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Prospects for solar synthesis

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Abstract — Natural sunlight is a powerful source of energy to carry out useful chemical re-
actions. Polymers can be designed to control and catalyze important photochemical processes
such as "artificial photosynthesis", production of hydrogen peroxide, and removal of water
contaminants such as polynuclear aromatics (PNA's) and polychlorinated biphenyls (PCB's).
This paper describes preliminary explorations of ways to use the world's most abundant source
of energy to power novel chemical processes by employing simple polymeric devices.

Canada is a very large, cold country and Canadians have the dubious distinction of using more energy
per capita than any other country in the world; and it is not just because of that cold climate. It is
primarily due to the size of our vast country that stretches nearly 5000 miles from one side to the other
and three thousand miles north and south. A large part of our energy budget is used in transportation,
and as you probably know, the world is beginning to run out of the natural resources that sustain our
industrial and technological society. The native people in Canada lived here for more than 10,000 years
in a very creative relationship with their environment. Their energy systems were essentially all solar
driven, that is, they used animals and plants, plants being the primary converter of solar energy and
animals the secondary ones, and were able to survive without infringing on the environment in any ap-
preciable way for thousands and thousands of years. Four hundred years ago, the first European set-
tlers came to Canada and founded Montreal and Quebec City, two of the first early European settle-
ments in North America. They also depended primarily on solar energy, that is, they used trees to
build and heat their houses, they used animals and their own strong backs and legs for their propulsion
mechanisms.

My ancestors came to Canada 160 years ago, and were still using these same solar–based types of
energy. In fact, it wasn't until nearly the end of the Nineteenth century that we began to use addition-
al resources which were based on the stored solar energy of past millenia, such as coal, oil and natural
gas.

And even today, the largest source of energy in Quebec, based on hydroelectricity, is annually renewed
by the water which has been evaporated by solar energy to form clouds, moved by solar–driven winds
over northern Quebec and falls as rain to refill the lakes. It is interesting that the total output of elec-
tricity from most hydroelectric power systems is roughly only one thirtieth of the amount of solar
power reaching the surface of the lakes. Clearly we need to learn a lot more about solar energy conver-
sion if we are only getting a few percent of the total available solar power. Water power is called a
"renewable" resource, but it is renewable only because it uses the sun's energy.

For some years my students and I have been interested in energy generation from solar sources. Maybe
we could make a plastic leaf! Maybe we could find some cheap way of converting sunlight into useful
power. One of the first possibilities that must be considered is the use of silicon solar cells. Silicon
cells work well, particularly in southern latitudes where you don't need much energy to warm your
house. They don't work too well running vehicles, although someone has flown an airplane across the
English Channel with solar power, and there are some races going on right now with solar–powered
vehicles of various kinds, but they don't go very fast, except in the desert. However the problem for
Canada is that we get our energy in the summer time and we need it in the winter.

A solar power plant has been constructed just outside of Los Angeles, which fits well with solar con-
cepts, because the largest demand for electricity in California is in the summer, for air conditioning.
This supplements the generating plants, and reduces the need to build another power plant. However,
it is not cost–efficient because of the high cost of installation: approximately $200/m² of collector area.

Does it make any sense to think about solar energy in Canada? The solar intensity in southern Canada
is about 350 Langleys per day averaged over 365 days of the year. California and Florida have only
about 450, which is only a 25% increase. Thus we would have to build slightly larger collectors to
make the same amount of electricity. The problem is with the annual distribution of solar power. In
Canada and other northern countries there is very little solar energy in the winter and a large amount
in the summer.

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The problem with solar driven systems is that we don't know how to store large quantities of electricity. One possibility would be to generate electricity with solar cells and use it to hydrolize water, making hydrogen. However, hydrogen is also difficult to store in large quantities. What we really need is to synthesize a storable fuel which we can generate in the summer, and use in the winter. In this paper I will describe some possible ways that this might be done, involving the use of macromolecules.

Firstly, does it make any sense to think of making chemicals with sunlight? Table 1 shows calculations of the theoretical yield of a one hectare solar chemical plant, roughly the size of a football field (100 meters by 100 meters). With the normal average solar intensity of 300 watts/m² (Montreal or Toronto) you could make 32 tons a day of a chemical like Vitamin D. That is many times the entire annual consumption of Vitamin D in Canada. With radiation in the visible region, there is about 4000 kilowatts of solar energy which could theoretically produce about 200 tons of chemicals a day, comparable to the production of a full scale chemical plant (ref. 1)

Table 1. Theoretical production of a 1-hectare solar plant

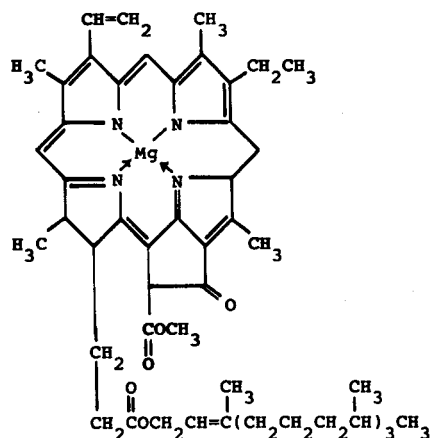| Wavelength range (nm)	KW, noon	Production tons/day
Near UV — 270-400	900	32
Visible — 400-700	4,000	267
Near IR — 700-1000	22,000	212
IR — 2910	2,900	279

Fig. 1. The structure of chlorophyll.

The first and most efficient of all solar chemical systems is that of the green plant. The green plant does most of its work with a compound called chlorophyll, which consists of a porphyrin ring, often with a metal complexed at the centre, attached to a long hydrocarbon tail called a phytol (Fig. 1). The active centre, where chemical reaction takes place usually consists of two of these porphyrin rings, and two quinones in a very special relationship with each other in the crystal structure. The process which drives photosynthesis is the transfer of an electronic excitation from the porphyrin ring to an anthraquinone moiety, which gives two radical ions which are the first chemical intermediates in natural photosynthesis.

We attempted to make a polymeric model of the active site in natural photosynthesis (ref 2). We synthesized the compound shown below which contains a porphyrin, and a methacrylate group (I). This monomer was copolymerized with an excess of acrylic acid. In addition we made another copolymer containing the porphyrin group and a few quinone groups (II). The presence of acrylic acid made them water–soluble.

I

II
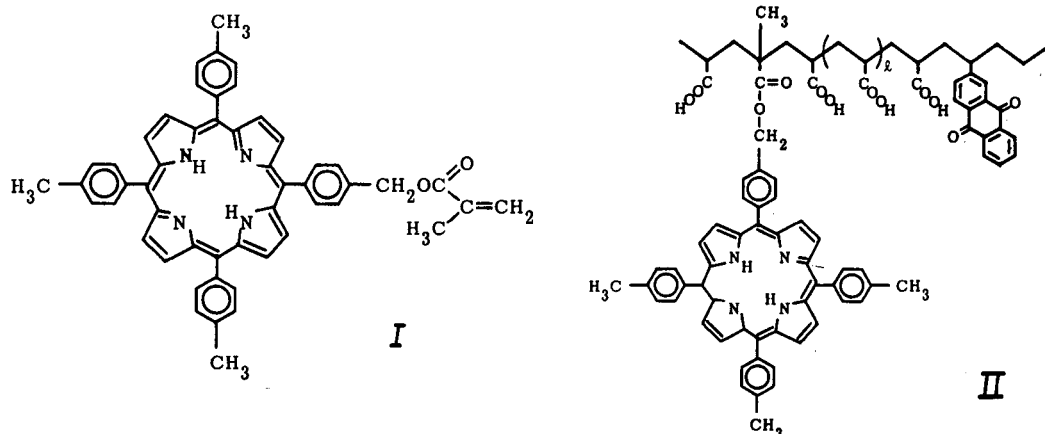
Aqueous solutions of the two polymers were studied in an ESR spectrometer, while irradiating with light absorbed only by the porphyrin. The ESR spectrum of the positive radical ion from the porphyrin and the negative radical ion from the quinone were observed (ref. 2). These signals were very similar to those observed using natural chloroplasts from a green plant in the ESR spectrometer. We conclude that it is possible to synthesize a polymeric compound capable of carrying out the first chemical step of natural photosynthesis.

However photosynthesis is more complicated than that, because the natural system contains what are called "antennas". In the leaf of a green plant the chlorophyll, which is green, is not distributed evenly throughout the leaf, but is localized in small units called chloroplasts. Furthermore, the arrangement is not even uniform within the chloroplasts. In a single photosynthetic unit, there is one active centre, similar to that described previously, plus about 200 extra chlorophyll units embedded in a lipid bilayer membrane. The purpose of these extra units is to act as antennas so that the light absorbed will be delocalized through the system and eventually will reach the active centre to drive the process of photosynthesis.

It is proposed that the hydrocarbon tails are projecting down into the lipid layer, and the porphyrin rings are in the outer protein layer. If the chlorophyll is removed from this bilayer and dissolved in a solvent, at the same concentration, it no longer shows this delocalization of photon energy. The energy is simply converted into heat and there is no "antenna effect" at all. It is believed that the purpose of this bilayer arrangement is to keep these rings just far enough apart so that the energy can travel along the layer very rapidly, but not be converted to heat.

A number of years ago (ref. 3), polymer scientists discovered that aromatic polymers such as poly-(vinylnaphthalene) and poly(naphthylmethacrylate) have exactly the same properties. If these polymers are irradiated with near–UV light, an excitation on one of the naphthalene groups is localized for only a few picoseconds before it hops along the chain to some other adjacent group. In fact, it will move back and forth in a random walk until it is trapped or the energy is emitted as a photon of fluorescence. This is an example of what we call the "antenna effect", or "photon harvesting" in polymeric molecules. A polymer antenna is a polymer which, in solution, looks something like Fig. 2 where the N's are naphthalene, and A is anthracene. This random coil in solution is capable of absorbing near ultraviolet light, and transferring the excitation from the absorbing naphthalene groups — there may be a thousand of them — to a single anthracene trap in the middle. The fluorescent spectrum of the polymer is shown in Fig. 3. The emission intensity from the thousand naphthalene groups is less than that of the one anthracene on the chain. Clearly the energy absorbed by the naphthalene has been transferred to the anthracene. Over the last decade or so we have been looking at various ways in which one can use this energy–harvesting process to do useful chemistry.
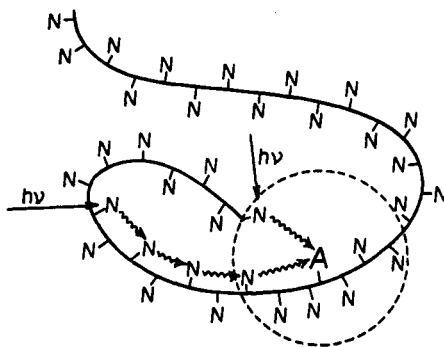

Fig. 2. A conceptual illustration of energy transfer in an antenna polymer.

In early studies we used naphthalene and anthracene because their photophysics is well known, but many other aromatic or non–aromatic components can be built into these systems. In an organic solvent at high dilution, you can isolate polymer molecules so that you can look at only the processes occuring within a single molecular chain. It is now well established (ref. 3) that the energy is transferred by means of a singlet energy transfer (Förster) mechanism due to dipole–dipole interactions between the various groups in the chain. The efficiency of this process approaches 95%, so we can build antennas which are just as good as nature's antennas at collecting photons. The lifetime over which this excitation moves is very very short, of the order of 10–20 ns, or 10^{-8} s. After that there is a chance that the excitation will convert to a triplet which has a much longer lifetime, of the order of 0.1–2 s.

PHOTOZYMES

These new polymers are usually copolymers of a vinyl aromatic compound like vinylnaphthalene with styrenesulphonate or methacrylic or acrylic acid. These unusual polymers behave normally in an organic solvent to form something like a random coil, but if dissolved in water, they form pseudo–micellar structures in which the hydrophobic groups tend to go on the inside, and the hydrophyllic groups on the outside (Fig. 4). There is nothing very surprising about this except that one might have expected that with polyelectrolytes the repulsions between the ionic groups would spread the chain out into a linear rod–like chain. Apparently the hydrophobic interactions are too strong and the polymer adopts this kind of micellar conformation, which has very interesting properties.
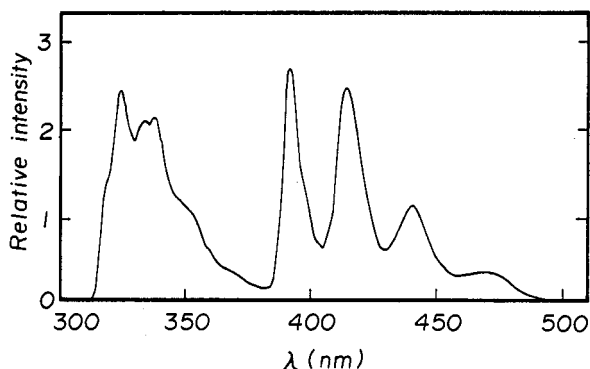
Fig. 3. Fluorescence spectrum of a copolymer of 1–naphthylmethyl methacrylate with 0.665 mol % 9–anthrylmethyl methacrylate in 2–methyl THF at 77 K, on excitation of the naphthalene chromophore at 280 nm.
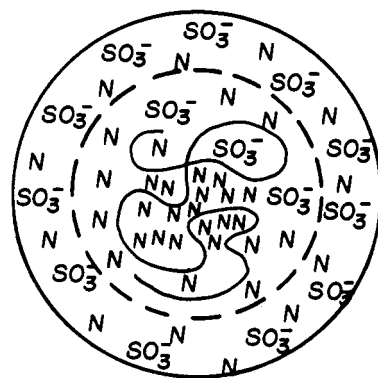

Fig. 4. Possible photozyme structure.

For example if the polymer is dissolved in water in the presence of a hydrophobic organic material, the organic compounds will seek out the centre of the "hydrophobic pocket". If the solution is then irradiated with light, light will be absorbed by the many naphthalene groups and their energy transferred either or directly or electronically, to the molecules in the centre, inducing extremely rapid photochemical reactions. Because of the analogy between these pseudo–micelles and an enzyme, which also has a hydrophobic pocket, and which is capable of doing rapid and rather specific chemical reactions in living systems — we have called them "photozymes".

The exact molecular conformation of these polymers in water has not yet been determined. They are random polymers. All of the naphthalene cannot be in the centre and all of the sulphonates on the outside. Clearly there must be some distribution where the larger sequences of vinylnaphthalene are in the centre and the individual sulphonic acids are towards the outside. Light scattering data indicate that the effective hydrodynamic radii are are larger than one would predict from a random coil model, presumably because of the repulsion of the charged ionic groups within (ref. 4). Studies by light scattering, quasi–elastic light scattering, and by ultracentrifuge, indicate that there is no coagulation of these polymers (ref. 5). They are single molecules in solution with molecular weights from 50,000 to 200,000, and they appear to be spherical. They do not contain nobs and nodules as have been proposed for certain types of polyelectrolytes.

We have also synthesized block copolymers, in this case poly(vinylphenanthrene), with blocks of polymethacrylic acid. There it is easier to conceive of a realistic conformation. One can imagine the hydrophobics crowded together in a very small kernel surrounded by a long coil of polyelectrolyte which maintains the polymer in solution (ref.6).

Most of our studies of photozymes to date have used a copolymer of nearly equal proportions of sodium styrene sulfonate and 2–vinylnaphthalene, denoted PSSS–VN, with a molecular weight of about 200,000 (by ultracentrifuge) The fluorescence of a very dilute solution of this polymer (of the order of 10 or 100 ppm) shows two emission bands, one from the naphthalene "monomer" and the second from what is called an excimer of naphthalene (Fig. 5, curve a). If a very small quantity of perylene is added to this solution, the naphthalene emission decreases and superimposed on it is a strong characteristic emission from the perylene, even though it represents only one part in a thousand of the total composition (Fig. 5, curve b). This is clear evidence for energy transfer from naphthalene to perylene via the antenna effect.
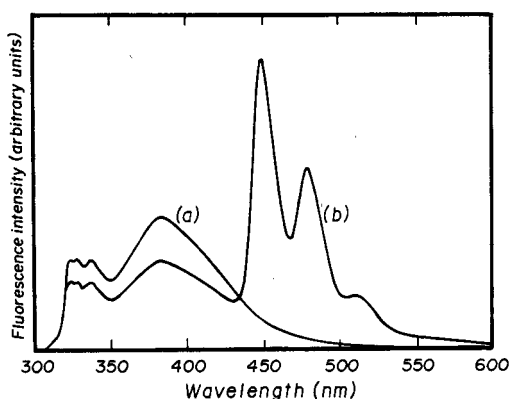
Fig. 5. Steady–state fluorescence spectrum of PSSS–VN in aqueous solution (a) and the corresponding spectrum of the system containing solubilized perylene (b) ($\lambda_{ex} = 280$ nm, $c_{pol} = 0.01$ g dm^{-3}, $c_{per} = 1.07 \times 10^{-6}$ M).
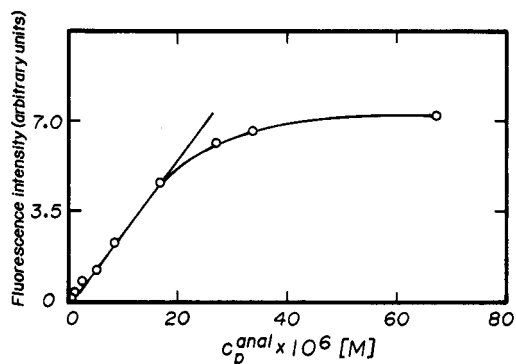
Fig 6. Emission from perylene as a function of concentration at constant polymer concentration.

If the concentration of polymer is increased, the amount of perylene solubilized also increases. Increasing the perylene (at constant polymer concentration) the fluorescence emission reaches a constant value, indicating that the polymer is fully saturated (Fig. 6). From these data the partition coefficient between water and the interior of the hydrophobic pocket can be calculated. Table 2 shows the number of aromatic probe molecules at saturation in PSSS–VN. Six molecules of anthracene can be dissolved in each polymer molecule, two of diphenyl anthracene and only one of perylene. The partition coefficients are greater than 10^8. Thus nearly all of the aromatic compounds present in an aqueous solution will be localized inside the hydrophobic pocket of the photozyme.

Table 2. Partition coefficients K and solubility of various aromatic probes in PSSS-VN

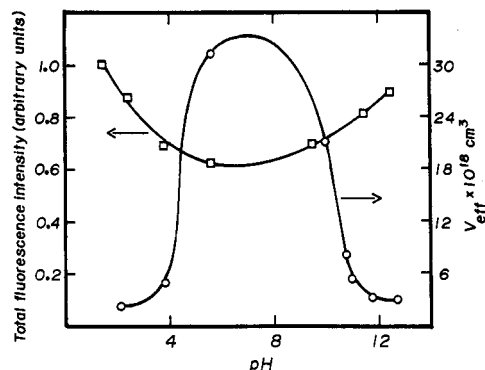| Wavelength range (nm)	$K \times 10^{-7}$ ($\pm 5\%$)	Mol/mol of polymer
Anthracene	12.70	6
9,10-Dimethylanthracene	15.80	3
9,10-Diphenylanthracene	36.70	2
9-Methylanthracene	0.36	10
Perylene	1870.00	1

Fig. 7. Perylene emission intensity and PSSS–VN hydrodynamic volume as a function of pH (ionic strength).

The dimensions of these polymer coils can be changed by adjusting either the pH or the ionic strength. At high pH or ionic strength, the coil is compressed and so has a low volume. At low and high pH (and high ionic strength) the volume decreases by an order of magnitude. However the solubility does not change very much, indicating that even though the photozyme is not as non–polar when it is expanded, it still retains its affinity for the hydrophobic probe molecules (Fig. 7).

Irradiation of photozyme solutions of aromatic molecules in the presence of oxygen leads to very rapid conversion of the aromatic, such as dimethylanthracene, into an endoperoxide which eventually is converted to a quinone.
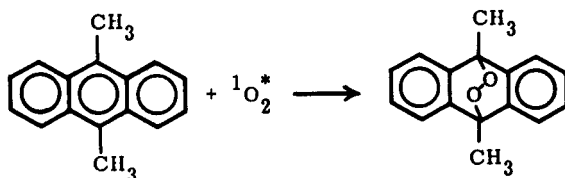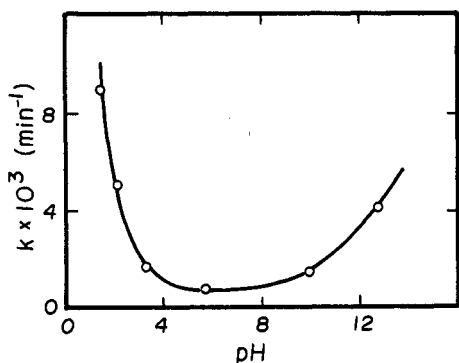
Fig. 8. Effect of pH (ionic strength) on rate of singlet O_2 addition of perylene in PSSS–VN.

Since this compound does not fluoresce, there is an immediate decrease in the fluorescence intensity. The rate can thus be followed by fluorescence measurements. However, in this case the rate of photooxidation does depend on the expansion of the coil (Fig. 8).

In the highly expanded form, the singlet oxygen may be generated too far away from the probe for reaction to occur. Thus, in this type of photozyme reaction, the rate can be adjusted by the simple addition of salt or acid. Since the photozyme is in equilibrium with the aqueous solvent, the photochemical reaction can be carried out sequentially. More substrate can be added after reaction and this process repeated many times. By analogy to an enzyme there is a cycling of the reagents through the catalyst, hundreds of cycles can be carried out in some of these systems to produce substantial yields of product. There are also indications that there is a certain selectivity to the chemical reactions within the photozyme (ref. 7,8).

Polychlorinated biphenyls (PCBs) have solubilities of the order of 1 ppb in ordinary water, but many people think that they are so toxic that their concentration must be reduced to parts per hundred trillion. That represents a technical problem because the law of mass action predicts that the rate of any reaction is proportional to concentration. With only 1 ppb of one reagent, the rate of reaction will be very slow unless a large excess of the other reagent is used. Fortunately, the enzyme–like nature of photozymes means that the PCB can be concentrated in the reactive centre. We have found that the photozyme PSSS–VN is very efficient to dechlorinate typical PCBs. For example, solar irradiation of hexachlorobiphenyl, a model PCB, results in substantial conversion to less toxic compounds, often after only a few days of solar radiation. Figure 9 (ref. 9). It seems that the photozyme itself plays a part in the mechanism by forming a complex with the PCB before the halogen is removed. Further studies with commercial Arochlor samples confirm the efficacy of the photozyme Fig. 10 (ref.10).
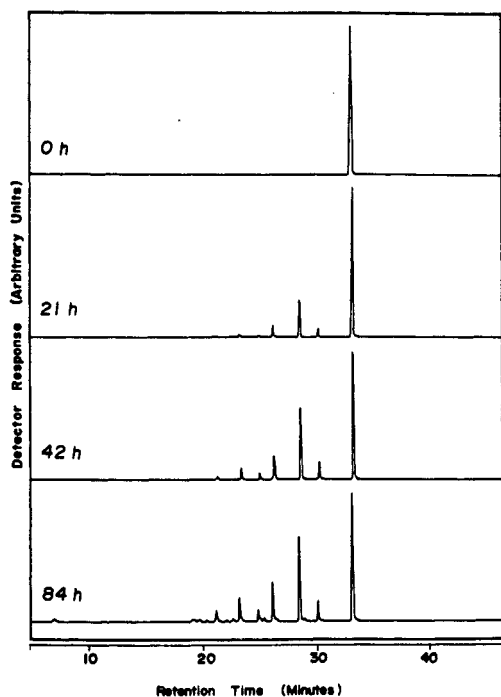

Fig. 9. Rate of dechlorination of hexachlorobiphenyl in aqueous PSSS–VN (simulated solar radiation).
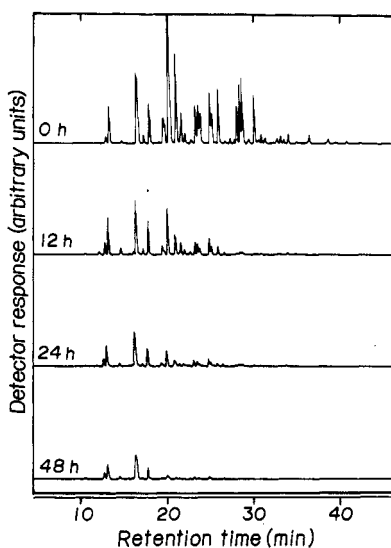

Fig. 10. Rate of dechlorination of Arochlor PCB's in aqueous PSSS–VN (simulated solar radiation).

A typical Arochlor consists of hundreds of chlorinated biphenyls, and as you see, the higher components are eliminated over a period of time. Those which are the most dangerous toxicologically, are gradually transformed. In a possible application the photozyme could be added at parts per million levels to a tailings pond containing contaminated water. The rate of dechlorination is probably 100 times greater than if the water is irradiated directly.

According to current theories there was no oxygen present in the earliest periods of the Earth's history. Oxygen was produced by living organic systems. As a result, there was little ozone, which suggests that the earth was subjected to very deep UV radiation. The only molecules that could survive would be compounds without ester or amide groups in them. The natural polymers we know today (i.e., proteins, cellulose, nucleic acids) would not survive very long under these conditions. On the other hand, something like sulfonated polystyrene, which could have been made by simple chemistry in volcanoes and other geologic reactors is very resistant to UV and other forms of radiation. This could be the beginning of a photozyme replica system. Living systems depend more than anything else on exact replication, so chemical systems are required which are capable of doing very specific kinds of chemical reactions. One might speculate that photozymes might have evolved in prebiotic systems which modelled the very specific enzyme systems adapted by living organic molecules.

SOLAR SYNTHESIS OF A STORABLE FUEL

In these experiments we attempted to synthesize a plastic membrane which would produce a useful fuel, hydrogen peroxide, when irradiated with sunlight (ref. 11). A hydrogel system was prepared from hydroxyethylmethacrylate (HEMA) and an anthraquinone–containing monomer (isopropenyl anthraquinone) 2% to prepare a solid film. On irradiation with light, the anthraquinone moiety is photoreduced to the anthrahydraquinone. After reaction with oxygen, the anthrahydraquinone is oxidized back to anthraquinone, producing hydrogen peroxide which diffuses through the hydrogel and is carried away in a flow of water (Fig. 11). The process is cyclic, involving the $AQ-AQH_2$ redox couple. This is similar to the current commercial method for production of hydrogen peroxide. The commercial process involves a hydrogen reduction of a substituted anthraquinone to the anthrahydroquinone, then exposure to oxygen to make the hydrogen peroxide followed by separation in a counter current extraction.
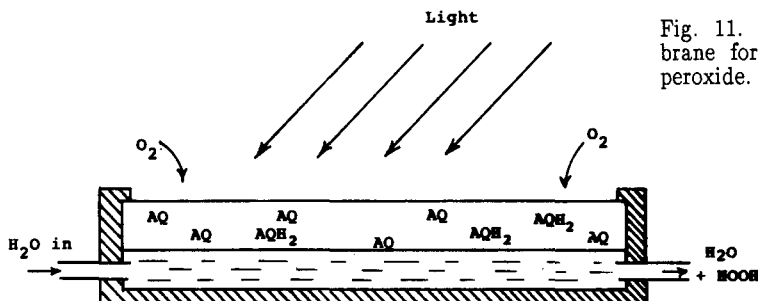

Fig. 11. Schematic of hydrogel membrane for solar production of hydrogen peroxide.

The reaction can be followed by UV spectral measurements, shown in Fig. 12. At the start of a run the anthraquinone spectrum is shown and as it is reduced it is converted to the anthrahydroquinone which has a strong absorbance at 380 nm. The occurrence of an isobestic point strongly suggests that only two compounds are involved. If you then expose the films to oxygen, the peak for AQH_2 is reduced and that for AQ increases. At least 100 cycles have been demonstrated, with more than 100 moles of H_2O_2 produced per mole of AQ.
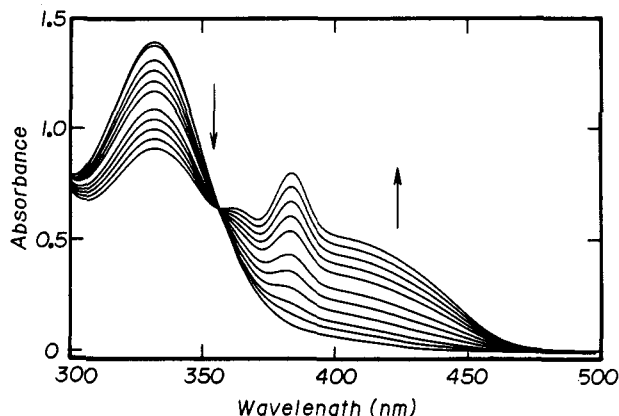

Fig. 12. Photoreduction of IPA swollen P–AQ hydrogels at 313 nm. $I_0 = 2.2 \times 10^{-5}$ Einstein/L s.

In sunlight, the complete cycle can be done in about 300 s (6 min) in Toronto summer sun. The actual power of sunlight is impressive. It would be very difficult to expose an area the size of a square meter with an electrically driven source that would give you an equivalent intensity. The rate is comparable to that observed with a very high intensity mercury lamp used for making microcircuits for microelectronics.

Hydrogen peroxide is in some ways an ideal fuel. It decomposes with a metal catalyst to give you heat, oxygen and water. (No pollutants.) It can be stored for quite long periods of time in water. It can be pumped along steel pipes. It has many many advantages. It was used during the two world wars as fuel for submarines and rockets, and it also has great value in improving the paper industry, because it can replace the sulfur compounds used for bleaching paper, with a considerable reduction in both air and water pollution. In the presence of an alcohol such as isopropanol, the quantum yield of AQH_2 production approaches unity. There are some side reactions which we now understand and think we can eliminate, but we haven't yet built a solar driven plant. Nevertheless, the results are sufficiently promising to expect that this is just the beginning of a new field of solar photochemistry.

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