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Applications of the chemical-molecular viewpoint in the calculation of properties of polymeric systems proved very fruitful in this project.

In the area of methodology, we have perfected the band theory code MOSOL, which is based on the semiempirical MNDO (and its closely related versions, AM1 and PM3) all developed with some AFOSR support. In the course of this work we have included a screw axis of symmetry for polymers; extended the method to metallic systems and improved the convergence of the calculations. We have introduced methodology applicable to a wide class of polymers and properties based on the oligomer approach. We have developed a new analytical theory for the calculation of the elastic modulus, Y, of polymers. →

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We have applied the methods described above for the comparative study of polysilane and a series of simple related polymers: poly(difluorosilane), poly(methylsilane), poly(dimethylsilane), poly(diethylsilane), polygermane. We have used an array of semiempirical approaches and _ab initio_ calculations followed by vibrational analysis derived that the fact that the experimental spectra correspond to somewhat disordered conformations, and that the spectrum is conformation dependent.

We have calculated the most stable geometry of several ladder type polymers. In the case of the ladder polymers the main issue has to do with whether the most stable structures correspond to the highest possible symmetry, or a broken symmetry geometry. Our calculations presented strong evidence in favor of the latter and also provided interpretation of IR, optical, ENDOR and conductivity data.

We have applied the general methodology for elastic moduli described above to _all_-_trans_-PE and various forms of PA. The agreement with experiment, where available, is excellent. In the case of _trans_-PA the result is consistent with the fact, that a conjugated polymer has a more rigid backbone than a saturated one (PE), and its Y value is larger. Surprisingly, the _cis_ conformations have a _lower_ elastic modulus. This sensitivity of a mechanical property on overall conformation of a polymer is very significant, and should be measurable. We plan to follow up on this problem by continuing elastic modulus calculations of polymers in various conformations. In contrast to the sensitivity to conformation, Y depends on charge transfer (CT) only weakly. In doped PA we calculated a mere 7% change of Y upon doping up to 0.25e/CH unit, a very high doping level. The corresponding calculations gave geometry changes in quantitative agreement with X-ray data. Consequently, the mechanical properties should not be very sensitive to the amount of charge transfer, in contrast to simplistic arguments, that CT occurs to antibonding or from bonding states. Therefore, highly conductive polymers should maintain high maximal elastic moduli and other mechanical properties, in agreement with Heeger's general observations.

FINAL TECHNICAL REPORT

TITLE: Development of Effective Quantum Chemical
           Methods for Polymers and Solids

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SENIOR RESEARCH PERSONNEL: Dr. Sung Y. Hong
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PUBLICATIONS:

[1]   "Torsional Potentials of Si.,le Polysilane Derivatives"
      Cui, C.X.; Karpfen, A.; Kertesz, M. Macromolecules 1990, 23,
      3303-3308.

[2]   "Dependence of Young's Modulus of Trans-Polyacetylene Upon
      Charge Transfer"
      Hong, S.Y.; Kertesz, M. Phys. Rev. Lett. 1990, 64, 3031-
      3034.

[3]   "Extraction of Polymer Properties from Oligomer
      Calculations"
      Cui, C.X.; Kertesz, M.; Jiang, Y. J. Phys. Chem. 1990, 94,
      5142-5179.

[4]   "Theoretical Evaluation of Young's Moduli of Polymers"
      Hong, S.Y.; Kertesz, M. Phys. Rev. B. 1990, 41, 11368-11378.

[5]   "Assignment of the Vibrational Spectra of Polysilane and its
      Oligomers"
      Cui, C.X.; Kertesz, M. Macromolecules, 1992, 25, 1103-1108.

[6]   "Electronic Structure of Heterocyclic Ladder Polymers"
      Hong, S.Y.; Kertesz, M.; Lee, Y.S.; Kim, O.-K. Chem.
      Mater., 1992, 4, 378-383.

[7]   "Geometrical and Electronic Structures of a Benzimidaxo-
      benzophenanthroline - type Polymer (BBL)"
      Houg, S.Y.; Kertesz, M.; Lee, Y.S.; Kim, O.K. (to be
      published).

[8]   "What Determines the Polarizability and Vibrational Spectra
      of Doped Poly-p-phenylene: Geometry or Charge Transfer?"
      Cui, C.X.; Kertesz, M. to be published.

Summary of results from the AFOSR grant #89-0229

Under the completed grant (AFOSR grant # 89-0229, duration from December 1, 1988 through November 30, 1991) our work has proceeded in five closely related areas. We summarize below the current status and scientific achievements in each. The following material properties were in the focus of the work:

-Conformational energetics, structural data, energetics of alternative forms;

-Vibrational frequencies and intensities;

-Electronic structure as related to linear and non-linear optical spectra, thermochromism;

-Electrochemical data as pertaining to the energy gaps of the materials;

-Elastic moduli.

1. Methodological developments

In the study of extended systems, solids and polymers, energy band theory is preeminent[1], because the use of reciprocal space (k-space) reduces the calculations to a size characteristic of the repeat unit. We have perfected such a band theory code[2], which is based on the semiempirical MNDO[3] (and its closely related cousins, AM1[4] and PM3[5]) all developed with some AFOSR support. In the course of this work we have included a screw axis of symmetry for polymers [1]*; extended the method to metallic systems [2]; and improved the convergence of the calculations.

In comparison to band theory, sufficiently large oligomer and cluster calculations can certainly provide the same quality data for polymers and solids. These are generally considered as a non-viable alternatives due to the prohibitive costs associated with large oligomers and clusters. We have found [3], however, that for a wide class of polymers and properties this is not the case, and that oligomers can provide a viable alternative to band theory, moreover for vibrational calculations the oligomer approach is superior[8]. Several authors have observed[6], that properties, such as geometry, charge distribution, or the energy per repeat unit, $E(N)$, as calculated by the finite difference method

$$E(N) = e(N+1) - e(N) \qquad (1)$$

converge very often extremely fast, and reasonable results can be had for N as small as 2. Here $e(N)$ is the total energy of the N-mer. We have shown [3] that this fast convergence is a consequence of the fast convergence of the density matrix in the middle unit cell of the oligomer. This in turn is a consequence of the fact that the oligomer molecular orbitals (MO's) can be mapped in the k-dependent crystal orbitals. By introducing an extremum condition for the functional

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*Numbers in [ ] brackets correspond to references on the summary page of the report listing papers supported by the grant.

$$X(q) = \sum_r \left| \sum_j C_{rj}(n) \, \sin(q\pi j/(N+1)) \right| \qquad (2)$$

we assigned a particular **k** value to each MO, which is defined as the q value for which X(q) is maximum. In (2) j refers to the j-th repeat unit, r to the atomic orbital in a given unit, n is the MO index, $C_{rj}(n)$ the corresponding MO coefficient. Thus a **k** value is chosen for which the MO most closely resembles an orbital with periodic boundary condition. This criterion produces well defined **k** values, as documented by the published data. This correspondence can also be used to map the MO energies to energy bands. Comparison with full band theory calculations shows that tetramers can produce quantitative results. Limitations of the approach are related to quasi-degenerate ground states and are discussed in [3].

We have developed a new analytical theory [4] for the calculation of the elastic modulus, Y, of polymers. This is based on any available force field, and its development was motivated by the fact that second derivatives of the total energy are available and used in the solid state methods described above. The calculated Y values depend on the geometry of the polymer, which is available from the calculations described above, and on the selection of the force constants. We have demonstrated, that force constants, which produce good vibrational frequencies also give excellent Y values. In this context, it is worthwhile to note, that the MNDO family of Hamiltonians is generally not accurate enough to produce reliable vibrational frequencies even if empirical scaling is used[7]. However, scaled MNDO predictions of Y values are satisfactory for planar zig-zag polymers, such as polyethylene (PE) and polyacetylene (PA), where torsion does not play a predominant role.

The new analytical theory of Young's modulus is described in detail in [4]. One of its important features is, that it allows decomposition of Y into components corresponding to various internal coordinates. This has lead to the surprising result that a large number of coordinates contribute to Y significantly. For instance, in polyethylene, 37% is due to bond length elong tion, 33% to CCC bond angle opening and the rest 30% to various coupling terms, most of which involves the seemingly innocent hydrogens. The accuracy of the approach as compared to experiment is very good, further applications to rigid rod and ladder polymers are planned.

2. Conformational energetics and vibrational properties of simple polysilanes

We have applied the methods described above for the comparative study of polysilane and a series of simple related polymers: poly(difluorosilane), poly(methylsilane), poly(di-methylsilane), poly(diethylsilane), polygermane. We have used an array of semiempirical approaches and _ab initio_ calculations [1], followed by vibrational analysis of polysilane at the AM1 and 6-31G [5] levels. Concerning conformations, the AM1 torsional potentials can be used only for trends and location of important local minima. As compared to the _ab initio_ results, the barrier heights separating these minima or the relative values of these minima are

often wrong. However, trends, such as increase of the barrier separating the all-trans conformation from the gauche of poly(di-alkylsilane) as a function of the size of the alkyl chain length are believable. Concerning vibrational spectra the MNDO family is too rough to be generally useful, while ab initio at the modest 6-31G level is accurate enough, so that it can be used for vibrational assignments in polysilane. The root mean square error for trans-polysilane was 36 cm^{-1} using uniform scaling [5]. This relatively large value (as compared to PE's 6 cm^{-1}) is due to the fact that the experimental spectra correspond to somewhat disordered conformations, and that the spectrum is conformation dependent.

3. Electronic structure of heterocyclic ladder polymers

In one of the early applications of the band theory version of MNDO[9] we have shown in collaboration with J.J.P. Stewart that full in-plane geometry optimization provides a good overall description for polyacene, PAC, the prototypical conjugated ladder polymer[10]. We have calculated the most stable geometry of three such polymers [6,7]: polyphenothiazine (PTL, L for "ladder"), polyphenoxazine (POL) and poly(pheno-quinoxaline) (PQL). The MNDO band theory employed gives very reasonable geometries for these types cf materials and can be used as a basis for calculating their electronic structures by extended Huckel theory (EHT). This procedure (MNDO band theory geometry optimization followed by EHT for one electron properties) has proven before to produce results which correlate very well with experimental data including the sensitive issue of the stability of alterative forms of the polymers.[2b,11] In the case of the ladder polymers the main issue has to do with whether the most stable structures correspond to the highest possible symmetry, or a broken symmetry geometry. Our calculations presented strong evidence in favor of the latter and also provided interpretation of IR, optical, ENDOR and conductivity data.

4. Elastic moduli of selected carbon backbone polymers

We have applied the general methodology for elastic moduli described above to all-trans-PE and various forms of PA [2]. The agreement with experiment, where available, is excellent. In the case of trans-PA the result is consistent with the fact, that a conjugated polymer has a more rigid backbone than a saturated one (PE), and its Y value is larger. Surprisingly, the cis conformations have a lower elastic modulus. This sensitivity of a mechanical property on overall conformation of a polymer is very significant, and should be measurable. We plan to follow up on this problem by continuing elastic modulus calculations of polymers in various conformations.

In contrast to the sensitivity to conformation, Y depends on charge transfer (CT) only weakly [2]. In doped PA we calculated a mere 7% change of Y upon doping up to 0.25e/CH unit, a very high doping level. This conclusion is independent of whether a

delocalized (band) model or a localized (soliton) model was used. The corresponding calculations gave geometry changes in quantitative agreement with X-ray data. Consequently, the mechanical properties should not be very sensitive to the amount of charge transfer, in contrast to simplistic arguments, that CT occurs to antibonding or from bonding states. Therefore, highly conductive polymers should maintain high maximal elastic moduli and other mechanical properties, in agreement with Heeger's general observations[12].

5. Preliminary studies in non-linear optical properties

Hunt et al. have recently established a direct relationship between the vibrational Raman intensities and the hyperpolarizabilities of molecular systems[13]. In our efforts to interpret the Raman spectra of doped and undoped poly(p-phenylene), we have discovered [8], that the geometry of the rings (quinoid or aromatic) is more important in determining the polarizability and Raman spectrum (both frequencies and intensities), than the charge state of the system. It appears that the primary role of doping is to induce a structural transition from the aromatic (undoped neutral) to the quinoid (acceptor or donor doped) structure, and that the latter structure inherently has a qualitatively larger polarizability. This finding opens up new possibilities to design materials with inherently large hyperpolarizabilities, and we plan to pursue such calculations on several σ- and π-conjugated polymers in the near future. Our results [8] showed, that the calculations reproduce the main features of the Raman spectrum correctly without any reference to the experimental spectrum of the polymer.

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