Dynamic helicity-reversal defects in polytetrafluoroethylene chains

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Propagation of the excitation that changes a left-handed helix to a right-handed helix is studied as a model for the mechanism of certain phase transitions in polytetrafluoroethylene. Although energy considerations cause these dynamic helicity-reversal defects to decelerate after creation, the particular morphology of this polymer appears to permit them to traverse a lamellar thickness in times of the order of 10 ns.

(Keywords: dynamics; PTFE; defects)

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a commercially important simple polymer with the rich phase diagram shown in *Figure 1*. In the high-pressure phase III, the conformation of the helix is that of a planar zigzag, or 2_1 helix[1]. In the low-pressure phases I, II and IV, the polymer molecules are helical with a gentle twist away from the zigzag conformation. This twist is caused by the repulsion between the fluorine atoms on alternate carbon atoms[2]. In phase II, the helix is incommensurate with a pitch of 2.910 rad per monomer, corresponding to approximately 2.159 CF_2 units per turn of the helix. The unit cell of this phase is triclinic and has been reported to contain two helical chains with opposite handedness[3,4]. In phases I and IV, the helix is thought to be a commensurate 15_7 helix having the helices packed in a hexagonal array[2,5]. The unit cell in these phases has usually been considered to contain one chain[5,6], which has the consequence that only a single handedness can be present. As pointed out by Farmer and Eby[7], this implies that every other chain must reverse its handedness in going from the low temperature phase to the high temperature phases; for this to be the case a mechanism must exist to allow for the reversal of the helicity at a low cost in energy. The reversal of handedness of the helical molecule was proposed early as a possible defect in the crystal phases[8]. Both infrared absorption[9] and Raman scattering[10,11] in the band 570–640 cm^{-1} show anomalies with increasing temperature which have been explained in terms of thermally activated helicity-reversal defects[9–11]. There is also evidence from nuclear magnetic resonance spectra[12] of growing dynamic disorder with increasing temperature.

Conformational energy calculations[6,13–15] show that there are two degenerate minima for conformations about $\pm 16°$ off the *trans* conformation, in close agreement with experiment. The potential barrier between these minima is less than 1 kcal mol^{-1} †, which suggests that it might be relatively easy to form a defect consisting of a reversal of the helicity. Some simple conformational energy calculations of such a defect have been performed[9,16] with the results that the conformational energy of a chain containing one such defect is also about 1 kcal mol^{-1} higher than the energy of a perfect helix.

The purpose of the present paper is to show that such a defect separating two regions of opposite helicities appears as a natural *dynamic* state in the PTFE chain. This entity has been given the name *ambidextron*[17]. We have calculated the size and dispersion relation of the ambidextron, and we will argue that the creation of ambidextrons may play a significant role in the transition from the low temperature phase to the high temperature phases of PTFE.

The existence of dynamic helicity-reversal defects in PTFE was first discussed qualitatively by Clark[18], who speculated that such defects may provide a mechanism for large angular displacements about the chain axes at temperatures below 19°C without significantly changing the X-ray diffraction spectrum of PTFE. Discussion of propagating solitary-wave defects without helicity reversal has a longer history[19]; most recently Syi and Mansfield[20] have proposed that such a mechanism can be used as a molecular model for α-relaxation in numerous crystalline helical polymers. In the present paper we concentrate on the dynamics of helicity-reversal defects. We will find that a certain topological constraint limits the applicability of the model, but that the exceptional lamellar thickness[21] of PTFE makes the ambidextron a possible candidate for relaxation processes in this particular material.

CALCULATION OF THE DYNAMICS OF THE AMBIDEXTRON

We start by deriving an effective Hamiltonian for an isolated PTFE chain, with parameters determined by a combination of conformational energy calculations and data derived from observation of the vibrational spectrum of PTFE. We denote by θ_m the rotation of the mth CF_2 unit about the helical axis relative to a fixed direction

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† 1 kcal≈4.2 kJ

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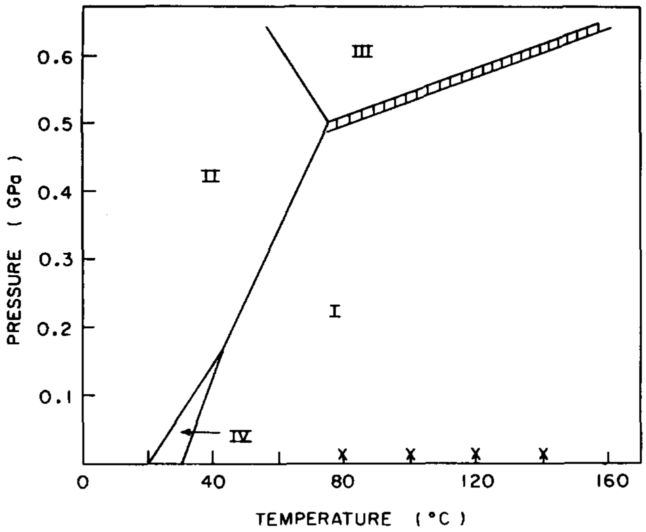

Figure 1 Part of the phase diagram of PTFE

in space, and make the assumption that the potential energy can be written

$$U = \sum_m V_1(\theta_{m+1} - \theta_m) + \sum_m V_2(\theta_{m+1} - \theta_{m-1}) \quad (1)$$

For convenience we have replaced θ_m by $\theta_m + \pi$ for all odd m, so that a conformation with all $\theta_m = 0$ will represent the planar zigzag all-*trans* conformation. While the first term in equation (1) is minimized in this all-*trans* conformation, the second term represents the repulsion between the next-nearest fluorine groups. In the ground-state conformation, $|\theta_{m+1} - \theta_m| \ll 1$, so we define $\eta_m \equiv \theta_{m+1} - \theta_m$ and proceed by expanding equation (1) in η_m and $\eta_m + \eta_{m-1}$. Symmetry considerations require that the expansion have the form

$$U = \sum_m (\alpha_1 \eta_m^2 + \alpha_2 \eta_m^4 + \cdots) - \gamma \sum_m [(\eta_m + \eta_{m-1})^2 + \cdots] + \text{constant} \quad (2)$$

where

$$\alpha_1 = \frac{1}{2} \frac{d^2 V_1(x)}{dx^2}\bigg|_{x=0} \quad (3a)$$

$$\alpha_2 = \frac{1}{4!} \frac{d^4 V_1(x)}{dx^4}\bigg|_{x=0} \quad (3b)$$

and

$$\gamma = \frac{1}{2} \frac{d^2 V_2(x)}{dx^2}\bigg|_{x=0} > 0 \quad (3c)$$

By rearranging equation (2), and defining

$$\frac{1}{2} J_1 = \alpha_1 \quad (4a)$$

$$\frac{1}{2} J_2 = \gamma \quad (4b)$$

and

$$\theta_0^2 = \frac{4\gamma - \alpha_2}{2\alpha_1} \quad (4c)$$

we obtain

$$U = \frac{1}{2} J_1 \sum_m [(\theta_{m+1} - \theta_m)^2 - \theta_0^2]^2 + \frac{1}{2} J_2 \sum [(\theta_{m+1} - \theta_m) - (\theta_m - \theta_{m-1})]^2 \quad (5)$$

To derive the equations of motion for vibrations of the monomers about their equilibrium positions, we denote by I the moment of inertia of a monomer unit about the helical axis, and write the Hamiltonian as

$$H = \frac{1}{2} I \sum_m \left(\frac{\partial \theta_m}{\partial t}\right)^2 + \frac{1}{2} J_1 \sum [(\theta_{m+1} - \theta_m)^2 - \theta_0^2]^2 + \frac{1}{2} J_2 \sum_m [(\theta_{m+1} - \theta_m) - (\theta_m - \theta_{m-1})]^2 \quad (6)$$

We take θ_0 to be the observed deviation from the *trans* conformation in the 15_7 helix, and then require that $\frac{1}{2} J_1 \theta_0^4 = \varepsilon_b$, where ε_b is the calculated potential barrier between the minima of these conformations. The parameter J_2 is calculated from the fluorine–fluorine interactions using the approach outlined in the Appendix. Finally, the moment of inertia I is determined by requiring that the small-amplitude librational vibrations about $\eta_m = \theta_0$ found from equation (6) have a frequency ω_0 at the Brillouin zone centre corresponding to the observed frequency [22,23] of 6.1 THz. The values of θ_0, ε_b, J_1, J_2 and I and the calculated parameters of the ambidextron are presented in *Table 1*.

To analyse the equations of motion resulting from the Hamiltonian, we use a continuum representation to write the Hamiltonian density as

$$H = \frac{I}{2a}\left[\frac{\partial \theta(z)}{\partial t}\right]^2 + \frac{1}{2a} J_1 \left[a^2 \left(\frac{\partial \theta}{\partial z}\right)^2 - \theta_0^2\right]^2 + \frac{a^3}{2} J_2 \left(\frac{\partial^2 \theta}{\partial z^2}\right)^2 \quad (7)$$

where a is the separation of the monomer units along the chain axis, which we take to be in the z-direction. The continuum approximation is appropriate when

$$\frac{a^2}{2}\left|\frac{\partial^2 \theta}{\partial z^2}\right| \ll 1$$

We will further discuss the validity of this approximation later in this paper.

The equation of motion obtained from equation (7) is

$$\frac{I}{a} \frac{\partial^2 \theta}{\partial t^2} = 2a^3 J_1 \frac{\partial}{\partial z}\left\{\frac{\partial \theta}{\partial z}\left[\left(\frac{\partial \theta}{\partial z}\right)^2 - \frac{\theta_0^2}{a^2}\right]\right\} - a^3 J_2 \frac{\partial^4 \theta}{\partial z^4} \quad (8)$$

Table 1 Parameters for the Hamiltonian (eq. 6) and calculated parameters for the ambidextron

Parameter	Value
θ_0	0.21 rad
ε_b	0.25 kcal mol^{-1} (ref. 15)
a	2.21 Å
I	4.32×10^{-46} kg m^2
J_1	1.28×10^2 kcal mol^{-1}
J_2	19.4 kcal mol^{-1}
ε_0	1.04 kcal mol^{-1}
a^*/a	1.56
v^*	1.4×10^3 m s^{-1}
ω_0	38.1×10^{12} rad s^{-1} (refs. 22, 23)

We look for wave-like solutions with the ansatz

$$\theta(z,t)=\theta(z\mp vt) \tag{9}$$

substitution of which in equation (8) gives

$$\frac{I}{a}v^2\theta''=2a^3J_1\frac{\mathrm{d}}{\mathrm{d}z}\left\{\theta'\left[(\theta')^2-\frac{\theta_0^2}{a^2}\right]\right\}-a^3J_2\frac{\mathrm{d}}{\mathrm{d}z}\theta''' \tag{10}$$

where $\theta'\equiv \mathrm{d}\theta(z)/\mathrm{d}z$. Integrating once, and defining $\varphi(z)\equiv\theta'(z)$, we finally arrive at the relation

$$a^3J_2\varphi''=2a^3J_1\varphi^3-\left(\frac{I}{a}v^2+2a\theta_0^2J\right)\varphi \tag{11}$$

Equation (11) is the familiar and well studied φ^4 equation[24]. Two solutions of (11) are the trivial static solutions given by $\varphi=\pm\theta_0/a$, which represent right- and left-handed regular helices. A non-trivial solution of (11) is the φ^4 kink:

$$\varphi(z\mp vt)=\varphi^{\pm}\tanh\left[\left(\frac{Iv^2+2a^2\theta_0^2J_1}{2a^4J_2}\right)^{1/2}(z\mp vt)+\delta\right] \tag{12}$$

where

$$\varphi^{\pm}=\pm\left(\frac{Iv^2+2a^2\theta_0^2J_1}{2a^4J_1}\right)^{1/2} \tag{13}$$

and δ is an unimportant phase.

The solutions (12) represent a reversal of the helicity from the pitch given by $\pm\theta_0/a$ at $z\to-\infty$ to $\mp\theta_0/a$ at $z\to+\infty$ travelling with a velocity $\pm v$. The ends of the chain at $z\to\pm\infty$ rotate in opposite directions with an angular velocity $v\varphi^{\pm}$. The ambidextrons represented by (12) are localized within a distance

$$a(v)=\left(\frac{2a^4J_2}{Iv^2+2a^2\theta_0^2J_1}\right)^{1/2}\approx a^*\left[1-\frac{1}{3}\left(\frac{v}{v^*}\right)^2\right] \tag{14}$$

for $(v/v^*)\ll 1$, with

$$a^*=\frac{a}{\theta_0}\left(\frac{J_2}{J_1}\right)^{1/2} \tag{15}$$

and

$$v^*=\left(\frac{4}{3}\frac{a^2\theta_0^2J_1}{I}\right)^{1/2} \tag{16}$$

Their energies ε are given by

$$\varepsilon\approx\varepsilon_0\left[1-\frac{3Iv^2}{4a^2\theta_0^2J_1}\right]+\frac{L}{a}\frac{Iv^2\theta_0^2}{2a^2} \tag{17}$$

with L the overall length of the chain and with

$$\varepsilon_0=\frac{4}{3}\theta_0^3(J_1J_2)^{1/2} \tag{18}$$

being the energy of a static ambidextron.

From (17) and (18) we see that the ambidextron has an effective mass, m^*, given by

$$m^*=\frac{I\theta_0^2}{a^2}\left[\frac{L}{a}-2\left(\frac{J_2}{J_1}\right)^{1/2}\right]\approx\frac{I\theta_0^2}{a^2}\frac{L}{a} \tag{19}$$

This expression differs from those commonly encountered in soliton theory in containing a term proportional to the length L of the chain. The origin of this term lies in the topological constraint imposed on any solution for a continuously varying angle $\theta(z,t)$; the 'winding number', equal to the number of times θ rotates about the axis in passing from one end of the chain to the other, cannot change if the ends of the chain are at rest. Keeping the ends of the chain fixed thus results in a force that tends to prevent free motion of the soliton. This problem is avoided if at least one end of the chain is free to rotate, but then the bulk of the chain must participate in the excitation of the soliton, and a correspondingly large term appears in the expression for the energy. The effective mass is then almost entirely due to the moment of inertia of the chain.

The calculated values for ε_0, a^* and v^* are included in *Table 1*. First we see that the energy ε_0 of the static ambidextron calculated in this indirect way agrees well with values obtained by other authors. Brown[9] finds a value of 1.2 kcal mol^{-1} from analysis of the infrared absorption peaks at 625 cm^{-1} and 640 cm^{-1} and compares this with an energy of 1.4–2.6 kcal mol^{-1} obtained from a conformational calculation, while Corradini and Guerra[16] arrive at a value of about 1.0 kcal mol^{-1}.

The solutions (12) represent ambidextron states where the two ends of the molecule rotate in opposite directions. Such a state is not very likely to occur in crystalline PTFE, where the chains are folded in lamellae of thicknesses[25] of the order of 1 μm and no stem in the lamellae is then likely to have two ends both of which are free to rotate. However, on physical grounds there must exist solutions of (8) that satisfy a boundary condition in which only one end is kept fixed. Such solutions cannot be obtained by a Lorentz transformation of (12), since to satisfy energy conservation such defects cannot travel with constant velocity. An ambidextron travelling from the free end towards the fixed end of the chain thus does so with a velocity that decreases with the distance travelled. Although we have not been able to obtain such a solution in closed form, we can estimate the time it takes for such a defect to traverse a typical lamella thickness of PTFE. We consider an ambidextron created at $t=0$ at a free end of a PTFE chain, so that this end rotates as the ambidextron travels along the chain. When losses are ignored, the energy E of this ambidextron is then approximately

$$E=\varepsilon_0+\frac{1}{2}m_0^*v(t)^2+\frac{I}{2a}z(t)(\varphi^+)^2v^2 \tag{20}$$

Here m_0^* is the effective mass associated with the local structure of the defect and this effective mass is a function only of the spring constants J_1 and J_2; $z(t)$ is the distance that the ambidextron has travelled in a time t and the last term in (20) is the kinetic energy of the rotating section of the chain. From (20) we have

$$v=\left[\frac{E-\varepsilon_0}{\frac{1}{2}m_0^*+\frac{I}{2a}z(t)(\varphi^+)^2}\right]^{1/2} \tag{21}$$

from which we obtain

$$z(t)=\frac{2a}{I(\varphi^+)^2}\left[\left(\frac{E-\varepsilon_0}{2}\right)^{1/3}\left(\frac{3I(\varphi^+)^2}{4a}t\right)^{2/3}-\frac{1}{2}m_0^*\right] \tag{22}$$

For an initial energy E of 2 kcal mol^{-1}, we then obtain a traversal time of the order of 10^{-8} s.

DISCUSSION

For the ambidextrons considered in this paper to provide a mechanism for relaxation in the transition between phases I and IV, there must then be a high ratio of free ends to stems in a crystal lamella. The molecular weight of PTFE is[7,25] typically about 10^6, while the stiffness of the PTFE chains causes the lamellar thickness to have an exceptionally high value of about[21] 1 μm. Thus each molecule in a lamella folds only a few times, which means that the ratio of free ends to stems is indeed high.

This consideration raises the more general question of whether a continuum soliton model is capable of describing molecular motion in helical polymers in which the chains are more tightly folded. To treat the case of isotactic polypropylene, for example, it may be necessary to model the ambidextron in terms of a two-dimensional solitary wave $(r(z, t), \theta(z, t))$, in which not only the angle θ but also the amplitude r can change with position. An amplitude that passes through zero would then correspond physically to a backbone bond passing through the helix axis. This process would change the winding number of the polymer chain, and hence allow the motion of the ambidextron without rotation of large segments of the chain. The energy barriers to be overcome in forming this type of excitation would appear to be sufficiently large that a discrete rather than a continuum model would be necessary.

In the particular case of PTFE, the continuum approximation to the Hamiltonian appears to be justified. As previously stated, this approximation is valid when

$$\frac{a^2}{2}\left|\frac{d^2\theta}{dz^2}\right| \ll 1$$

For the ambidextron, we obtain

$$\frac{a^2}{2}\left|\frac{d^2\theta}{dz^2}\right| \sim 0.1$$

which is in accord with this condition. Furthermore, Schmidt[26] has examined the continuum approximation of the discrete φ^4 chain, and finds the continuum approximation to be reasonably accurate for $a/a^* < 0.6$. In our case, we have $a/a^* \approx 0.6$.

CONCLUSIONS

We have shown that a dynamic helicity reversal, termed an ambidextron, appears as a natural consequence of the equation of motion for the monomers in a PTFE chain. The properties of the ambidextron are such that it will propagate with position-dependent velocities in the range from 40 to 1000 m s^{-1} at a cost of energy of the order of 1 kcal mol^{-1}. These ambidextrons are, however, such that one end of the chain in which they propagate must be free to rotate. Hence, for the ambidextrons to provide a mechanism for relaxation in crystalline PTFE, there must be a high ratio of free ends to stems in the crystal lamellae. This is indeed the case for PTFE, because the stiffness of the molecular chains causes the fold length of PTFE to be exceptionally long. Thus the ambidextrons provide a mechanism for the reversal of helicities which may occur in the transition from the low temperature phase to the high temperature phases of PTFE.

In the present paper, we have only considered a single chain of PTFE and have ignored the effects of interchain interactions in the crystalline phases of PTFE. Conformational calculations[16] indicate that the interaction between a chain with one ambidextron and a perfect helical chain is about the same as the interaction between two perfect helices, and so we have no reason to believe that the inclusion of interchain interactions will qualitatively change any results obtained here. However, because neighbouring chains of opposite helicities interlock more readily than chains of the same helicity, there exists the possibility of a weak long-range interchain interaction between ambidextrons; if one helix reverses its helicity, the neighbouring chains can lower the interchain interaction energy somewhat by reversing their helicities to bring the ambidextrons into greater proximity. The properties of a lattice of chains, each described by the Hamiltonian equation (6) and interacting with one another, will be the subject of future work.

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REFERENCES

1 Flack, H. D. *J. Polym. Sci.* 1972, **10A2**, 1799
2 Brown, C. W. and Howells, E. R. *Nature* 1954, **174**, 549
3 Weeks, J. J., Clark, E. S. and Eby, R. K. *Polymer* 1981, **22**, 1480
4 Farmer, B. L. and Eby, R. K. *Polymer* 1981, **22**, 1487
5 Clark, E. S. and Muus, L. T. S. *Krist.* 1962, **117**, 119
6 D'Ilario, D. and Giglio, E. *Acta Cryst.* 1974, **B30**, 372
7 Farmer, B. L. and Eby, R. K. *Polymer* 1985, **26**, 1944
8 Klug, A. and Franklin, R. E. *Discuss. Faraday Soc.* 1958, **25**, 104
9 Brown, R. G. *J. Chem. Phys.* 1964, **40**, 2900
10 Koenig, J. L. and Boerio, F. J. *J. Chem. Phys.* 1969, **50**, 2823
11 Hannon, M. J., Boerio, F. J. and Koenig, J. L. *J. Chem. Phys.* 1969, **50**, 1819
12 English, A. D. and Vega, A. J. 'Polymer Characterization by ESR and NMR', (Eds A. E. Woodward and F. A. Bovey), American Chemical Society, Washington, D.C., 1980, p. 169
13 Iwasaki, M. *J. Polym. Sci.* 1963, **1**, 1099
14 de Santis, P., Giglio, E., Liquori, A. M. and Ripamonti, A. *J. Polym. Sci.* 1963, **1**, 1383
15 Banerjea, A. and Taylor, P. L. *J. Appl. Phys.* 1982, **53** (10), 6532
16 Corradini, P. and Guerra, G. *Macromolecules* 1977, **10**, 1411
17 Wright, N. F. *Bull. Am. Phys. Soc.* 1988, **33**, 248
18 Clark, E. S. *J. Macromol. Sci. Phys.* 1967, **B1**, 795
19 For a review, see Boyd, R. H. *Polymer* 1985, **26**; 323, 1123
20 Syi, J.-L. and Mansfield, M. L. *Polymer* 1988, **29**, 987
21 Bunn, C. W., Cobbold, A. J. and Palmer, R. P. *J. Polym. Sci.* 1958, **28**, 356
22 Krimm, S. *Fortschr. Hochpolym.-Forsch.* 1960, **2**, 51
23 Masetti, G., Cabassi, F., Morelli, G. and Zerbi, G. *Macromolecules* 1973, **6**, 700
24 See, for example, Dodd, R. K., Eilbeck, J. C., Gibbon, J. D. and Morros, H. C. 'Solitons and Nonlinear Wave Equations', Ch. 7, Academic Press, London, 1984
25 Sperati, C. A. and Starkweather, H. W. *Forschr. Hochpolym. Forsch.* 1961, **21**, 465
26 Schmidt, H. *Phys. Rev.* 1979, **B20**, 4397

APPENDIX

In this appendix, we estimate the coefficient J_2 of equation (5). We denote by $\varepsilon_v + \varepsilon_e$ the interaction energy between the fluorine atoms on carbon atom $m-1$ and those on carbon atom $m+1$. Here ε_v is the van der Waals interaction between a fluorine atom at $\boldsymbol{r}_1$ and a fluorine atom at $\mathbf{r}_2$. This energy is given by

$$\varepsilon_v(\mathbf{r}_1 - \mathbf{r}_2) = -\frac{A}{|\mathbf{r}_1 - \mathbf{r}_2|^6} + \frac{B}{|\mathbf{r}_1 - \mathbf{r}_2|^{12}} \tag{A1}$$

where[15] $A = 276.5$ kcal mol^{-1} Å^6 and $B = 2.332 \times 10^5$ kcal mol^{-1} Å^{12} (1 Å $= 10^{-1}$ nm). The electrostatic contribution ε_e is given by

$$\varepsilon_e(\mathbf{r}_1 - \mathbf{r}_2) = \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{A2}$$

In equation (A2), q is the effective charge on each fluorine atom[15], $q = -0.173e$, where e is the proton charge.

It is easy to show that

$$J_2 = -\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}(\varepsilon_v + \varepsilon_e)|_{\phi=0} \tag{A3}$$

where $\phi = \theta_{m+1} - \theta_{m-1}$. By using the values of q, A and B given above, we conclude after some algebra that $J_2 = 19.35$ kcal mol^{-1}.