Using Crystal Optics to Demonstrate Single-Layer Localization of a Solid-State Chain Reaction

by **Kevin L. Pate** and **J. Michael McBride***

Department of Chemistry, Yale University, Box 208107, New Haven, CT 06520-8107, USA
(e-mail: j.mcbride@yale.edu)

Dedicated with admiration to Professor *Albert Eschenmoser* on the occasion of his 75th birthday

Upon warming to 225 K, single crystals of 11-bromoundecanoyl peroxide (BrUP), in which radicals have been created by photolysis at lower temperature, undergo partial decomposition by a radical chain reaction *ca.* 40 cycles long. FTIR allowed monitoring two chain products: CO_2 and an α-lactone that decomposes further at 260 K. When initiation is confined to alternate molecular layers by polarized photoselection, the chain reaction reduces the crystal symmetry from tetragonal to monoclinic. Desymmetrization is easily observed by optical microscopy, although it is difficult to detect by X-ray diffraction. Accurate monitoring of birefringence using a *Sénarmont* 1/4-wave plate, and comparison with FTIR kinetics, proves that the chain reaction occurs within single molecular layers 2 nm thick.

1. Introduction. – 1.1. *Constrained Orientation and Location.* Constraints on the *orientation* and *location* of reactive intermediates and product molecules are responsible for important differences between fluid-state and solid-state reactions. In addition to influencing chemical transformations, these constraints permit tailoring nano-patterned materials for technological applications, and they allow studying reaction intermediates in fine detail.

One often thinks of X-ray diffraction as the ultimate tool for determining structure in solids, and it has been used effectively to study solid-state reactions (see, *e.g.*, [1]). But, as the present paper illustrates, simpler techniques can be more sensitive for answering certain structural questions about reactions in solids. It is usually impossible using X-ray diffraction to identify *which* unit cells have reacted.

Many spectral properties, such as anisotropic magnetic interactions and absorption of polarized light, can allow one to determine molecular *orientation* precisely, often to within a few degrees of arc, but for individual molecules of intermediate or product deep within a crystalline sample it is much more difficult to establish the absolute or relative *location* on the molecular scale of nanometers¹). The high resolution of scanning-probe microscopy is available only for molecules located on a crystal surface.

Magnetic coupling between odd electrons, measured by electron paramagnetic resonance (EPR) spectroscopy, has been used to track the relative location of the two free radicals generated as a pair by partial photolysis of pure diacyl peroxide single crystals [2]. This tool can be accurate within ±0.01 Å, but it becomes useless once the

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¹) Diffraction from gratings photochemically generated by laser interference can be useful on the scale of hundreds of nm.

two odd-electron spins have separated by more than 15 Å, either through molecular motion or through radical-molecule reaction.

Below, we report a photo-initiated, thermal chain reaction in a diacyl peroxide crystal and show how easily a polarizing microscope provides evidence for localization of the reaction chains within individual molecular layers when X-ray diffraction fails.

1.2. *Intermediates in Diacyl Peroxides.* Photolysis of an individual molecule in a single crystal of a pure diacyl peroxide at cryogenic temperature generates a pair of alkyl radicals separated by a pair of CO_2 molecules. As this assembly is warmed, the radicals ultimately become sufficiently mobile to react with one another by coupling or disproportionation, or with adjacent lattice molecules by H-abstraction. EPR Spectroscopy has shown that these reaction paths are tightly controlled by constraints on molecular orientation and location. In the case of 11-bromoundecanoyl peroxide (BrUP), EPR spectroscopy established the following sequence of well-defined intermediates during warming to 220 K after brief photolysis at 20 K [3][4]:

20 K:	a pair of primary 10-bromodecyl radicals
55 K:	the same pair equilibrating between two new, slightly different conformations
115 K:	a primary/secondary radical pair formed when one of the 10-bromodecyl radicals abstracts a specific α-H-atom next to a C=O group in an adjacent peroxide molecule
130 K:	a pair of two secondary α-radicals that remain close enough together to undergo electron exchange.

At 225 K, the two α-radicals formed at 130 K become separated (see *Scheme*, below) so that splitting due to electron exchange disappears from their EPR spectrum. Preliminary FTIR studies show a simultaneous increase in CO_2 concentration, suggesting a chain decomposition of BrUP [5]. By 235 K, the α-radicals have been mostly transformed into secondary radicals located nearer the end of the alkyl chain.

The purpose of the present work was to confirm the occurrence of chain decomposition and to establish the extent to which the reaction chain remains localized in the crystal lattice.

2. Results. – 2.1. *FTIR Evidence for the BrUP Chain Reaction. Fig. 1* displays FTIR spectra from a single crystal of BrUP measured at 17 K. The trace labeled 23 K was measured after UV photolysis at 23 K had decomposed *ca.* 1 molecule in 2,000 at random within the crystal. Preferential decomposition near the crystal surface was avoided by using light of wavelength >330 nm that is very weakly absorbed by the tail of the diacylperoxide chromophore. The spectrum shows CO_2 peaks near 2336 and 2347 cm^{-1} [6], but no absorption in the 1158–1172 cm^{-1} region.

Previous work had shown that warming a lightly photolyzed crystal from 20 K to 220 K results in a sequence of IR frequency changes in the 2330–2350 cm^{-1} region corresponding to the local structural changes seen by EPR. During these transformations, the peaks remain sharp, and their integrated absorbance varies only within the narrow range ($\pm 50\%$) consistent with reorientation of a constant number of CO_2 molecules [6].

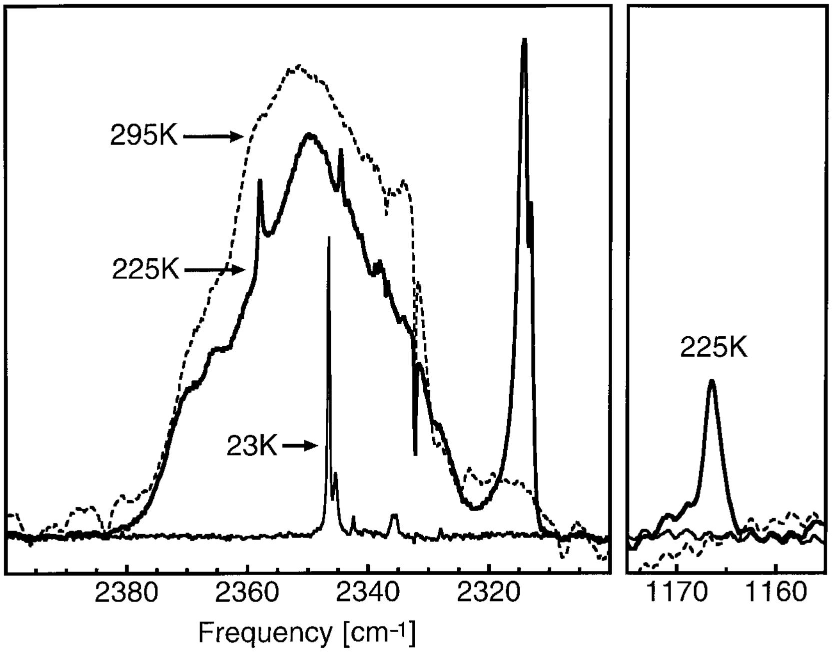

Fig. 1. *FTIR Difference spectra in CO_2 and α-lactone regions from a single crystal of BrUP after photolysis at 23 K* (light solid line), *and after warming briefly to 225 K* (heavy solid line) *and to 295 K* (dashed line). All spectra were measured at 17 K and corrected by subtracting a spectrum measured before photolysis.

The trace labeled *225 K* in *Fig. 1* shows that, after brief warming to 225 K, the CO_2 signal increases 20- to 50-fold in intensity and broadens substantially, indicating that each initial radical pair generates many new CO_2 molecules in a variety of local environments. Probably, the CO_2 molecules are near enough to one another to give additional broadening from vibrational coupling.

The *Scheme* shows a plausible mechanism for producing a large amount of CO_2. Fragmentation of the α-radical yields an α-lactone, CO_2, and a primary 10-bromodecyl radical that can abstract an α-H-atom from an adjacent intact peroxide to continue the chain²). Formation of an α-lactone is confirmed by appearance of its characteristic peak at 1167 cm^{-1} ³), which grows in strict proportion to the increase in CO_2 and subsequently disappears on warming to 295 K.

For conversions of 0.1% or more, crystal damage can be observed by polarizing microscopy, as described below. When a crystal was photolyzed at room temperature through a sharp mask, the damage was not observed to extend beyond the irradiated region. This shows that the intermediates and products of the 40-molecule reaction chains are not freely mobile over several microns, even at room temperature.

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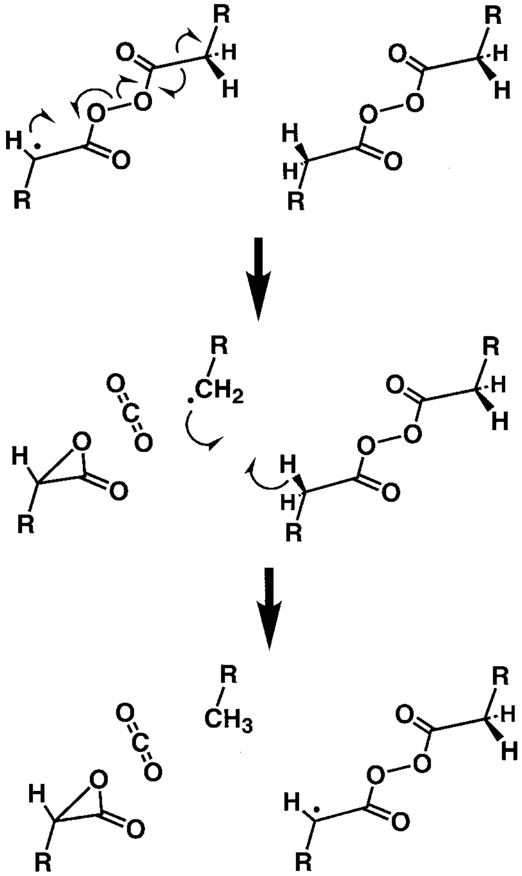
²) The distance between the radical C and the H to be transferred is 3.03 Å; the CH–C angle is 159° [4].

³) *Chapman* and *Adam* reported [7] a characteristic α-lactone ring-deformation mode at 1163 cm^{-1}. They and others reported C=O stretching in the range of 1890–1935 cm^{-1} for alkyl-substituted α-lactones. In BrUP, a peak at 1937 cm^{-1} grows and decays in parallel with the 1167 cm^{-1} peak. Other peaks also grow in the 1895–1940 cm^{-1} region at 225 K, but they do not decay at 295 K.

Scheme. *Chain Propagation Involving the Central Portions of two BrUP Molecules that are Adjacent along the Crystallographic [110] Direction*. Drawn to scale. R = $Br(CH_2)_9$



Still, one may ask whether lattice constraints are sufficient to prevent motion of the intermediate radicals on the more 'molecular' scale of a few nanometers. The high symmetry of BrUP provides a powerful tool for addressing this question.

2.2. *Crystal Layering and Desymmetrization.* BrUP is a layered crystal (space group $P4_12_12$) [8]. The adjacent molecules shown in the *Scheme* are related by a unit translation along both the *a*- and *b*-axes. Repetition of this translation generates a line of molecules parallel to [110] along which a strictly controlled reaction chain would propagate.

Repeated displacement of the [110] line diagonally toward the reader (along the *a*- or *b*-axis) generates a horizontal, two-dimensional (001) layer of molecules related by pure translation. One could easily imagine that radical mobility of a few Å (or α-abstraction by undecarboxylated acyloxyl radicals) could make a reaction chain jump from one [110] line to the next within the layer [9]. The thickness of (001) molecular layers is 21.4 Å, so if there were mobility of *ca.* 2 nm, abstracting radicals might propagate the reaction chain between layers.

In BrUP, the (001) layers stack along the vertical 4-fold screw axis (c) with favorable Br–Br interactions imposing a 90° rotation about c between successive layers [8]. The resulting tetragonal symmetry makes the crystal uniaxial, meaning that plane-polarized light propagates undisturbed along the c-axis. In crystals of lower symmetry, the light would, in general, become elliptically polarized.

The diacylperoxide chromophore is photolyzed by light polarized along its O–O bond [10]. In BrUP, this bond is nearly perpendicular to c, and it is rotated by 90° about c in the two immediately adjacent layers. By choosing polarization along the [110] diagonal of the square (001) crystal plate, one may selectively decompose molecules in alternate layers without damaging molecules in the intervening layers.

A reaction confined to alternate layers would destroy the crystal's tetragonal symmetry and might be detected by a technique sensitive to desymmetrization. If the technique could not detect the desymmetrization resulting from a small amount of initial selective photolysis, it might still detect the desymmetrization after amplification by chain decomposition. But *desymmetrization will be amplified only if the reaction chains are confined within individual layers.*

In principle, absorption spectroscopy could be used to detect desymmetrization, but monitoring the loss of peroxide would involve measuring a small difference between large absorptions, and the products lack a convenient chromophore, except in the IR, where background absorption is strong and polarized experiments are tedious. Instead, we chose to try X-ray diffraction and polarized microscopy.

2.3. *X-Ray Diffraction*. Existence of 4-fold screw symmetry along the c-axis of BrUP forbids ($00l$) X-ray reflections unless $l = 4n$, where n is an integer. Desymmetrization by selective reaction in alternate molecular layers should convert the 4-fold screw into a 2-fold screw and change the condition on ($00l$) to $l = 2n$. That is, after desymmetrization an ($00l$) scan should show peaks with $l = 4n + 2$, forbidden by $P4_12_12$ symmetry, between the allowed $l = 4n$ reflections.

Fig. 2 shows an ($00l$) scan of a 1.2 × 0.9 × 0.5 mm BrUP crystal after polarized photolysis at room temperature to *ca.* 0.5% conversion. In the range (004) to (00 92), no forbidden reflections are clearly evident. Possibly (00 18) and (00 70) appear in the trace amplified by a factor of 30, but they are only marginally larger than noise and could never be relied upon for quantitative purposes. A second X-ray scan 3 h later also failed to reveal desymmetrization, although, as described below, polarized microscopy demonstrated strong desymmetrization both before and after the X-ray scans⁴).

Perhaps it is not surprising that X-ray diffraction is rather insensitive to desymmetrization, since less than 1% of the sample reacts, and in such a way that the most strongly scattering atoms might not be significantly displaced⁵).

2.4. *Birefringence*. 2.4.1. *Observation*. Polarized light transmitted along the 4-fold symmetry axis of a tetragonal crystal maintains its plane polarization, so that the crystal appears dark between crossed polars⁶). For lower crystal symmetry, the light maintains

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4) The *Sénarmont* α before X-ray diffraction was 16.2°; after it was 21.7°, see below.

5) Scattering from adjacent planes of Br-atoms dominates ($00l$) scattering to give the 'sin^2' intensity profile with nodes near $l = 21$ and $l = 65$ in the ($00l$) scan of *Fig. 1*. 'Forbidden' reflections might become visible in other regions of reciprocal space, but the ($00l$) reflections should be particularly sensitive to desymmetrization.

6) For a full discussion of crystal optics and the polarizing microscope, see [11].

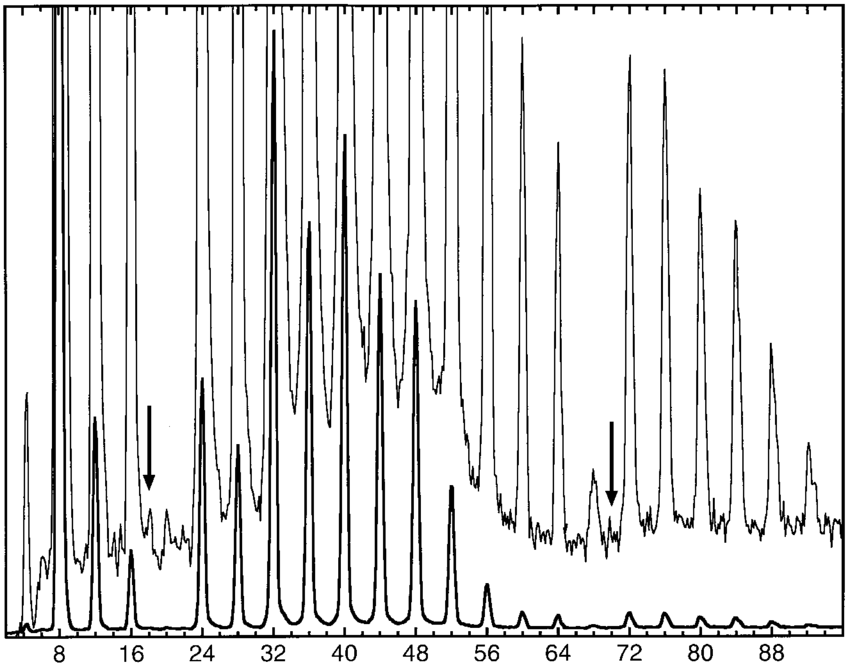

Fig. 2. *(001) X-Ray intensities of a BrUP crystal after desymmetrization by* ca. *0.5% decomposition in alternate molecular layers.* Upper trace amplified 30-fold. Arrows indicate possible forbidden reflections.

its polarization within the crystal only if its electric vector aligns with the direction of maximum or minimum crystal polarizability. Other polarizations propagate within the crystal as two waves, one polarized in the direction of maximum polarizability, the other in the direction of minimum polarizability. These waves have different velocity within the crystal, so that, upon emerging from the crystal, they are out-of-phase with one another, and combine to yield elliptical polarization, which cannot be extinguished by a polarizing filter. The photolyzed crystal from the failed X-ray experiment, described above, revealed its desymmetrization by appearing light between crossed polars.

The relative retardation of the two light waves in a slightly desymmetrized crystal results in characteristic interference colors from *Newton*'s series⁷). The direction in the sample that has lower electric polarizability, and thus faster propagation, can be identified by inserting a filter of known birefringence that is either reinforced or partially cancelled by the birefringence of the sample. The use of such a 'lambda' filter with the photolyzed BrUP crystal showed that, as expected, the polarizability was reduced in the direction of the electric vector of the light that has been used for photolysis.

That the molecular chromophores preferentially removed by the chain reaction have the same orientation as those of the photolyzed molecules is consistent with predominant peroxide decomposition within individual crystal layers where all

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7) This is the phenomenon that makes color photomicrographs of polycrystalline samples worth putting on calendars.

molecules are related by translation. Measuring the extent of this predominance requires quantitative determination of the relative retardation.

2.4.2. Sénarmont *Quantification*. In 1840, *Henri Hureau de Sénarmont* showed that inserting a quarter-wave plate after a weakly birefringent sample, with axes at 45° both to the polarization of the incoming light and to the principal directions of the quarter-wave plate, converts emerging elliptically polarized light into plane-polarized light whose plane is rotated from that of the incoming light by an angle α [11]. This angle is proportional to the sample's relative retardation[8]). A microscope with a rotatable analyzer allows quantifying the sample's relative retardation simply by measuring the amount of rotation necessary to achieve extinction.

Fig. 3 plots the relative retardation (*Sénarmont* α) as a $1.2 \times 0.8 \times 0.3$ mm crystal of BrUP is warmed on a microscope cold stage after brief polarized photolysis at 215 K. Birefringence is negligible until the sample is warmed to 230 K, whereupon α increases from 0° to 7° over 70 min. Birefringence then remains constant to 260 K, at which temperature α rises to 12.8° over 60 min.

2.4.3. *First-Order Kinetics.* The solid line in *Fig. 4* shows that the growth of birefringence at 230 K is kinetically first-order with a half-life of 15 min. The dashed line from FTIR shows that growth of CO_2 from chain decomposition at *ca.* 225 K is also first-order with a half-life of *ca.* 12 min. The time and temperature values for the FTIR experiment are approximate because each point represents a 17 K spectrum measured after cycling the sample to a temperature measured as 225 K by a thermocouple mounted opposite the crystal on a CsI plate in the cryostat. Within this uncertainty, the FTIR and birefringence curves are identical.

The agreement between the solid and dashed lines of *Fig. 4* leaves little doubt either that the *Sénarmont* α is measuring the same chain process that produces CO_2 or that, at this low conversion, α is linear in the amount of conversion. It is significant that CO_2 production parallels, and does not outlast, the development of birefringence. If reaction chains were initiated in alternate layers but propagated to the intervening layers, production of birefringence would die away more rapidly than production of CO_2. *Clearly the reaction chains are confined to individual molecular layers.*

The rate of the radical chain process should be proportional to the number of propagating radicals, but effectively independent of the amount of remaining peroxide, of which only *ca.* 1% is consumed. Thus, the observed rate law for the reaction chain must be the same as that for destruction of the propagating radicals.

In solution, the rate law for a free-radical chain reaction is typically second-order, because termination is by radical-radical reaction. In solid BrUP, the rate law is first-order, meaning that termination is not by radical-radical reaction but rather by random conversion of a propagating radical into one that fails to propagate[9]). This could involve either encounter with a crystal defect that halts propagation or random conversion of a secondary α-radical (or of a 10-bromodecyl or 11-bromoundecanoyloxyl radical) into the non-propagating secondary radical located nearer the molecular terminus, the same radical whose formation is observed by EPR at this temperature.

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[8]) The proportionality constant is $\lambda/180° = 3.03$ nm/° for the green light used in our microscope.

[9]) Termination by reaction between radical progeny from single initiating molecule would also be first-order.

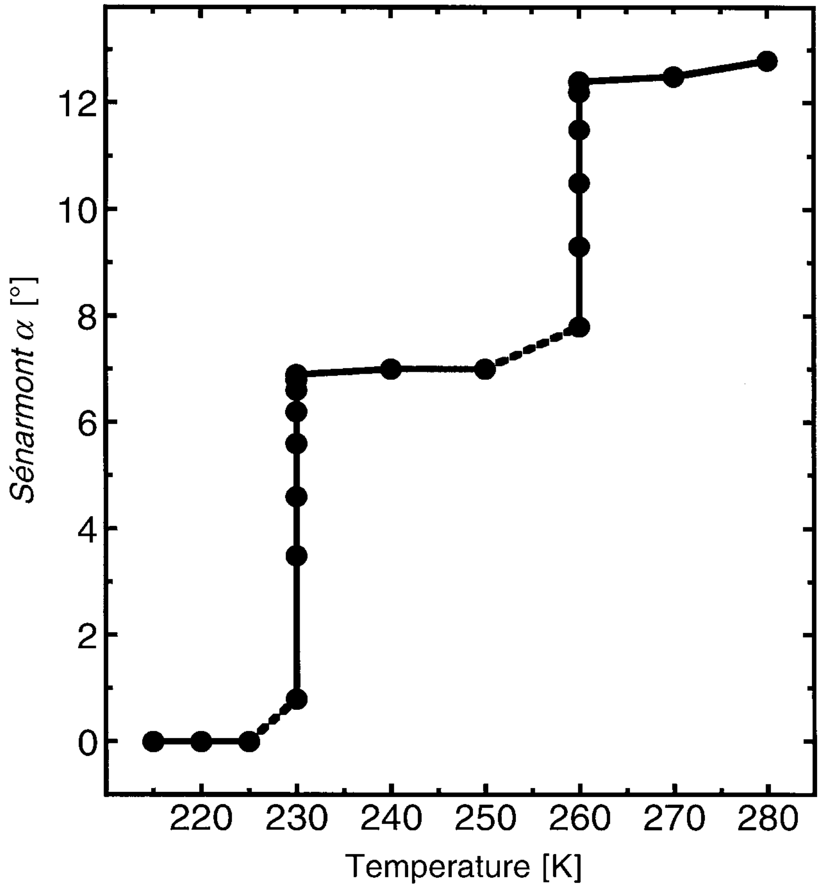

Fig. 3. *Growth of birefringence upon warming a crystal of BrUP after polarized photolysis at 215 K.* During the steps at 230 K (chain reaction) and 260 K (α-lactone decomposition), measurements were made at 10-min intervals.

2.4.4. *α-Lactone Decay.* The increase in birefringence at 260 K is presumably due to decay of the α-lactone formed in the 230 K chain reaction, because its characteristic FTIR peak at 1167 cm^{-1} disappears near the same temperature. The kinetics of this increase in birefringence appears to be first-order as would be expected for unimolecular decarboxylation of the α-lactone. Such a reaction would be consistent with identification of carbene products, alkene, and alkylcyclopropane [3]. Since the 1167 cm^{-1} lactone peak disappears completely, one might expect the CO_2 intensity to double, if the lactone, formed together with CO_2 at 230 K, decays by decarboxylation. That the intensity increase for CO_2 at 295 K in *Fig. 1* is less than 5% suggests a competing pathway for α-lactone decay, or a significant change in preferred CO_2 orientation and extinction coefficient[10]).

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[10]) CO_2 Loss from a lightly damaged BrUP crystal at 295 K is not observed on the time scale of our experiments.

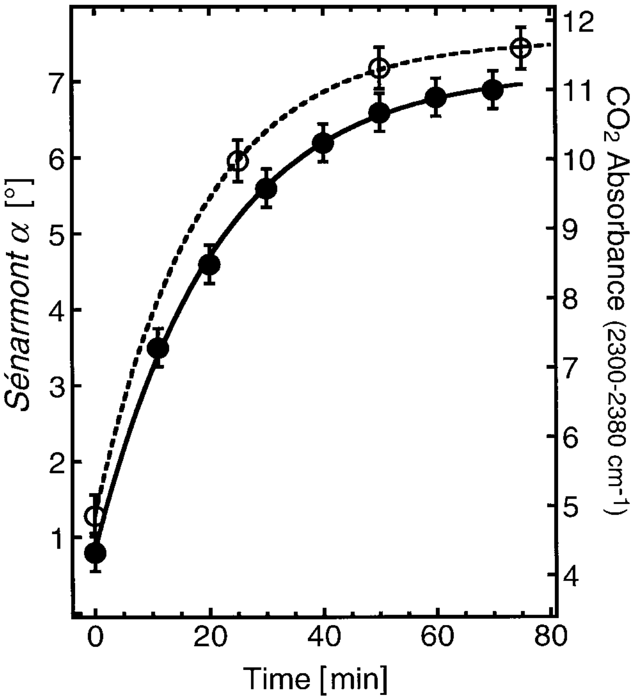

Fig. 4. *Growth of birefringence at 230 K* (solid points) *and of CO_2-integrated IR absorbance at* ca. 225 K (open points, the scale and offset from the solid curve are arbitrary) *during chain decomposition of BrUP.* Lines are fit to the data by least squares assuming first-order kinetics. Time set at 0 on measurement of first point. Note that CO_2 production does not outlast the growth in birefringence.

2.4.5. *Long Photolysis.* For longer photolysis, chains should begin to interfere with one another, as a propagating radical from one chain dead-ends by being created next to either a previously decomposed peroxide molecule from another chain or a reaction-generated lattice defect that prevents propagation. Photolyzing BrUP crystals of varying thickness (0.10 to 0.64 mm) at room temperature showed that α increases linearly with thickness and with photolysis time during the first hour of photolysis, but then grows more slowly over the next hour to reach a nearly constant value. For room-temperature photolysis, only crystals that have undergone relatively high conversion seem to cloud significantly in the photolyzed region, while crystals that have been photolyzed at low temperature to much lower conversion cloud upon warming to room temperature.

The limiting *Sénarmont* α is 130° per mm of crystal thickness, roughly twice the value at which the growth ceases to be linear in time. One might guess that removing the peroxide chromophore in the damaged layer would make that layer nearly optically isotropic with a refractive index like the lower index of the intact crystal (1.552 along the *c*-axis, 1.560 in the *ab*-plane). This allows a very rough estimate that 130°/mm corresponds to *ca.* 3% conversion within the damaged layers, which would be the conversion at which chain decomposition becomes inefficient.

3. Conclusions. – Of course, reaction chains in a crystalline solid propagate more rapidly between centers that are within 4 – 5 Å than between centers that are separated by 20 Å. Still, it is possible that, upon annealing a molecular crystal with significant local damage, small intermediates might occasionally have enough translational freedom, perhaps with assistance from local defects, to carry a reaction chain from one molecular layer to the next. The results presented above show that, in BrUP 114° below its melting point the frequency of such an excursion is very much less than once in a sequence of *ca.* 40 repeated near-neighbor reactions. While it may not be surprising, definitive information of this nature is rare for reactions in organic solids and is potentially relevant to nanoscale tailoring of materials.

The optical desymmetrization technique that made this demonstration easy is unusually simple and inexpensive and could have been used 150 years ago. Because of its null background, this relative, dispersion-based method is more sensitive than absorption spectroscopy or X-ray diffraction. Still, it cannot be considered very general, since it provides little information on molecular structure and requires a crystal of unusually high symmetry. In fact, most BrUP crystals were rejected for our study because their optical symmetry was already slightly lower than uniaxial *before* polarized photolysis. That is, they were optically anomalous, presumably because of growth-induced defect structures or local strain [12]. One might imagine achieving greater generality by directing polarized photolysis and microscopy along an optic axis of a biaxial crystal, but this would be challenging because the orientation of such optic axes is wavelength dependent.

We are grateful to Profs. *B. Kahr* (University of Washington) and *M. D. Hollingsworth* (Kansas State University) for important background work for the birefringence and FTIR studies, respectively. This work was supported by Grant N00014-90-J-4015 from the *Mechanics Division* of the *Office of Naval Research* and by a *Dox Fellowship* to *K. L. P.*

Experimental Part[11])

Bis(11-bromoundecanoyl) peroxide was prepared from the peroxy acid and acid chloride by a literature procedure [8]. Single crystals were grown by evaporation in the dark at r.t. from 100 mg of BrUP in *ca.* 5 ml of hexane/AcOEt/CH_2Cl_2 2 : 1 : 1 in 5 dram vials. For the best optical quality, a cap with a 5-mm hole was replaced by one with two pinholes when the first crystallites appeared.

Clear (001) crystal plates for FTIR were of uniform 0.2 to 0.5-mm thickness and free from visible defects that might lead to poor thermal conductivity or to cracking on temp. cycling. Plates for optical microscopy met the same standards and also were free from detectable birefingence when viewed along [001]. Very few crystals met the last standard.

Crystals were photolyzed using light from an *Osram HBO 200W/2* high-pressure Hg lamp focused by a quartz lens and filtered with 10 cm of 0.3M aq. $CuSO_4$ to remove heat and at wavelengths shorter than 300 nm. Polarization was achieved with a *Glan/Thompson* prism (*Rudolph*). Light was transferred to the FTIR sample or to the microscope stage by reflection from a front-silvered mirror.

FTIR Spectra were measured with a *Nicolet Magna 550* spectrometer. Crystals for FTIR study were glued with a very thin layer of *Devcon 5 Minute Epoxy* adhesive to a CsI plate and masked with a piece of aluminum tape. A gold-chromel thermocouple was epoxied to the opposite face of the CsI plate just opposite the crystal after the plate was mounted in an *APD Displex DE202* cryostat with an *APD-E* controller.

The (00*l*) X-ray scan was measured in the ω-2θ mode using an *Enraf-Nonius CAD-4* diffractometer with monochromatized Mo radiation and an 0.5-mm vertical slit.

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[11]) For further details, see [13].

Optical measurements were made with a *Leitz Labolux 12 Pol S* microscope equipped with a *Mettler FP84* temp. controller cooled by a stream of dry N_2.

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