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Conformational disorder in conjugated polymers

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Conformational disorder plays an important role in determining the electronic properties of conjugated polymers. To obtain a better theoretical description of the role and extent of conformational disorder, we derive the π electron correlation length and the bond correlation length in terms of the effective torsional potential and geometry of the conjugated polymer chains. These quantities are related to the conjugation lengths and persistence lengths of the chain, which are computed for polyacetylene, polydiacetylene, polythiophene, and polypyrrole. In spite of uncertainties in the torsional potential parameters for these materials, good qualitative agreement is found between experiment and theory.

INTRODUCTION

Certain conjugated polymers show remarkable changes in their optical properties when the solvent is modified or when the temperature is varied. Qualitative explanations of these solvatochromic and thermochromic effects have been provided by a model^{1,2} which links the optical properties to the effective conjugation length of the polymer and the latter to the solvent or temperature. The conjugation length is, loosely speaking, the length at which the π orbitals of a unit in the polymer are no longer parallel to (i.e., conjugated with) the π orbitals at the origin. In this paper, we define and calculate the temperature dependence of the conjugated length for model effective potentials and, using the same ideas, compute the persistence length³ of the polymer. We then apply these concepts to a number of polymers of current interest and compare to experiment where possible.

We consider a simple model to describe the conformational properties of conjugated polymers. Our model is applied to chains consisting of a series of alternating single and multiple carbon-carbon bonds (polyacetylene and polydiacetylene) and to chains consisting of a sequence of aromatic rings (polythiophene and polypyrrole). Our "course graining" unit is the single aromatic ring (in the case of polythiophene and polypyrrole) or the single rigid platelet in the case of polyacetylene and polydiacetylene (see Fig. 1). We take the relative position of the atoms within a single unit to be fixed; therefore, a unit can be completely specified in relation to other units by giving its center of mass and its orientational coordinates (Euler angles). We describe the polymer chains as consisting of a sequence of such units. The standard methods³ found in the literature to deal with the statistical mechanics of chain molecules are readily applied to our chains, with the coarse grained units playing the role of the backbone atoms in the standard treatment.

Our model owes much to the earlier theoretical work of Dobrosavljevic and Stratt,⁴ Schweizer,⁵ and Soos and Schweizer,⁶ who were concerned with the effects of confor-

mational disorder on the optical properties of conjugated polymers. Dobrosavljev and Stratt treat polydiacetylenes only, in a model similar in spirit to the present paper. They use an Ising model (to mimic the hydrogen bonding interactions along the chain) which includes correlations between adjacent hydrogen bonds, a model which has enough cooperativity to produce a sharp change in the correlation length with temperature. They then use a tight binding (Hückel) model for the electronic states to discuss the effect of disorder on those states. In the present paper, we focus on the definition of the conjugation length using a model with no cooperativity, but which stresses the role of the torsional potential and allows continuous low energy conformational defects. This makes our simple model applicable to a number of conjugated polymers. If cooperativity is important (as may be the case in polydiacetylene), our model would have to be generalized in the direction of Dobrosavljevic and Stratt.

Schweizer⁵ and Soos and Schweizer⁶ treat the effect of conformational disorder on the optical properties of polymers in two limiting cases: (1) the strong disorder limit in which the defects completely disrupt the conjugation, so that

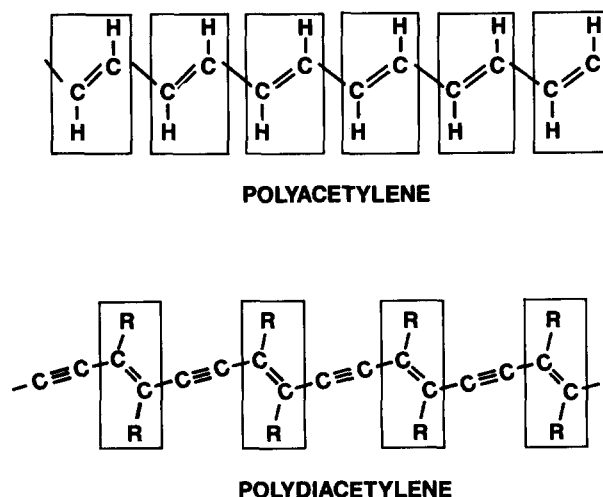


FIG. 1. Examples of coarse graining units for polyacetylene and polydiacetylene.

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a polymer is a connected system of shorter length conjugated units, and (2) the weak disorder limit in which the weak conformational disorder does not affect the energy levels but only the dipole transition moments and hence the optical absorption. The latter model, although similar in spirit to ours, is on the one hand less detailed than ours (in the treatment of the torsional energy and distribution of defects) and on the other hand more detailed (in the treatment of the transition moments and optical absorption). The former model (which implicitly allows only two torsional angles 0 and $\pi/2$) is quite different in spirit to either our model or that of Dobrosavljevic and Stratt.⁴

Available data from Raman and infrared spectroscopy, as well as *ab initio* quantum mechanical calculations suggest that different energy scales are associated with different possible distortions of the molecular structure.⁷⁻¹⁰ For example, when the various distortions of a two ring molecule are parametrized in terms of simple quadratic potentials

$$V(\eta) = K_\eta \eta^2/2 \quad (1)$$

(here η represent the generalized coordinate associated with the distortion and K_η is the force constant associated with that coordinate), one can distinguish three different energy scales: $E_{\text{torsion}} \ll E_{\text{wags}}, E_{\text{bends}} < E_{\text{stretch}}$.

An analysis of the conformational structure of the polymer chain should reflect this difference in energy scales.

The bond vectors joining successive rings are denoted by $\hat{u}_1, \hat{u}_2, \dots, \hat{u}_N$ and the unit vectors perpendicular to the planes of the rings by $\hat{\sigma}_1, \hat{\sigma}_2, \dots, \hat{\sigma}_N$. We expect correlations between the directions of the bond vectors as well as correlations between the directions of the planes to fall off exponentially with distance:

$$\langle \hat{u}_0 \cdot \hat{u}_L \rangle = e^{-L/\lambda_p} \quad (2)$$

$$\langle \hat{\sigma}_0 \cdot \hat{\sigma}_L \rangle = e^{-L/\lambda_\sigma} \quad (3)$$

Equation (2) and (3) define the two correlation lengths λ_p and λ_σ , respectively. The bond correlation length λ_p obtained from Eq. (2) coincides [up to order $O(1/\lambda_p)$] with the standard³ persistence length a (see appendix A for details). We also introduce the conformational conjugation length λ_c by

$$\langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L)^2 \rangle - \langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L) \rangle^2 \sim e^{-L/\lambda_c}, \quad (4)$$

where $\langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L)^2 \rangle_0$ is the value of $\langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L) \rangle^2$ when the allowed motions of the bonds are unhindered ($V=0$). The length λ_c defined by Eq. (4) is a measure of the coplanarity of the coarse graining units. It is important to realize that it is λ_c and not λ_σ that provides the correct measure of the conjugation along the chain in all cases. This is best seen via an imaginary chain where all the \hat{u} 's are parallel to each other ($\lambda_p = \infty$) and the angle between adjacent $\hat{\sigma}$'s has the same probability of being either 0 or π : in this case $\langle \hat{\sigma}_0 \cdot \hat{\sigma}_L \rangle$ vanishes (i.e., $\lambda_\sigma = 0$) but λ_c is infinite, as expected for the conjugation length in this situation.

In addition, the length λ_c is the correct order parameter for the optical properties due to π electron conjugation. This

can be seen by examining how the optical gap scales with λ_c within the simplest model for such effects: a one-dimensional, nearest-neighbor-coupling Hückel Hamiltonian applied to an alternating bond structure, such as in polyacetylene. In the planar form, the nearest-neighbor matrix elements alternate between β_d and β_s (double and single bonds); in the molecule with torsional motion about the single bonds, these will alternate between β_d and a value depending on the torsion about that bond $\beta_s(\phi_\eta) = \beta_s \cos \phi_\eta$. In the Born-Oppenheimer approximation, we can take the ϕ_η [and hence the $\beta_s(\phi_\eta)$] to be constant. The eigenvalues of this electric Hamiltonian (or the equation $\det |\lambda \mathbf{1} - \mathbf{H}|$) are functions of $[\beta_s(\phi_\eta)]^2$. If we assume that all the torsional angles ϕ_η are independent, we may average the determinantal equation and find that, to lowest order, we can replace $\cos \phi_\eta$ by $\langle \cos^2 \phi_\eta \rangle^{1/2}$ everywhere. Therefore, to find the eigenvalues of H averaged over the possible values of the torsional angle to this order, we make this replacement.

In this simple model, the band gap is given by

$$E_g = 2|\beta_d|(1 - \chi \langle \cos^2 \phi \rangle^{1/2}), \quad (5)$$

where $\chi = \beta_s/\beta_d$ and we have assumed that the average of $\cos^2 \phi_\eta$ is independent of η . The band gap in the absence of torsion E_g^0 is $2|\beta_d|(1 - \chi)$, so that

$$E_g - E_g^0 = 2|\beta_d|\chi \{1 - \langle \cos^2 \phi \rangle^{1/2}\} \quad (6)$$

$$= 2\beta_s \left\{ 1 - \left[\frac{1}{2} + \frac{\langle \cos 2\phi \rangle}{2} \right]^{1/2} \right\}. \quad (7)$$

In Sec. III we will show that

$$\langle \cos 2\phi \rangle = e^{-1/\lambda_c}$$

so that

$$E_g - E_g^0 = 2\beta_s \left\{ 1 - \left[\frac{1}{2} + \frac{1}{2} e^{-1/\lambda_c} \right]^{1/2} \right\}. \quad (8)$$

In the limit that λ_c is large compared to 1,

$$E_g - E_g^0 \cong \beta_s/2\lambda_c. \quad (9)$$

Therefore, the band gap is inversely related to the conjugated length λ_c in agreement with the usual formula used to interpret conjugation lengths from fitting the band gap of finite sized (N repeat units = n double bonds) conjugated chains (e.g., polyenes)¹¹:

$$E_g - E_g^0 \propto \frac{1}{N}. \quad (10)$$

The exact quantitative relationship between λ_c and N can only be found by more elaborate calculations. Here we are content with the qualitative relationship $\lambda_c \sim N$.

Even at the coarse graining scale we have chosen, a treatment of the conformational problem which allows all the distortions listed above and accounts for long range excluded volume effects requires a large scale Monte Carlo simulation. At present such a treatment will, however, prove of little value because of the large uncertainties in the various input parameters (potentials associated with the distortions). It seems, therefore, sensible to adopt a less comprehensive approach and to make full use of the fact that most conformational properties will be controlled by distortions occurring at the lowest energy scale.

Sections II and III are devoted to the treatment of the lowest level of approximation: only torsions around bonds connecting the platelets are allowed. We assume that the torsion potential depends only on nearest neighbor interactions: i.e., only on the angle ϕ between the directions of two adjacent platelets. This should be a reasonable approximation since conjugated chains are known to be fairly rigid and since our coarse graining scale is already of the order of a few atomic units.

With the scheme just outlined, simple expressions are obtained in Sec. III relating the form $V(\phi)$ of the torsional potential to the conformational conjugation length λ_c defined in Eq. (4). These relations are new: to our knowledge, in spite of its obvious usefulness as a conformational measure of conjugation, λ_c has not been introduced before in the literature. A straightforward application of the classical methods ordinarily used to treat the conformational statistics of ideal chains³ also allows us to obtain relations between $V(\phi)$ and the persistence length λ_p . Only simple one-dimensional integrals are involved: therefore, it is very easy to study the dependence of λ_c and λ_p on different choices of the potential. In Sec. III we apply these results to the treatment of particular systems: polyacetylene, polydiacetylene, polythiophene, and polypyrrole. It will be seen that, at this level of approximation, there is some uncertainty on our results due to the uncertainty in the form of the input potential $V(\phi)$.

We shall not make any attempt to include in our treatment the effect of stretches in the interunit distance, since the energy scale involved is so large compared to kT . In addition, we neglect the effect of long range excluded volume interactions. We consider this approximation reasonable since the ratio of chain length to persistence length is on the order of ten or less for the relatively stiff polymers of interest here.

II. CHOICE OF POTENTIALS

The full potential for the motions of polymer segments in solution is, of course, not known. We can estimate the potential for torsional motion in the gas phase based on Raman spectroscopy and in solution by NMR spectroscopy. Although these estimates are crude, we can use them to get a qualitative picture of the conjugation lengths in polymers.

In this description, we use model *effective* potentials for torsional motion of the form

$$V(\phi) = -E_c \cos(2\phi) - E_s \cos \phi, \quad (11)$$

where the first term is a "conjugation" energy part and the second a "steric hindrance" part. The parameters E_c and E_s are the effective energy values after solvent effects, etc. are taken into account.

Note that the conjugation energy part has the usual $\cos(2\phi)$ form; this term has periodicity π with a minimum at $\phi = 0$ (when the platelets are aligned) and a maximum at $\phi = \pi/2$. The second term in Eq. (5) represents a contribution having periodicity 2π . Terms of this form could have their origin in steric hindrance, examples being polythiophene and its alkyl substituted derivatives, and polyacetylene. A specific interaction between substituent groups, such as the attractive hydrogen bonding in polydiacetylene, would

also be represented by a term of this form.

For the calculations presented in the next section, the energies E_c and E_s appearing in Eq. (5) are free input parameters. We shall look at the values of E_c and E_s in the region $0 < E_c, E_s < 15kT$. If $E_s < 4E_c$, the potential has a minimum at $\phi = \pi$; such a situation is realized in both polythiophene and polypyrrole.

III. CALCULATION OF CONJUGATION LENGTH

A. The simplest case—infinite persistence length

In this case the "bond vectors" \mathbf{u}_i are assumed parallel to each other. Therefore, if only torsions around the bonds are permitted, the persistence length λ_p is infinite. For the purpose of obtaining the conjugation length λ_c , the chain can be idealized in terms of the set of unit vectors $\hat{\sigma}_i$ located on the sites of a one-dimensional lattice. Only rotations in a plane perpendicular to the direction of the chain are allowed (see Fig. 2). An example where this case would be an excellent approximation is poly(*p*-phenylene).

The potential associated with the relative rotation by an angle ϕ of two adjacent platelets is denoted by $V(\phi)$; one can then define the partition function³

$$\begin{aligned} Z &= \int_0^{2\pi} \frac{d\phi_1}{2\pi} \int_0^{2\pi} \frac{d\phi_2}{2\pi} \dots \int_0^{2\pi} \frac{d\phi_N}{2\pi} \prod_{j=2}^N e^{-V(\phi_j)/kT} \\ &= \left[\int_0^{2\pi} \frac{d\phi}{2\pi} e^{-V(\phi)/kT} \right]^{N-1}. \end{aligned} \quad (12)$$

Here ϕ_j is the angle between $\hat{\sigma}_{j-1}$ and $\hat{\sigma}_j$. We consider first the correlation function

$$\begin{aligned} \langle \hat{\sigma}_i \cdot \hat{\sigma}_{i+n} \rangle &= \frac{1}{Z} \int_0^{2\pi} \frac{d\phi_1}{2\pi} \int_0^{2\pi} \frac{d\phi_2}{2\pi} \dots \int_0^{2\pi} \frac{d\phi_N}{2\pi} \\ &\quad \times \prod_{j=2}^N e^{-V(\phi_j)/kT} (\hat{\sigma}_i \cdot \hat{\sigma}_{i+n}) \end{aligned} \quad (13)$$

and note that the torsional potential $V(\phi)$ has periodicity 2π . We note that

$$\begin{aligned} \hat{\sigma}_0 \cdot \hat{\sigma}_L &= \cos(\theta_{0L}) = \cos(\theta_{0L-1}) \cos \phi_L \\ &\quad - \sin(\theta_{0L-1}) \sin \phi_L, \end{aligned} \quad (14)$$

where θ_{0L} is the angle between $\hat{\sigma}_0$ and $\hat{\sigma}_L$; furthermore, since

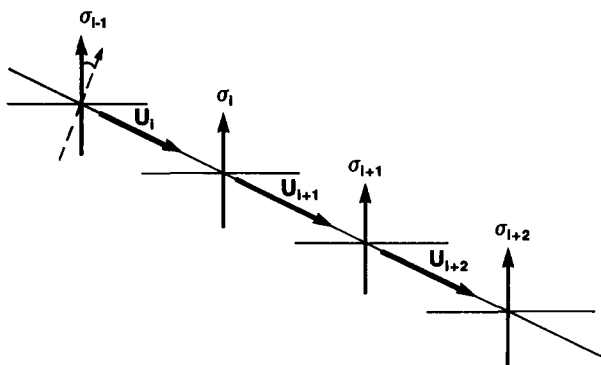


FIG. 2. Geometry in the case of all bond vectors, \mathbf{u}_i , parallel (infinite persistence length). The vectors σ_i can rotate in the plane perpendicular to \mathbf{u}_i .

$V(\phi)$ is symmetric around $\phi = \pi$, we have

$$\int_0^{2\pi} d\phi \sin \phi e^{-V(\phi)/kT} = 0. \quad (15)$$

Therefore, Eq. (13) can be rewritten as

$$\langle \hat{\sigma}_0 \cdot \hat{\sigma}_L \rangle = \xi \langle \hat{\sigma}_0 \cdot \hat{\sigma}_{L-1} \rangle = \xi^L = e^{-L |\ln \xi|}, \quad (16)$$

where

$$\xi = \langle \cos \phi \rangle \frac{\int_0^{2\pi} d\phi \cos \phi \exp^{-V(\phi)/kT}}{\int_0^{2\pi} d\phi \exp^{-V(\phi)/kT}}. \quad (17)$$

From Eqs. (3) and (16) one is finally led to

$$\lambda_\sigma = \frac{1}{|\ln \xi|} = \frac{1}{|\ln \langle \cos \phi \rangle|}. \quad (18)$$

When the torsional potential has periodicity π , [i.e., $E_s = 0$ in Eq. (17)] the numerator in the right-hand side of Eq. (17) vanishes and so does λ_σ .

Next we consider the correlation function

$$C(L) = \langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L)^2 \rangle - \langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L) \rangle^2. \quad (19)$$

Here $\langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L) \rangle = 1/2$ is the value of $\langle (\hat{\sigma}_0 \cdot \hat{\sigma}_L) \rangle$ if $V(\phi) = 0$. We define

$$c_L = \langle \cos^2(\theta_{0L}) \rangle \quad (20)$$

$$s_L = \langle \sin^2(\theta_{0L}) \rangle = 1 - c_L \quad (21)$$

as well as

$$\langle \cos 2\phi \rangle = \frac{\int_0^{2\pi} d\phi \cos 2\phi \exp^{-V(\phi)/kT}}{\int_0^{2\pi} d\phi \exp^{-V(\phi)/kT}}, \quad (22)$$

so that applying Eqs. (20) and (21) to the analogs of Eq. (14) and making use of

$$\int_0^{2\pi} d\phi \sin(2\phi) e^{-V(\phi)/kT} = 0 \quad (23)$$

we obtain

$$c_L = (c_{L-1} - 1/2) \langle \cos 2\phi \rangle + 1/2. \quad (24)$$

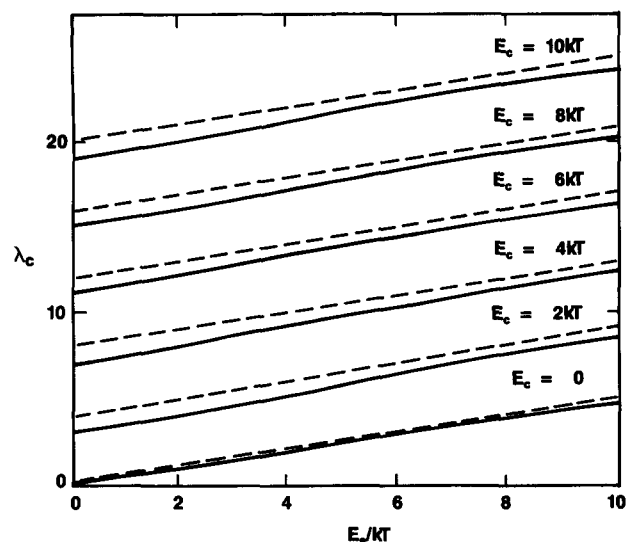


FIG. 3. Plot of the conjugation length λ_c for various values of E_c and E_s using the potential of Eq. (5). The dashed line represents the approximate result for λ_c given by Eq. (B13).

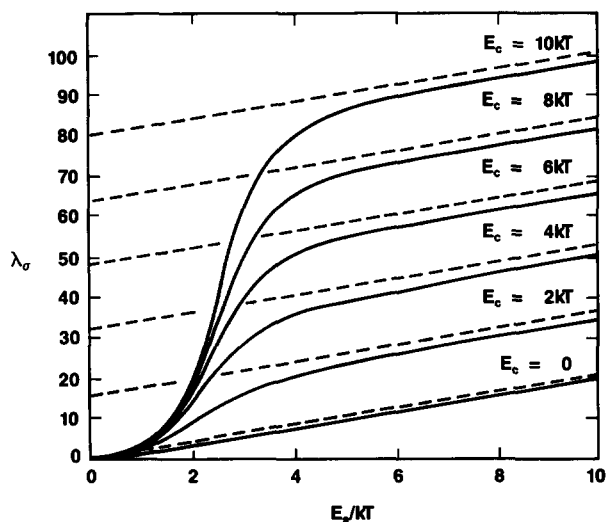


FIG. 4. Plot of correlation length λ_σ for various values of E_c and E_s using the potential of Eq. (5). Note that λ_σ goes to zero for small E_s in contrast to the behavior of λ_c . The dashed line represents the approximate result for λ_σ given by Eqs. (27) and (B13).

Therefore we have

$$C(L) = \langle \cos 2\phi \rangle^L \quad (25)$$

which compared with Eq. (4) gives

$$\lambda_c = 1/|\ln \langle \cos 2\phi \rangle|. \quad (26)$$

Note that for torsional potentials in which $E_s \gg E_c$, $\langle \cos \phi \rangle \approx e^{-2\langle \phi^2 \rangle}$ so that

$$\lambda_c = \lambda_\sigma/4. \quad (27)$$

In Figs. 3 and 4 we plot values of λ_c and λ_σ using the model potential of Eq. (5) for various values of E_s and E_c .

B. Nonparallel \mathbf{u}_i ; only torsions allowed

In the previous subsection we have restricted ourselves to the case where the bond vectors \mathbf{u}_i are parallel to each other so that the bond correlation length λ_p is infinite and is unaffected by torsions. In most cases this condition is not met (see Fig. 5); however, it is easy to adapt to our model chains the classical methods³ used to study the conformational statistics of polymers, and to treat in this way the case when the angle between adjacent \mathbf{u}_i is different from 0.

Again let us consider the case when *only* torsions around connecting successive units are allowed (i.e., the bond angle between adjacent \mathbf{u}_i is restricted to a given value $\Theta = \Theta_0$). This restriction ensures that the center of mass of a platelet and the point where the axes of the two bonds relative to that platelet intersect are fixed with respect to each other (see Fig. 6). One can regard the intersection of the bond axes as backbone atoms of a fictitious chain and proceed to introduce the standard³ rotation matrices T_i for that chain. Since the bond angles are fixed (see Fig. 2), and our torsional potentials satisfy Eq. (11), one gets

$$\langle T \rangle = \begin{pmatrix} \cos \Theta_0 & \sin \Theta_0 & 0 \\ -\xi \sin \Theta_0 & -\xi \cos \Theta_0 & 0 \\ 0 & 0 & -\xi \end{pmatrix}, \quad (28)$$

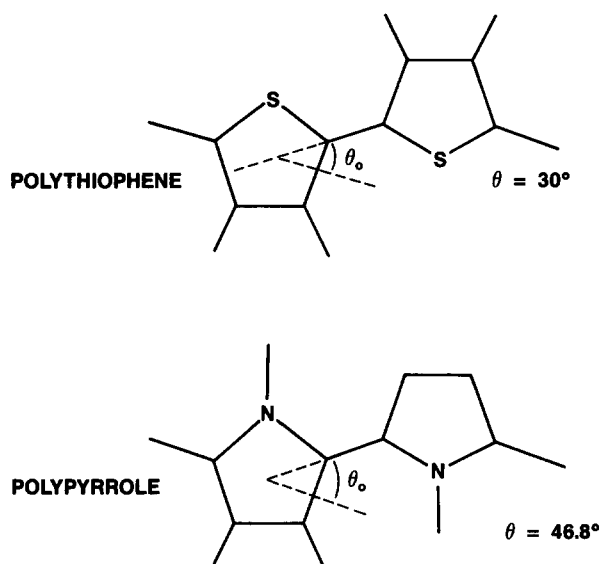


FIG. 5. Geometry for polythiophene and polypyrrole indicating nonzero Θ_0 , the angle between two successive interring bonds. Bond angles from Brédas *et al.* (Ref. 16).

where $\xi = \langle \cos \phi \rangle$ is defined in Eq. (17). It is easy³ from Eq. (28) to find the “bond correlation length” λ_p and the persistence length a (See Appendix A). The latter is directly related to measurable quantities (i.e., C_∞ and the radius of gyration of the chain); its expression in terms of Θ_0 and ξ is

$$a = \frac{1}{2} \left[\left(\frac{1 + \cos \Theta_0}{1 - \cos \Theta_0} \right) \left(\frac{1 + \xi}{1 - \xi} \right) + 1 \right]. \quad (29)$$

It should be stressed that the quantities ξ and Θ_0 controlling the persistence length a are different from the parameters determining the conformational conjugation length λ_c ; therefore, in general, there is no direct relation between two lengths. It should also be noted that, since λ_c depends only on ξ , the persistence length a is directly related to λ_c and Θ_0 alone.

It is straightforward to obtain a rough estimate of how our result (28) for the persistence length would change if wags and bends were allowed. Suppose that distortions from the equilibrium position $\Theta = \Theta_0$ are controlled by a potential of the form

$$V(\Theta) = K_\Theta (\Theta - \Theta_0)^2/2 \quad (30)$$

and are decoupled from the torsional part: i.e., $V(\Theta, \phi) = V(\Theta) + V(\phi)$. Under these assumptions Eq.

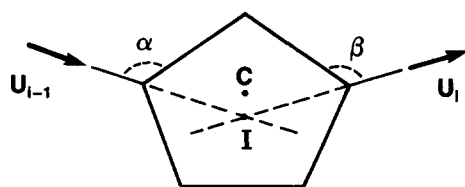


FIG. 6. Geometry for nonparallel \mathbf{u} , showing that the center for mass of the platelet and the point I (intersection of \mathbf{u} , and \mathbf{u}_{i-1}) are fixed with respect to each other if only torsional motion is allowed. Note, if blends and wags (changes in α and β) are allowed, this is no longer true.

(28) should be replaced by

$$\langle T \rangle = \begin{pmatrix} \gamma \cos \Theta_0 & \gamma \sin \Theta_0 & 0 \\ \gamma \xi \sin \Theta_0 & -\gamma \xi \cos \Theta_0 & 0 \\ 0 & 0 & -\xi \end{pmatrix}, \quad (31)$$

where

$$\gamma \cong 1 - kT/2K_\Theta \quad (32)$$

accounts for the effect of $V(\Theta)$ within the harmonic approximation. Using the form (31) of the rotational matrices, one obtains for the persistence length

$$a = \frac{1}{2} \left(\frac{1 + \gamma \cos \Theta_0 (1 + \xi) + \gamma^2 \xi}{1 - \gamma \cos \Theta_0 (1 - \xi) - \gamma^2 \xi} + 1 \right). \quad (33)$$

In the next section we shall use Eq. (33) to get rough estimates of lower limits on the persistence length.

IV. RESULTS FOR SPECIFIC POLYMERS

A. Polyacetylene

Though soluble versions of polyacetylene have not been made, we will consider it first since the torsional potential can be inferred from Ackerman and Kohler's results¹⁰ on octatetraene (four double bonds): $E_c = 4.5$ kcal/mol and $E_s = 1.5$ kcal/mol. These values lead to the following results for λ_c and a :

$T = 250$ K	$\lambda_c = 19$	$a = 184$,
$T = 300$ K	$\lambda_c = 15$	$a = 112$,
$T = 350$ K	$\lambda_c = 13$	$a = 71$.

We obtain $\lambda_c = 15$ at room temperature. Polyene units of this length would display optical properties very similar to those of polyacetylene. Thus if polyacetylene could be made soluble by addition of substituent groups which did not significantly alter this potential (did not interfere with the planar structure), we predict long conjugation lengths and optical properties (linear and nonlinear) similar to polyacetylene. Our results, however, also suggest a relatively stiff backbone, which would make solubilization of this molecule difficult. We can also infer that polyenes in solution with lengths up to about 15 units should remain relatively ordered in solution, a result which is consistent with recent experimental observations up to a length of 13 units.¹²

B. Polydiacetylene

Because of the cylindrical symmetry of the triple bond in the polydiacetylene backbone, we expect a very soft potential for polydiacetylene (with $R = H$ in Fig. 1), certainly less than that of polyacetylene. Estimates¹³ in the literature for E_c range from 0.2 to 2 kcal/mol. (Recent calculations by Brédas¹⁴ yield $E_c \sim 0.5$ kcal/mol.) Taking E_c and E_s equal to 1 kcal/mol as reasonable estimates for the H -substituted material, we find from Fig. 6 $\lambda_c = 3$ units at room temperature. Soluble polydiacetylenes have been synthesized and extensively studied. Solubility is effected by introducing a large, complicated R group. The most extensively studied examples have R groups which are capable of intramolecular hydrogen bonds. In a good solvent the hydrogen bond network is interrupted to a substantial degree. An estimate of the conjugation length from disruption of the hydrogen

bond network yields 3–4 units,¹ which compares favorably to our λ_c estimate. The “optical conjugation length” is estimated from experiment to be 6–7 units. In relatively poor solvents, extensive hydrogen bonds reinforce the planar backbone and optical properties very similar to that of the crystalline solid are obtained. The estimate of the strength of the hydrogen formation corresponds to E_s . For large E_s , Eqs. (26) and (27) can be used to estimate $\lambda_c = 13$ units, results which are consistent with the long conjugation lengths suggested by experiment.¹

Our results can also be applied to oligomers of these polymers. We would expect conformational disorder to play a role in the behavior of oligomers when the oligomer length approaches the λ_c value, i.e., in the polydiacetylene case for lengths on the order of 3 units. In fact, Wudl and Bitler's¹⁵ results on polydiacetylene oligomers indicate progressively more disordered structures as the length is increased from 3 to 19 repeat units.

Because of the specific architecture of the polydiacetylene backbone, our estimate of the persistence length is essentially infinite. In fact, even in good solvents it is found experimentally to be quite large (~ 33 units).¹⁶ A complete calculation of the persistent length must include other motions of the backbone as has been done with some success by Allegra *et al.*¹⁷

C. Polythiophene

We use the form of the torsional potential quoted from Bucci *et al.*¹⁸

$$V[\phi] = V_1(1 - \cos \phi)/2 + V_2(1 - \cos(2\phi))/2 + V_3[1 - \cos(3\phi)]/2 \quad (34)$$

with $V_1 = 0.585$ kcal/mol, $V_2 = 5.0 \pm 1.0$ kcal/mol, and $V_3 = -0.371$ kcal/mol. These values correspond to a fairly large conjugation energy $E_c = V_2/2$ with small steric hindrance contributions from V_1 and V_3 . Our results for the “conformational conjugation length” λ_c and for the persistence length a are summarized below. To obtain a we have taken¹⁹ $\Theta_0 = 30^\circ$ (see Fig. 5):

$$\begin{aligned} T = 250 \text{ K} & \quad \lambda_c = 8.6 \pm 2.0 & a = 12.4 \pm 0.3 & (10.8 \pm 0.3) \\ T = 300 \text{ K} & \quad \lambda_c = 7.0 \pm 1.8 & a = 11.6 \pm 0.2 & (9.9 \pm 0.2) \\ T = 350 \text{ K} & \quad \lambda_c = 5.8 \pm 1.5 & a = 11.0 \pm 0.2 & (9.3 \pm 0.3) \end{aligned}$$

All lengths given here are in polymer repeat units (or platelets). These values of the persistence length are about twice as large as they would be in the case of equally likely *cis* and *trans* configurations; unlike λ_c , a changes very little with temperature. The uncertainties in λ_c and a quoted above are due to the uncertainty on the value of V_2 . The numbers in parentheses given on the far right are values of the persistence length a calculated using Eq. (33) and choosing for K_Θ the unrealistically small value $K_\Theta = 20$ kcal/mol; therefore, these numbers are a lower limit on the value of a when the torsional potentials has the form given by Eq. (34). These results are in remarkably good agreement with experiment. The experimental values for a , measured by neutron scattering, is 16 units.²⁰ The experimental value for the conjugation length is about 6 units.^{2,21}

Recent quantum chemistry calculations¹⁴ on bithienyl

suggest a form of the potential somewhat different from that quoted above.¹⁸ These calculations yield a torsional potential best fitted with a potential having the form given in Eq. (16), with $E_s = 1$ kcal/mol and $E_c = 0.8$ kcal/mol. This leads to the following results for λ_c and a :

$$\begin{aligned} T = 250 \text{ K} & \quad \lambda_c = 3.1 & a = 105.9 & (44.2), \\ T = 300 \text{ K} & \quad \lambda_c = 2.1 & a = 60.3 & (33.2), \\ T = 350 \text{ K} & \quad \lambda_c = 2.0 & a = 49.7 & (26.1). \end{aligned}$$

The values for the persistence length found in this case are much larger than those obtained above because, in the potential of Eq. (34) the difference in energy between the *trans* and *cis* configurations is very small [$V(\phi = 0) - V(\phi = \pi) \sim 0.2$ kcal/mol]. On the other hand Brédas¹¹ finds [$V(\phi = 0) - V(\phi = \pi) \sim 2$ kcal/mol], i.e., the two values for the *cis-trans* energy barrier differ by an order of magnitude. The larger difference between the results for the persistence length for the two choices of $V(\phi)$ examined here shows how crucial it is in an analysis of this type to have reliable experimental data or theoretical calculations on these torsional potentials. In fact, since the persistence length appears to be so sensitive to the form of $V(\phi)$, one might even be in a position where one gets better information on $V(\phi)$ —in particular on the difference $V(\phi = 0) - V(\phi = \pi)$ —from direct measurements of a than from other methods. According to our results, the potential of Bucci *et al.*¹⁸ gives better agreement with experimental values of λ_c and a .

The numbers quoted in parentheses in the last column were again obtained from Eq. (33) with the very soft form of $V(\Theta)$ as before. Since in this case $V(\phi)$ alone gives a very large value of a , the effect of wags and bends is more appreciable.

D. Polypyrrole

We have used a fit of the form of Eq. (34) to the bipyrrrole potential $V(\phi)$ given by Brédas *et al.*²² We find $V_1 = 1.9$ kcal/mol, $V_2 = 2.75$ kcal/mol, and $V_3 = 0.6$ kcal/mol. This potential has a much shallower minimum, at $\phi = \pi$, than the potentials used in the case of polythiophene. Choosing $\Theta_0 = 46.8^\circ$ (see Fig. 5)¹⁹ we find for λ_c and a :

$$\begin{aligned} T = 250 \text{ K} & \quad \lambda_c = 7.4 & a = 90.2 & (39.9), \\ T = 300 \text{ K} & \quad \lambda_c = 5.6 & a = 52.7 & (27.5), \\ T = 350 \text{ K} & \quad \lambda_c = 4.4 & a = 33.9 & (20.2). \end{aligned}$$

Although Θ_0 is considerably larger for polypyrrole than for polythiophene and although large Θ_0 correspond to shorter persistence lengths [see Eq. (33)], the value for a is larger than the corresponding value for polythiophene. This is because ξ is larger (closer to 1) in the polypyrrole case, owing to the large difference between $V(\phi = 0)$ and $V(\phi = \pi)$.

V. CONCLUSIONS

In this paper we have introduced a new model to study the conformational properties of conjugated polymers. In this model we work at the coarse graining scale of a single ring or unit. We have introduced a conformational conjugation length λ_c which is a measure of the coplanarity of the different units and therefore a measure of conjugation and

find simple expressions relating λ_c to the torsional potential. We also include in our model the classical methods used to study the conformational statistics of ideal chains and obtain expressions relating the torsional potential to the persistence length. We find that in this framework, the conformational correlation length and the persistence length are quantities whose values are controlled by different statistical averages.

We have applied this formalism to study a number of actual systems, notably polyacetylene, polydiacetylene, polythiophene, and polypyrrole. Since there is a general uncertainty in the form of the input potential needed in our analysis, our final results have considerable uncertainties; however, we find good qualitative agreement with the known experimental behavior of these polymers.

It must be emphasized that we have assumed that the effective torsional potential is separable from the other degrees of freedom in the polymer. We have also neglected the effect of bending, wagging, and stretching motions on λ_c based on energetic considerations. In those cases for which the torsional potential is very stiff, these other degrees of freedom will play a role.

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APPENDIX A: RELATION BETWEEN a AND λ_p

Usually the persistence length a is defined as the average sum of the projections of all bonds $j > i$ on bond i in an indefinite long chain: i.e., if ψ_{ij} is the angle between the directions of bond i and bond j (and if all bonds have equal length l) the persistence length is

$$a = l \sum_{j=i+1}^{\infty} \langle \cos \psi_{ij} \rangle. \quad (\text{A1})$$

For chains with large a , we can see that this coincides with our definition in Eq. (2).

Consider a classical "Heisenberg type" model for the bond-bond interaction: then denoting with \hat{u}_i the unit vector in the direction of bond i , one finds

$$\langle \hat{u}_0 \cdot \hat{u}_n \rangle = \eta \langle \hat{u}_0 \cdot \hat{u}_{n-1} \rangle = \eta^n = e^{-n |\ln \eta|}, \quad (\text{A2})$$

where

$$\frac{\int_0^{2\pi} d\psi \cos \psi \exp^{-\beta V(\psi)}}{\int_0^{2\pi} d\psi \exp^{-\beta V(\psi)}} \quad (\text{A3})$$

and ψ is the angle between two adjacent bonds; in this case one can define a bond correlation length λ_p as

$$\lambda_p = \frac{1}{|\ln \eta|}. \quad (\text{A4})$$

It is easy to see that in this model λ_p and a coincide in order $(1/\lambda_p)$: in fact, according to Eq. (A2)

$$\langle \cos \psi_{ij} \rangle = \eta^{|j-i|} \quad (\text{A5})$$

so that (letting $l = 1$)

$$a = \sum_{\kappa=1}^{\infty} \eta^\kappa = \eta/(1-\eta). \quad (\text{A6})$$

On the other hand $(1-\eta)$ is small

$$\frac{1}{\lambda_p} = |\ln \eta| \approx \frac{1-\eta}{\eta} + \frac{1}{2} \left(\frac{1-\eta}{\eta} \right)^2 + \dots \quad (\text{A7})$$

so that

$$\frac{1}{\lambda_p} = \frac{1}{a} + \frac{1}{2a^2} + \dots, \quad (\text{A8})$$

namely,

$$a = \lambda_p [1 + O(1/\lambda_p)]. \quad (\text{A9})$$

Similar considerations apply in the case of more complicated forms of the interbond potential.

APPENDIX B: CALCULATIONS OF $\langle \cos \phi \rangle$ AND $\langle \cos 2\phi \rangle$

Note that the partition function for a bond with torsional potential given by Eq. (5) can be written as

$$q = 1/2\pi \int d\phi \exp \left\{ \frac{E_c \cos 2\phi}{kT} + \frac{E_s \cos \phi}{kT} \right\} \quad (\text{B1})$$

so that

$$\langle \cos \phi \rangle = \frac{\partial \ln q}{\partial (E_s/kT)} \quad (\text{B2})$$

and

$$\langle \cos 2\phi \rangle = \frac{\partial \ln q}{\partial (E_c/kT)}. \quad (\text{B3})$$

The use of standard Bessel function identities leads to

$$q = \sum_{n=-\infty}^{+\infty} I_n(E_c/kT) I_{2n}(E_s/kT), \quad (\text{B4})$$

where $I_n(Z)$ are the modified Bessel functions. This formula is unwieldy, except when either E_c or E_s is very small. For example, if $E_c = 0$

$$\langle \cos \phi \rangle = I_1(E_s/kT)/I_0(E_s/kT), \quad (\text{B5})$$

$$\langle \cos 2\phi \rangle = I_2(E_s/kT)/I_0(E_s/kT) \quad (\text{B6})$$

and if $E_s = 0$

$$\langle \cos \phi \rangle = 0,$$

$$\langle \cos 2\phi \rangle = I_1(E_c/kT)/I_0(E_c/kT). \quad (\text{B7})$$

In addition, the formula for q can be used to give a naive estimate of λ_c when E_c and E_s are large compared to kT . In this case

$$q \approx \int d\phi e^{(E_c + E_s)/kT} e^{-(2E_c + E_s)/2} \phi^2/kT} \quad (\text{B8})$$

$$q \approx e^{(E_c + E_s)/kT} \left(\frac{2\pi kT}{4E_c + E_s} \right)^{1/2} \quad (\text{B9})$$

and thus

$$\langle \cos 2\phi \rangle = 1 - \frac{2kT}{4E_c + E_s} \quad (\text{B10})$$

and

$$\lambda_c = (|\ln \langle \cos 2\phi \rangle|)^{-1} \quad (\text{B11})$$

$$\lambda_c \approx \left(\left| \ln \left[1 - \frac{2kT}{4E_c + E_s} \right] \right| \right)^{-1} \quad (\text{B12})$$

$$\lambda_c \approx \frac{4E_c + E_s}{2kT}. \quad (\text{B13})$$

The first approximation equation (B12) is quite good for almost the entire range of E_c and E_s considered here.

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