Stretching of conjugated polymers in dilute solution

A. Viallat* and P. A. Pincus†
Materials Department, University of California, Santa Barbara, CA 93106, USA

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A theoretical approach is proposed to describe the behaviour of stretched soluble conjugated polymers. Flexible, lightly doped chains are subjected either to a static field or to a pure longitudinal flow. In both cases, the rigid portions of the chain that contain electrons (conformons) are not dramatically altered. While many-electron conformons tend to break in small portions of low charge density, the optimum length of short one-electron segments increases slightly.

(Keywords: soluble conjugated polymers; dilute solution; stretching; extensional flows; conformon)

INTRODUCTION

The statistical structure of soluble conjugated polymers is complex: π-electron delocalization enhances chain rigidity and favours planar configurations, whereas random motions of the chain backbone occurring in solution tend to limit conjugation and conformational order. The characterization of this structure has recently received great attention since these systems are of potential interest for the processing of high conducting polymers. Several models have been proposed to describe conformational and electronic properties of these systems[1–4] but, until now, calculations have dealt mostly with polymer chains in the undeformed state, i.e. in the absence of an external perturbating field. The aim of this study is to describe the behaviour of conjugated chains under mechanical deformation. The stretched state is obtained either by applying a pulling force at both chain extremities or by subjecting the dilute solution to a pure elongational flow. In the latter case, it has been known for many years that flexible saturated chains undergo coil-stretched transition under high velocity gradients[5–11].

In this paper, we shall follow closely the theoretical framework developed by Pincus, Cates and Rossi described in Reference 1 and use their notation. Their model suggests that each additional electron is associated with a local rigid region of the chain (conformon) which is, in many respects, similar to the polaron of standard solid state physics. Recent numerical calculations have shown evidence of the existence of conformons and have given a quantitative description of a number of their statistical properties[12].

Here, we deal with lightly doped chains in dilute solution; we study the modification of the chain rigidity and the evolution of various conformon properties (average length, average number of confined electrons, effective interaction between electrons) with stretching. At this stage we emphasize that our discussion is essentially qualitative.

The main features of our theoretical framework are reiterated below. Then we consider a static extensional force field applied to lightly doped chains; we first analyse the simple situation of an ideal Gaussian chain and then examine how predictions are modified when excluded volume interactions are introduced. We then study the behaviour of a chain subjected to a pure longitudinal flow in the presence of a high velocity gradient.

THEORETICAL FRAMEWORK

When solubilized in a good solvent a chain undergoes fluctuations of large amplitude. Random rotational motions occur along the backbone, leading to an

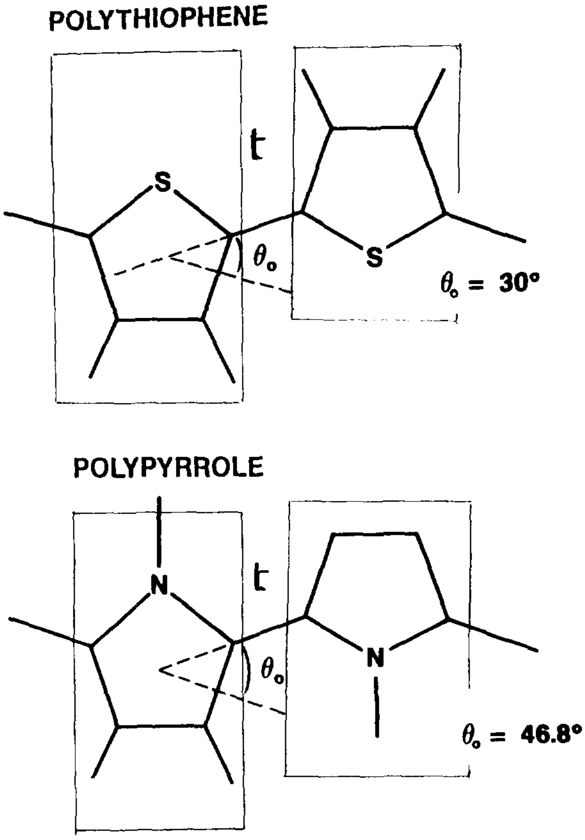

Figure 1 Examples of soluble conjugated polymers; t is the transfer integral between neighbouring platelets

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* Permanent address: Laboratoire de spectrométrie physique, Université scientifique, technique et médicale de Grenoble, BP 87, 38402 St Martin d'Hères cedex, France

† To whom correspondence should be addressed

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alteration of the ordered planar structure characteristic of the chain conformation in solid state. Therefore, the probability for a π-electron to hop from one unit cell to the next is modified: hopping constants depend on the relative orientation of the lobes of the p_z atomic orbitals. The resulting coupling between the electronic structure and the configurational degrees of freedom in the chain is treated according to the model proposed in Reference 1: the hopping constant between two adjacent unit cells (see *Figure 1*) has the usual $t\cos^2\phi$ form, where t is the transfer integral and ϕ is the rotational angle between the two cells[4]. It is assumed that, to a first approximation, the lobes of the p_z orbitals are perpendicular to the planes defined by the two platelets.

Electronic energy

The electronic Hamiltonian is obtained from the standard tight binding approximation. For simplicity, we work with spinless electrons and consider the very simple case where the hopping constants are either equal to 0 or 1 (i.e. $\cos^2\phi=1$ or 0). Therefore, the electronic energy of a rigid segment composed of l unit cells and containing r electrons is

$$U_l\cong(t/6)\left(\frac{\pi}{l+1}\right)^2 r(r+1)(2r+1) \tag{1}$$

where the harmonic approximation has been used in order to linearize U_l (Reference 1).

Configurational entropy

When a rigid segment of l monomers is created in the chain, the rotational degrees of freedom, associated with the $l-1$ corresponding angles ϕ, become frozen. The resulting cost of configurational entropy can be written as $\Delta S_l=l\beta$. The constant β is the entropy lost per unit cell when a platelet is forced to be aligned with the preceding platelet. β depends on the local chain structure within the size scale of a monomer. More precisely, as most soluble conjugated polymers contain large sidegroups, β is introduced to account for ordering effects arising from all possible sidegroup interactions.

Statistical properties of conformons

Minimizing the free energy of the rigid segment, $F_l=U_l+kT\,\Delta S_l$ one obtains the optimum length for the conformon[4]:

$$l^*(r)\sim l_c(r+\tfrac{1}{2}) \tag{2}$$

where $l_c=(2\pi^2 t/3\beta kT)^{1/3}$.

The statistical structure of the polymer can be investigated by representing the chain as a succession of random coil segments and conformons: at a given electronic concentration, one can derive, for example, the average number of conformons per chain and the conformon charge. At a low electronic concentration c, where c is less than the statistical weight for creating a conformon, only small one-electron conformons exist, while at high electronic concentrations, large conformons containing many electrons are more stable. In other words, an effective attraction between electrons originating in the configurational disorder of the chain skeleton is observed.

ELONGATIONAL FORCE: UNIAXIAL STRETCHING

When one applies a pulling force f at both ends of a Gaussian chain, the resulting stretching affects the statistical structure. To describe these effects, we calculate the partition function for small elongation ($\langle r\rangle \ll Na$ or $f\ll T/a$, where a is the length of the polymer structural unit and N is the number of units of the chain):

$$Z_f=\left(\frac{3}{2\pi Na^2}\right)^{3/2}\int_0^\infty \exp(-3r^2/2Na^2)\exp(f\cdot r/kT)4\pi r^2\,dr \tag{3}$$

where a is the monomer length and N the degree of polymerization (we consider a freely jointed chain). The reduction of configurational entropy upon stretching is obtained from equation (3):

$$\Delta S_f=\frac{\partial(kT\log Z_f)}{\partial T}=-\beta\frac{f^2Na^2}{6(kT)^2} \tag{4}$$

where the constant β introduced in formula (4) has been added to take into account the local geometry of the chain.

As the total chain entropy decreases upon deformation, the cost of entropy per monomer for creating a stiff segment in a stretched chain is also reduced. Per monomer, $\Delta S_{l,f}$ is given by

$$\Delta S_{l,f}=\beta\{1-f^2a^2/6(kT)^2\}l \tag{5}$$

The approach detailed in the previous section is valid for stretched chains, provided β is replaced by $\beta'=\beta\{1-f^2a^2/6(kT)^2\}$. One can have a clear idea of the chain behaviour under stretching by expressing β' as a function of the mechanical deformation. For a Gaussian chain, the relative average elongation under a force f is $\langle r\rangle=fR_0^2/3T$ where $R_0=N^{1/2}a$ is the size of the undeformed chain. We define the relative elongation ratio $\lambda=\langle r\rangle/R_0$ and the deformation ratio in the direction of elongation, x, $\alpha^2=\langle x^2\rangle/x_0^2$. In the Gaussian approximation $\alpha^2=3\lambda^2+1$.

The optimum length for a stiff segment containing r electrons is then

$$l_f^*(r)=l^*(r)(1-3\lambda^2/2N)^{-1/3} \tag{6}$$

and the conformon length per electron is

$$l_{c,l}=l_c(1-3\lambda^2/2N)^{-1/3} \tag{7}$$

These two equations tell us that the deformation has a very small effect on the conformon length: for fairly large elongation ratios ($\lambda\approx 10$) and $N>500$, one has $\Delta l_f^*/l_f^*\ll 10\%$. For smaller values of N, $\lambda\approx 10$ corresponds to a fully stretched chain. In this case, the chain is in rod conformation and has an infinite conjugation length. The conformon concept then becomes meaningless since the electronic structure can be described in the standard solid state framework. It should be emphasized that conjugated polymers in solution usually have a rather long persistence length (e.g. >20 monomers for polythiophene). Then the polymer structural unit, which is the unit step for the Gaussian chain, contains many monomers and consequently the total number of unit steps N may be fairly small, of the order of 100 for instance.

The free energy f_f needed to create a new conformon is $f_f\sim(3/4)\beta l_c(1-3\lambda^2/2N)^{2/3}$. As might naively be expected, less energy is required to create a conformon in a stretched chain since its structure is more ordered. Following the model developed in Reference 1 we consider various doping levels; we define the overlap concentration of conformons $c_f^* = 1/l_{c,f}$ and the statistical weight for creating a conformon $\sigma_f = \exp(-f_f/kT)$ (we denote by c^* and σ the corresponding values in the relaxed state). Equations (6) and (7) yield

$$c_f^* = c^*(1-3\lambda^2/2N)^{1/3}, \qquad c_f^* \leqslant c^* \tag{8}$$

$$\sigma_f = \sigma^{(1-\lambda^2 3/2N)^{2/3}}, \qquad \sigma_f \geqslant \sigma \tag{9}$$

We are now able to examine the modification of the chain structure as a function of the stretching ratio and the electronic density along the chain, c, where $c = n/N$ and n is the number of electrons in the chain. According to the predictions of Reference 1, when $c \ll \sigma$, undeformed chains contain only one-electron conformons of size l_c. At small elongation, conformons are slightly longer since $l_{c,f} > l_c$. For stretching ratios large enough that $c > c_f^*$ (i.e. $3\lambda^2/2N > 1-(c/c^*)^3$), one-electron conformons become so long that $l_{c,f} > c^{-1}$: the electronic concentration is beyond c_f^*. Conformons overlap and, consequently, the polymer becomes stiff.

When $c \gg \sigma$, one has, for small elongation, $c \gg \sigma_f$. Then the number of conformons, $p_f = N(\sigma_f c)^{1/2}$, slightly increases while the average number of electrons per conformon, $\bar{r} \approx (c/\sigma_f)^{1/2}$, decreases.

Starting from $l^*(r)$ in the undeformed state, the typical conformon length $l_f^*(r)$ decreases as large elongation ratios are reached. Eventually, all initial conformons can break into one-electron conformons when λ is large enough that $c < \sigma_f$. At very large elongational forces, the chain is stiff and complete electronic delocalization is achieved along the chain backbone.

Let us now turn towards the case of a single chain with excluded volume. Configurational entropy is smaller than in the ideal situation since only self-avoiding configurations are allowed. For large N the entropy per monomer is constant. The entropy loss for a one-monomer rigid segment can be written $\Delta S_{l,\mathrm{excl\,vol}} = \gamma l$, where γ is a constant that accounts for the additional loss of configurations due to excluded volume effects.

Considering now the self-avoiding chain subjected to an elongation $\boldsymbol{R}$, the reduction of entropy due to stretching is $\Delta S(\boldsymbol{R}) = \log w(\boldsymbol{R})$, where $w(\boldsymbol{R})$ is the distribution function of end-to-end chain vectors. For small stretching ratios $R \ll R_F$, the distribution function scales[13] as $w(\boldsymbol{R}) = (\boldsymbol{R}/R_F)^{1/3}$. Then the entropy per monomer has the form $\Delta S(\boldsymbol{R}) \sim (1/N)\log N$, which can be neglected when $N \gg 1$: statistical properties of conformons are not significantly affected under weak stretching.

For large deformations, the distribution function has the asymptotic behaviour[13], $w(\boldsymbol{R}) = \exp\{-(\boldsymbol{R}/R_F)^{5/2}\}$. Then the entropy per monomer is $\Delta S(\boldsymbol{R}) = -(1/N)(\boldsymbol{R}/R_F)^{5/2}$ and the corresponding loss of entropy in our rigid segment is $\beta' l(1-\lambda^{5/2}/N)$. This yields an optimum conformon length

$$l^*_{\mathrm{excl\,vol,f}} = l^*_{\mathrm{excl\,vol}}(1-\lambda^{5/2}/N)^{-1/3} \tag{10}$$

This result shows that conformon properties predicted for ideal chains are not strongly altered by excluded volume effects: $l^*_{\mathrm{excl\,vol,f}}$ and l_f^* have formal identical forms. At high deformation, one finds 5/2 for the λ exponent, while it was only 2 for the ideal case: the distribution of conformon lengths for self-avoiding chains is slightly more sensitive to elongational effects. Yet these effects remain very small as long as the chain is not fully stretched.

STRETCHING UNDER LONGITUDINAL FLOW

We now discuss the case of a simple conjugated chain in an extensional flow. Pure elongational flows have an interesting property: frictional forces derive from a potential and so the deformation can be studied by equilibrium theories. Furthermore, in extensional flows, flexible chains are known to exhibit sharp coil-stretched transitions under high longitudinal velocity gradients. We consider here a one-dimensional longitudinal velocity gradient $v(\boldsymbol{r}_n) = sx_n\boldsymbol{u}$. The term $\boldsymbol{r}_n$ is the position of the nth monomer and s is the velocity gradient along the x direction. Neglecting hydrodynamics interactions and excluded volume effects, the total force experienced by each monomer is the sum of the elastic force (Rouse contribution) and hydrodynamics friction forces:

$$\boldsymbol{f}_n = (3kT/a^2)\,\partial \boldsymbol{a}_n/\partial n + s\xi x_n \boldsymbol{i} \tag{11}$$

with

$$\boldsymbol{a}_n = \boldsymbol{r}_{n+1} - \boldsymbol{r}_n$$

Following the approach described in Reference 8 we can obtain the associated potential energy V and the entropy reduction due to the deformation. V can be simply written as

$$V = (3kT/2a^2)\sum_n (a_n^2 - \mu x_n^2) = (2NkT/4a^2)\sum_i (i^2 r_i^2 - \mu x_i^2) \tag{12}$$

Here $\mu = s\tau/3N^2$ where $\tau^{-1} = T/\xi(Na)^2$ is the characteristic Rouse relaxation time for chain deformation (proportional to N^2). The second term is obtained from a 'Fourier transform' where $i = p\pi/N$, $p = 1, 2, \ldots, N$. Then the partition function is

$$Z = \prod_{i=\pi/N}^{\pi} \iiint_{x,y,z} \mathrm{d}x_i\,\mathrm{d}y_i\,\mathrm{d}z_i \times \exp\left[-\frac{3N}{4a^2}\{(i^2-\mu)x_i^2 + y_i^2 + z_i^2\}\right] \tag{13}$$

The free energy is

$$\Delta F = kT/2\sum_i \log(1-\mu/i^2) \sim kT/2\log(1-\mu N^2/\pi^2)$$

By denoting the critical velocity gradient for which ΔF diverges by $s_c = 3\tau/\pi$, the loss of entropy due to the chain deformation is

$$\Delta S = \left[-\frac{1}{2}\log\left(1-\frac{s}{s_c}\right) - \frac{1}{2}\frac{s}{s_c}\frac{1}{(1-s/s_c)}\right]\beta \tag{14}$$

where the geometrical constant β has been added as in equation (4). The corresponding entropy loss for a one-monomer rigid segment is then

$$\Delta S_{1,s} = \beta l(1-(\log u - 1 + u^{-1})$$

where $1 - s/s_c = u$. We express l_s^* as a function of the chain elongation ratio. To a first approximation, transverse dimensions are essentially unchanged in the Gaussian regime, while the parallel dimension, $\langle x^2\rangle = (Na^2/3)u^{-1}$, exhibits a divergence when u tends to 0. This yields $\langle x^2\rangle/\langle x_0^2\rangle=\alpha^2=3\lambda^2+1=u^{-1}$. Then, minimizing the free energy, one finds for the optimum conformon length

$$l_s^*=l^*[1-(2Nu)^{-1}]^{-1/3}$$
$$l_s^*\sim l^*[1-3\lambda^2/2N]^{-1/3} \qquad (15)$$

where the term N^{-1} has been neglected in the second expression. This equation is identical to equation (6), obtained in the case of a static stretching force: all results obtained in the previous section can be directly applied to the case of a longitudinal flow. Therefore, no drastic change of the statistical properties of the conformons is expected until the chain undergoes the stretched-coil transition.

SUMMARY

In this paper, we have discussed in a very simplified way statistical properties of conformons in an elongated conjugated chain in solution. Large approximations have been made, which require that our conclusions be compared with experimental results. Such results are not yet available. We have considered Gaussian chains where electrons had been added to an otherwise empty band. Statistical structures of a chain under an extensional static force and, in a more realistic situation, under longitudinal flow are similar. For incompletely stretched chains, statistical properties of conformons are hardly modified. The effective attraction between electrons which favours many-electron conformons decreases while the length of one-electron conformons increases due to a longer conjugation length.

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