Copyright © 2001 by Humana Press Inc.
All rights of any nature whatsoever reserved.
0273-2289/01/9601-3/0135/$12.25

Theoretical Study of Electronic Structures and Conduction Properties of Copolymers Based on Poly(cyclopentadienylene)

A. K. Bakhshi*,[1] and Pooja Rattan[2]

[1]*Department of Chemistry, University of Delhi, Delhi 110007, India, E-mail: akabakhshi@yahoo.com; and*
[2]*Department of Chemistry, Panjab University, Chandigarh 160014, India*

Abstract

Various quasi-one-dimensional superlattices (copolymers) $(A_mB_n)_x$ of two novel donor-acceptor polymers PPDCF ($[A]_x$) and PPDCN ($[B]_x$) based on poly(cyclopentadienylene) (PPD) and belonging to the class of type II staggered superlattices were investigated using a negative factor counting method in the tight-binding approximation. Both PPDCF and PPDCN consist of a bicyclopentadienylene unit bridged by an electron-accepting group $>C=CF_2$ in PPDCF and $>C=C(CN)_2$ in PPDCN. The trends in the electronic structures and conduction properties of the copolymers $(A_mB_n)_x$ as a function of the block sizes *m* and *n*, arrangement of the units (periodic or random) in the copolymer chain, and length of the copolymer chain are discussed.

Index Entries: Conducting polymers; electronic structure; conduction properties; superlattice; designing of polymers; band gap.

Introduction

Among the various strategies presently followed for designing novel conducting polymers, one very exciting possibility is provided by the donor-acceptor polymers based on the approach suggested by Havinga et al. *(1)*. The principal idea behind this strategy is that the conjugated polymers with alternate donor and acceptor moieties in the main chain are expected to have a small band gap. Using this approach, novel thermally stable polymers, polysquaraines, and polycroconaines, with band-gap values as low as 0.5 eV, and poly-4H-cyclopenta-dithiophene-4-one (PCDT) and polydicyano-methylene-cyclopenta-dithiophene (PCNTh), the two polymers with experimental band-gap values of 1.2 and 0.8 eV, respectively, have been synthesized *(2,3)*. We have recently proposed on the basis

*Author to whom all correspondence and reprint requests should be addressed.

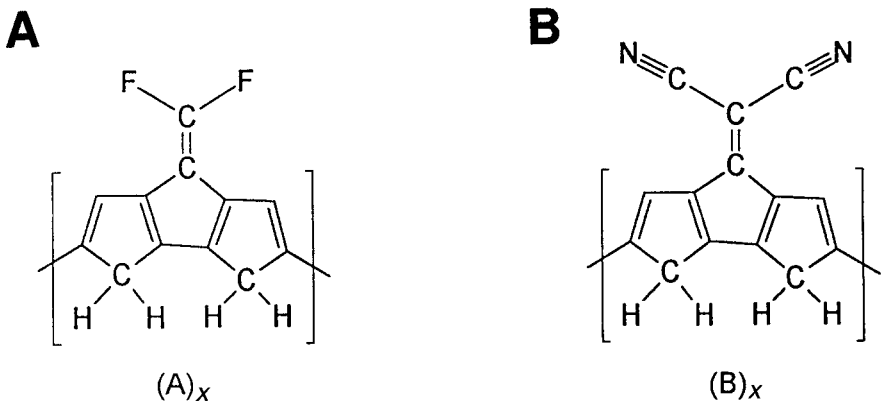

Fig. 1. Schematic structures of **(A)** PPDCF and **(B)** PPDCN.

of ab initio Hartree Fock crystal orbital method two small band-gap donor-acceptor polymers based on poly(cyclopentadienylene) (PPD) *(4)*. The repeat unit of these polymers is a bicyclopentadienylene unit bridged by an electron-accepting group Y (Y is $>C=CF_2$ in PPDCF and $>C=C[CN]_2$ in PPDCN) (Fig. 1), and, therefore, these polymers can be considered as $-CH_2$-containing analogs of PCDT and PCNTh. Our results have shown that the presence of weakly interacting CH_2 group in these two polymers considerably improves both their intrinsic and extrinsic conductivities. Using these band structure results as input, we report in this article the results of the electronic structures and conduction properties of various periodic and random copolymers (quasi-one-dimensional superlattices) of PPDCF and PPDCN using the negative factor counting method in tight-binding approximation.

Depending on the band alignments of the two constituent polymers, quasi-one-dimensional copolymers (polymeric superlattices) such as the inorganic superlattices are divided into four types *(5)*: type I, type II staggered, type II misaligned, and type III (Fig. 2). The band alignments of the two component homopolymers (PPDCF and PPDCN) show that they belong to the class of type II (staggered) superlattices (Fig. 3). The values of the two fundamental parameters, the conduction band discontinuity ΔE_c, and the valence band discontinuity ΔE_v controlling the electronic properties of the PPDCF-PPDCN copolymers are 1.321 and 0.898 eV, respectively. (ΔE_c is defined as the difference in the electronic affinities of the two components, while ΔE_v equals the corresponding difference in the ionization potentials). Since the ab initio Hartree Fock crystal orbital method is known to overestimate the electronic properties owing to the basis set truncation and neglect of correlation effects, the results given herein should be considered only as qualitative predictions referring to a stretched energy scale. The results obtained are expected to provide important guidelines for the synthesis of the copolymers of PPDCF and PPDCN with tailor-made conduction properties.

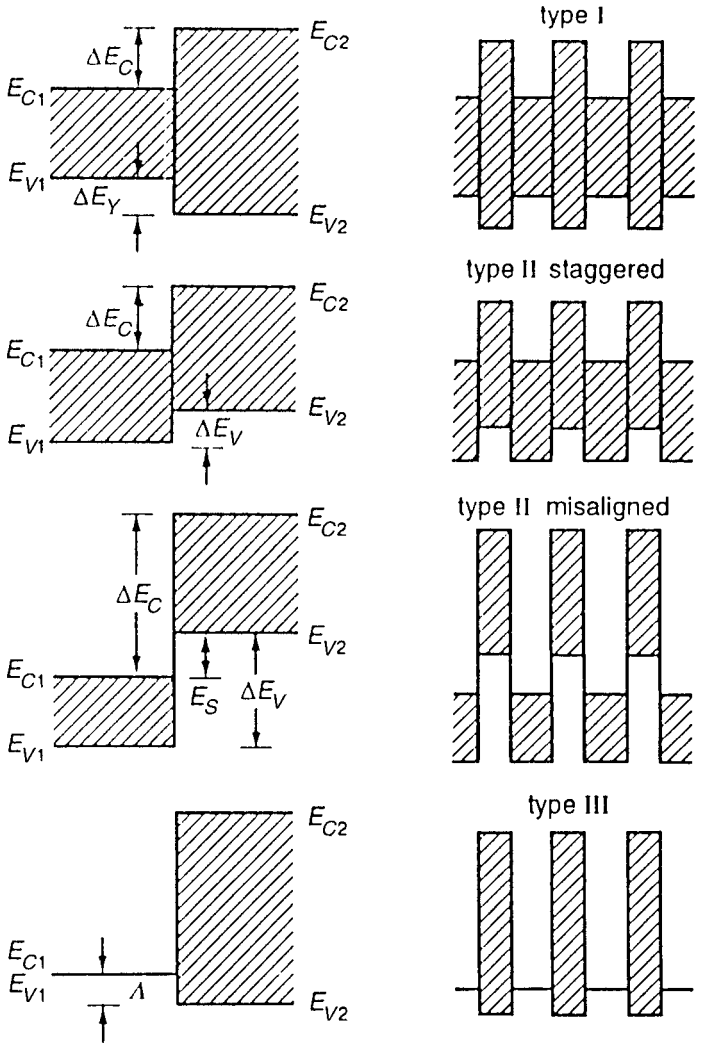

Fig. 2. Types of superlattices.

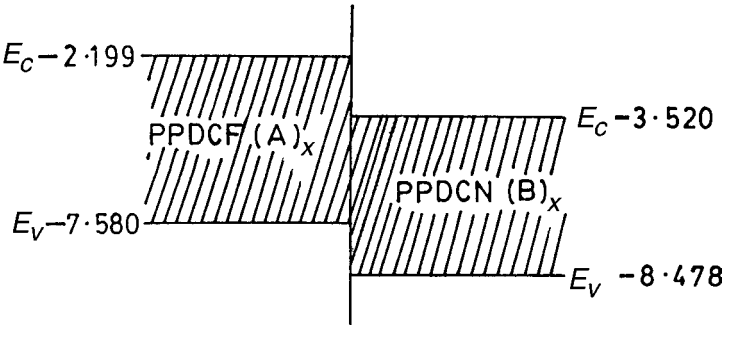

Fig. 3. Band alignments of PPDCF and PPDCN.

Methodology

The electronic density of states (DOS) of a quasi-one-dimensional copolymer $(A_mB_n)_x$ chain can be determined using a simple negative factor counting method *(6,7)* based on Dean's eigenvalue theorem *(8,9)*. The DOS are determined from the secular determinant that is tridiagonal in the case in which only first-neighbor interactions are taken into account (tight-binding approximation). The number of eigenvalues of the tridiagonal secular determinant, which is smaller than a given trial energy λ, equals the number of negative factors $\varepsilon_i(\lambda)$ obtained by the following relations:

$$\prod_{i=1}^{N} (\lambda_i - \lambda) = \prod_{i=1}^{N} \varepsilon_i(\lambda) \tag{1}$$

$$\varepsilon_1(\lambda) = \alpha_1 - \lambda \tag{2}$$

$$\varepsilon_1(\lambda) = \alpha_1 - \lambda - \frac{\beta_j^2}{\varepsilon_{i-1}(\lambda)} \tag{3}$$

Equations 2 and 3 are obtained by transforming the tridiagonal determinant into a didiagonal determinant by applying successive Gaussian eliminations. α_i and β_j are the diagonal and off-diagonal matrix elements, respectively, of an effective one-electron Hamiltonian, and λ is its eigenvalue. The diagonal (α) and off-diagonal (β) matrix elements of the secular determinant are determined from the corresponding band structure results of each component (PPDCF and PPDCN) *(4)* constituting the copolymer chain. The band structure results of PPDCF and PPDCN were obtained on the basis of the ab initio Hartree Fock crystal orbital method using their geometries *(4)* that were obtained from the MNDO-AM1 solid-state calculations considering all the valence electrons. For all the geometry optimizations, the polymers were assumed to possess planar conformations, except the hydrogen atoms attached to sp^3-hybridized carbon atoms. The unit cells of both PPDCF and PPDCN consist of three fused rings, containing two electron-donating ($>CH_2$) and one electron-accepting ($>C = CF_2$ in PPDCF and $>C = C[CN]_2$ in PPDCN) groups (Fig. 1). The helical angle for the polymer chain is 180°. The computations were performed using Clementi's 7s/3p minimal basis set for the heavy atoms and four primitive Gaussian functions contracted to one s function for the hydrogen atoms. For a given band, α of a component is taken to be the middle point (or weighted middle point) of the corresponding band, assuming the dispersion of the band to be given by the simple relation

$$\varepsilon_A(K) = \alpha_A + 2\beta_{A,A}\,\mathrm{Cos}(Ka) \tag{4}$$

in which $\beta_{A,A}$ is taken to be one-fourth of the bandwidth if the same component is repeated. If, on the other hand, component A is followed by compo-

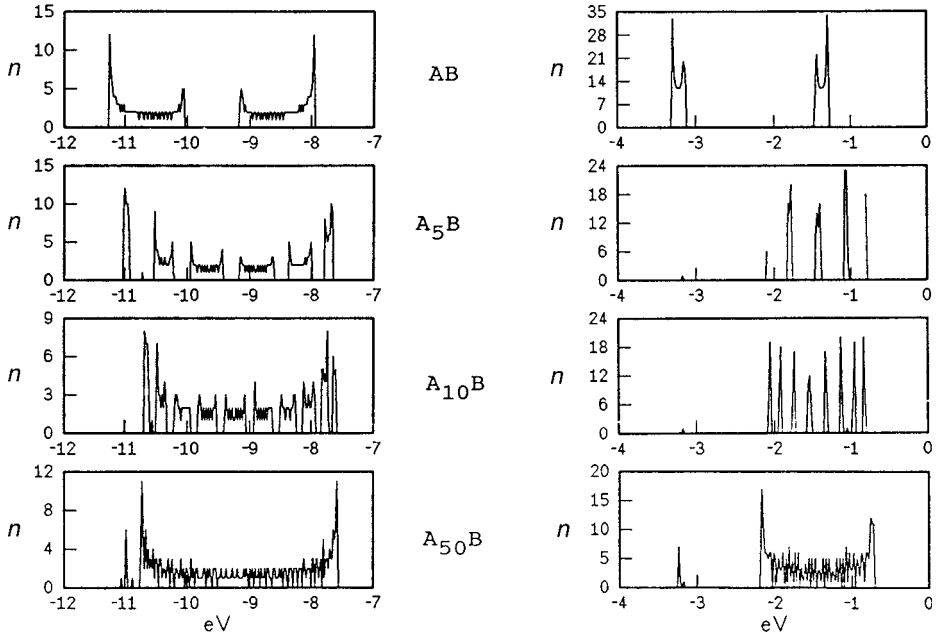

Fig. 4. DOS curves of some periodic block copolymers (energy in electron volts; *n* is the number of states). A = PPDCF; B = PPDCN.

nent B, then the off-diagonal matrix element $\beta_{A,B}$ is assumed to be given by the simple relation

$$\beta_{A,B} = \tfrac{1}{2}(\beta_{A,A} + \beta_{B,B}) \quad (5)$$

The DOS calculations were done for a chain of 300 units using an energy grid of 0.02 eV.

Results and Discussion

The copolymers we studied were modeled on the basis of the general formula $(A_mB_n)_x$ in which *m* and *n* are the block sizes of A and B, respectively (in which $[A]_x$ = PPDCF and $[B]_x$ = PPDCN). Three types of copolymers were studied: $(AB_n)_x$ with $m = 1$; $(A_mB)_x$ with $n = 1$; and $(A_mB_n)_x$ with $m = n$. For each type, both periodic and random copolymers were studied. A copolymer is taken as periodic if the arrangement of repeating units is periodic, and random if this arrangement is random or aperiodic. Various sequences of the periodic and random copolymers of the three types were generated by means of a computer program.

The DOS curves for both the valence and the conduction bands of the periodic and aperiodic copolymers of the type $(A_mB)_x$ are shown in Figs. 4 and 5, respectively. The calculated electronic properties such as ionization potential (*IP*), electron affinity (*EA*), and band gap (E_g) of various periodic and aperiodic copolymer chains of the aforementioned three types are given in Tables 1 and 2, respectively.

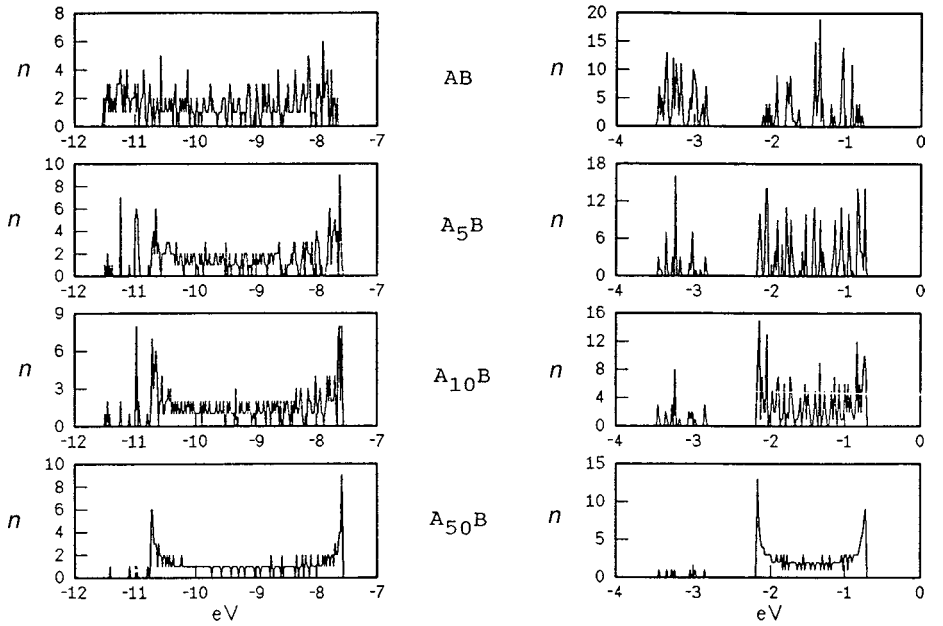

Fig. 5. DOS curves of some random block copolymers (energy in electron volts; n is the number of states). A = PPDCF; B = PPDCN.

DOS of Copolymers

In the case of periodic copolymers, the DOS curves consist of relatively narrower and well-separated peaks. In contrast, the DOS distributions of the random copolymers consist of relatively broader regions of allowed states with fewer gaps in between. The result is that the band gap for a random copolymer is less than that for the corresponding periodic copolymer. These features are a result of the continuously changing environment of a unit in a random copolymer chain in contrast to the periodic chain in which the environment of a unit throughout the chain remains the same. Since similar features are present in the DOS curves of other periodic and aperiodic copolymers, we do not show them here.

Electronic Properties

Periodic Copolymers

In the case of the $(AB_n)_x$ copolymers (Table 1), an increase in the block size n of PPDCN (B) increases both the *IP* and *EA*. The band-gap E_g is also seen to increase with an increase in block size n. Since the decrease in *IP* decreases the band gap while an increase in *EA* also decreases it, the observed increase in the band gap in these systems implies that the increase in *IP* is much more than the corresponding increase in *EA* values. It therefore means that the copolymers of $(AB_n)_x$ type become better candidates for n-doping with an increase in the block size n of B. Increasing the proportion of PPDCF (m) in the copolymer chains of the type $(A_mB)_x$, however, has the

Table 1
Calculated Electronic Properties (eV) of Periodic Copolymers[a]

		IP	*EA*	E_g
Homopolymers	$(A)_x$	7.580	2.199	5.381
	$(B)_x$	8.478	3.520	4.958
Type $(AB_n)_x$	$(AB)_x$	7.959	3.300	4.659
	$(AB_2)_x$	8.079	3.400	4.679
	$(AB_5)_x$	8.199	3.480	4.719
	$(AB_{10})_x$	8.219	3.500	4.719
	$(AB_{20})_x$	8.239	3.500	4.739
	$(AB_{50})_x$	8.239	3.500	4.739
Type $(A_mB)_x$	$(AB)_x$	7.959	3.300	4.659
	$(A_2B)_x$	7.799	3.240	4.739
	$(A_5B)_x$	7.659	3.240	4.419
	$(A_{10}B)_x$	7.599	3.240	4.359
	$(A_{20}B)_x$	7.579	3.240	4.339
	$(A_{50}B)_x$	7.579	3.240	4.339
Type $(A_mB_n)_x$	$(AB)_x$	7.959	3.300	4.659
	$(A_2B_2)_x$	7.899	3.380	4.519
	$(A_5B_5)_x$	7.719	3.460	4.259
	$(A_{10}B_{10})_x$	7.619	3.500	4.119
	$(A_{20}B_{20})_x$	7.579	3.500	4.079
	$(A_{50}B_{50})_x$	7.579	3.500	4.079

[a]A = PPDCF; B = PPDCN.

opposite effect; that is, both *IP* and *EA* values decrease while the band gap decreases and are therefore better intrinsic conductors and better candidates for p-doping.

The band gap is also found to decrease with an increase in the block size of PPDCF (m) and PPDCN (n) for a given composition m/n. This decrease in the E_g values of the copolymer chain, however, is the result of a decrease in the *IP* and an increase in the *EA*. An increase in the block sizes m and n for a given composition has, therefore, the effect of increasing both the intrinsic conductivity and dopantphilicity (both p- and n-) of the copolymer. In the case of these copolymers, the calculated band-gap values are found to be largely determined by the low band-gap component PPDCN (E_g = 4.958 eV) rather than the other (PPDCF) (E_g = 5.381 eV), and although both *IP* and *EA* values lie generally between those of PPDCN and PPDCF, E_g values are found to be generally lower than that of PPDCN.

Random Copolymers

From Table 2 one can see that the trends in the electronic properties of the random copolymers are nearly similar to those for the corresponding periodic chains except that in the random copolymers, the saturation in the electronic properties is reached much faster. This is owing to the fact that some blocks of sufficient size n of the low band-gap component PPDCN will occur in the random sequence. However, since their probability of

Table 2
Calculated Electronic Properties (eV) of Random Copolymers[a]

		IP	*EA*	E_g
Homopolymers	$(A)_x$	7.580	2.199	5.381
	$(B)_x$	8.478	3.520	4.958
Type $(AB_n)_x$	$(AB)_x$	7.659	3.480	4.179
	$(AB_2)_x$	7.659	3.500	4.159
	$(AB_5)_x$	7.719	3.500	4.219
	$(AB_{10})_x$	7.719	3.500	4.219
	$(AB_{20})_x$	7.719	3.500	4.219
	$(AB_{50})_x$	7.859	3.500	4.359
Type $(A_mB)_x$	$(AB)_x$	7.659	3.480	4.179
	$(A_2B)_x$	7.599	3.460	4.139
	$(A_5B)_x$	7.579	3.460	4.119
	$(A_{10}B)_x$	7.579	3.460	4.119
	$(A_{20}B)_x$	7.579	3.460	4.119
	$(A_{50}B)_x$	7.579	3.440	4.139
Type $(A_mB_n)_x$	$(AB)_x$	7.659	3.480	4.179
	$(A_2B_2)_x$	7.619	3.500	4.119
	$(A_5B_5)_x$	7.579	3.500	4.079
	$(A_{10}B_{10})_x$	7.579	3.500	4.079
	$(A_{20}B_{20})_x$	7.579	3.500	4.079
	$(A_{50}B_{50})_x$	7.579	3.500	4.079

[a]A = PPDCF; B = PPDCN.

occurrence in the random chain is less, the DOS values at the band edges are relatively smaller. On the other hand, in the case of periodic copolymers, it was found that saturation in the electronic properties is not reached even for m or n = 50, because the electronic structure was found to be changing still, in particular the heights of the peaks and the distance between the peaks. By Gerschgorin's theorem, the lower edge of the conduction band cannot be lower than $\alpha_B^C - 2 \max(\beta_B^C, \beta_{AB}^C)$, in which α_B^C, β_B^C denote the conduction band parameters of the low band-gap component, and the edge of the upper valence band cannot be higher than $\alpha_B^V + 2 \max(\beta_B^V, \beta_{AB}^V)$, in which α_B^V, β_B^V denote the valence band parameters of the low band-gap component (β_{AB} is the linking parameter between the two different components). The band edge values $\alpha_i^c - 2\beta_i^c$ and $\alpha_i^V - 2\beta_i^V$ (l = 1,2) can obviously be reached for sufficiently large m and n. This means that tuning the electronic properties to certain values between PPDCF and PPDCN is easier by synthesizing periodic copolymers, while achieving an electronic property characteristic of the low band-gap component PPDCN and almost independent of PPDCF is possible by preparing random copolymers. It is interesting to note from Tables 1 and 2 that random copolymers in general have lower *IP* and E_g values but higher *EA* values than their periodic counterparts. This means that, for a given composition, random copolymers are

expected to be better candidates for both intrinsic and extrinsic conductivities than the corresponding periodic copolymers.

Note that the calculated values of band gap for various periodic and random copolymers are rather large (~4.0 eV) because the ab initio band structure results of PPDCF and PPDCN obtained using minimal basis set were used as input for these calculations. The results of ab initio band structure using minimal basis set, although reproducing the experimental trend, are known to overestimate band-gap values by a factor of 4 to 5, and, thus, the same overestimation is carried over to the band-gap values of copolymers. In view of this, the present values should be considered as qualitative predictions referring to a stretched energy scale. Although by using better basis sets and by taking into consideration electron correlation effects, the calculated band-gap values will come nearer to the experimental results, as has been observed earlier in the case of polyacetylene, such calculations are highly time-consuming, because they require, among other things, polarization functions in the basis set and a four-index transformation, followed by a transformation to Warnier functions with optimized phases.

Conclusion

We have studied systematically the electronic structures and conduction properties of periodic and random copolymers of PPDCF $(A)_x$ and PPDCN $(B)_x$, which represent the prototypes of the quasi-one-dimensional superlattices of the type II staggered. Our results show that a higher percentage of PPDCN is desirable if n-doping is desired in a copolymer. For p-doping, however, a higher percentage of PPDCF is necessary. To have a copolymer with prospects for both n- and p-doping as well as better intrinsic conductivity, increasing the block sizes of both PPDCF and PPDCN for a given composition is the best solution. Finally, random copolymers are predicted to be better intrinsic and extrinsic conductors of electricity than the corresponding periodic copolymers.

References

1. Havinga, E. E., ten Hoeve, W., and Wynberg, H. (1993), *Synth. Met.* **55–57,** 299–306.
2. Lambert, T. L. and Ferraris, J. P. (1991), *J. Chem. Soc. Chem. Commun.* 752–754.
3. Ferraris, J. P. and Lambert, T. L. (1991), *J. Chem. Soc. Chem. Commun.* 1268–1270.
4. Bakhshi, A. K. and Rattan, P. (1998), *J. Chem. Soc. Faraday Trans.* **94,** 2823–2826.
5. Smith, D. L. and Maithio, C. (1990), *Rev. Modern Phys.* **62,** 173–234.
6. Seel, M. (1979), *Chem. Phys.* **43,** 103–109.
7. Ladik, J., Seel, M., Otto, P., and Bakhshi, A. K. (1986) *Chem. Phys.* **108,** 203–214.
8. Dean, P. (1960), *Proc. R. Soc. London Ser. A* **254,** 507.
9. Dean, P. (1961), *Proc. R. Soc. London Ser. A* **260,** 263.