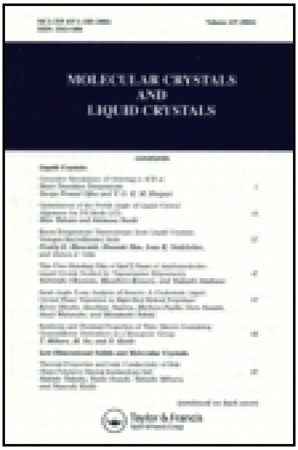

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THE EVOLUTION OF STRUCTURE DURING THE ALKALI METAL DOPING OF POLYACETYLENE AND POLY(p-PHENYLENE)

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Abstract

The progression of phases which evolve during the alkali metal doping of polyacetylene and poly(p-phenylene) is examined using newly developed structure concepts, crystal packing analysis, and diffraction and electrochemical data. At least for alkali metals larger than Li^+, at dopant concentrations above a few percent the alkali metal ions aggregate in columns within the host polymer lattice. Structural variations result for polyacetylene both from the degree these columns are filled and the chain-to-column ratio. More limited phase variation results for poly(p-phenylene), where 2,3, and 4 chain/column structures are observed, but the metal-metal spacing within the columns is fixed. Structural models are presented for the 2 chain/column complex of poly(p-phenylene) and the 3 chain/column complexes of K and Rb doped trans polyacetylene.

INTRODUCTION

Much of the important theoretical work on explaining the physics of highly conducting polymer complexes has focused on the properties of isolated polymer chains. This simplification was convenient both because of the theoretical difficulties in handling three-dimensional interactions and the absence of concrete crystal structure data for the polymer complexes. On the other hand, it is clear that carrier transport (both in the chain direction and in orthogonal directions for polymers having limited conjugation lengths) cannot be explained without incorporation of three-dimensional structure information in the theoretical models.

The problem with deriving crystal structures is that there is so little useable diffraction data obtainable for the presently available samples of conducting polymers. This difficulty is in part due to intracrystallite disorder, polycrystallinity, inhomogeneous doping, and sometimes the coexistence of more than one phase of a polymer complex.

We will here focus on identifying the sequence of structures formed during the doping of polyacetylene, PA, and poly (p-phenylene), PPP, with alkali metals. First we will develop simple structural concepts that facilitate the construction of model structures. Next we will use these concepts to propose models consistent with available data. Systematic features in the nature and evolution of structures will be of specific interest. The models proposed should be viewed as trial structures consistent with the presently available data, but with uncertainties resulting from limitations in this data. It is hoped that these structures will provide a foundation for both theoretical calculations of three-dimensional properties and future refinements of structure. Although solvating molecules are often incorporated in alkali-metal doped polymers, the present analysis and experimental data pertains to the solvent-free polymer complexes.

DEVELOPMENT OF SIMPLE STRUCTURAL CONCEPTS

It is important to realize that, with the possible exception of lithium, the alkali metals occupy channels in the polyacetylene or poly(p-phenylene) host lattice. Random distribution of alkali metal ions is precluded at alkali metal concentrations higher than at most a few percent by the high strain energies required to open cavities between parallel polymer chains.[1] These strain energies can be eliminated if the alkali metal ions aggregate into columns or layers. Layer structures, in which alkali metal ions are in nearest-neighbor proximity in a 2-D array, are excluded for these polymers by unfavorable electrostatic interactions compared with those for channel structures. For the case of alkali metal complexes of PA and PPP in which solvating molecules are present, which is not dealt with in the present work, layer structures are feasible in which the solvating species and the alkali metal ions form a layer. Similarly, we show here structures in which the alkali metal columns form layers, but the columns within these layers are separated by polymer chains.

Since we are dealing with channel structures, we can designate the structures of the alkali metal complexes in a quite simple way by the number of polymer chains per alkali metal column (m) and the number of chemical units in a chain segment with the same length as the average alkali-metal separation in the alkali metal column (n). We will show for K-doped PA and for Li-doped and K-doped PPP that m decreases with increasing dopant concentration from 4 to 3 and from 3 to 2. Only the results for m=4 are somewhat ambiguous. Lower values than m=2 are not obtained. Non-integer values of m would result only for structures which have subunits containing different chain-to-column ratios.

Integer values of n result for commensurate complexes in which all columns are equivalent. PA and PPP provide two extreme cases relevant to formation of commensurate complexes. In trans PA the chain-direction separation of CH units (1.24Å, which is over one-half the monomer repeat length) is much shorter than the shortest possible separation between metal ions (M^+) in the alkali metal column, while for PPP the center-to-center separation between phenyls (4.35Å) is within 25% of the shortest observed $M^+...M^+$ separation typical of alkali metal complexes. For example, the shortest $M^+...M^+$ separation in alkali metal-TCNQ salts is 3.50-3.69Å and the shortest $M^+...M^+$ distances in MC_6 and MC_8 graphite complexes are 4.26Å and 4.92Å, respectively.[2] Hence, a metal-metal separation equal to the chain repeat length is highly favorable (and observed, i.e., n=1) for PPP complexes, while the smallest value of n which provides a sufficiently long $M^+...M^+$ separation for polyacetylene is n=3, corresponding to a metal-metal separation of 3 x 1.24 = 3.72Å. Upper limits on n are provided by the requirement that there is not too much void space in the alkali metal columns, since it costs interchain van der Waals energy to make these columns. This energy cost should generally decrease with a decrease in the radius of the alkali metal since, decreased dimension channels are usually required. Hence, n might tend to be increased at a particular dopant level for a smaller radius ion. Values of n between 3 and 5 can be obtained for K-doped PA ($M^+...M^+$ separations of 3 x 1.24Å = 3.72Å to 5 x 1.24Å = 6.20Å), while n=2 for PPP ($M^+...M^+$ separation of 2 x 4.35Å = 8.70Å) appears to be too high. Hence, alkali-metal-doped PA displays a variety of phases which are not found for the corresponding PPP complexes. According to the present notation, the simple commensurate phases of PA are designated $(C_nH_n)_mM$ and the corresponding phases of PPP are $(C_6H_4)_mM$.

Other criteria used in the construction of model structures are that the structure should have the highest packing density consistent with non-overlapping van der Waals volumes and favorable arrangement of chains and columns to minimize Madelung energy. The latter constraint means that alkali metal columns are well separated by intervening chains, the overlap of π-orbitals (containing negative charge) of neighboring chains is minimized, the number of chains nearest-neighbor to each metal column is maximized, and carbon-metal nearest-neighbor interactions are favored over hydrogen-metal nearest-neighbor interactions. Within these constraints, the chains and dopant columns are arranged so as to reproduce the observed diffraction spacings. The longest observed diffraction spacing provides the most useful guide and the shorter spacings are checked for consistency after the model has been formulated. For the present model constructions we use the following van der Waals radii: H(1.17Å), C(1.70Å), K^+(1.33Å), and Rb^+(1.45Å).[2] For reasons discussed earlier,[3] the center of the H is located 1.04Å from the bonded carbon in these rigid atom calculations. For PPP, the geometry used is a 1.40Å in-ring carbon-carbon bond length, a 1.50Å carbon-carbon bond between phenyls, and 120° for C-C-H and C-C-C bond angles. An average C-C bond length of 1.396Å, a C-C-C angle of 125.3°, and a C-C-H angle of 117.35° are used for PA. This geometry provides the observed separation of -HC=CH- units in trans polyacetylene (2.48Å).[4]

RESULTS AND DISCUSSION

We have previously reported the structure of the $(C_nH_n)_2M$ complex, where M is Na, K, Rb, or Cs[1,2]. This is a tetragonal structure shown in Figure 1, where each alkali metal column is nearest neighbor to four polyacetylene chains.

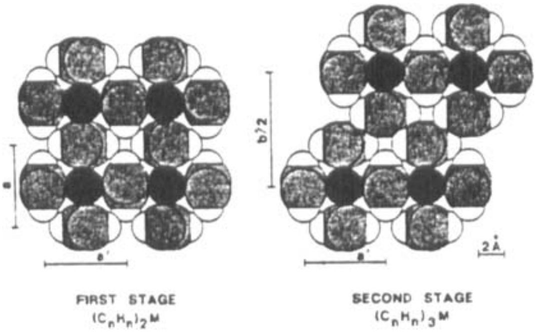

FIGURE 1 Chain-axis projection for the $(C_nH_n)_2K$ and $(C_nH_n)_3K$ complexes. The K^+ are black, the carbons are shaded, and the hydrogens are white.

As shown in Figure 1, this structure is in good agreement with the guidelines used to construct models: the structure is close packed without the existence of overlapping van der Waals volumes, negative charges on the chain are well-separated as are the alkali metal columns, and each alkali metal has maximum coordination with carbon atoms. If the alkali metal ions sit above the midpoint of carbon-carbon bonds, a location which provides calculated carbon-metal distances in very good agreement with those in graphite complexes, each alkali metal is nearest neighbor to 8 carbon atoms.[2]

A comparison of theoretical compositions calculated for commensurate phases with diffraction and electrochemical data[5] on K-doped samples suggests that there exists a range of compositions for this tetragonal phase: from $(C_4H_4)_2K$ to $(C_3H_3)_2K$ on dopant insertion and from $(C_3H_3)_2K$ to $(C_5H_5)_2K$ on dopant extraction.

This hysteresis is quite reasonable, since unfavorable kinetics for changing the chain-to-column ratio (changing m) compared with changing the filling factor of columns (changing n) can provide higher n values and lower m values at a given y for dopant extraction compared with dopant insertion. The maximum predicted dopant level (y=0.167, corresponding to $(C_3H_3)_2K$) compares well with values derived from (1) elemental analysis (y=0.17), (2) the observed meridional spacing (3.5 - 3.8Å) at maximum dopant level (y=0.16-0.18), and analysis of diffraction intensities (y=0.16-0.17).[2] The structure $(C_4H_4)_2M$ has a composition (y=0.125). This is about equal to the lowest dopant level obtained from analysis of diffraction intensities for the tetragonal phase during dopant insertion (y=0.13) and the transition point between two-phase and continuous-transformation regions in electrochemical curves (voltage versus y) during dopant insertion (y=0.12).[2,5] The same transition occurs at y=0.10 on dopant extraction,[5] a y value which equals the predicted composition for $(C_5H_5)_2K$.

A major question pertaining to the properties of doped polyacetylene is whether or not bond alternation disappears upon doping. We cannot establish on the basis of the present arguments whether or not the difference in bond lengths becomes too small for measurement. However, we can say that there are no arrangements of the alkali metal atoms for the $(C_nH_n)_mM$ structures for which all bonds are equivalent with respect to alkali metal proximity. Furthermore, the equivalence of CH groups in undoped trans-PA is removed for all but the $(C_4H_4)_2M$ structure. If the alkali metal atoms are coordinated above the midpoints of carbon-carbon bonds, with relative shifts in location of ions in columns on opposite sides of a chain so as to minimize ion-ion repulsion energies, then the sequence of bonds and CH units are, respectively, $[a_1,a_1,b_0]$ and $[A_1,B_2,A_1]$ for $(C_3H_3)_2M$, $[a_1,b_0,a_1,b_0]$ and $[A_1,A_1,A_1,A_1]$ for $(C_4H_4)_2M$, and $[a_1,b_0,b_0,a_1,b_0]$ and $[A_1,B_1,C_0,B_1,A_1]$ for $(C_5H_5)_2M$, where different small letters represent distinguishable bonds and different capital letters represent distinguishable carbon atoms for a particular phase. The subscript numbers denote the number of alkali metal ions coordinated with a particular carbon-carbon bond or coordinated with bonds associated with a particular CH unit (subscripts on small letter and capital letters, respectively). The basis for distinguishability is the proximity of alkali metal ions in the two columns surrounding each chain. Consideration of more distant ion-chain interactions will further increase the number of distinguishable bonds and distinguishable CH units.

Since n is unity for alkali-metal-doped PPP, the sequence of phases is much simpler than for the case of alkali-metal doped PA. Possible phases are $(C_6H_4)_mM$ corresponding to $C_6H_4M_y$ where y is 1.00, 0.50, 0.33, 0.25, and 0.20 for m=1,2,3,4, and 5, respectively. The maximum observed doping level from elemental analysis and from the number of coulombs passed during electrochemical doping and dopant extraction is 0.50,[5] corresponding to the 2 chain/column structure (m=2). Transitions are observed in electrochemical curves (Li and K) at the compositions expected for the m=3 and m=4 structures.[5] There is no evidence for structures having m values greater than 4 (4 chains/column).

We will now describe particular crystal packing models developed for $(C_nH_n)_3K$, $(C_nH_n)_3Rb$, and $(C_6H_4)_2K$. Although very few x-ray diffraction lines are observed for the above polyacetylene complexes, structure evaluation is made possible by the existence of a long diffraction spacing (8.0-8.2Å for K and 7.7-7.9Å for Rb) that can readily be explained using the key elements of the $(C_nH_n)_2M$ structure as building blocks for the $(C_nH_n)_3M$ structure. As shown in Figure 1, the model structure for the more dilute phase is obtained from the tetragonal $(C_nH_n)_2M$ phase by adding an additional plane of polymer chains between the dopant-containing planes - analogous to the change in going from stage 1 graphite to stage 2 graphite. While each polymer chain is nearest neighbor to two alkali metal columns in the $(C_nH_n)_2M$ structures, one-half of the polymer chains in the $(C_nH_n)_3M$ structures are coordinated with only one alkali metal column. Staging has been reported previously in acceptor-doped polyacetylene.[6,7] Also, J. Tanaka has interpreted the observation of two isobestic points in the spectroscopy of Na-doped PA as due to staging[8] and M. Fouletier et al.[9] make the same association based on their electrochemical studies of Li-doped PA.

The long diffraction spacings derived from the packing calculation (8.18Å for K and 8.34Å for Rb) are in good agreement with the observed spacings (8.0-8.2Å for K and 7.7-7.9Å for Rb). Depending upon sample preparation, there is difficulty in unambiguously separating diffraction lines at shorter spacings due to the $(C_nH_n)_3M$ phases from contributions due to undoped PA and $(C_nH_n)_2M$. Nevertheless, observed diffraction lines have positions and relative intensities that are consistent with the proposed model for $(C_nH_n)_3M$. Another complication results from the observation of a diffraction spacing at 11.7Å in some of the K-doped samples, appearing sometimes in addition to lines attributed to the $(C_nH_n)_3M$ phase. This 11.7Å line (observed, for example, in PA electrochemically doped to y=0.055) is likely due to a metastable phase, since it disappears upon annealing (150°C for 2 hrs).

The packing calculations for the $(C_nH_n)_3M$ structure provide an orthogonal cell in which the unit cell parameters normal to the chain direction are a=5.94Å, b=16.37Å for K and a=6.16Å and b=16.68Å for Rb. As shown in Figure 1, all chains have a setting angle of either 0 or 90°. The separation of polymer layers containing chains with backbones normal to the b axis are successively 5.94Å and 2.25Å for the K-complex and 6.16Å and 2.18Å for the Rb complex. Twice the sum of these numbers for each complex corresponds to the b-axis repeat length. The relative coordinates of the polymer chains in the chain-axis direction are not reliably established. The close-packed model shown in Fig. 1 results if type A chains (chains coordinated to two alkali metal columns) have carbons at a c-axis coordinate which is shifted by 2.48Å/4 relative to carbons in the type B chains (chains coordinated to one alkali metal column). Due to the smaller number of coordinating alkali metal columns for the type B chains, more of the donated charge will be on type A chains than on type B chains.

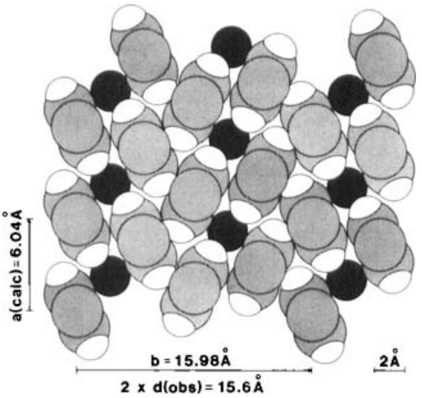

FIGURE 2 Chain-axis projection of the proposed structure for $(C_6H_4)_2K$. Atoms are designated as in Fig. 1

The structural model proposed for $(C_6H_4)_2K$ is shown in Figure 2. The longest observable x-ray diffraction spacing for this structure is calculated to be 7.99Å, the (020) reflection, which is in good agreement with the longest observed spacing for PPP heavily doped with K(7.81Å). The PPP backbone is approximated as planar, while deviations from planarity are expected due to the repulsion of the ortho hydrogen atoms. From structural studies on alkali metal complexes of the biphenyl anion, where the angle between phenyl rings is 7.2 to 9.7°,[10-11] this deviation is not of major significance for the packing analysis.

The proposed structure for $(C_6H_4)_2K$ is orthohombic (or pseudo-orthorhombic), space group P_{bam}, with a=6.04Å, b=15.98Å, and c=4.35Å (chain axis). There are four phenyls and two potassiums in this cell. The potassium is sandwiched between phenyls on parallel neighboring chains so that a perpendicular to the two rings from the center of HC-CH bonds intersects the K site, which is a center of symmetry. An alternative structure, in which the K ions sit above the center of the phenyl rings does not provide a calculated long diffraction spacing which is in agreement with the observed value. The calculated setting angle of the phenyls with respect to the (010) plane is 25.1°, which is reasonably close to the setting angle which we derive for undoped PPP (31-33°) using oligomers as model compounds. The calculated fractional cell coordinates of the center of the phenyl is (0.357, 0.147, 0.000).

The suggested coordination of K with HC-CH bonds in PPP is interesting as is the suggested occurrence of a dimer structure. Extrapolating from structural measurements on biphenyl and the biphenyl(-1) anion,[10,11] charge transfer results in dimensional changes from an aromatic structure toward a quinoidal structure. Hence, if the donated charge is largely present in bonds parallel to the chain direction, the derived coordination of the K with these bonds is reasonable. Note also from the structure of the $(C_6H_4)_2K$ complex (Fig. 2) that this coordination produces a high molecular dipole normal to the chain direction and results in three chemically-distinguishable carbon atoms, in contrast with the two chemically-distinguishable carbon atoms in the undoped polymer.

The prediction of properties based on these structural models will be the subject of future communications. This work and related electrochemical data[5] show that over most of the available composition range for PA (K-doped between $0.005<y<0.125$ on dopant insertion and $0.005<y<0.10$ on dopant extraction) and for PPP (Li or K-doped with $y>0.02$) a change in dopant concentration results in a change in the relative fraction of compositionally different phases. Therefore, a multi-phase model is necessary to explain the changing properties of these materials over most of their obtainable composition range.

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