not work. The topological polarization fluctuates in the k-space of the extended polymeric system, as shown in Figure 8(b) and (c)-(e). We only stress here that in order to have more realistic physical pictures for magnetic polymer systems statistical mechanics oriented treatments based on microscopic description can apply to polymeric magnetic systems. The traveling wave approach also predicts that a series of *p*-topological polymers characterized by extended π-conjugation of segments manifest paramagnetism in some favorable cases. Either inter-polymer antiferromagnetic or ferromagnetic interaction hampers their intra-polymer magnetic properties, but the possible occurrence of organic polymer spin-glass states results from amorphous magnetic polymer materials based on extended π-conjugation polymers.

Two-Dimensional Infinite or Extended Polymeric Spin Systems: Topology of Inter-Polymer Contacts (Inter-polymer Connectedness)

Finally, let us consider two-dimensional magnetic polymer systems in terms of the traveling wave approach, focusing on inter-polymer connectedness. Figure 9 illustrates in the **k**-space the band structure of the first two-dimensional ferromagnetic model polymer with topologically controlled robust spin polarization. The band structure manifests the C_3 translation symmetry of the system. The NBCO appearing at zero energy with both an infinitely thin bandwidth and delocalized nature corresponds to the highest occupied band, which accommodates N parallel π-spins in the ground state. Because of the robust spin polarization stemming from the topology of the π-conjugation of the segment this two-dimensional polymer is expected to be a high-Tc organic ferromagnet or a superparamagnet in certain materials conditions. Also due to the particular topology of the π-conjugation and inter-segment linkage mode the lowest antibonding and highest bonding bands are characterized by infinitely thin bandwidths. Both the probability amplitudes on the carbon site in each crystal orbital and the spin density distribution in the zero energy traveling wave (NBCO) are modulated in a complex fashion in the two-dimensional **k**-space, closely depending on the inter-segment linkage mode in this model polymer.

In order to gain a physical insight of general features of this modulation the most possibly simplified two-dimensional model polymer can be a quasi two-dimen

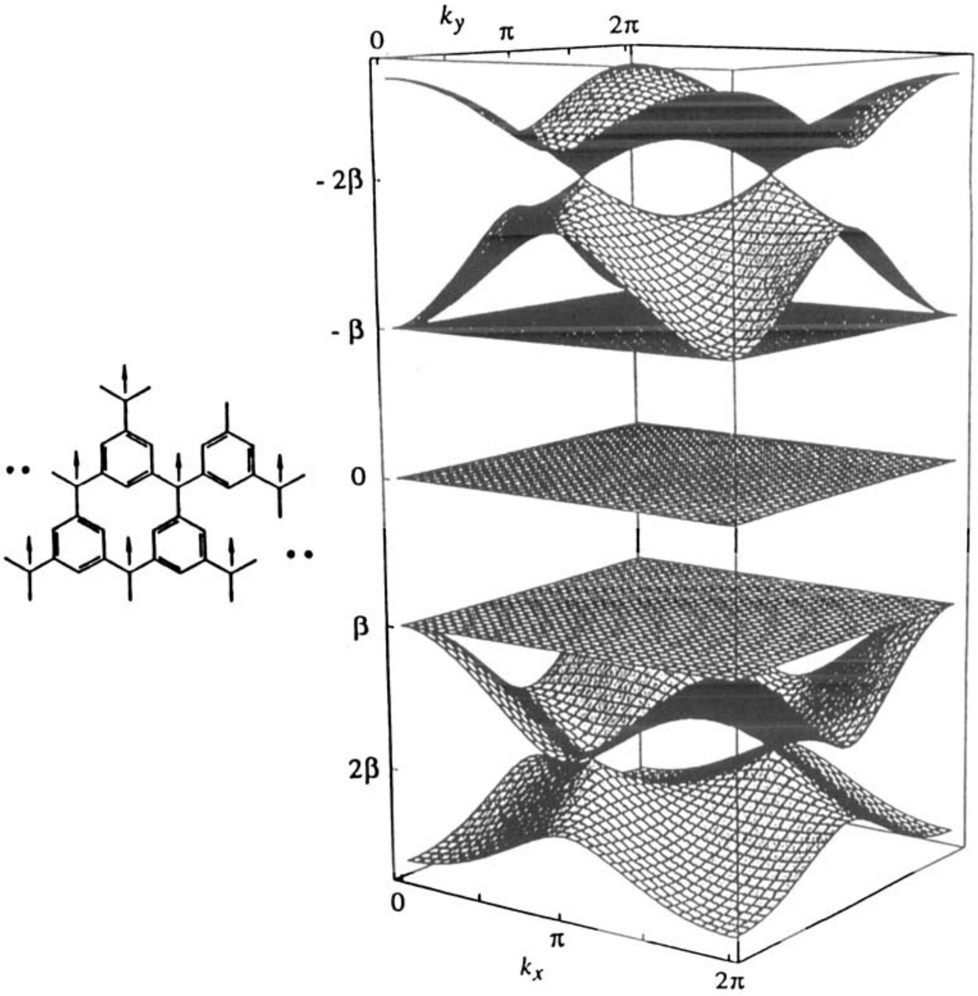

FIGURE 9 2D k-space representation of the band structure of the first two-dimensional polymeric model spin system for organic ferromagnets and superparamagnets. The NBCO appearing at zero energy manifests an infinitely thin bandwidth and delocalized nature. Infinitely thin bandwidths feature also in the lowest unoccupied ABCO and the highest occupied BCO.

sional one which is comprised of the *m*-topological polymer in Figure 7(a), and which has an antiferromagnetic contact between the site 3 of one segment and the site 6 of the nearest-neighbor segment. The 3 and 6 site-contact constitutes the translation symmetry of the z component of the wavevector k, as shown in the inset of Figure 10. The N-fold superdegenerate nonbonding zero-energy band with N delocalizing π-electrons still keeps an infinitely thin bandwidth, predicting the ferromagnetic ground state and possible purely organic superparamagnets in certain materials conditions. On the other hand, the lowest antibonding and highest bonding

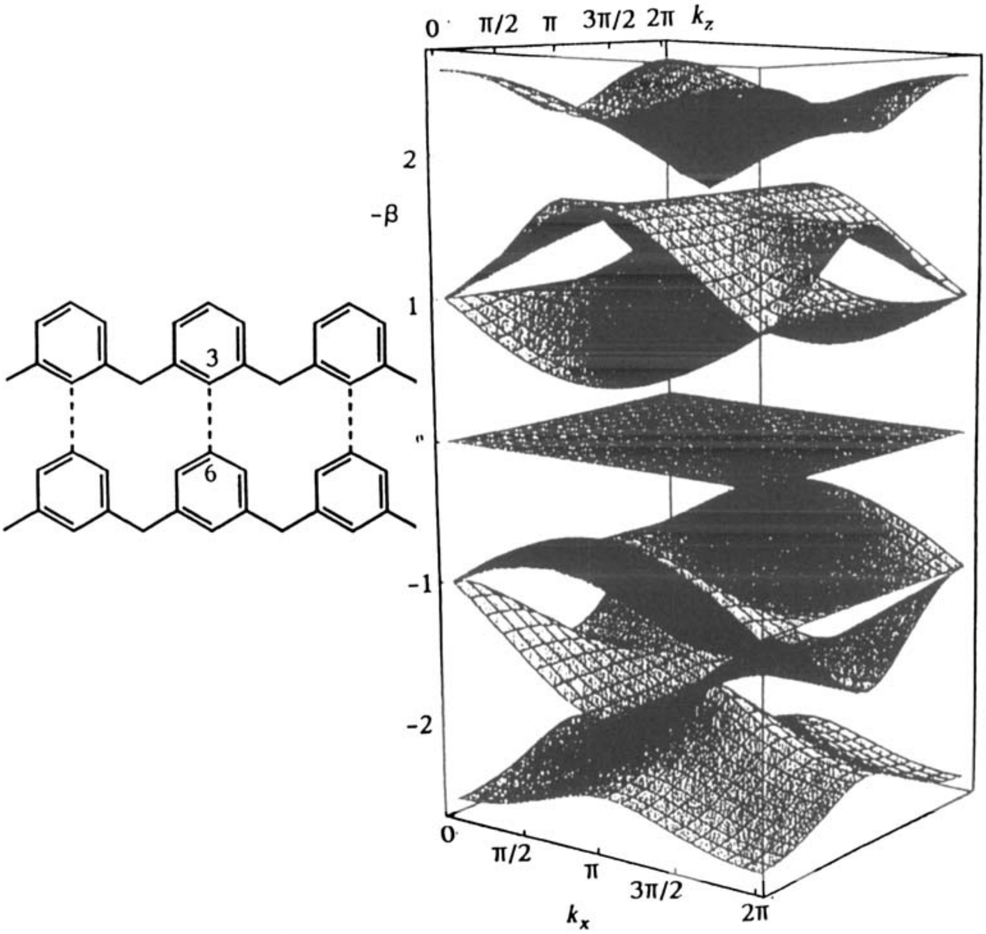

FIGURE 10 2D k-space represetation of the band structure of a quasi 2D magnetic model polymer with an antiferromagnetic inter-polymer contact. The 3 and 6 site-contact is along the z component of the wavevector **k**.

bands are strongly modulated through the antiferromagnetic inter-polymer (inter-1D chain) interaction and they are not superdegenerate any longer, resulting in finite bandwidths for both of the bands. The π spin density distribution on the carbon sites undergoes a considerable amount of complexion which depends on the strength of the inter-polymer antiferromagnetic contact. Lifting of the superdegeneracy is due to the large amplitude of the traveling wave at the 3 carbon site of the non-interacting one-dimensional polymer. The topology of inter-polymer contacts crucially influences the on-carbon-site probability amplitude of the traveling wave of two-dimensional polymers. An increase in the number of inter-polymer contacts gives rise to more and more complex modulations of band structures and topological spin polarization, predicting the potential multifunctionalities such as opto-spinics (optical spin-manipulated electronics) and purely organic ferromagnetic polymer conductivity inherent in extended polymeric spin systems.[29] These functionalities cannot be foreseen in a straightforward manner from the argument confined to finite organic spin systems. In real magnetic polymer materials in amorphous states there occur both competing ferro- and antiferro-magnetic inter-polymer contacts, possibly constituting multi-potential well structures as the consequence of spin frustration taking place in the bulk materials. The above physical picture of the modulation of the topologically controlled spin polarization can be an underlying microscopic mechanism behind organic spin-glass states.

As previously described, the present model approach applied to non-alternant hydrocarbon-based polymeric spin systems shows constraint. The model is applicable to most systems where one-electron terms predominates in the two-center/-one-electron approximation, but not to the systems where one-center/two-electron interaction is contributing. Hubbard model Hamiltonian approach can be invoked in order to predict intriguing materials properties of the latters.

A VB PICTURE OF SPIN STRUCTURES OF INFINITE POLYMERIC SPIN SYSTEMS IN TERMS OF TRAVELING WAVE/CRYSTAL ORBITAL APPROACH

In this section, we introduce a facile and conceptually useful method for the description of spin structures of infinite or extended organic polymeric spin systems. Particularly, in spin chemistry VB descriptions can afford a useful theoretical formalism which is not only essential for rationales for underlying mechanisms in spin alignment, but also easy to understand because of its localized nature. The method is based on a VB picture for non-interacting organic molecules in terms of molecular orbital calculation in any level of approximation.[25] The method can be readily extended to infinite systems their band structure of which is describable in terms of the traveling wave approach. A VB picture of spin structures can be described in terms of localized spin structures, i.e., atomic orbital (AO)-based Slater determinants $|\cdot\cdot\chi_r\cdot\cdot\bar{\chi}_s\cdot\cdot|$ where the π AOs are used in our tight-binding (LCAO) approximation (r and s denote atomic site numbers). In order to evaluate the relative importance of contributing AO-based Slater determinants we identify only any desired AO-based ones and calculate their contributing weights of any desired spin structures in terms of traveling wave (crystal orbital: CO) based Slater determinants

$\Sigma_k C_k | \cdot\cdot\Psi_i \cdot\cdot \overline{\Psi}_j \cdot\cdot |_k$, where i and j denote band indexes for crystal orbitals accommodating α spin and β spin, respectively. The employed methodology is general, but the degree of the numerical accuracy obtained depends on the level of approximation of the traveling wave solution. Usually, the different-spin-for-different-orbital (DODS) approach tends to enhance the difference in the relative contribution from various important AO-based determinants,[25c] nevertheless, the generalization is not simple in the k-space. The contribution of any desired AO-based Slater determinant $| \cdot\cdot\chi_r \cdot\cdot \overline{\chi}_s \cdot\cdot |$, which is defined as $<| \cdot\cdot\chi_r \cdot\cdot \overline{\chi}_s \cdot\cdot \| \cdot\cdot\Psi_i \cdot\cdot \overline{\Psi}_j \cdot\cdot |>$, can be evaluated by decomposing CO-based Slater determinants $| \cdot\cdot\Psi_i \cdot\cdot \overline{\Psi}_j \cdot\cdot |$, which we can identify for a particular state of the system under study, into the components, i.e., AO-based Slater determinants.[29] The magnitude and phase of the contribution from any desired AO-based determinant are obtained. The magnitude gives the relative weight of the desired localized VB spin structure in the identified CO-based Slater determinants. The phase can be interrelated to the group-theoretical symmetry of the system.

To illustrate the usefulness of the method, we return to the one-dimensional model polymer in Figure 3. Figure 11 depicts in the k-space the contribution of three wanted VB spin structures (A), (B), and (C) which correspond to localized spin structure, $|\chi_1\overline{\chi}_2\chi_3|$, $|\chi_1\chi_2\overline{\chi}_3|$, and $|\overline{\chi}_1\chi_2\chi_3|$, respectively. We assume that in the ferromagnetic ground state the N-fold superdegenerate nonbonding crystal orbital accommodates N π-electrons with all α spins. The contributions W_i (i = A, B, C) from the spin structure (A), (B), and (C) are given as

$$W_A\text{: } <|\chi_1\overline{\chi}_2\chi_3 \| \Psi_1\overline{\Psi}_1\Psi_2|> = -(1+4\cos k)/(3+2\cos k) \qquad (12)$$

$$W_B\text{: } <|\chi_1\chi_2\overline{\chi}_3 \| \Psi_1\overline{\Psi}_1\Psi_2|> = -(1+\cos k)/(3+2\cos k) \qquad (13)$$

$$W_C\text{: } <|\overline{\chi}_1\chi_2\chi_3 \| \Psi_1\overline{\Psi}_1\Psi_2|> = 1/2(3+2\cos k) \qquad (14)$$

in the k-space, respectively. They are the exact analytical solution for the simplified linear chain model polymer in Figure 3. Figure 11 shows that the VB spin structure (A) is dominant in the most region of the k-space but not in all the space, particularly for $k = \cos^{-1}(-1/4)$ the VB spin structure (A) is not a leading one any longer, and the other two structures predominate, although the corresponding state density is relatively small. For the finite system with the same segment structure the contribution of the VB spin structure corresponding (A) predominates. Thus, the finding that the VB spin structure (A) does not always predominate in the infinite system cannot be expected from an intuitive extension of the results for the

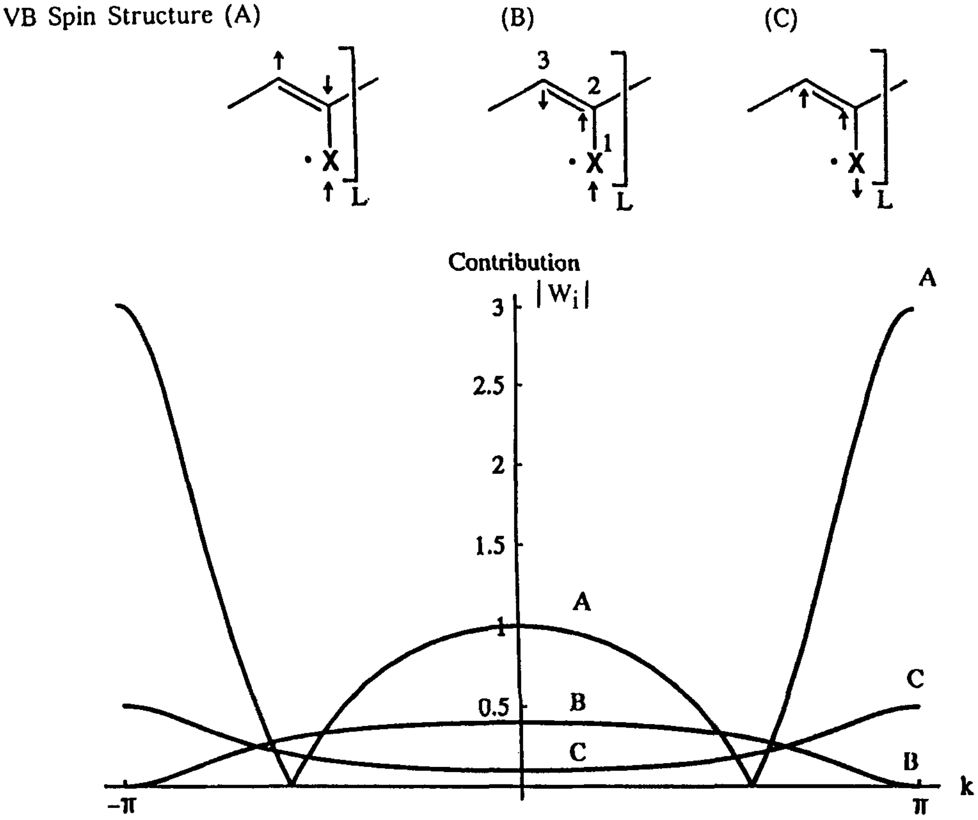

FIGURE 11 k-Space representation of the contributing localized VB spin structures of the one-dimensional polymeric model spin system as shown in Figure 3. Solid curves show the weights W_is of the contributing structures in the ferromagnetic ground state.

finite one. On the other hand, for $k = \cos^{-1}(-1)$ where the spin densities ρ_1 and ρ_2 on the site 1 and 2 become zero due to the apparently vanishing electron correlation effect, the VB spin structure (A) is dominant in nearly one order of magnitude. Totally, the localized VB spin structure (A) featuring in the infinite system expounds that the robust topological spin polarization (π-spin density wave) takes place in the ferromagnetic ground state. Naturally, in the VB picture the contributing weight of a particular AO-based spin structure undergoes fluctuation in the k-space as the physical consequence of the inter-segment interaction in the present infinite system.

CONCLUSIONS

Infinite or extended organic polymeric spin systems have been treated in terms of electronic band structure calculations, illustrating that concepts inherent in the infinite systems are required in order to disclose their potential physical properties and to design intriguing organic multifunctionality materials. The simplified traveling wave (crystal orbital) approach has been invoked to obtain band-structure pictures. The concepts obtained in this work serve for expounding underlying mechanisms of spin alignment in novel extended organic polymeric spin systems. Simple and intuitive extensions from the results for finite systems are not applicable to the infinite spin systems.

The context of a polymer version of the topological π-spin polarization has been described which is interrelated to the topological superdegeneracy of nonbonding crystal orbitals (traveling waves) of one- and two-dimensional infinite or extended organic polymeric systems. Inter-polymer contacts between the polymeric spin systems have been elucidated in the context of the topology of the contacts, i.e., the inter-polymer connectedness, exemplifying two-dimensional polymeric model spin systems. The occurrence of the contacts gives rise to the prominent modulation of band structures, and as a result, topological spin polarizations, showing the possible utilization of the various types of contacts in materials design for novel functionality polymeric spin systems, as models for spinics (= spin manipulated electronics) devices.

A k-space VB representation of infinite or extended organic polymeric spin systems has been made for the first time, showing that the localized VB spin structure with π-spin density wave characteristics features in a one-dimensional model magnetic polymer systems. The VB representation has disclosed such physical aspects inherent in infinite spin systems that cannot be expected from the simple or intuitive extension obtainable for finite spin systems. It has turned out that the VB localized model is useful in understanding the spin structure in infinite spin systems and the method invoked in this work is general and facile in order to obtain their VB picture.

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15. The first conceptual advance in organic magnetism can date back to the two proposals of its possible occurrence on the theoretical side.[1,2] The two proposals are based upon completely different theoretical grounds. The other approach exploits intermolecular interaction such as charge-transfer interaction between organic donors and acceptors, where subtle crystal packing modes are required to be controlled and tuned in crystalline solids[2] (through-space approach/McConnell-Breslow's approach). It is not until recently that the first purely organic crystalline ferromagnet (Curie temperature Tc~0.6K) based on a through-space approach has been found (Kinoshita-Sugano-Awaga model).[16] The molecular building spin block was a neutral doublet radical, *p*-nitrophenyl nitronyl nitroxide. The through-space approach associated with crystal packing modes includes Yamaguchi model where CT components have stable doublet radical moieties.[12a-c] Yamaguchi model can be termed as a CT-radical hybrid approach while the through-space approach originally proposed by McConnell[2a] and various modified varieties[17-20] can be termed as genuine CT approaches. Quite recently, a novel

through-bond approach to polymeric organic ferromagnets has been proposed[21] (polaronic ferromagnet approach), where doping processes of diamagnetic polymers designed in terms of the π-topological symmetry of conjugated systems give rise to ferromagnetically coupled spins induced in the π-systems. Molecular design of diamagnetic polymers employed in this approach is also based upon the π-topological symmetry argument which is essentially the same as in the topological spin polarization approach (Itoh-Mataga's approach). One of the strong motivations behind Fukutome's polaronic ferromagnet approach is to find a way to organic ferromagnetism without exploitation of chemically reactive spin sites during the course of synthetic or preparation processes. A challenging and elaborate experiment by Dougherty's group has demonstrated the occurrence of high-spin ground states from a doped polymer.[22] It turned out that the magnetic polymer employed was air-sensitive, hampering the originally proposed advantage. This through-bond approach is required to undergo further detailed evaluation of magnetic properties and electronic spin structures of model polymers from the microscopic viewpoint.

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