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Solid-State Photopolymerization of Diacetylenes

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ABSTRACT: A detailed study of the UV photopolymerization of a highly radiation-sensitive diacetylene is presented. The polymerization kinetics, quantum yield, and variation of optical properties on polymerization are analyzed and discussed. The polymerization rate for irradiation of thin diacetylene films is found to decrease markedly as the polymer concentration increases. Quenching of the monomer excited state by the polymer chains present in the partially polymerized samples is shown to provide a reasonable explanation for this behavior. This quenching is probably an important limiting factor in determining overall polymer conversion in the photopolymerization of diacetylenes.

I. Introduction

The solid-state polymerization of diacetylene crystals provides a prime example of a lattice-controlled solid-state reaction.[1] The reaction proceeds via 1,4 addition and can be initiated by heat,[2,3] pressure, UV irradiation,[4,5] high-energy irradiation,[1,6] or exposure to certain gases.[7] In favorable cases, the reaction product is a single-crystal, fully conjugated polymer of macroscopic dimensions.

Much of the work in the poly(diacetylene) area has centered on the kinetics and mechanism of the polymerization process. The thermal polymerization process is temperature activated by about 1 eV, which should represent roughly the energy difference between the monomer and the dimer intermediate to chain propagation. Energetic arguments[3] and recent ESR experiments[8,9] strongly suggest a biradical (rather than a bicarbene) structure for the dimer. At this stage, the dimer can revert to the monomer (which it probably does with highest probability[10]) or proceed forward to initiate a chain. Each propagation event, i.e., each addition of a monomer unit to the chain, is exothermic by ~1.6 eV.[3] Little is known about the chain termination event.

For photopolymerization, the process is viewed to be much the same except that the activation barrier is overcome via the photon energy.[5] Since the photopolymerization process is strictly linear in light intensity (at least in the vicinity of room temperature),[5,11] the dimerization event must involve a monomer excited state interacting with a monomer ground state. Figure 1 illustrates schematically the energetics of these processes.[3] Since the absorbed photon can initiate a chain reaction, quantum yields can be quite high.[5,11] The quantum yield is defined as the number of poly(diacetylene) repeat units produced per absorbed photon and is equal to nq, where q is chain initiation probability and n is the propagation length. Values ranging from $nq = 10^{-4}$ to 50 have been reported for various diacetylenes.[5,11-14] The exothermic nature of the photopolymerization process has been conclusively demonstrated with photoacoustic spectroscopy.[11]

In this paper, we present a detailed study of the UV photopolymerization of a highly radiation-sensitive diacetylene.[6] We discuss the polymerization kinetics, the factors limiting quantum yields, and the variation in optical properties on polymerization. Experimental details are given in section II. Results are presented section III and discussed in section IV.

II. Experimental Section

The diacetylene chosen for this study is 4BCMU, $RC\equiv C-C\equiv CR$, where R is $(CH_2)_4OCONHCH_2COO(n\text{-}C_4H_9)$. BCMU stands for [(butoxycarbonyl)methyl]urethane. This particular diacetylene displays high reactivity to UV or γ irradiation but virtually no thermal reactivity.[6] Some of the experiments described herein employ 4BCMU single crystals, which typically grow as thin platelets (1 × 5 × 0.01 cm).[14] However, most of our photopolymerization studies have been carried out on thin films of 4BCMU. These films, with thicknesses ranging from 1000 to 20 000 Å, were deposited on quartz slides with an air brush. A drop of paraffin oil (purified by passage through silica gel) was then placed on the slide and inserted in a standard 1-cm quartz cuvette so that the paraffin oil formed an interface between the 4BCMU film and the inner surface of the quartz cuvette. This arrangement was used to minimize scattering, which can be quite a problem with an air/film interface. Water and paracyclophane[15] were also used as "index matching" media to ensure that our results were unaffected by the paraffin oil. Spectra were taken before irradiation and after various irradiation dosages. The irradiation source was a 150-W xenon arc lamp with a 260-nm, 10-nm band-pass interference filter and a Corning 754 UV filter. The incident irradiation intensity was typically 2×10^{13} photons/(cm^2·s), determined with a calibrated EG&G photodiode. The band-pass for the spectra was 1 nm.

At the end of the experiment the amount of polymer on the slide was determined by dissolving the film in 2 mL of $CHCl_3$ and measuring the absorbance of the resulting polymer solution ($\epsilon_{max} = 17\,000$ L/(mol·cm) at 470 nm).[16] Average film thickness was

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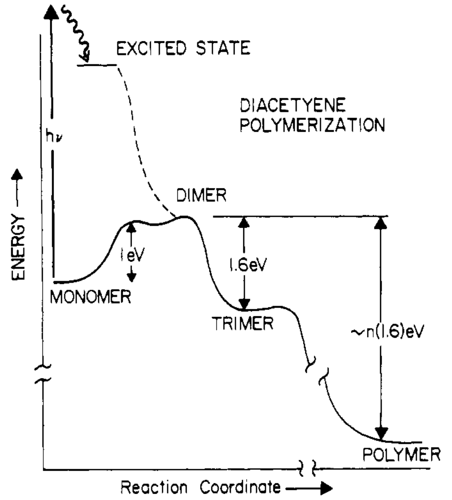

Figure 1. Reaction diagram illustrating the energetics of diacetylene polymerization. Energetic parameters are taken from ref 3.

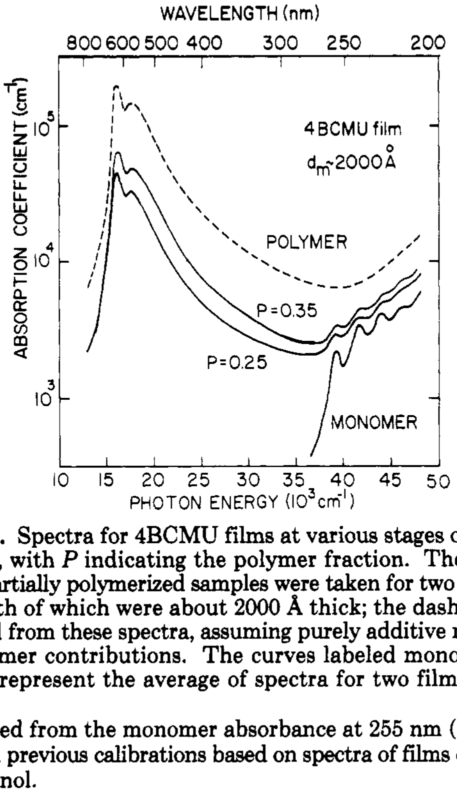

Figure 2. Spectra for 4BCMU films at various stages of polymerization, with P indicating the polymer fraction. The spectra for the partially polymerized samples were taken for two different films, both of which were about 2000 Å thick; the dashed curve is derived from these spectra, assuming purely additive monomer and polymer contributions. The curves labeled monomer and polymer represent the average of spectra for two films.

determined from the monomer absorbance at 255 nm ($\alpha = 2100$ cm^{-1}) and previous calibrations based on spectra of films dissolved in methanol.

III. Results

Typical results for the evolution of the optical properties of 4BCMU on UV polymerization are shown in Figure 2. The main features of the monomer absorption spectrum are in good agreement with that obtained by Takabe et al.[17] for 2,4-hexadiyne-1,6-diol. The monomer peaks show a progression of about 2300-cm^{-1} spacing, consistent with values for the triple-bond stretching frequencies observed in Raman spectra.[18] Weak absorption found by Takabe et al.[17] in the onset region (33 000–36 000 cm^{-1} with $\alpha \sim$ 100–300 cm^{-1}) is not observed in 4BCMU—probably because of the difficulty in obtaining films sufficiently free of polymer to detect such weak absorption. The monomer peak at 255 nm probably contains a significant contribution due to the urethane functionalities in the side group of 4BCMU.[11] As shown previously,[11] polymerization occurs with excitation anywhere within the monomer absorption band.

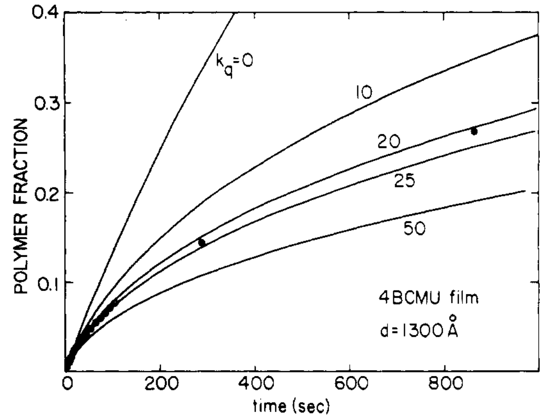

Figure 3. Polymer fraction vs. irradiation time for a 4BCMU film, 1300 Å thick. The theoretical curves are obtained for the kinetic model with indicated values of quenching parameter, k_q. The incident light intensity was 2×10^{13} photons/(cm^2·s) at 260 nm.

After UV irradiation, spectra such as those shown in Figure 2 are obtained. The polymer fraction indicated in the figure is obtained from spectra of dissolved films as described in section II. The polymer absorption band measured for these films agrees well with that of the single crystal,[14] suggesting that crystallite sizes in the films are large enough to have no effect on the spectra. The main polymer absorption band peaks at 16 000 cm^{-1} (followed by a vibrational sideband) and then monotonically decreases up to about 35 000 cm^{-1}. Above 35 000 cm^{-1}, a gradual increase in polymer absorption (up to the highest energies studied) is indicated by the data. This conclusion comes largely from the dashed curve in Figure 2, which we derive assuming additive polymer and monomer contributions to the spectra for the partially polymerized samples. Both the $P = 0.25$ and $P = 0.35$ spectra gave the same results within experimental error. In spite of the care and precautions we have taken with regard to scattering, we cannot with certainty rule out increased scattering in the partially polymerized samples as the cause of the apparent increase in absorption beginning at 35 000 cm^{-1}.

Note that visual inspection of the data would seem to suggest some broadening of the monomer absorption peaks in the partially polymerized samples. An intrinsic source of this broadening could be lifetime reduction due to nonradiative quenching of the monomer excited state by the polymer chain. As will be apparent shortly, we believe this quenching to be an important effect with regard to polymerization kinetics. However, it is probably not a significant effect with regard to line broadening, at least at room temperature. The fact that the derived polymer absorption spectrum is featureless in the monomer absorption region suggests that there is no significant intrinsic broadening and that the apparent broadening is due to the combination of decreased monomer absorption and increased polymer absorption in the region. The same is probably true in the experiments of Bloor et al.[19]

In principle, the polymer absorption spectrum could be obtained by simply irradiating long enough for the polymer concentration, P, to closely approach unity. We have found, rather surprisingly, that large P values are not readily obtainable for 4BCMU with UV irradiation, in spite of the fact that the film thicknesses are much less than the absorption depths. The reason for this behavior is that the polymerization rate decreases much faster than would be expected based on the disappearance of monomer. Typically at $P \sim 0.1$, the polymerization rate, $\mathrm{d}P/\mathrm{d}t$, is about 5 times smaller than the value near $P = 0$. At higher

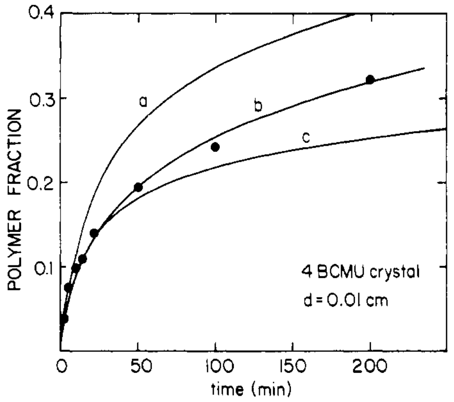

Figure 4. Polymer fraction vs. irradiation time for a 4BCMU single crystal, 0.01 cm thick. The irradiation source was 260 nm (uncalibrated). The theoretical curves are obtained from the kinetic model with (a) $\alpha_p/\alpha_m = 1$, $k_q = 0$, (b) $\alpha_p/\alpha_m = 1$, $k_q = 20$, and (c) $\alpha_p/\alpha_m = 3$, $k_q = 0$.

conversion there is a monotonic decrease in dP/dt. This behavior is illustrated in Figure 3. These results are quite representative in that they are virtually unaffected by (1) film thickness variation in the 1000–20 000-Å range, (2) excitation wavelength variation (220–260 nm), and (3) variation of the index matching medium (water, paraffin oil, paracylcophane, or air).

In numerous experiments such as that summarized in Figure 3, we find dP/dt constant (i.e., P linear with time or dosage) for $P \lesssim 0.03$. This is in contrast to the results of Bhattacharjee and Patel[20] on 4BCMU, who were unable, due presumably to sensitivity restrictions, to obtain a linear P vs. time regime. For this reason they were only able to estimate a lower limit for the quantum yield, $nq > 50$, in spite of careful calibration prcedures. We have taken less care with calibration procedures, using calibrated photodiodes, but are able to estimate $nq = 70$ in the linear regime with an uncertainty of about a factor of 2. This value is almost 10 times larger than that estimated from photoacoustic experiments on 4BCMU.[11] It now seems clear that the photoacoustic experiments substantially underestimate nq because of differences in the thermal properties of monomer and polymer.[21]

Figure 4 illustrates a parallel series of experiments carried out on 4BCMU single crystals. In this case, the polymer fraction is determined from the optical density measured with light polarized perpendicular to the chain,[14] with a final calibration at the end of the experiment obtained by dissolving the crystal in $CHCl_3$ and measuring the optical density of the resulting solution at 470 nm. Because the crystal thickness is rather large compared to the absorption depth, it is difficult to identify any abnormal qualities in the curve shape of Figure 4. We will return to these results in section IV.

IV. Discussion

A kinetic model for the photopolymerization process has been discussed in previous papers,[5,11] where it is shown that the inhomogeneity of the UV polymerization process can be an important effect. This conclusion is particularly evident when the sample thickness is much larger than either the monomer or the polymer absorption depths.[5] For the film experiments discussed here, the sample thickness is quite small and inhomogeneity does not play an important role either in the kinetics or as a limiting factor in the overall yield. We believe these thin-film experiments allow the identification of another important limiting factor—quenching of the excited monomer by the polymer chains produced during the reaction. This process is quite evident with diacetylenes having fluorescent substituent groups.[12,22,23] However, since these diacetylenes do not fluoresce,[24] a direct probe of the quenching of the diacetylene excited state by the polymer is not available. Instead, we argue here based on a comparison of experiment and a kinetic model including quenching. Note that the kinetic model applies to arbitrary values of monomer and polymer absorption coefficients and, therefore, includes the filtering effect of polymer absorption.

The differential equation governing the photopolymerization process is[5,11]

$$dP(x,t)/dt = nq'\alpha_m I(x,t)M(x,t)/\rho \tag{1}$$

where n is the chain propagation length, q' is the chain initiation probability, α_m is the monomer absorption coefficient, x is the distance measured from the crystal surface, $P(x,t)$ is the polymer concentration (polymer repeat units/cm^3) at time t and distance x, $M(x,t)$ is the monomer concentration $[M(x,t) = \rho - P(x,t)]$, and ρ is the density (molecules/cm^3), which is essentially the same for monomer and polymer. $I(x,t)$ is the photon intensity (photons/(cm^2·s)) at time t and distance x into the crystal and is given by

$$I(x,t) = I_0 \exp\left[-\alpha_p \int_0^x P(x',t)/\rho \, dx' - \alpha_m \int_0^x M(x',t)/\rho \, dx'\right] \tag{2}$$

where α_p is the polymer absorption coefficient. The polymerization rate is given by

$$\frac{dP(t)}{dt} = \int_0^d \frac{dP(x,t)}{dt} \, dx \tag{3}$$

where d is the crystal thickness.

The inclusion of quenching requires a redefinition of q. Previously, q was defined as[5,11]

$$q = \xi_i/(\xi_i + \xi_d) \simeq \xi_i/\xi_d \tag{4}$$

where ξ_i is the rate constant for chain initiation and ξ_d is the sum of all other rate constants for deactivation of the excited state. If ξ_q is the second-order rate constant for quenching by the polymer chain, we have for q' in eq 1

$$q' = q/(1 + k_q P(x,t)/\rho) \tag{5}$$

where we have defined $k_q = \xi_q/\xi_d$. The latter definition amounts to scaling the energy transfer rate constant to the intrinsic lifetime (ξ_d^{-1}) as is usually done.[25] The form for the quenching in eq 5, and in particular the proportionality to $P(x,t)$, is chosen to be consistent with quenching measurements in mixed molecular crystals, where Förster transfer is thought to be the dominant energy transfer mechanism.[25] It should be emphasized that the mechanism for energy transfer from the diacetylene monomer to the polymer may be quite different and our approach here should be recognized as a first approximation.

The polymer fraction, P, is obtained as $P(t)/\rho d$ after numerical integration of eq 3 over x and numerical integration of $dP(t)/dt$ over time. The model results are compared to the film experiment in Figure 3. Since there is a well-defined linear regime, k_q is the only adjustable parameter in the fit, which yields $k_q \sim 20$. The crystal data of Figure 4 are less straightforward to interpret, since the inhomogeneity of the reaction affects the results so that the fit depends on α_p/α_m and k_q. Though $\alpha_p/\alpha_m \sim 3$ can be estimated from Figure 2, there is an unknown contribution due to scattering. Nevertheless, it is clear that the

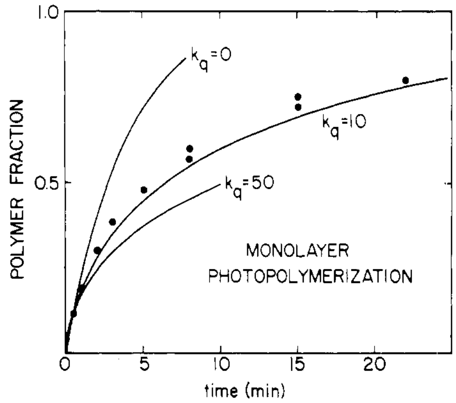

Figure 5. Polymer fraction vs. irradiation time for diacetylene multilayers, consisting of 32 monolayers (~1000 Å thick) from Tieke and Wegner.[12] The theoretical curves are all adjusted to pass through the first data point.

crystal data can be adequately represented by the kinetic model.

Finally, in Figure 5 we compare to the experiments of Tieke and Wegner[12] on diacetylene multilayers, where the small-thickness limit applies. We find $k_q \sim 10$ yields a satisfactory description of their data.

V. Conclusions

There are a number of factors which limit the photoreaction yields. They can be divided conveniently into two classes: those that affect the propagation length, n, and those that affect the chain initiation probability, q. Examples of the former are strain caused by mismatch between monomer and polymer lattice dimensions and chain-blocking impurities (which can be other chains at high conversions[10]). In this paper we have dealt with effects on q and have identified a possibly important limiting factor—quenching of the monomer excited state by the polymer chains in the partially polymerized materials. We suggest this quenching to be an important factor in UV polymerization and perhaps in γ-ray polymerization as well.[5] The rate constant describing this quenching should be a function of the details of the packing arrangements in the crystal. However, the rate constants were found to be of similar magnitude for the 4BCMU films studied herein and the diacetylene multilayers studied by Tieke and Wegner.[12] Confirmation of this mechanism is required via either a broader study of diacetylene polymerization or perhaps via low-temperature line width measurements of the monomer absorption band in partially polymerized crystals.

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