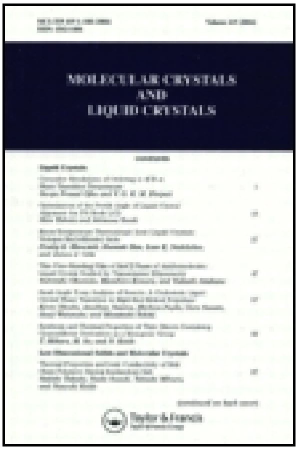

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MECHANISMS OF THE SPECTRAL SENSITIZATION OF THE DIACETYLENE POLYMERIZATION

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Abstract A short survey is given of experiments using surface active dyes in order to sensitize the photopolymerization of diacetylenes to visible light in Langmuir-Blodgett multilayers. Among the different mechanisms discussed, the preferred one is based on an electron transfer between the photoexcited dye and the diacetylene moiety.

1. INTRODUCTION

The photopolymerization of pure diacetylenes is restricted to UV or high energy irradiation because the monomeric diacetylene chromophore absorbs in the UV-range only. To extend the spectral sensitivity substituents might be used that absorb visible light. However the choice of the substituents is limited by steric effects. The polymerization of diacetylenes occurs in the solid state only and is strictly lattice controlled.[1,2] Therefore the substituent acting as the chromophore must not disturb the packing necessary to bring about the solid state reactivity.

Such steric problems can be overcome with Langmuir-Blodgett multilayers. It was shown that multilayers can be built up with amphiphilic diacetylenes such as

$$C_{12}H_{25}-C{\equiv}C-C{\equiv}C-C_8H_{16}-COOH$$

preferably in the form of the Cd-salt.[3,4] The multilayer can be polymerized by UV-irradiation with retention of the crystalline order and layer structure.[5]

The incorporation of the surface active dyes is achieved by adding a small amount of the dye to the solution of monomer diacetylenes prior to the spreading at the air-water interface. Fig. 1 shows schematically the arrangement of the surface active dye in a monolayer.

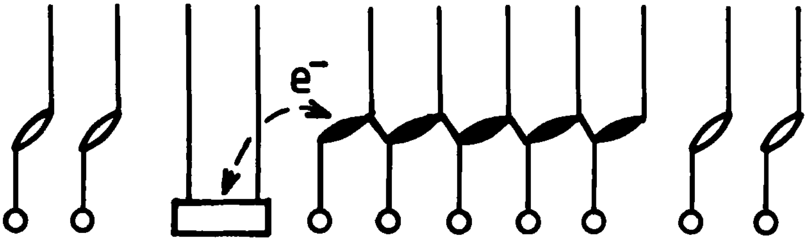

FIGURE 1. Partially polymerized monolayer and an electron transfer between the surface active dye and the oligomer.

Since they were published recently[6-8], the experiments designed to study the sensitization capability of a series of surface active dyes are here only briefly summarized. The aim of this paper is to present a refined discussion of the mechanisms that account for the sensitization.

2. SENSITIZATION EXPERIMENTS

Several surface active dyes with optical absorptions in the range between 400 and 600 nm have been used as sensitizers of the photopolymerization of diacetylenes in multilayers: five different cyanine dyes[6,7] as well as one acridinium and one anthraquinone dye.[8] The general characteristics of the sensitization by these dyes is quite similar. Irradiation of the multilayer in the range of the absorption band of the dye leads to a polymerization of the diacetylene units. The action spectrum of the reaction rate corresponds exactly to the dye absorption spectrum.[7] This is the proof, that the diacetylene polymerization is sensitized by the optical excitation of the dye.

The polymer yield is related to the integral polymer absorption A, evaluated between 13500 and 30500 cm^{-1}. At the beginning of the irradiation the time dependence of the conversion obeys an empirical law $A \sim t(c+t)^{-1}$, c being a constant. At longer irradiation times a maximum of A is observed.

Within the experimental error A_{max} is the same for the different sensitizer dyes described above. Furthermore, A_{max} is independent of the dye concentration in the range between 0.02 and 3 mole percent. It is important to note that the same A_{max} values are obtained either by the sensitized polymerization or by a direct UV-excitation of the triple bond system. Taking into account the lowest dye concentration of 0.02 mole percent used so far, we conclude that one dye molecule must be able to sensitize the polymerization of approximately 5000 monomer units in order to reach the high conversion observed.

The quantum yield Q of the sensitized photopolymerization is defined as the number of monomer molecules polymerized per number of photons absorbed by the dye. At the beginning of the conversion Q is of the order of 10^{-3} to 10^{-2}.

The intensity of the fluorescence of the dyes strongly decreases as the polymer product is formed whereas the absorption of the dyes decreases only slowly due to a photodegradation process. Two different mechanisms may account for the fluorescence quenching: firstly a Förster type energy transfer or secondly an electron hopping or tunneling process from the dye to an adjacent oligomer chain.

3. SENSITIZATION MECHANISMS

3.1 INITIATION REACTION

The lowest electronic excitation energies of monomeric diacetylenes are observed at 3.7 eV[9] and 3.1-3.2 eV[10] for the singlet and triplet states, respectively. Since the optical transitions of the sensitizer dyes are excited at considerably lower quantum energies a transfer of electronic excitation energy from the dye to the diacetylene monomer is not possible. Therefore other possibilities have to be considered. We suggest two possible mechanisms.

First we describe a model that is based on an electron transfer between the photoexcited dye and the diacetylene creating reactive radical-ion states. To substantiate this process, the knowledge of the absolute potentials of the various ground and excitation states is crucial. The highest occupied molecular orbital of the diacetylene monomer is located -7 ± 1 eV below the vacuum level as determined by ESCA.[11] Therefore the singlet and triplet excitation states of the diacetylene monomer are expected at the potentials -3.3 eV and -3.8 to -3.9 eV. However, these levels are known only with an uncertainty of ± 1 eV due to the experimental error of the ESCA data.

The level E^* of the excited state ionization energy of the cyanine dyes can be approximated from the oxidation potential E_{ox} and the optical excitation energy.[12] Using the data of polarographic investigations[13] E^* is calculated. The series of cyanine dyes that sensitize the diacetylene polymerization has values of E^* in the range between -2.7 eV and -3.3 eV. Therefore it is feasible that an electron can be transferred from the photoexcited cyanine dye acting as donor to the diacetylene unit by a tunneling or hopping process. The sensitization by the surface active anthraquinone and acridinium dyes can be explained similarly.[8] Although reliable data on the reduction potentials of these dyes in the multilayer environment are not available at present, we assume that they act as electron acceptors due to their low lying gas phase ionization potentials.

The reactive ion-radical states thus created can initiate the diacetylene polymerization. By means of ESR-investigations of diacetylene single crystals at low temperatures a multitude of diradical and carbene like centres were characterized as reaction intermediates.[14] However, whether some of these paramagnetic centres exist at neutral or ionic chain ends is not known at present.

A second model for the sensitization mechanism might consist of a transfer of vibronic energy from the dye to the diacetylene.[7] Vibronic quanta are generated during the relaxation of the photoexcited dye. A vibronically excited monomer state acting as a precursor state of the diacetylene polymerization was postulated previously.[15,16] However, this model is not in accordance with several observations.

The Stokes shift of the dye can be estimated to be a rough measure for the probability that vibronic energy is generated. If the polymerization is initiated via the exchange of vibronic quanta a correlation should exist between the Stokes shift of the dye and the quantum yield Q. This is not observed.[8]

In addition, dyes that deactivate radiationlessly should be sensitizers as well, because they convert their whole excitation energy to vibrons and phonons. A preliminary result of current investigations is that a surface active azo dye that is nonfluorescent does not sensitize the diacetylene polymerization.[17] A consequence of the model of a vibrational initiation of the polymerization is the expectation that a selfsensitization by the polymer is possible, if the irradiation is performed in the range of the main polymer absorption band. The polymer absorption at 2 eV is due to an excitonic state.[18,19] The undisturbed polymer does not fluoresce. Therefore the whole excitation energy decays radiationlessly into vibronic energy. To excite the postulated vibronic precursor states more quantum energy than necessary is present. As described below the excitonic state of the polydiacetylene does not initiate further polymerization. Therefore a selfsensitization by the excitonic state of the polydiacetylene does not exist.

Based on these arguments, we conclude that an initiation reaction by transfer of vibronic energy is improbable.

3.2 CHAIN PROPAGATION REACTION

Once the polymerization is initiated as described above, a chain propagation reaction takes place. The growth of the polydiacetylene chain is thermally activated.[20] In diacetylene single crystals the kinetic chain length n was determined.[21] At the beginning of the conversion n is in the order of 50 to 100 units. At higher conversions values of n up to 1000 were reported. Since the kinetic chain length could not be determined in the multilayers so far, we assume that n is in the same order of magnitude. The high polymer yield per sensitizer molecule that is obtained after long irradiation times is greater than n. Therefore the dye molecules must act several times as a sensitizer. Consequently a regeneration of the dye is necessary. One might therefore consider a back reaction of the electron transfer after an oligomer chain is formed.

3.3 SELFSENSITIZATION

As mentioned above, it is essential for an understanding of the sensitization process to know the effect of the already formed oligomer chains on the propagation reaction. Therefore the photoresponse of pure monomeric and partially polymerized multilayers were compared.[22] It was found that the spectral sensitivity of a partially polymerized layer is considerably redshifted with respect to a monomeric layer. The action spectrum of this effect, which we call selfsensitization, is quite similar to the action spectrum of the photoconductivity.[23] It does not correspond to the polymer absorption band that was shown to be of an excitonic nature.[19,20] Therefore we concluded that the band-to-band transition and consequently mobile charge carriers on the oligomer chain contribute to the chain propagation.[22] Since the π-electron system of the polydiacetylene chain is fully conjugated, the charge carriers have an extraordinary high mobility, in the order of 10^5 $cm^2\ V^{-1}\ s^{-1}$.[24] They can easily reach the chain end which is assumed to be a trap.[25] The electronic structure of the chain end may be changed from a nonreactive to a reactive state. This can reinitiate a chain growth.

A more detailed picture of the charge carrier generation is based on the Onsager theory for the geminate recombination in one-dimensional systems.[26] After the optical generation by the band-to-band transition, the carrier pair rapidly looses its initial excess kinetic energy and becomes thermalized at a mutual distance b. In polydiacetylenes b is in the range between 50 and 100 Å.[19,27] Now the question arises, whether really free charge carriers are operative in the selfsensitization or only those that are generated within a distance b/2 from the chain end.

In one-dimensional systems the probability for the occurance of free charge carriers that can escape geminate recombination increases linearly with an applied electric field.[19,26,27] Therefore the photopolymerization of a PTS crystal was studied under the action of an electric field up to 40 kV cm^{-1} applied at the surface along the polymer chain direction.[16] The crystal was exposed to continuous UV-irradiation of 360 nm. The polymerization was monitored during the irradiation by the transmission of the crystal at 575 nm. It was found firstly, that the selfsensitization effect exists too in partially polymerized PTS single crystals and secondly, the reaction rate did not change if the electric field was switched on or off.

This result was used to question the contribution of charge carriers to the sensitization,[16] but without considering the following: firstly, a transmission experiment probes the polymerization of the bulk of the crystal that is not influenced by the electric field, because of the surface electrode arrangement. Therefore the measuring sensitivity is low. Secondly, we expect that the probability that charge carriers can reach the chain end is not further enhanced by the electric field if they are generated within a distance b/2 from the chain end.

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