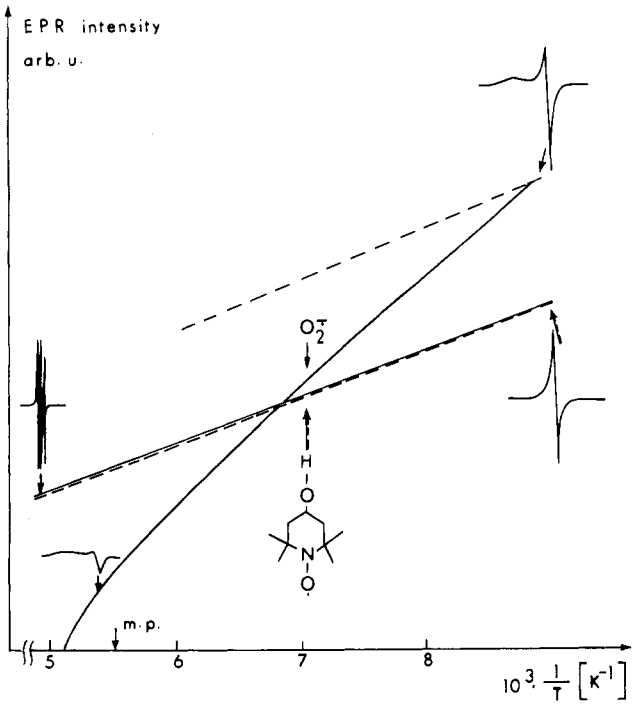

Figure 2. Plot of relative ESR signal amplitude versus reciprocal temperature for (a) O_2^- and (b) the TEMPOL radical in propionitrile. The broken line represents the expected change of intensity with temperature on the basis of the Curie law.

temperature and (b) g-anisotropy remains virtually unchanged over a wide range of temperature and is observed even in the liquid phase.

The remarkably similar temperature dependence of the ESR signal of O_2^- in butyronitrile or propionitrile solution, frozen solutions of dimethyl sulfoxide,[9] or O_2^- generated on a silica gel surface[29] can be explained by assuming that the dominant temperature-dependent effect arises from changes in the mobility of O_2^- entities in the solvent matrix and variation of spin–lattice relaxation time.[30] The major temperature-dependent term effecting the mobility is presumably related to fluctuations in the O–O bond length (z-axis). This term would explain the pronounced line broadening of $g_{\parallel}$ that is observed with increasing temperature. The nature of the organic solvent or matrix should not effect this phenomenon to any significant extent as appears to be the case from experimental data. However, when the solvent is in the liquid phase, and in absence of large orbital momentum contribution or orbital degeneracy, a one-line symmetrical spectrum of O_2^- would normally be expected, due to complete averaging of the g-anisotropy caused by rapid tumbling of O_2^- entities. However, an *asymmetric* one-line spectrum is observed, whose amplitude continues to decrease rapidly with temperature, even in the liquid phase. To understand this interesting and relatively unusual phenomenon, one has to bear in mind that (i) the matrix of the frozen solvent softens and remains soft at temperatures much below the melting point and (ii) that a certain degree of order may be preserved at temperatures above the melting point accompanied by retention of relatively high viscosity. The large drop in signal intensity over a wide temperature range encompassing both the frozen state and solution phase can be rationalized in terms of these two phenomena. The increased mobility of O_2^- with increasing temperature and spin–lattice relaxation would lead to enhanced averaging of the g-anisotropy resulting in a broad line in the solution phase instead of two separate lines corresponding to $g_{\parallel}$ and $g_{\perp}$. However, the retention of an anisotropic spectrum of O_2^- in the liquid phase indicates that g-anisotropy is too large to be completely averaged out.

A study with TEMPOL (Figure 2) shows that in contrast with O_2^- (i) the expected (Curie) dependence of integrated signal intensity on temperature is observed and (ii) hyperfine structure is observed to be resolved at temperatures immediately above the melting point of the solvent. TEMPOL is a large molecule relative to O_2^- with an almost totally quenched orbital momentum and almost zero g-anisotropy. Under these circumstances, the temperature dependence of the ESR signal intensity simply mirrors changes in viscosity. In contrast the very small change in g-anisotropy indicates that the orbital momentum of O_2^- is modulated by the fluctuations in the O–O bond length[29,30] leading to a shortened spin relaxation time with increasing temperature.

The spectrum of O_2^- in frozen solvent was essentially independent of the preparation technique (KO_2 dissolution in the presence of crown ether or electrolytic generation). It was also found that no change in the line shape of the ESR signal could be detected in the solution phase after bubbling argon through the solvent to remove molecular oxygen. This indicates that negligible electron exchange occurs between O_2 and O_2^- on the ESR time scale in the solution phase. The stability of O_2^- solutions in the organic phase over the temperature range of interest was confirmed by the constancy of repeated experiments performed after a number of freeze–thaw cycles.

As a precursor to performing the electrochemical generation of O_2^-, cyclic voltammetric measurements on the reduction of O_2 were made with mercury, glassy carbon, platinum, and gold electrodes in butyronitrile. The formal reversible potentials, calculated as the average of the reduction and oxidation peaks, are −1.01 (Hg), −1.01 (glassy carbon), −1.00 (Pt), and −1.05 (Au) V vs SCE. The formal potentials are essentially independent of electrode material as expected theoretically. However, the values in butyronitrile are more negative than in dimethyl sulfoxide.[31] The large difference between the formal potentials reported in butyronitrile and the standard potential of O_2/O_2^- redox couple in water (E° = −0.33 V vs NHE)[32] can be attributed to solvation affects.[5]

Registry No. TEMPOL, 2226-96-2; O_2^-, 11062-77-4.

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Light-Sensitive Oscillations in the Hydrogen Peroxide Oxidation of Ferrocyanide[1]

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We recently designed a new pH oscillator using a continuous-flow stirred tank reactor (CSTR) in which sulfite ions and hexacyanoferrate(II) ions are simultaneously oxidized by hydrogen peroxide in water solution.[3] Further study of this system reveals that, in a significant excess of H_2O_2, pH oscillation occurs without sulfite in the hexacyanoferrate(II)–hydrogen peroxide reaction. This new mode of oscillation is extremely sensitive to visible light.

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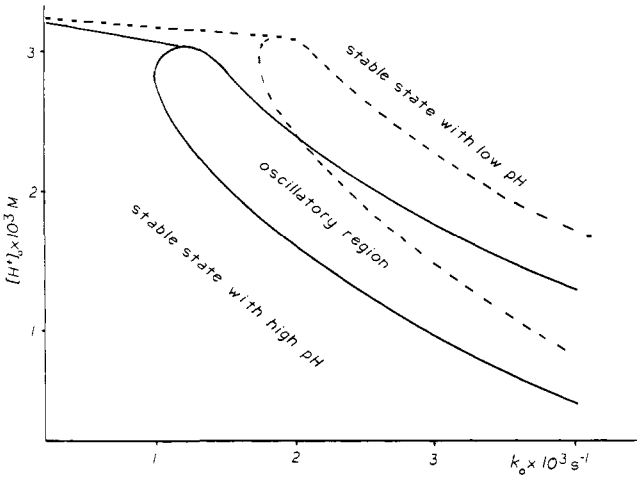

Figure 1. Phase diagrams taken in the dark (solid lines) and in light (500 lx, dashed lines) at 25 °C with $[H_2O_2]_0 = 1.0 \times 10^{-1}$ M, $[Fe(CN)_6^{4-}]_0 = 3.33 \times 10^{-3}$ M.

Light can initiate oscillatory behavior in a system showing no oscillation in the dark; in other instances light can suppress oscillations that exist in its absence.

Stock solutions of H_2O_2, H_2SO_4, and $K_4Fe(CN)_6$ were stored under argon in darkness. The reaction was followed by continuous measurement of pH and light absorbance in a CSTR.[3] To suppress bubble formation, which can alter the volume of liquid and disturb the stability of the reactor, Triton WR-1339 surfactant was introduced into the H_2O_2 input stream at a concentration of 0.25 ppm. No effect of the surfactant on the chemistry of the reaction was found. The light source for illumination was a GM no. 308-11/49CP type tungsten lamp (30 W). The light intensity was measured at the window of the CSTR.

With a significant excess of hydrogen peroxide and appropriate input concentrations of hydrogen ion and hexacyanoferrate(II) ion, oscillations in pH and light absorbance occur when the reaction takes place in a CSTR protected from light. The periodic pH change can be as large as 2 pH units. The amplitude of the oscillation in $[Fe(CN)_6^{3-}]$ (calculated from the light absorbance) is quite low, barely exceeding 1% of its total concentration.

Oscillatory behavior occurs over a range of input concentrations and flow rates. There are two stable steady states which differ in pH. The one found at high values of $[H^+]_0$ and k_0 has a pH of about 5.5, while the other state shows a pH of about 7.5. No bistability is observed. If $[H^+]_0 > [Fe(CN)_6^{4-}]_0$, the low pH state is found at all flow rates. A phase diagram obtained in the dark is shown in Figure 1 (solid lines). Here we have fixed the temperature, $[H_2O_2]_0$, and $[Fe(CN)_6^{4-}]_0$ and determined the state of the system at various values of $[H^+]_0$ and k_0. Similar phase diagrams are obtained at $[H_2O_2]_0 = 0.2$ and 0.5 M. The oscillatory region narrows and shifts to higher flow rates as $[H_2O_2]_0$ is increased. No oscillation is found when the $[Fe(CN)_6^{4-}]_0/[H_2O_2]_0$ ratio is near or above the stoichiometric value.

The amplitude, period, and even the existence of oscillations in this system are remarkably sensitive to visible light. The dashed lines in Figure 1 show how the phase diagram changes when the system is illuminated. In Figure 2 we demonstrate how increasing the intensity of illumination under some conditions causes the amplitude of oscillation to decrease until oscillations finally cease (oscillation can be restored by turning off the light or by increasing the flow rate), while at other concentrations illumination can induce oscillations. In another experiment, oscillations were established in the CSTR maintained in darkness, and the solution of hexacyanoferrate(II) was illuminated before being introduced into the reactor. The effect was similar to that caused by illumination of the reactor. The effect of light on the stock solution is reversible; the original behavior of the dark reaction is reestablished about 20 min after the illumination ceases.

During oscillation, the fate of the hydrogen peroxide alternates between reduction (eq 1) by hexacyanoferrate(II) when the pH is low and oxidation (eq 2) by hexacyanoferrate(III) at higher pH values.

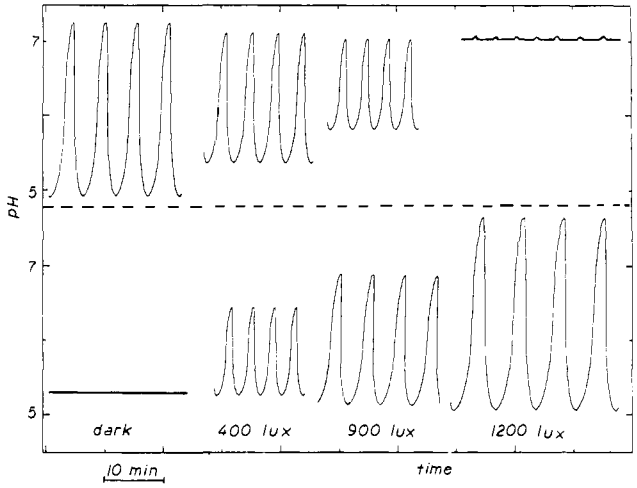

Figure 2. Effect of illumination on oscillatory behavior. When the input concentrations (top) are $[H_2O_2]_0 = 5.0 \times 10^{-2}$ M, $[Fe(CN)_6^{4-}]_0 = 3.3 \times 10^{-3}$ M, and $[H^+]_0 = 1.8 \times 10^{-3}$ M at a flow rate of $k_0 = 1.9 \times 10^{-3}$ s^{-1}, the amplitude decreases with increasing light intensity. At input concentrations of $[H_2O_2]_0 = 5.0 \times 10^{-2}$ M, $[Fe(CN)_6^{4-}]_0 = 3.33 \times 10^{-3}$ M, and $[H^+]_0 = 2.33 \times 10^{-3}$ M at a flow rate of $k_0 = 3.0 \times 10^{-3}$ s^{-1}, illumination induces oscillation (bottom). $T = 25$ °C.

Table I. A Plausible Mechanism for the Oscillatory Reaction

step no.	reaction
M1	$HFe(CN)_6^{3-} + H_2O \xrightleftharpoons{\text{light induced, slow}} Fe(CN)_5H_2O^{3-} + HCN$
M2	$Fe(CN)_5H_2O^{3-} + H_2O_2 \rightarrow Fe(CN)_5H_2O^{2-} + OH^- + OH^\bullet$
M3	$Fe(CN)_6^{4-} + Fe(CN)_5H_2O^{2-} \rightarrow Fe(CN)_6^{3-} + Fe(CN)_5H_2O^{3-}$
M4	$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$
M5	$Fe(CN)_6^{4-} + OH^\bullet \rightarrow Fe(CN)_6^{3-} + OH^-$
M6	$Fe(CN)_5H_2O^{3-} + HO_2^\bullet + H^+ \rightarrow Fe(CN)_5H_2O^{2-} + 2OH^\bullet$
M7	$Fe(CN)_6^{3-} + O_2^- \rightarrow Fe(CN)_6^{4-} + O_2$
M8	$H^+ + Fe(CN)_6^{4-} \rightleftharpoons HFe(CN)_6^{3-}$
M9	$HO_2^\bullet \rightleftharpoons H^+ + O_2^-$
M10	$H_2O \rightleftharpoons H^+ + OH^-$

$$2Fe(CN)_6^{4-} + H_2O_2 + 2H^+ \rightarrow 2Fe(CN)_6^{3-} + 2H_2O \quad (1)$$

$$2Fe(CN)_6^{3-} + H_2O_2 + 2OH^- \rightarrow 2Fe(CN)_6^{4-} + 2H_2O + O_2 \quad (2)$$

In Table I, we present the outlines of a mechanistic description for the behavior portrayed above. Since the iron–hexacyano complexes are kinetically sluggish, the key step of the proposed mechanism, and the one responsible for the photosensitivity, is the light-induced formation (M1) of the more reactive monoaquapentacyanoferrate(II). The destabilization of the steady state is generated by autocatalytic production of $OH^\bullet$ radicals in steps M4 and M6, mediated by the monoaqua complex, $Fe(CN)_5H_2O^{3-}$. A similar autocatalytic production of $OH^\bullet$ radical has been proposed in the ferroin–hydrogen peroxide reaction.[4] This mechanism is similar to that of the iron-catalyzed decomposition of H_2O_2 proposed first by Haber and Weiss[5] and modified by Barb et al.[6] Preliminary calculations based on reactions M1–M10 show oscillations similar to those found experimentally.

The influence of light on several other oscillatory reactions has been investigated in some detail,[7-9] in some cases leading to new

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mechanistic insights. The present system is significantly more sensitive to visible light than either the Belousov–Zhabotinskii[8] or the Briggs–Rauscher[9] reactions, and it should provide an ideal system for experiments on periodic perturbation of chemical oscillators[10] or even for chemical image processing.[11]

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Design and Synthesis of New Ferroelectric Liquid Crystals. 9.[1] An Approach to Creation of Organic Polymer Thin Films with Controlled, Stable Polar Orientation of Functional Groups

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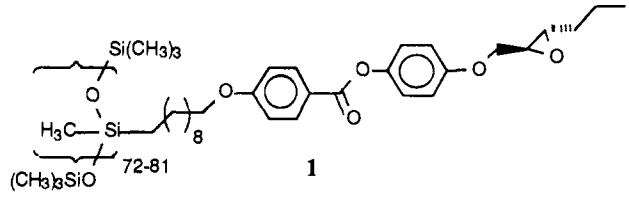
For many microelectronic and optoelectronic applications, organic thin films with controlled, polar orientation of functional groups relative to a substrate surface hold great potential. Several possible solutions of this problem are currently under active investigation, including the growth of single crystal films,[2] polar deposition of Langmuir–Blodgett multilayers,[3] electrically poled polymer films,[4] and self-assembled multilayers.[5] In this communication, we describe a new approach for achieving designed organic thin films with thermodynamically stable, polar orientation of functional groups using ferroelectric liquid crystal polymers (FLCPs).



X —95→ C* —147→ I
"glass" ←85— C* ←147— I

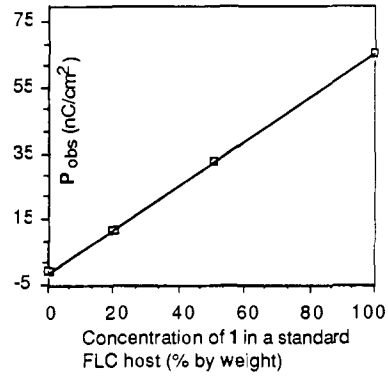


Figure 1. Structure, phase sequence, and polarization of FLC polymer **1** and polarization of some host–guest mixtures.

Due to the useful physical properties of polymer films and the spontaneous polar order present in ferroelectric liquid crystal assemblies, a large effort has recently been launched directed toward the synthesis of FLCPs.[6,7] The small spontaneous polarization (P) observed for materials reported to date coupled with the choice of chiral moieties incorporated into the mesogenic units, however, precludes real insight into the functional group orientation occurring in these systems. Reported herein is the synthesis and characterization of the first FLCP to incorporate a mesogen possessing interpretable sign and large magnitude of P.

Thus, following literature procedures,[7a,8] hydrosilylation of 4-[(*S*,*S*)-2,3-epoxyhexyloxy]phenyl 4-(ω-decenyloxy)benzoate[9] with commercially available polymethylhydrosiloxane[10] (MW = 4500–5000) catalyzed by dicyclopentadienylplatinum(II) chloride gave a white, crystalline solid after precipitation from a benzene solution with methanol. The ^{1}H NMR ($CDCl_3$) and infrared spectra ($CHCl_3$) of the new material are consistent with the desired polymer **1** (Figure 1). Optical microscopy on the neat polymer, mixing studies with a low molar mass smectic C* host, and dielectric spectroscopy combine to show unequivocally that the new

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