

QUANTUM YIELD OF SOLID STATE POLYMERIZATION OF DIACETYLENES

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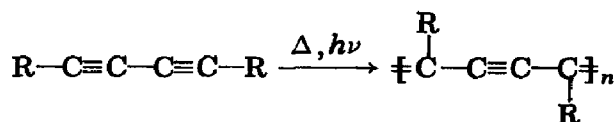
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Summary

Chemical actinometry was used to make the first reliable determination of the quantum yield of the solid state polymerization of two diacetylenes $R-C\equiv C-C\equiv C-R$, the first compound being 5,7-dodecadiyn-1,12-bis(*n*-butoxycarbonylmethylene urethane) (4BCMU) where $R \equiv (CH_2)_4-OCONHCH_2COO(CH_2)_3CH_3$ and the second being 2,4-hexadiyn-1,6-bis(*p*-toluenesulfonate) (1_p TS) where $R \equiv -CH_2OSO_2-\text{C}_6\text{H}_4-CH_3$. The number of monomer molecules polymerized on irradiation at 254 nm was determined by absorption spectroscopy. A quantum yield of above 50 was observed for 4BCMU while 1_p TS gave the much lower value of 0.06 ± 0.03 . The lower quantum yield for 1_p TS is explained by the low molecular weight chains provided by polymerization.

1. Introduction

The solid state polymerization of the diacetylenes $R-C\equiv C-C\equiv C-R$ [1, 2] with high energy radiation is an ideal example of a visible photochemical reaction. Color development on radiation- or thermally induced polymerization [1, 2] of diacetylenes is due to the formation of a highly conjugated backbone:



The rates of polymerization on either radiation or thermal annealing are different for diacetylenes with different substituent groups. Some diacetylenes are almost inactive, *i.e.* they do not polymerize, while others are highly active and polymerize quantitatively, at least on the surface, in a few seconds when exposed to high intensity UV light [3]. Often a diacetylene can be crystallized into either active or inactive phases by selecting proper solvents [3].

Observation of color development with the naked eye indicates that the process of polymerization of the diacetylenes should be very fast. We decided to utilize chemical actinometry [4] to evaluate the quantitative aspects of the rate of polymerization by measuring the actual quantum yields of these solid state photochemical processes. The chemical method employs a photochemical reaction possessing a known and accurately reproducible quantum yield.

There is only scant information available on the quantum yields of solid state photopolymerization processes [5 - 7]. In a recent paper Tieke and Wegner [7] utilized photopolymerization of diacetylenes prepared in multilayers. However, meaningful quantum yields are difficult to measure because polydiacetylenes are insoluble in most solvents. Recently, a new class of polydiacetylenes has been discovered which shows a high solubility in common organic solvents. In this paper we report the determination of the quantum yield of two monomers which provide solvent-soluble polymers. One is 2,4-hexadiyn-1,6-bis(*p*-toluenesulfonate) (1_p TS) ($R \equiv -CH_2OSO_2-\text{C}_6\text{H}_4-CH_3$) and the other is 5,7-dodecadiyn-1,12-bis(*n*-butoxycarbonylmethylene urethane) (4BCMU) ($R \equiv -(CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$). Although poly(1_p TS) is insoluble at high conversions where the molecular weight of the polymer is high, it can be conveniently dissolved in solvents such as *N,N*-dimethylformamide at low polymer conversions. Most of the previous attempts to determine the quantum yields of photopolymerization of diacetylenes appear to be based on assumptions which might not be reliable. Several of the potential sources of error in these determinations are as follows.

(a) The calibration of the sources was poor and the uncertainties were as high as 50%.

(b) The time-dependent conversion rate was not determined by the more accurate method of obtaining continuous absorption spectra of the polymers in solution.

(c) The quantum yield was reported for high conversions only, thus ignoring the fact that the polymerization rate decreases with increasing conversion.

(d) An assumption of complete absorption of the incident beam by the solid monomer was not warranted.

(e) Most significantly, no attempt was made to use colorless solid monomer depositions as the starting materials.

In the work reported here we used chemical actinometry to measure light intensities, thus avoiding problem (a), and we measured the rates of reaction by spectrophotometric analysis of solutions made by dissolving irradiated samples: this allowed accurate monitoring even at low conversions. We also worked under conditions of virtually complete absorption of the exciting light by the samples.

The 1_p TS and 4BCMU monomers were selected so that a slow color development (1_p TS) could be compared with a rapid color development (4BCMU). Determination of $G(-m)$, the number of monomer molecules

reacting per 100 eV of ^{60}Co γ rays, reveals that for 4BCMU [8] the number is $200\,000 \pm 50\,000$ compared with only 66 for 1_pTS [8, 9]. Consequently, we might expect a much lower quantum yield value for 1_pTS than for 4BCMU. However, a survey of the literature [5, 6] shows that almost the same ranges of quantum yield value were cited for both. Furthermore, some of the variations might be attributed to variation in the reactivity of different polymorphic forms of the same diacetylene. However, we were not convinced that this was the principal reason for the erratic character of the reported results.

2. Experimental details

The synthesis of the 1_pTS and 4BCMU monomers used in the present investigation has been described elsewhere [9, 10]. The monomers were crystallized twice from available solvents to obtain high purity. Figure 1 shows UV spectra of the 4BCMU monomer both in the form of a solid thin film (uniformly coated inside the wall of a cuvette) and in spectral grade methanol solvent. Both spectra appear to be identical in showing the first major peak at 254 nm. All the absorption spectra were recorded using a Beckman DK-2A ratio-recording spectrophotometer. The light source used for the irradiation of the monomers and for running actinometry was a high pressure 1000 W mercury (xenon) arc lamp (Hanovia L5173) and the output of the lamp, after passing through a cooling distilled water jacket device and

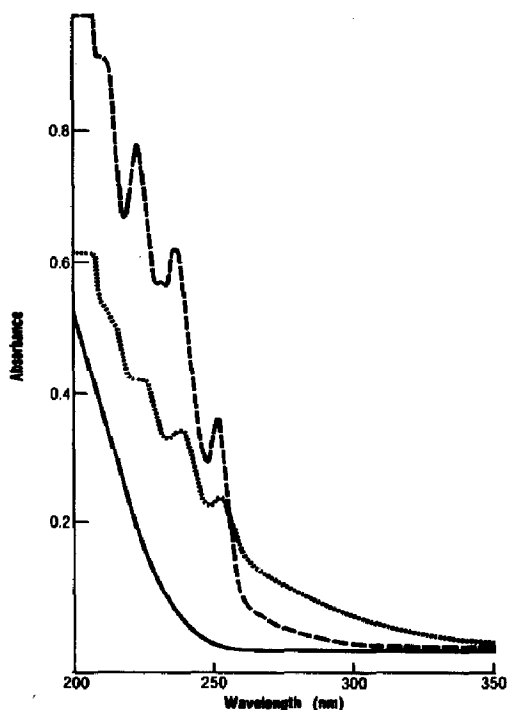


Fig. 1. UV absorption spectra of 4BCMU monomer: ---, 4BCMU in methanol; —, methanol; ···, solid thin film of 4BCMU (uniformly coated inside the wall of a cuvette).

a light baffle, was focused by a quartz lens on the entrance slit of a Bausch and Lomb monochromator (a grating of 1200 lines mm^{-1} blazed at 210 nm). This entrance slit was varied from 3 to 1.5 mm and the similar variations in exit slit were from 1.5 to 0.5 mm. The irradiations of the solid-monomer-coated samples were made at a single wavelength of 254 nm which is the first absorption peak in the monomer spectrum of both 1_pTS and 4BCMU. If we know the lamp profile and arbitrarily take the lamp intensity at 250 nm to be equal to unity, the action spectra (from 250 to 325 nm) are found to bear a close resemblance to the absorption spectra of the monomers within the spectral region studied. In order to obtain the action spectra, the 4BCMU-monomer-coated filter papers were irradiated by monochromatic light and the changes in absorbance at $\lambda = 470$ nm were monitored as a function of the time of irradiation by dissolving the polymers in suitable solvents (see Section 2.2 for details).

Ferrioxalate actinometry was used to measure the light intensities, following the general procedure of Hatchard and Parker [4]. Reproducible results were obtained by mixing the irradiated ferrioxalate solution, an acetate buffer and freshly prepared *o*-phenanthroline solution and waiting 0.5 h for reaction completion before taking the absorbance of the solution at 510 nm. The wavelength was adjusted by the monochromator and the light output at 254 nm was evaluated by running actinometry for 16 min of irradiation in each case. The lamp decay and instability were negligible. The total light intensity from the lamp was checked periodically with a radiometer and fluctuations in light intensity of only about 5% were observed, apparently resulting from very occasional feeble fluctuations of the intensity of the arc lamp. In any case the determination of the quantum yields was repeated at least four times for each monomer on different days and the experimental order of operations was alternated. All experiments were carried out at room temperature. Typical intensities of about 2×10^{-8} and 8×10^{-8} einsteins s^{-1} were obtained at the sample position with the two different slit settings of the monochromator. The light was focused on an area of approximately 1.5 cm \times 0.5 cm in each case. The actual intensity I_0 was calculated for each irradiation.

2.1. Sample preparation

Colorless solutions containing 20 g per 100 ml of both the monomers were prepared in acetone. Two techniques for putting the monomer coatings on the filter paper were used. Using the first technique the solution was sprayed uniformly on the strips (9 mm \times 100 mm) of filter paper arranged side by side to give a coating thickness of about 1 mm in each case. In the second technique the samples were prepared by dipping strips of filter paper of the same size in the solution, drying in air for about 10 s and repeating the process 10 times to obtain a monomer coating approximately 1 mm thick on each individual strip. The coated paper strips were then dried under vacuum for 10 min, thereby ensuring removal of all the acetone. All the coating and drying work was carried out under a red safelight to prevent any

photopolymerization prior to irradiation. To compare the results at longer periods of exposure (greater than 30 s), a few samples were made by yet a third technique where the inside of a 2 mm quartz cell was packed with known weights of solid monomer powders. In this case the total polymer contents of the irradiated samples were obtained by subtracting the polymer contents of the starting materials. (The starting material was very faintly blue which corresponds to a polymer conversion of less than 0.05%.) It should be emphasized that the last technique of sample preparation was employed only to draw a comparison with the other two techniques where the materials used were more reliable colorless monomers.

2.2. Determination of the quantum yield

During irradiation the cell was held in a fixed position on the optical bench. Monomer-coated filter strips were exposed to UV light (254 nm) by placing the individual strip vertically within the front-window side of the same quartz cell also used for running actinometry. This optical arrangement ensured that both the actinometer solution and the sample-coated paper strips received the same quantity of front-face illumination. The samples were irradiated for different periods of time, up to a maximum of 4 min for 4BCMU and up to a maximum of 10 min for 1_p TS. Irradiated 1_p TS solids appeared pink, thus evidencing only partial polymerization. The same partial polymerization produced a blue coloration in the 4BCMU. Observation by eye revealed that the color change was limited only to the very front of the surface area, thus making it certain that complete light absorption occurred in each sample. No metallic color appeared in either polymerization process even at maximum exposure time. To measure the polymer content, each strip was placed in an acetone bath to remove most of the unreacted monomer. After a few minutes the strips were transferred very carefully to test tubes containing either spectral grade *N,N*-dimethylformamide (for 1_p TS) or chloroform (for 4BCMU). The dissolution of poly(4BCMU) in chloroform was very fast, while poly(1_p TS) required slight warming for it to dissolve in *N,N*-dimethylformamide. Solutions of low conversion poly(1_p TS) were pale yellow whereas the solutions of poly(4BCMU) in chloroform were bright yellow. Each solution was diluted quantitatively by the respective solvents to the required amounts and optical absorption spectra were recorded. The spectral shapes of both polymeric solutions have been published previously [10, 11]. The number M_p of moles of monomer polymerized per unit time was calculated from the absorbance readings of individual solutions at 450 nm for poly(1_p TS) (whose extinction coefficient is $5600 \text{ M}^{-1} \text{ cm}^{-1}$) and at 470 nm for poly(4BCMU) (whose extinction coefficient is $17\,500 \text{ M}^{-1} \text{ cm}^{-1}$).

3. Results and discussion

The lower extinction coefficient for poly(1_p TS) solution probably indicates the presence of very low molecular weight chains (with a degree of

polymerization of approximately 20). Thus for poly(1_p TS) the meaningful absorbance values could be recorded only for samples which were irradiated for 2 min and over. The quantum yield values were obtained by taking the ratio of M_p to I_0 .

A number of investigators have established that the rate of polymerization of 1_p TS is almost constant up to about 10% conversion, after which point autocatalytic polymerization occurs. In contrast, 4BCMU polymerizes asymptotically and so in this case the quantum yield of photopolymerization can be expected to decrease markedly with the time of exposure. Hence, in order to compare the quantum yields of different diacetylenes, the values should be determined at zero dose by extrapolation.

Figure 2 shows a plot of quantum yield values against the time of irradiation for 4BCMU. The line was drawn through the average of at least four different values for each irradiated sample.

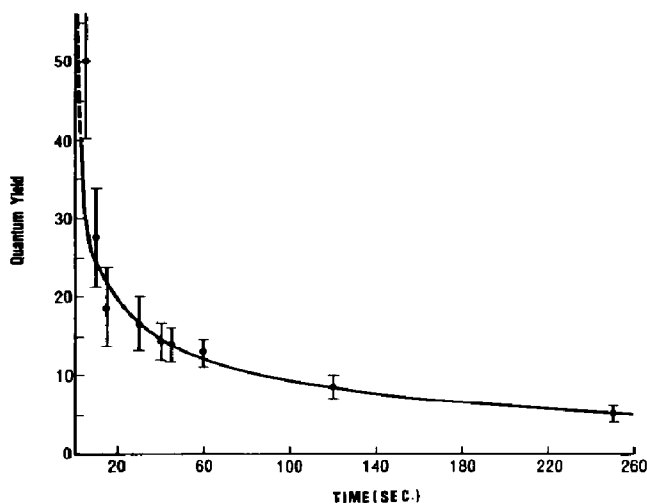



Fig. 2. A plot of quantum yield against time of irradiation at 254 nm for 4BCMU.

The initial quantum yield $(QY)_i$ at zero dose obtained by extrapolating the curve in Fig. 2 to zero time turned out to be at least 50 and possibly very much larger for 4BCMU. This value reduced to 6.0 ± 2 when the sample was irradiated for a little more than 4 min. The meaningful quantum yield value for 1_p TS polymerization could be calculated only for 8 and 10 min of irradiation in our present experimental set-up and as expected the value obtained was low, only 0.06 ± 0.03 . At lower exposure times the results varied from 0.04 to 0.08. The results are compared with corresponding $G(-m)_i$ values in Table 1. Thus, similar behavior is observed in both γ ray and UV photopolymerization.

The high value of the quantum yield of polymerization for 4BCMU appears to be unique and we believe that this is the first reliable quantitatively determined value for such polymerization processes. Such a high value is possible for 4BCMU because of the production of longer chains (2500 repeat

TABLE 1

(QY)_i and G(-m)_i for 1_pTS and 4BCMU

Diacetylene	R	(QY) _i	G(-m) _i
1 _p TS	-CH ₂ OSO ₂ -  -CH ₃	0.06 ± 0.03	66 ± 5
4BCMU	-(CH ₂) ₄ OCNHCH ₂ COO(CH ₂) ₃ CH ₃	> 50	200 000 ± 50 000

units) by radical propagations. In 1_pTS the propagation of reactive sites to a longer length is restricted because strains build up in the 1_pTS crystals; these strains are generated by a 5% mismatch along the *b* axis [2, 12] between the monomer and the polymeric repeat unit. The *b* axis is the fiber axis or the axis of chain propagation. No such mismatch is noticed for poly(4BCMU). The significance of this work lies in the fact that we were able to obtain a very reliable high quantum yield value for 4BCMU at zero conversion. The methods for preparing colorless monomer samples, coupled with the complete light absorption by the solids, are the major contributing factors for obtaining such results. The influence of the monomeric side groups on the quantum yield is also established in this work. The decrease in quantum yield at higher conversions is due to the decrease in the rate of polymerization.

Acknowledgments

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