Mechanism by which pressure and a field affect the electrical conductivity of conjugated polymers with insulator bridges

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A model proposed here explains the abrupt change in conductivity, by several orders of magnitude, observed in a polymer film with a filamentary polymer structure upon a slight change in external conditions. The propagation of a conductivity pulse along the polymer chain is of a soliton nature. The new model is used to derive a current-voltage characteristic for a polymer film. © *1995 American Institute of Physics.*

1. INTRODUCTION

The mechanism responsible for the rapid formation and disappearance of conducting channels in several polymers containing oxygen is of considerable interest and the subject of widespread research.[1–5] Several models involving metal whiskers growing away from the electrodes or phase transitions have been proposed,[6,7] but they fail to explain why the switching is very sensitive to external agents which could affect only the surface properties of the polymer film and would not directly affect its interior properties.

In this paper we propose a mechanism for switching, or for the formation of a conducting phase, which involves a transformation of the polymer chain. This mechanism can explain most of the experimental results of thin films: the abrupt, reversible change in the conductivity, by several orders of magnitude, when a small uniaxial pressure, $\sim 10^2$ Pa, and/or an electric field is applied; the insensitivity of the properties of the film to hydrostatic pressure; the absence of an effect in thick films; the occurrence of an effect when crushed glass is added; the memory of the conducting state under special conditions; and the destruction of this memory by a weak external perturbation. This mechanism also explains the "butterfly" current-voltage characteristic.

2. STRUCTURE OF THE POLYMER CHAIN

The observation that a very low external pressure can cause a change of many orders of magnitude in the conductivity of films is evidence that this effect does not stem from a change in volume due to the pressure, because such changes are small.

The polymer film apparently switches from a nonconducting state to a conducting one because of the structure of the monomer unit (Fig. 1), which can be in two modifications for the given class of polymers. In the first modification, a carbon atom C is in an sp^3 hybridization, and the chain of conjugation of the monomers with each other is broken. In the second modification, a C atom has an sp^2 hybridization, which leads to a conjugation of a monomer unit with the neighboring units. Figure 1 shows the progressive conversion from the nonconducting state to the conducting one. We show below that this situation is described by a soliton solution.

In a nonconducting bridge $-\overset{|}{\underset{|}{\mathrm{C}}}-$, in which case the C atom has an sp^3 hybridization, the plane of the benzene ring of the side group (in our case, a phthalide radical) is perpendicular to the main chain: $\varphi=0$, where φ is the angle between the plane of the benzene ring of the side group and the direction of the main chain. In a conducting bridge $\overset{|}{\underset{|}{\mathrm{C}}}$ in which case the carbon acquires an sp^2 hybridization, the plane of the side-group benzene ring becomes parallel to the main chain: $\varphi=\pi/2$. The structure of the bridges is characterized by the angle φ, which takes on not only the two extreme values just mentioned but also all intermediate values.

The interaction potential is periodic in the angle and can be approximated by[8]

$$U_n=U\,\frac{1-\cos 4\varphi_n}{4}+A\,\frac{1-\cos 2\varphi_n}{2}$$

for monomer (unit) n.

We introduce operators a_{in}^{+} and a_{in}, which create and annihilate an electron with an energy ε_n in the nth monomer unit of the ith polymer filament. We write the Hamiltonian of the system:

$$\begin{aligned}H=&\sum \varepsilon_n a_{in}^{+}a_{in}+\frac{J_1}{4}\sum \sin^2\varphi_{in}\sin^2\varphi_{i,n+g}(a_{in}^{+}a_{i,n+g}\\&+a_{i,n+g}^{+}a_{in})+\frac{J_2}{4}\sum \sin^2\varphi_{in}\cos^2\varphi_{i,n+g}(a_{in}^{+}a_{i,n+2g}\\&+a_{i,n+2g}^{+}a_{in})+\sum J_{ij}a_{in}^{+}a_{jn}+\sum (M_{in}^{z})^2/2I\\&+\frac{U}{4}\sum(1-\cos 4\varphi_{in})+\frac{A}{2}\sum(1-\cos 2\varphi_{in}).\end{aligned}\qquad(1)$$

Here J_1, J_2, and J_{ij} are parameters; M is the angular momentum, and I is the moment of inertia. The Hamiltonian (1) describes the behavior of a 3D polymer film as a system of

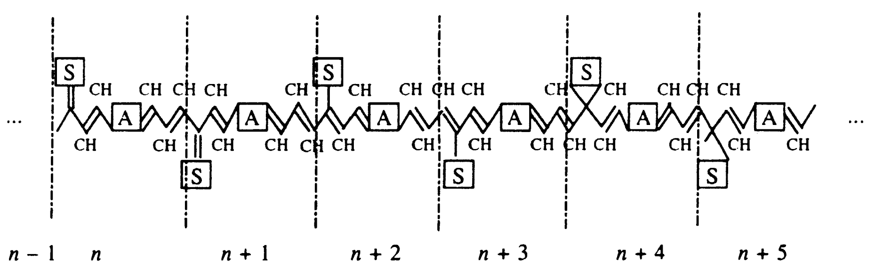

FIG. 1. Schematic structure of a polymer with bridges. S—Side group; A—part of the main chain; n—index of a monomer unit. Units n and $n+1$ are conducting, $n+2$ and $n+3$ are transitional, and $n+4$ and $n+5$ are nonconducting.

polymer filaments. In a first approximation, we assume that jumps of carriers between filaments are improbable and that the corresponding parameter J_{ij} is small.

The first term in (1) describes the state of the monomer (the unit), and the second describes the exchange interaction between neighboring monomer units. If we have $\varphi_{in}=\pi/2$, i.e., if neighboring units are in a conducting state, then an exchange interaction occurs between the units, and this term is nonzero. If at least one of two neighboring units is in a nonconducting state, i.e., if $\varphi_{in}=0$, then there is no exchange interaction between the units. The third term in (1) describes the exchange interaction between next-nearest neighbors. This term is important if one of the angles of neighboring monomers is zero. This third term plays an important role in the transition region, in which a rotation through an angle up to $\pi/2$ in one of the monomers leads to a rupture of the bond and to a restructuring of the conjugation chain within the unit. As a further result, electrons become able to interact through the unit, rupturing the bond between neighbors. This process leads to a shift of a biradical state. The last three terms in the Hamiltonian describe internal rotation of a side group.

Rotation of the plane of a side group in a monomer to the state $\varphi_{in}=0$ adds one electron to the π shell, which is responsible for the existence of the highly conducting state. Its population is accordingly increased by an amount $\sin^2\varphi_{in}$.

The part of the polymer molecule in which the angles φ_{in} are equal to, or approximately equal to, $\pi/2$ is conjugated and thus highly conducting. The other part, with $\varphi_{in}\simeq 0$, is an insulator. These two regions may be either in direct contact or separated by a transition region. The value of the angle φ_{in} along the molecular chain characterizes the conductivity of the polymer.

For the angle φ_{in} we have the equations of motion

$$
\begin{aligned}
&i\frac{d}{dt}\varphi_{in}=-\frac{i}{I}M_{in}^{z},\\
&I\frac{d^2}{dt^2}\varphi_{in}=-U\sin 4\varphi_{in}-A\sin 2\varphi_{in}\\
&\qquad -J_1\sum \sin\varphi_{in}\cos\varphi_{in}\sin^2\varphi_{i,n+g}\\
&\qquad \times(a_{in}^{+}a_{i,n+g}+a_{i,n+g}^{+}a_{in})\\
&\qquad -\frac{J_2}{2}\sum[\sin\varphi_{in}\cos\varphi_{in}\cos^2\varphi_{i,n+g}\\
&\qquad \times(a_{in}^{+}a_{i,n+2g}+a_{i,n+2g}^{+}a_{in})\\
&\qquad -\sin\varphi_{in}\cos\varphi_{in}\sin^2\varphi_{i,n+g}(a_{i,n-g}^{+}a_{i,n+g}\\
&\qquad +a_{i,n+g}^{+}a_{i,n-g})].
\end{aligned}
\tag{2}
$$

We will use these equations to study the change in the structure of a unit and the band structure of the polymer.

3. SOLITON WHICH TRANSFORMS THE POLYMER FROM A NONCONDUCTING STATE TO A CONDUCTING ONE

We take the quantum-mechanical expectation value of expression (2). The electron variables and the nuclear variables are not correlated with each other, because of the difference in time scales for the development of the corresponding processes. We can thus write

$$
\begin{aligned}
&\langle \sin 2\varphi_{in}\cos^2\varphi_{i,n+g}a_{in}^{+}a_{im}\rangle\\
&\quad \simeq\langle \sin 2\varphi_{in}\cos^2\varphi_{i,n+g}\rangle\langle a_{in}^{+}a_{im}\rangle.
\end{aligned}
$$

For other combinations of $\sin\varphi$ and $\cos\varphi$ we adopt corresponding assumptions. In addition, the energy spectrum of the rotation of the side groups is continuous because of the large value of I, and the angle φ_{in} is a nonquantum quantity. In other words, we can use the approximation

$$\langle \sin\varphi_{in}\rangle=\sin\langle\varphi_{in}\rangle=\sin[\varphi(n,t)].$$

We introduce

$$
\begin{aligned}
\alpha&=\frac{J_1}{2}\langle a_{in}^{+}a_{i,n+g}+a_{i,n+g}^{+}a_{in}\rangle\\
&\quad -\frac{J_2}{2}\langle a_{i,n-g}^{+}a_{i,n+g}+a_{i,n+g}^{+}a_{i,n-g}\rangle,\\
\beta&=\frac{J_2}{4}\langle a_{in}^{+}a_{i,n+2g}+a_{i,n+2g}^{+}a_{in}\rangle.
\end{aligned}
\tag{3}
$$

These quantities vary slowly in time; the subscript n is independent of g.

Working from all these arguments, and carrying out some trigonometric transformations, we can write the expectation value of (2) as follows:

$$
\begin{aligned}
I\frac{d^2\varphi(n,t)}{dt^2}&=-U\sin[4\varphi(n,t)]-A\sin[2\varphi(n,t)]\\
&\quad +\frac{\alpha-\beta}{8}\{\sin[2\varphi(n,t)+2\varphi(n+1,t)]\\
&\quad +\sin[2\varphi(n,t)+2\varphi(n-1,t)]\}
\end{aligned}
$$

$$-\frac{\alpha}{4}\{\sin[2\varphi(n+1,t)]+\sin[2\varphi(n-1,t)]\}-\frac{\beta}{2}\sin[2\varphi(n,t)]$$
$$-\frac{\alpha+\beta}{8}\{\sin[2\varphi(n,t)-2\varphi(n+1,t)]+\sin[2\varphi(n,t)-2\varphi(n-1,t)]\}. \qquad (4)$$

In the continuum approximation, the difference in the angles between two neighboring monomers can be assumed small. Replacing $\varphi(n,t)+\varphi(n+g,t)$ by $2\varphi(n,t)$, and carrying out a series expansion in the small difference $\varphi(n,t)-\varphi(n+g,t)$, we then find

$$\frac{d^2y}{dt^2}=-\frac{4U-\alpha+\beta}{I}\sin y-\frac{4A}{I}\sin\frac{y}{2}-\frac{2(\alpha+\beta)}{I}\sin\frac{y}{2}$$
$$+\frac{\alpha+\beta}{4I}[y(n+1,t)+y(n-1,t)-2y(n,t)],$$

where $y=y(n,t)=4\varphi(n,t)$. We introduce the coordinate $x-x_0=nb$, where b is the size of a monomer unit, and we also introduce the new variables

$$t'=t\sqrt{\frac{4U-\alpha+\beta}{I}},\quad x'=2x\sqrt{\frac{4U-\alpha+\beta}{\alpha+\beta}}.$$

We find

$$\frac{\partial^2y(x',t')}{\partial t'^2}-\frac{\partial^2y(x',t')}{\partial x'^2}+\sin[y(x',t')]=-\lambda\sin\left[\frac{y(x',t')}{2}\right], \qquad (5)$$

where $\lambda=[2(\alpha+\beta)+4A]/(4U-\alpha+\beta)$. This equation is a double sine-Gordon equation. In the zeroth approximation, in which U is large, while $\alpha+\beta$ and A are small, we can discard the right-hand side of (5). We then have the standard sine-Gordon equation for determining the angle $\varphi(n,t)$:

$$\frac{\partial^2y}{\partial t'^2}-\frac{\partial^2y}{\partial x'^2}+\sin y=0. \qquad (6)$$

The types of solutions of (6) and, correspondingly, of (5) differ, depending on the boundary and initial conditions. These solutions may oscillate around $\varphi=0$ and $\varphi=\pi/2$. These solutions do not lead to a complete revamping of the band structure of the polymer, since, on the average, they conserve the value of the angle φ and describe vibrational motions of the side group in the conducting or insulating state of the monomer. These solutions are realized in polymer films and are manifested experimentally.[9-11] The most important solution of (6) is a single solution, which we write in the old coordinates:

$$\varphi(x,t)=\arctan\left\{\exp\left[\pm2\gamma\sqrt{\frac{4U-\alpha+\beta}{\alpha+\beta}}(x-x_0-v_st)\right]\right\}, \qquad (7)$$

where $\gamma=\sqrt{1-v^2}$, v is a constant, and

$$v_s=v\sqrt{\frac{\alpha+\beta}{4I}}$$

is the velocity of the soliton.

It follows from solution (7) that in the limit $x\rightarrow-\infty$, and in the case of the minus sign on γ, the angle φ is $\pi/2$. As x increases toward ∞, this angle varies monotonically to zero. The other solution, for the case of the plus sign on γ, describes the change in the angle from zero in the limit $x\rightarrow-\infty$ to $\pi/2$ in the limit $x\rightarrow\infty$. The choice of solution is determined by the boundary conditions at the ends of the polymer molecule.

4. BOUNDARY CONDITIONS

To formulate boundary conditions we assume that an external agent acts on a part of the polymer molecular adjacent to the surface of an electrode, at which we have $\varphi=\pi/2$ or $\varphi=0$. The resulting seed values then propagate along the chain in accordance with expression (7). The charges (Z) of the side groups of the polymer chain interact with the electrode with a potential energy $Ze/2x_*$, where x_* is the distance from the electrode to that charge at which the side group has a minimum potential energy. Near such minima (there are two of them: at x_* and x_1), the side group vibrates at a frequency ω, but it does not go from one minimum to the other. A transition from the minimum x_* to x_1 requires an activation energy.

If an active C–O bond in a side group has an energy E_b, the activation energy for rotation of the ring through an angle $\pi/2$ is $E_a=E_b-Z^2e^2/2x_*$. In an external electric field E, and during the simultaneous application of a uniaxial pressure P, the activation energy varies and can be written

$$E_a^{\pm}=E_a-a_1P\mp a_2E, \qquad (8)$$

where $a_1=Z^2e^2\delta/2x_*$ is a pressure coefficient, δ is the coefficient of linear compression, and $a_2=\sqrt{2E_a/\omega}$ is a field coefficient. Only the linear terms have been retained in expression (8). In a real situation, in which there may be several activation energies, because of the nonuniformity of the polymer, the number of molecules with changes of $\pi/2$ in the angle φ varies progressively as the conditions

$$E_a^i-a_1P\mp a_2E\leqslant k_BT$$

become satisfied, where E_a^i is the set of activation energies, and k_B is the Boltzmann constant.

Let us examine the effect of external agents on the boundary conditions. We first assume that the boundary side groups have an angle $\varphi=0$. The application of a pressure (or a field) to the electrode switches the boundary side group from an equilibrium state with a minimum energy U_0 at the point x_* to a new equilibrium state with a potential energy U_1 at the point x_1, by distorting the potential curve so that U_1 becomes smaller than U_0. The C–O bond is ruptured in the process, and the boundary side group assumes a position characterized by the angle $\varphi=\pi/2$. This situation determines the boundary conditions on Eq. (6). When the pressure (or field) is turned off, the potential curve reverts to its original form, in which the energy U_0 at the point x_* is smaller than U_1 at x_1, and the angle φ of the boundary side group becomes $\varphi=0$.

5. PERTURBATION THEORY FOR EQ. (5)

Solutions of the perturbed sine-Gordon equation have been studied quite thoroughly (Refs. 12–14, for example). Such solutions are sought in the form of a soliton of the unperturbed equation with modulated parameters. Following the procedure worked out in Ref. 14 for the sine-Gordon equation with an arbitrary perturbation, we find the following expression in place of (7) for our situation, in first-order perturbation theory:

$$\varphi(x,t)=\arctan\left\{\exp\left[\pm\frac{x-x_0-X(t)}{\sqrt{1-u^2(t)}}\ 1\right\},\tag{9}$$

where $u(t)=\pm\tanh(2\lambda t)$, $X(t)=\pm\ln[\cosh(2\lambda t)]$.

To work in higher-order perturbation theory, we use the change of variables

$$(x'+t')/2=\xi,\quad (x'-t')/2=\eta\tag{10}$$

to put Eq. (5) in the form

$$y_{\xi\eta}=\sin y+\lambda\ \sin(y/2).\tag{11}$$

We seek a solution of (11) in the form

$$y=4\ \arctan f,\quad f=\exp\ \theta.\tag{12}$$

With $\lambda=0$ we have the following result for the unperturbed sine-Gordon equation:

$$\theta^{(0)}=\pm\gamma[(1-v)\xi+(1+v)\eta].\tag{13}$$

This solution is distorted in the case $\lambda\neq0$; i.e., the velocity v_s and shape of the pulse change.

From (11) and (12) we find an equation for $\theta(\xi,n)$:

$$(\theta_{\xi\eta}-\lambda/2)\coth\ \theta=\theta_\xi\theta_\eta-1.\tag{14}$$

For $\lambda\neq0$ we seek a solution of (14) in the form $\theta=\theta(w)$, $w=a\xi-\gamma x_0=\eta/a$. From Eq. (14) we find in this case

$$\theta_{ww}-\theta_w^2\tanh\ \theta=\lambda/2-\tanh\ \theta,\tag{15}$$

$$w=\int d\theta\left(c\ \cosh^2\ \theta-\sinh^2\ \theta+\frac{\lambda}{2}\sinh\ 2\theta\right)^{-1/2}.\tag{16}$$

The coefficient c in (16) is found from the condition $w=\theta^{(0)}$ in the case $\lambda=0$: $c=1$. We thus finally find

$$w=\int d\theta\left(1+\frac{\lambda}{2}\sinh\ 2\theta\right)^{-1/2}.\tag{17}$$

To first order in λ we find from (17)

$$\theta^{(1)}=w\sqrt{1+\frac{\lambda}{2}\sinh\ 2w}$$
$$=\left(a\xi-\gamma x_0+\frac{\eta}{a}\right)\sqrt{1+\frac{\lambda}{2}\sinh\left[2\left(a\xi-\gamma x_0+\frac{\eta}{a}\right)\right]},\tag{18}$$

$$y=4\ \arctan\left\{\exp\left[\pm\gamma(x'-x_0'-vt')\sqrt{1\pm\frac{\lambda}{2}\sinh[2\gamma(x'-x_0'-vt')]}\right]\right\}.\tag{19}$$

Higher orders are calculated from the iterative formula

$$\theta^{(n)}=w\sqrt{1+\frac{\lambda}{2}\sinh(2\theta^{(n-1)}}).\tag{20}$$

Analysis of (19) and (20) shows that the perturbing term changes the shape and velocity of the soliton but does not destroy it.

6. BAND STRUCTURE OF THE POLYMER

The energy of elementary excitations of the electron subsystem is determined by the poles of the Fourier transforms of the functions $G_{nm}=\langle a_{in}^+(t)a_{im}(0)\rangle$. To determine them we have the equations of motion

$$\begin{aligned}i\frac{d}{dt}G_{nm}=\varepsilon_mG_{mn}&+\frac{J_1}{4}\sum\langle\sin^2\ \varphi_{i,n-g}\ \sin^2\ \varphi_{in}\rangle\\&\times(G_{n-g,m}+G_{n+g,m})\\&+\frac{J_2}{4}\sum[\langle\sin^2\ \varphi_{in}\ \cos^2\ \varphi_{i,n+g}\rangle G_{n+2g,m}\\&+\langle\sin^2\ \varphi_{i,n-2g}\ \cos^2\ \varphi_{i,n-g}\rangle G_{n-2g,m}]\\&+\sum J_{ij}\langle a_{jn}^+(t)a_{im}(0)\rangle.\end{aligned}\tag{21}$$

According to (7) we have

$$\tan[\varphi(x,t)]=\exp[\pm\gamma B(x-x_0-v_st)],$$

where $B=2\sqrt{(4U-\alpha+\beta)/(\alpha+\beta)}$. We thus find

$$\cos^2[\varphi(x,t)]=\frac{1}{2}\frac{\exp[\mp\gamma B(x-x_0-v_st)]}{\cosh[\gamma B(x-x_0-v_st)]},$$

where $x-x_0=bn$, and b is the "lattice" constant along the polymer chain.

Since we will be using the continuum approximation below, we assume $\varphi_{in}\simeq\varphi_{i,n+g}$. In the classical limit we then find

$$\langle\sin^2\ \varphi_{i,n+g}\ \sin^2\ \varphi_{in}\rangle=\langle\sin^4\ \varphi_{in}\rangle=\sin^4\langle\varphi_{in}\rangle$$
$$=\frac{1}{4}\frac{\exp[\pm2\gamma B(x-x_0-v_st)]}{\cosh^2[\gamma B(x-x_0-v_st)]}$$

and, correspondingly,

$$\langle\sin^2\ \varphi_{in}\ \cos^2\ \varphi_{i,n+g}\rangle=\langle\sin^2\ \varphi_{i,n-2g}\ \cos^2\ \varphi_{i,n-g}\rangle$$
$$=\frac{1}{4}\cosh^{-2}[\gamma B(x-x_0-v_st)].$$

The system is assumed to be uniform in the y and z directions. After taking Fourier transforms in the yz plane, which is perpendicular to the axis of the polymer molecule, we find from (21)

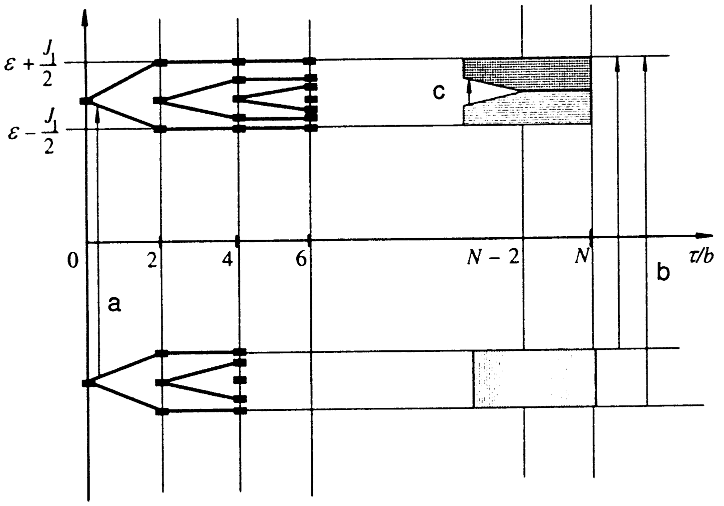

FIG. 2. Band structure of the polymer as a function of the slow time. At $\tau=0$, the levels are N-fold degenerate. At $\tau=2b$, two levels split off from the N-fold-degenerate system of levels, while the others remain degenerate. At $\tau=Nb$, the degeneracy is lifted completely. The arrows show optical transitions. The lower band is completely filled, and the upper half-filled. a—Absorption by the unconjugated part of the polymer; b, c—absorption and intraband absorption by the conjugated part of the polymer.

$$\begin{aligned} i\frac{d}{dt}G_{nm}(k_\perp,t)&=\varepsilon G_{nm}(k_\perp,t)+\frac{J_1}{8}\,\frac{\exp[\pm 2B\gamma(nb-v_st)]}{\cosh^2[\gamma B(nb-v_st)]}\\ &\quad\times\sum_{g=\pm1}G_{n+g,m}+\frac{J_2}{8}\,\frac{1}{\cosh^2[\gamma B(nb-v_st)]}\\ &\quad\times\sum_{g=\pm1}G_{n+2g,m}(k_\perp,t)\\ &\quad+2J\cos(k_\perp a)G_{n,m}(k_\perp,t). \end{aligned}\tag{22}$$

To find a solution, we discard from this expression the next-to-last term, which plays a role only in the (small) transition region; we approximate the second term by a step function; and we introduce a slow time $\tau=v_st$, which we use as a parameter. For the transition of the polymer from the nonconducting state to the conducting one, expression (22) then becomes

$$\begin{aligned} i\frac{d}{dt}G_{nm}&=[\varepsilon+2J\cos(k_\perp a)]G_{nm}+\frac{J_1}{2}\\ &\quad\times(G_{n+1,m}+G_{n-1,m})\qquad\text{for } n\leqslant\tau/b,\\ i\frac{d}{dt}G_{nm}&=[\varepsilon+2J\cos(k_\perp a)]G_{nm}\qquad\text{for } n>\tau/b. \end{aligned}$$

For $n>\tau/b$, each unit of the polymer chain is isolated from its neighbor along the chain. A multiply degenerate band with an energy

$$E_n=\varepsilon-2|J|\cos(k_\perp a),\quad n>\tau/b,\quad n=N+1,\ldots$$

thus forms in this part of the polymer.

In the case $n\leqslant\tau/b$, all the units $N=\tau/b$ form a conjugated chain of length τ. Expanding the function G_{nm} in a Fourier series in the variable n on this interval, and using $G_{N+1,m}=0$, we find

$$\begin{aligned} i\frac{d}{dt}G_{km}&=[\varepsilon+2J\cos(k_\perp a)]G_{km}\\ &\quad+J_1\cos\left(\frac{2\pi k}{N}\right)G_{km},\quad k=0,\ldots,N-1 \end{aligned}$$

and

$$\begin{aligned} G_{km}&=G_{km}(0)\exp\{-it[\varepsilon+2J\cos(k_\perp a)\\ &\quad+J_1\cos(2\pi k/N)]\}. \end{aligned}$$

Since the argument of the exponential function is independent of m, the energy levels for this part of the polymer chain are described by

$$E_k=\varepsilon-2|J|\cos(k_\perp a)-|J_1|\cos(2\pi k/N),\quad k=0,\ldots,N-1.\tag{23}$$

Half of these states are occupied by electrons which were previously in the σ shell.

Figure 2 shows the structure of the bands of energy levels for this polymer. We see that the onset of conducting chains causes a broadening of the absorption band for the $\pi\rightarrow\pi^*$ transition by an amount J_1 and gives rise to low-frequency absorption as a result of intraband transitions.

The gap for the intraband transitions depends on the slow time. As the conjugation chain grows when a kink moves, the gap shrinks, tending toward a limiting value of zero. This gap is described by the expression

$$\Delta(t)\simeq|J_1|(2\pi b/v_st),\tag{24}$$

from which we can determine the velocity of the soliton.

We can measure v_s by placing a pickup for a variable pressure with a frequency Ω at the contact of the polymer with an electrode. A pressure increase generates a soliton, which propagates along the polymer; after a half-period, with decreasing pressure, an antisoliton is generated. The latter propagates at the same velocity and limits the conjugated part of the polymer to a size $2\pi v_s/\Omega$. The gap depends on Ω and is given by

$$\Delta(\Omega)=|J_1|b\Omega/v_s.$$

Hence

$$v_s=|J_1|b\Omega/\Delta.$$

All quantities in this expression either are known or can easily be measured.

7. DISCUSSION OF RESULTS

7.1. Switching mechanism

The primary result of this study has been to establish that a traveling solitary wave forms and converts a polymer molecule from a nonconducting state to a conducting one, and vice versa. This result has not previously been obvious for the given class of polymers. The existence of such a solution suggests a model for the switching and for the formation of the conducting channels. Let us examine this model.

A bridge carbon atom in a polymer chain in the nonconducting ground state has sp^3 hybridization. The plane of a side ring attached to this atom is perpendicular to the main polymer chain ($\varphi=0$). The restructuring of the electron state begins with a rotation of the side ring through an angle of $\pi/2$, a rupture of the C–O bond near an electrode due to external agents, and the formation of C═C double bonds instead of the single bonds in the main chain. The restructuring of the C–C bonds into C═C bonds, and of C═C bonds into C–C bonds, occurs very rapidly. This restructuring occurs within a unit and is not explicitly reflected in the model. The visible result, which is incorporated in the model, is the rupture of a C–O bond in a neighboring unit, accompanied by the formation of a biradical excited state.

The change in the angle φ from 0 to $\pi/2$ propagates undamped along the polymer chain by virtue of indirect interactions through the electron subsystem, which are determined by the parameters α and β. This process apparently occurs in the following way. After the rupture of a bond, a molecule assumes a position which is favored from the energy standpoint, in which the plane of the side ring makes an angle of $\pi/2$ with the plane perpendicular to the main chain. This change puts one new electron in the π shell (this electron had previously been in the σ shell) and causes the electron to interact with an electron at a bridge carbon atom, which passes from a $\overset{|}{\underset{|}{\mathrm{C}}}{=}$ configuration to a $-\underset{\|}{\mathrm{C}}-$ configuration. In other words, the double bond rotates through an angle of $\pi/2$ without a change in the sp^2 hybridization of the bridge atom. As a result of this rotation, C═C double bonds in the main chain of the polymer are again replaced by single C–C bonds, and vice versa, and the process involves two more monomer units. As a result, the biradical state moves one step, and the conjugated chain grows at the expense of the unconjugated part, which shrinks.

These instabilities are apparently observed in polymers when an electric field and uniaxial pressure are applied.[3–5] An explanation of the experimental results of Refs. 3–5 on the basis of a combination of a high elasticity and a high polarity,[6,7] without consideration of the chemical structure of the polymer, does not draw a complete picture of the phenomenon.

The results found above make it possible to explain the experiments of Refs. 9–11 on polyarylenephthalides: A switching effect with a abrupt change in resistivity from 10^{14} to 10^3 $\Omega\cdot$cm was observed in thin films (less than 3 μm thick) in electric fields. The same effect occurred upon the application of a uniaxial pressure. The external perturbation which transformed the properties of the polymer was fairly low. For example, the threshold value of the uniaxial pressure for the transition was less than 10^2 Pa. The experiments showed that the conducting state was sometimes "remembered" by the polymer. This memory may have been due to a pinning of the rotation angle by impurities or other irregularities. In this situation, a switching off (the onset of the second solution) could be caused by a stronger external perturbation: brief current pulses, an external pressure, displacement of an electrode, etc.

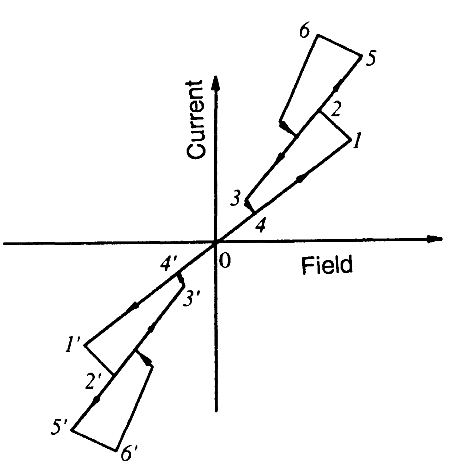

FIG. 3. Current-voltage characteristic of the polymer.

The generation of solitons is an improbable process. Accordingly, there are only a few transformed polymer chains, but their conductivity is high, and it determines the conductivity of the film. In the experiments on switching in Refs. 3 and 15, the observed surface density of conducting channels (the number of channels per unit area of the electrode) depended on the sample preparation conditions and the nature of the external agents. That density reflects the probability for the generation of a soliton under the given conditions.

7.2. Optical properties

When a polymer passes to a conducting state, a new band appears in optical spectra. It peaks at $E\simeq J_1$, has an abrupt cutoff on the high-energy side, and has a long tail on the low-energy side (Fig. 2). Since we have $J_1\sim 1$ eV, the formation of this new band causes a coloring of the polymer. The absorption bands observed in the nonconducting polymer broaden in the transition to the conducting state and acquire satellites on the high- and low-energy sides. These satellites are separated from the peak by amounts $J_1/2+J_0$ and $J_1/2-J_0$, where J_0 is the width of the lower band, from which the transition during the absorption begins. For most organic molecules we would have $J_0\geqslant J_1/2$.

Although the concentration of conducting molecules is small, their absorption coefficient is greatly increased because of the large conjugation length. This increase promotes a manifestation of an absorption spectrum of conjugated molecules.

These changes in spectra were apparently observed in Ref. 16, where the conducting state was formed by doping a system with iodine. The conductivity rose from 10^{-13} to 10^{-5} $\Omega\cdot$cm. Two new absorption bands were observed, at 1.05 and 3.2 eV. In its nonconducting state the polymer had absorption peaks at 4 and 4.5 eV, while in its conducting state these peaks shifted to 4.1 and 4.9 eV, respectively.

7.3. Electrical properties

Polymers of this class have a distinctive current-voltage characteristic (Fig. 3). In region 0–*1*, the film is in a nonconducting state and obeys Ohm's law. At point *1*, the field reaches a level at which the side group becomes able to overcome the barrier, and the film goes into a conducting state along path *1*–*2*. As the field is reduced, the conducting state is preserved, as is Ohm's law, to point *3*, because the activation energy for the transition $x_1 \rightarrow x_*$ is smaller than the activation energy for the transition $x_* \rightarrow x_1$. Then comes a transition to a nonconducting state. If we continue to increase the field after point *2* has been reached, Ohm's law holds again up to point *5*. At point *5*, side groups with a higher activation energy come into play, additional conducting channels form, and the current rises to its value at point *6*. The entire process then occurs again.

For a sample initially prepared in the conducting state, the switching events occur in a corresponding way, but the process involves the turning off of the conducting channels and the transition of the film to a nonconducting state.

These processes do not depend on the polarity, as can be seen on the left side of Fig. 3. When the sign of the field is changed, the only result is a change in the direction of the current; the shape of the characteristic remains the same.

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