CHAPTER III*

STUDY OF A SOLID STATE PHOTOREACTION

3.1 ABSTRACT

There is a considerable current interest in organic solid state photochemical reactions, their energetics, kinetics and topochemical factors in order to exploit them for specific molecular transformations. PAS appears to be a useful method in this connection not only because it is a convenient spectrophotometric tool for solids but also because of its selective sensitivity for the nonradiative deexcitation channel. A successful application of PAS to monitor several features of a solid state photoreaction is described in this chapter. The reaction chosen is ultraviolet radiation induced polymerization of a diacetylene to produce a fully conjugated linear polydiacetylene. The time profile, the wavelength dependence and the calorimetric features of the reaction have been investigated. Polarized PA spectra suggest a laminar alignment of the polymer chains in the crystal. A method has been described for obtaining the action spectrum of the photoreaction, which is simple, more convenient than the conventional sampling method and which appears to be of general use.

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3.2 **Introduction**

The most remarkable feature in the solid state is the tendency of its constituent atoms or molecules to arrange themselves in an ordered periodic pattern. As a consequence of the decreased translatory freedom, the reactions in the solid state occur with a minimum amount of atomic or molecular movements. The crystalline matrix provides an extraordinary spatial control on the initiation and progress of organic reactions, leading to the formation of products that could be difficult, if not impossible, to make by conventional solution methods. A given compound can react differently in the solid state and in the solution or gas phases; chemically closely related compounds can show significant differences in their chemical behaviour even in the solid state; the same compound, in different polymorphic modifications, has been shown to undergo different transformations (1). The underlying cause for all these observations is the influence of the crystalline matrix. Such a matrix influence is termed as "topochemical" influence (2). The molecule of interest can be tailored with a remarkable selectivity and stereospecificity if one can manipulate these topochemical factors. The importance of the study of solid state reactions is evident in order to augment our understanding of these subtle structural and geometrical factors involved. Photoacoustic spectroscopy would appear to be a useful method in such studies not only because it is a convenient spectrophotometric tool for solids but also because of its selective sensitivity for nonradiative decay processes.

In this context, we illustrate a comprehensive use of PAS in studying several features of a solid state photo reaction such as the wavelength dependence of the photo reaction, time profile of the reaction, conformation of the product, orientation of the product in the solid and photocolorimetry.
The reaction chosen is the ultraviolet radiation-induced polymerization of a crystal of a diacetylene monomer to produce the polydiacetylene.

Diacetylenes, \( \text{R}-\text{C} \equiv \text{C}-\text{C} \equiv \text{C}-\text{R} \), where \( \text{R} \) is a monovalent substituent group, polymerise in the solid state either upon heating or upon exposure to uv or radiation, to yield a fully conjugated, one-dimensional polymer crystal. Current interest in the solid state polymerization of diacetylenes has mainly been due to the initial work of Wegner (3-6). Most of polydiacetylenes are insoluble in common organic solvents, but after the recent synthesis of a new class of polydiacetylenes by Patel (7), that are highly soluble in organic solvents (chloroform, acetic acid, dichlorobenzene, dimethyl formamide etc.), considerable interest has been generated on the conformational features of the polymers in solution. The molecular weights, conjugation lengths, optical properties and conformational features of such polymers have been reported (8, 9). There has also been a great deal of recent interest in the optical properties of polydiacetylenes crystals, mainly due to the one-dimensional nature of the polymer (10-13), and their possible optogalvanic applications. Various techniques have been employed to study the solid state polymerization and optical properties of the polydiacetylenes. The most commonly used technique for monitoring the polymerization is monomer extraction (14-16), which is a tedious gravimetric method that requires large amounts of the material. Finite solubility of the polymer in the solvent chosen for the exclusive removal of monomer leads to an underestimation of the polymer conversion; conversely, any trapped monomer in the polymer lattice, especially at high conversion, can lead to an overestimation of the polymer conversion. Patel et al. have recently reported a new technique for determining the extent of polymer conversion (17). One of them is differential scanning calorimetric method, the principal requirement
of which is that the material should display separate monomer and polymer melting endotherms. The other is a simple and accurate spectroscopic method which requires the polymer to be soluble. The method of diffuse reflectance spectroscopy has also been used for an in situ study of the thermal and uv polymerization (13). Specular reflections were minimised by using a set of crossed polarisers in the optical path, and the spectra recorded in 2.5 nm steps over the desired spectral range. 20 separate measurements were made and averaged at each wavelength. The absorption spectrum was then obtained by the use of the Kubelka-Munk method of treating the date.

Considering the inherent difficulties involved in the calorimetric and the diffuse reflectance methods, and the efforts involved in treating the data in order to obtain the absorption spectrum, it would appear that photoacoustic spectroscopy would be superior, more convenient and of general use; the requirement here would be that the absorption spectra of the monomer and the polymer be well separated.

3.3 Materials and Methods

The monomer 3BCMU (4-6decadiyn-1,10-bis[(n-butoxy carbonyl)methyl urethane]) has the structure R-C≡C=C≡C-R, where R = -(CH₂)₃OCONHCH₂-COOC₄H₉ and produces upon polymerization the polymer hereafter referred to as poly (3BCMU). 3BCMU was the generous gift of Dr.G.N. Patel of Allied Chemical Corporation, Solvay, N.Y., USA. The monomer was purified by first dissolving in acetone and filtering off any traces of the polymer, and then by repeated recrystallization from acetone-hexane mixtures and stored in the dark below 10°C.
Photoacoustic spectra were recorded on a EG and G Princeton Applied Research model 6001 instrument. All PA measurements were done using a modulation frequency of 40 Hz, unless otherwise stated. Optical absorption spectra were recorded using a Cary 17D spectrophotometer. Polymerization of the monomer crystals was done using the source lamp of the PAS instrument, and, when necessary, using a model UV SL-25 multiband UV 'gun' made by Ultraviolet Products, USA.

**In situ** polymerization of 3BCMU was carried out on samples of the monomer adsorbed (from acetone solutions and subsequent solvent evaporation) on to filter paper strips, or on thin crystal platelets, using light from the source Xe lamp of the spectrometer (≈5 mW/Cm²). However, in experiments designed to monitor the time-dependent growth of the PA signals, a strip chart recorder attached to the instrument was used to follow the 630 nm and 580 nm peaks, and the sample in the PA cell was illuminated with an external UV-gun.

For photocalorimetry, the procedure suggested by Chance and coworkers¹⁵,¹⁶ was followed. The monomer in the crystalline or adsorbed state was placed in the cell with the light blocked, and the excitation wavelength for polymerization was chosen for the experiment (210, 225, 240 or 252 nm). The PA signal at the chosen wavelength obtained upon unmasking the sample cell was recorded as a function of time using a strip chart recorder.

For linear dichroism measurements, an Oriel UV-standard polarizer (model No. 2540-2) along with a precision rotator (model No. 1641) was incorporated into the optical path of the instrument and the PAS of the sample crystal recorded at 0° and 90° polarizer angles (with respect to the major c axis of
the 6 mm x 2 mm crystal platelet). Polarization of the emerging beam is always a problem associated with reflection optics. The polarization of a small fraction of the total radiation incident on the sample does not make any difference in the observed spectra for optically isotropic samples, provided the detector is not sensitive to the polarization of light. Thus PA signal will be proportional to the product $\beta(\lambda)I_c(\lambda)$; the second term $I_o(\lambda)$ is taken care of by normalizing the observed spectrum with the spectrum obtained for the carbon black sample. However, if the sample were optically anisotropic, then in spite of correcting for $I_o(\lambda)$ the spectrum would show an increased absorption when the plane of polarization of the incident light coincides with the orientation of the transition dipole of the sample, i.e. now the observed spectrum would be proportional to the product $\beta(\lambda)I_c(\lambda)P(\lambda)$ where $P(\lambda)$ is polarization factor at $\lambda$.

Indeed we have observed a spurious band at 425 nm with a crystal of poly(BCMU) in the EG&G PA spectra. Poly(BCMU) has no absorption maximum at 425 nm. The observed signal is due to the polarization of light incident on the sample. This could pose a problem if one attempts to record polarized PA spectra. We could solve this problem by normalizing the spectrum with carbon black spectrum recorded with a polariser with the same angle set in the optical path. Introducing the polarizer in the optical path, while recording the carbon black sample, will translate the change of the plane of polarization into a change of light intensity. Figure 3.1 shows the carbon black spectrum recorded with polarized light. These spectra were used for normalizing sample polarized spectra.

The approach taken to determine the action spectrum was to expose the monomer to radiation of a chosen wavelength in the instrument for a fixed period of time and to monitor the extent of polymerization by measuring the
Figure 3.1 PA spectra of carbon black recorded with polarized light.
polymer PA signal strength in the visible region 630 and or 580 nm. The monomer has no absorption and hence no PA bands above 300 nm. A direct comparison between two samples exposed to different wavelengths is prone to error due to variations in the sample size, and due to the variation of the source intensity with wavelength. These problems were overcome by two steps. Sample variation was minimized by dissolving 3BCMU in acetone and dipping filter paper strips (3 mm x 7 mm, Whatman No.1) in the solution and drying them, all in the dark and below 10°C. Then a given paper strip containing the adsorbed 3BCMU was irradiated at a chosen wavelength for 10 s, and the PA spectrum in the region 700-200 nm was recorded (curve a). Next, the same sample was irradiated with the external wide-band UV gun for several minutes to allow for complete polymerization and the spectrum of the fully polymerized sample was recorded in the same region (curve b). The fraction of the monomer that had polymerized upon 10 s exposure with the chosen wavelength was calculated from the ratio of the areas under the polymer band profiles (630,580 nm) of curves a and b. The variation in the spectrometer source intensity with wavelength was accounted for by normalizing the fraction (a/b) obtained to the light intensity at a given wavelength. This extent of polymer formed, corrected for power variation, was taken as the action parameter at the chosen wavelength, and plotted against wavelength to give the action spectrum of the photo-reaction.

A method of determining the action spectrum employing PAS has been used, and is described in the section on Results and Discussion. Briefly this uses the fact that in thermally thin ($\mu_s > t$) and optically transparent ($\mu_s > t$) samples, the ratio of the optical absorption (OA) spectrum to the photo-acoustic (PA) spectrum would be a wavelength-independent constant if the
molecules of the sample return to the ground state solely by nonradiative decay. If the sample were to fluoresce or undergo photoreactions as well, the OA/PA ratio would show wavelength dependence corresponding to the photo action. In this method, therefore, the OA spectrum of the monomer 3BCMU is compared with its PA and the ratio plotted.

3.4 RESULTS AND DISCUSSION

3.4.1 In situ polymerization:

Figure 3.2 shows the PAS record of the in situ polymerization of 3BCMU adsorbed on filter paper. The experiment was started by uncovering the light mask from the sample chamber and scanning the spectrum from 700 nm to 200 nm at a scan rate of 200 nm/min. Curve 1 is the spectrum of the pure monomer, and displays no bands in the visible region. Exposure of the monomer during this run to UV-radiation in the 300-200 nm region for 30 s is sufficient to start the polymerization; curve 2 reveals the presence of signals at 630 nm and 580 nm which correspond to the absorption bands of poly (3BCMU) reported by Chance et al. (20). Curves 3 to 7 show the progressive intensification of these bands, suggesting further photopolymerization of the sample. Curve 7 is essentially identical to curve 6 and suggests that, under these conditions, exposure of the monomer to UV radiation for a period of about 3 minutes was enough to polymerize the sample to the conversion limit.

In situ polymerization of a thin crystal shows exactly the same features but differs in the time required for reaching the conversion limit. Attenuation of the source power falling on the sample by introducing quartz plates in the light path led to the expected increase in the time required for reaching conversion limit. Use of a thicker crystal caused difficulties in measurements due to an increase in the sample thickness relative to the optical absorption length $\mu$, which resulted in PA saturation.
Figure 3.2  In situ photopolymerization of 3BCMU adsorbed on a filter paper strip. Curve 1 in the first run and 2-7 are subsequent ones on the same sample. Runs started at 750 nm and stopped at 200 nm.
The bands seen at 630 nm and 580 nm correspond to the planar conformation of poly (3BCMU); the band at 475 nm, seen in solution (20) and attributed to the nonplanar form of the polymer, is not seen in our experiments in the solid state.

That UV-radiation is needed for photopolymerization of 3BCMU was established by the following experiment. The monomer was exposed to radiation from 700 nm down to 200 nm during the first run in the instrument, leading to some polymerization. Subsequent runs were stopped at 300 nm, cycled in the range 700-300 nm, and the strength of the 630 nm (and 580 nm) band monitored. The absence of any increase in these signal strengths revealed that polymerization proceeds only when the monomer is exposed to UV-radiation. This observation was further confirmed in pulse excitation experiments, wherein the time variation of the 630 nm band was monitored as the external UV-illumination was turned on and off periodically. The results of such an experiment are illustrated in Figure 3.3 a which shows the PA signal to increase during the periods when the illumination is on and invariant during the dark.

3.4.2 Time profile of the reaction:

Wegner had studied (14) the UV-polymerization of a related diacetylene, PTS (where the substituent R group is p-toluene Sulfonyl), and concluded that the UV-polymerization is not autocatalyzed. However, reinvestigation of the reaction using diffuse reflectance spectroscopy by Chance and Patel (16) revealed that the reaction was autocatalytic and that the effect would be effectively masked in such UV experiments unless the optical absorption depth $\mu_p$ ($=1/\beta$ where $\beta$ is the optical absorption coefficient in cm$^{-1}$) of the crystal is comparable to or larger than the crystal thickness 1. In this connection, PAS would appear
Figure 3.3 (a) Variation of the PA intensity at 630 nm with time, as the external uv-gun illumination was switched on and off every 20 seconds. (b) Time-dependent growth of the 630 nm PA signal when the sample, 3BCMU (on filter paper), was constantly illuminated by an external uv-gun.
to be a convenient method to study this feature of the reaction under appropriate conditions.

In Chapter I, Table 1.1, we had considered six limiting cases concerning the relative magnitude of $\mu_\beta$, $\mu_5$, and $\lambda$, and the dependence of the PA signal on and in some detail. The particular case of interest here is that of an optically transparent sample ($\mu > 1$) which is also thermally thin ($\mu > \mu_5 > 1$) where the PA signal $I_{PA}$ is proportional to $\beta$, parallels the wavelength dependence of $\beta$, and varies as the inverse power of the modulation frequency ($\omega^{-1}$). In the present case of 3BCMU in the crystalline and adsorbed phases, it is clear that $\mu > 1$ and $\mu_5 > 1$, since the PA spectra in Figure 1 reveal well-resolved bands at 630 and 580 nm, PA saturation does not occur and the spectra parallel the absorption spectra in the wavelength dependence of $\beta$. We have also confirmed the dependence of the PA signal on $I$ by using samples of different thicknesses, and their $\omega^{-1}$ dependence by measuring the spectra at several modulation frequencies. Thus we are dealing with samples which meet the criterion for detecting any autocatalysis. The time evolution of the polymer PA signal at 630 nm is shown in Figure 3.3 b. The time profile of the reaction illustrated in the figure shows no features suggestive of autocatalysis, and confirms the earlier suggestion that photopolymerization of 3BCMU is not autocatalytic (17).

3.4.3 Photocalorimetry

Chance and Shand (18) have devised a PA photocalorimetric method to measure the heat energy involved in the photopolymerization of some diacetylene. The time-dependent variation of the PA signal at the exciting wavelength was analyzed using a kinetic model that was shown to agree with experimental results. In PA photocalorimetry, the time profile of the heat liberated,
arising from the exothermic photoreaction as well as that due to photon absorption by the sample, is measured. The calorimetric curve shown in Figure 3.4 for 3BCMU polymerization was prosaic, exhibiting a sharp rise in the PA signal (upon unblocking the light) which stayed essentially invariant (negligible rise) with time. Identical results were obtained when other excitation wavelengths were tried, such as 210, 240 or 252 nm (absorption peaks of monomer). This is in contrast to the curve for the higher homolog 4BCMU, where the signal showed a gradual fall with time after the instantaneous rise upon unmasking the light (18).

As the polymerization reaction proceeds, the amount of the polymer, which absorbs stronger than the monomer, increases, resulting in an increase of the signal with time. On the other hand, since the polymerization rate falls with time, the heat liberated due to polymerization, and hence the PA signal, should decrease with time. The experimentally measured signal would be a result of the above two factors. The heat liberated per photon absorbed may be represented as $h\nu + nq\Delta H$, where $h\nu$ is the photon energy, $n$ the length of the polymer repeat units produced per photon, $q$ the probability of the excited state initiating a polymer chain, and $\Delta H$ the heat liberated per polymerized unit. In the case of 4BCMU, $q$ has been estimated to be $3 \times 10^3$, $n$ as 2400, and $\Delta H$ as 1.6 eV, while for 3BCMU $n$ has been estimated to be 1000.

If one assumes the values of $q$ and $\Delta H$ to be the same as in 4BCMU, then, the heat liberated in the polymerization of 3BCMU would be expected to have a value that is $1000/2400$ times that of the polymerization of 4BCMU. The near constancy of the photocalorimeter curve for 3BCMU polymerization
Figure 3.4 Photocalorimetric profile of 3BCMU photopolymerization. PA signal intensity of the photopolymerization-initiating wavelength (225 nm) was followed with time upon the removal of the light-mask from the sample cell.
with time would then suggest that the contribution due to the heat of the reaction is effectively balanced by that due to the increased photon absorption by poly (3BCMU). The related diacetylene DCHD (where the substituent R group is methyl carbazole) also displays an essentially time-invariant PA photocalorimetric profile (19).

It is, however, possible that the parameter q need not be the same for 3BCMU as for its homolog 4BCMU. While these two monomers show essentially the same absorption characteristics and initiate photopolymerization from the same excited states, their molecular structures differ by a methylene group. Even such a subtle difference could reflect in the corresponding crystal packing and lead to different values of the chain initiation probability q for 3BCMU and 4BCMU. In the light of the near-constancy of the measured photocalorimetric curve for the polymerization of 3BCMU (Figure 3.4), it is also possible to conclude that the product nq is much smaller for 3BCMU compared to its higher homolog. The differences in 1, if any, are more than overcome by the large differences in n between two monomers.

Changing the modulation frequency between 40-200 Hz had no significant effect on the nature of photocalorimetric curve, except to decrease the magnitude of the initial signal. This is to be expected, since such a change would about equally affect both the factors that contribute to the photocalorimetric signal.

3.4.4 Action spectrum;

We next turn our attention to the measurement of the action spectrum of the photoreaction. In essence, an action spectrum describes the wavelength (energy) dependence of photo-action. In conventional methods, the amount
of the photoprodct formed is monitored as a function of the wavelength of excitation of the reactant. On the other hand since PAS measures the extent of partitioning of the absorbed energy into heat dissipation, it should be possible to exploit PAS to measure the action spectra of such molecules where no other competing deexcitation processes, such as luminescence, occur. We have tried both the approaches to determine the action spectrum of the 3BCMU photoreaction. In the first, a sample of the monomer adsorbed on filter paper strip was irradiated for a period of 10 s in the PA cell, using the PA spectrometer lamp and tuning the monochromator to UV-radiation of a chosen wavelength, and the PA spectrum in the 700-200 nm region was recorded. The experiment was repeated with several samples, each irradiated for the same time with light of a different wavelength. The data were analyzed, after correcting for the wavelength variation of the source power as described in the Materials and Methods section.

In the second method (21), we exploit the fact that the PA signal of an absorbing or optically transparent sample $I_{PA}$ will be proportional to the incident power absorbed by the sample ($P_{abs}$) and will depend on the efficiency, $\eta$, of the nonradiative decay to the ground state while the optical absorption signal $I_{OA}$ is indicative of $P_{abs}$. For a sample that neither fluoresces nor undergoes any photochemical reactions, $\eta = 1$ and the PA spectrum will parallel the optical absorption (OA) spectrum in the entire spectral range; i.e. a plot of the ratio of the absorption and PA signals [$I_{OA}/I_{PA}$] against wavelength will be a flat curve of zero slope. If, however, a part of the adsorbed energy were to be utilized towards emission or any photoreaction, the ratio $I_{OA}/I_{PA}$ would be expected to change with the wavelength, displaying the maximum changes at those wavelengths corresponding to the particular excited states from which emission or photoreaction occur. We have tested this with KMnO$_4$. 
and the dye thymol blue, compounds which neither fluoresce nor undergo any phototransformation, and in each case the ratio $I_\text{em}/I_\text{na}$ was seen to be independent of wavelength (figure 3.5 a). With the fluorescing dye Rhodamine 6G, such a plot displayed a peak at 525 nm indicating that the excited state corresponding to absorption at 525 nm was being deexcited partly through the fluorescence mode (Figure 3.5 a). Now, since diacetylenes such as 3BCMU do not fluoresce at room temperature but photopolymerize, the ratio $I_\text{em}/I_\text{na}$ as a function of wavelength in the UV-range would be expected to reflect the extent of photochemistry that occurs and thus yield the action spectrum. This method of obtaining the action spectrum of a photoprocess by PAS is being explored in greater detail in our laboratory. Figure 3.6, plot (a), shows the action spectrum obtained by the conventional method while plot (b) is the action spectrum obtained by the $I_\text{em}/I_\text{pa}$ ratio method; the resemblance between the two curves is gratifyingly close. Cahen and coworkers have utilized a similar method to monitor photoprocesses other than nonradiative decay in biological systems (22-24).

**3.4.5 Linear dichroism:**

Figure 3.7 shows the polarized PA spectra of poly (3BCMU) obtained by polymerizing the monomer crystal in situ. The bands at 630 nm and 580 nm are seen to have much higher intensities when the polarization is parallel to the major axis of the crystal than when it is perpendicular, suggesting that the transition dipoles of these bands in the highly conjugated system of the polymer lie along the major axis of the crystal. This observation is consistent with reports using normal incidence reflection spectra (20) on this class of polydiacetylenes, and indicates that the polymer chains are aligned along the c axis of the crystal. When the samples were taken as adsorbates on filter paper rather than crystals, no dichroism was observed on the resultant polymer suggesting random orientation on the paper surface.
Figure 3.5 Plot of the ratio of the optical absorption (OA) and PA signal (PAS) against wavelength for the aqueous solutions of (a) Thymol blue (b) Rhodamine 6G.
Figure 3.6 Action spectra of the photopolymerization of 3BCMU (a) using the conventional method and (b) by $I_{OA}/I_{PA}$ method described in the text.
Figure 3.7 Polarized PA spectra of poly (3BCMU) with the plane of polarization parallel (II) and perpendicular (⊥) to the major axis of the crystal.
3-5 Conclusion:

We have shown that PAS can be conveniently used to monitor several features of a solid-state reaction (i) the wavelength dependence of the photo-reaction, i.e. the action spectrum (ii) the time profile of the reaction (iii) the conformation of the product polymer (iv) the linear dichroism and orientation of the polymer in the solid and (v) the photocalorimetry of the reaction. The approach opens up the possibility of studying various organic photoreactions in the solid state and to understand the reactions in terms of the energy states involved in the reaction, and the effect of subtle geometric and structural changes on the course of the reaction. The method described here for the determination of the action spectrum of the photoreaction appears to be simpler and more convenient than the conventional sampling method.
REFERENCES:


