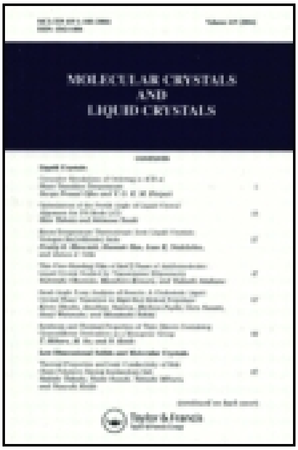

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New Experiments Concerning the Mechanism of the Solid State Photopolymerization of Di-Styrylpyrazine

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NEW EXPERIMENTS CONCERNING THE MECHANISM OF THE SOLID STATE PHOTOPOLYMERIZATION OF DISTYRYLPYRAZINE

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Abstract Defects in Distyrylpyrazine (DSP) monomer crystals haven been investigated by Transmission Electron Microscopy (TEM), light microscopy and synchroton topography. The onset of the photoreaction causes a multiplication of the defects. The course of the photoreaction as well as the product and stress distribution in the crystal are strongly wavelength dependent. Fracture of the crystals can be prevented under special irradiation conditions. A crystal structure analysis of a photoproduct in a four-center-type photopolymerization is available now for the first time. The chemical composition of these crystals has been determined by gelpermeation chromatography (GPC). The results are discussed with respect of the solid state reaction mechanism.

1. INTRODUCTION

1.1. General Features

Compounds such as Distyrylpyrazine are well known to undergo a four-center type photopolymerization (1) as schematically shown by Fig. 1. Although the reaction is known to be topochemical the question if it is a homogeneous (2) or a heterogeneous (3) solid state reaction has been discussed controversially in the past. The wavelength dependence of the reaction path (4) seems to be of critical importance for a detailed study of the reaction mechanism. It was, therefore, decided to investigate both the change in the perfection of the crystals and the product distribution as dependent on the irradiation conditions.

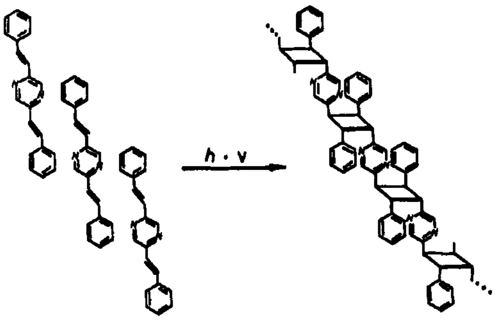

FIGURE 1. Reaction scheme for the four-center type photopolymerization of Distyrylpyrazine (DSP)

The change in spectral characteristics in the course of the photoreaction of DSP is shown in Fig. 2. Irradiation of DSP at 478 nm or at 436 nm excites the monomer molecules only. The double bonds of the photoexcited monomer can react either with a double bond of an adjacent monomer (I Fig. 3) or with the terminal double bond of an already formed oligomer molecule (II Fig. 3). The result of these two reactions is an oligomer of an average degree of oligomerization of 3.2

units ± 0.2 and an optical absorption characterized by the spectrum in Fig. 2 (5). Irradiation of the oligomer at i.e. 365 nm links the residual double bonds to produce high polymer material (III Fig. 3) (1,4).

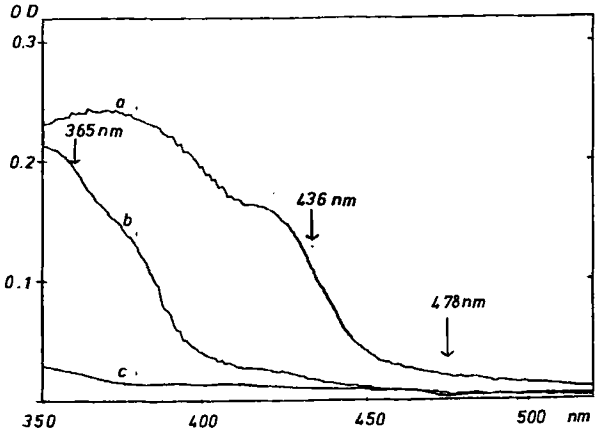

FIGURE 2. Absorption spectra of a polycrystalline film of a) monomer, b) oligomer and c) polymer DSP.

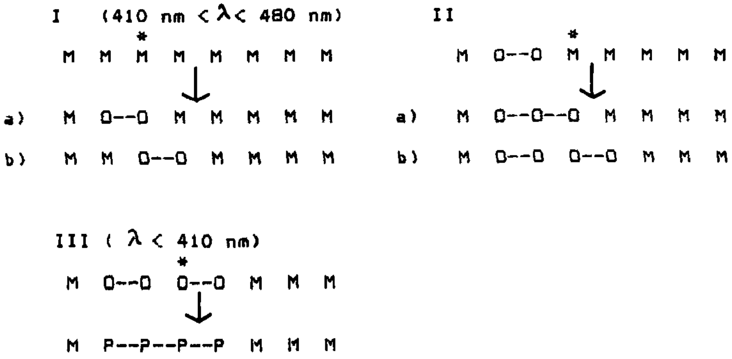

FIGURE 3. Scheme showing the formation of oligomer and polymer at different wavelengths (see text), M: Monomer; -O-: Oligomer base unit; -P-: Polymer base unit.

2. EXPERIMENTAL

2.1. Defects in DSP monomer

Defects sites in crystals are generally discussed as nucleation centers (6) for solid state product formation. In a TEM study on DSP monomer crystals grain boundaries were observed. The detailed structure of such a symmetrical small angle tilt boundary is shown in Fig.4 which is a (020) dark field electron micrograph. The boundary consists of piled-up individual dislocations. Each dislocation is seen end-on in this micrograph (7) and gives a contrast characterized by a single dot. Such grain boundaries were the only type of defect identified by TEM. Etching of crystals and evaluating the etch pit density suggests that the crystals are of high perfection (5). This is supported by synchroton topographs (8) one of which is shown in Fig. 5. From these results we conclude that the role of one-and two-dimensional defects in the solid state reaction of DSP should be negligible in the initiation of the reaction in the pure monomer crystal.

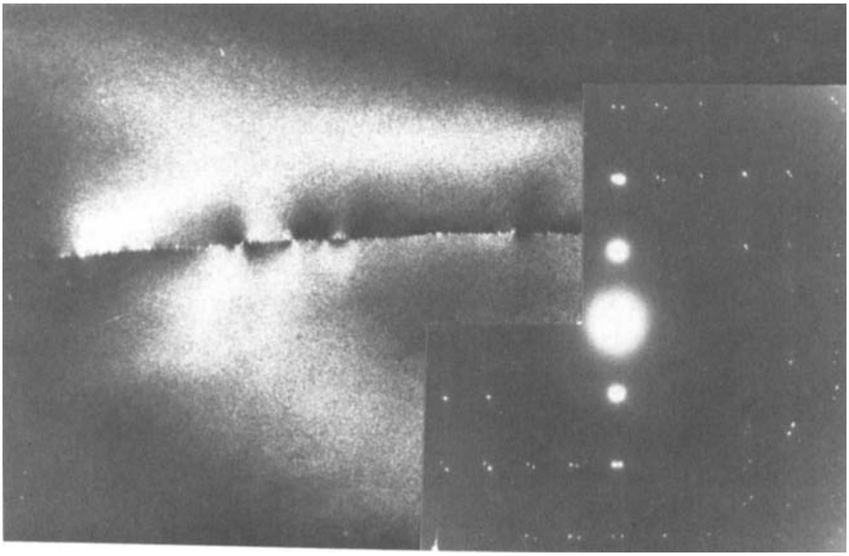

FIGURE 4. (020) dark field TEM micrograph of a tilt boundary in a DSP monomer crystal.

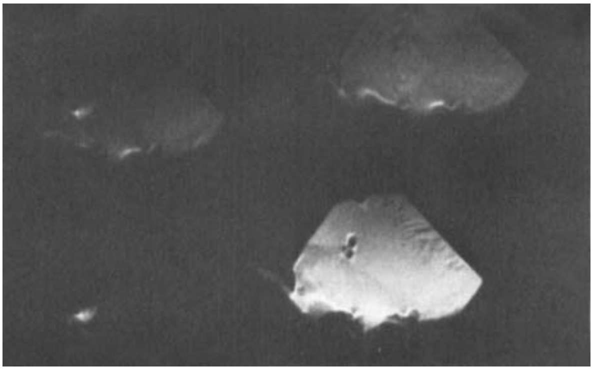

FIGURE 5. Synchroton topograph of a macroscopic DSP crystal in the Laue geometry

2.2. Deformation during the photoreaction

X-ray structure analyses of the pristine photoproducts of the four-center-photopolymerization are not available so far for the reason that the crystals usually fracture during the product formation. Looking in detail to the morphological changes which occur during the fracture process we observed two main features. The first is the appearance of cracks parallel to [001] and perpendicular to [010]. The trace of these cracks can be decorated by solvent etching as shown in Fig. 6. They are always formed, if the crystals are irradiated at wavelength $\lambda < .478$ nm i. e. shorter than the tail of the absorption band of the monomer. These cracks are indistinguishable from cracks caused by a stress applied to the (100) crystal surface (crack II Fig. 6) through a micro hardness indentor. In both deformation processes a slip system of [001]; (hk0) is involved.

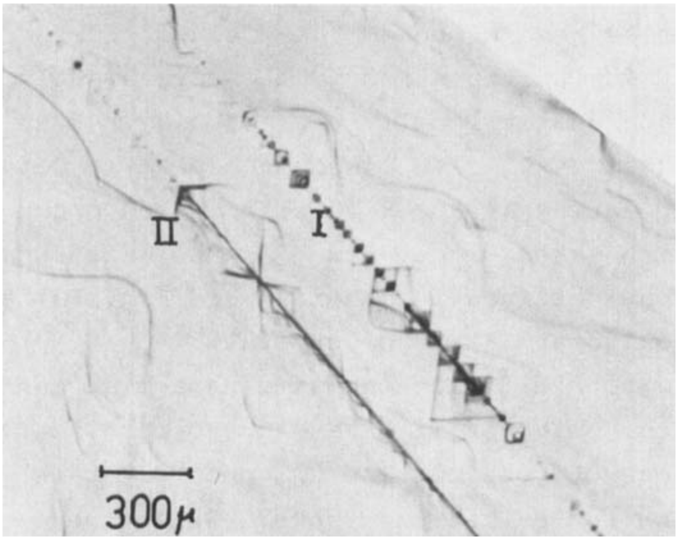

FIGURE 6. Decorated traces from cracks due to internal stresses from product formation (I) and due to external stress (II)

The connection between the course of the photoreaction and the build-up of stress can be understood by looking at the results of the X-ray structural investigation described below. The cracking of the crystals can be avoided by irradiation of the crystals in their long wavelength absorption edge. This is achieved by the 478 nm line of an argon-ion laser. Under these conditions the penetration of light into the crystal is nearly homogeneous as compared to irradiation at 436 or 365 nm where only the surface skin of the crystals will be affected. The internal stresses occuring from the oligomer formation are therefore distributed homogeneously over the crystals and the resulting macroscopic stress remains below the yield stress. Contrary, at 436 nm the stress occurs preferently in the surface and it locally becomes higher than the yield stress. As a consequence plastic deformation appearing as crack initiation and crack propagation takes place. Fig. 7 shows Weissenberg photographs obtained from a monomer (Fig. 7a) and from an oligomer (Fig. 7b) crystal.

Comparing both diffraction patterns a misorientation of the oligomer with respect to the initial monomer cannot be seen. The oligomer crystals were shown to be free of cracks. While the reflections along a* remain constant in position, the reflections in b* shift continuously from the initial monomer to their final oligomer position. There is no indication that a new phase appears during the oligomerization at 478 nm. A dramatic change in the morphology and the diffraction patterns appears, however, during the pre-irradiation of oligomer crystals with light of 365 nm. Fig.7c shows the same crystal as 7a, b after it had been pre-irradiated with light of 365 nm wavelength and after the polymerization had occured. New reflections corresponding to the polymer phase show up. Their orientational spread with respect to the oligomer shows the misorientation between

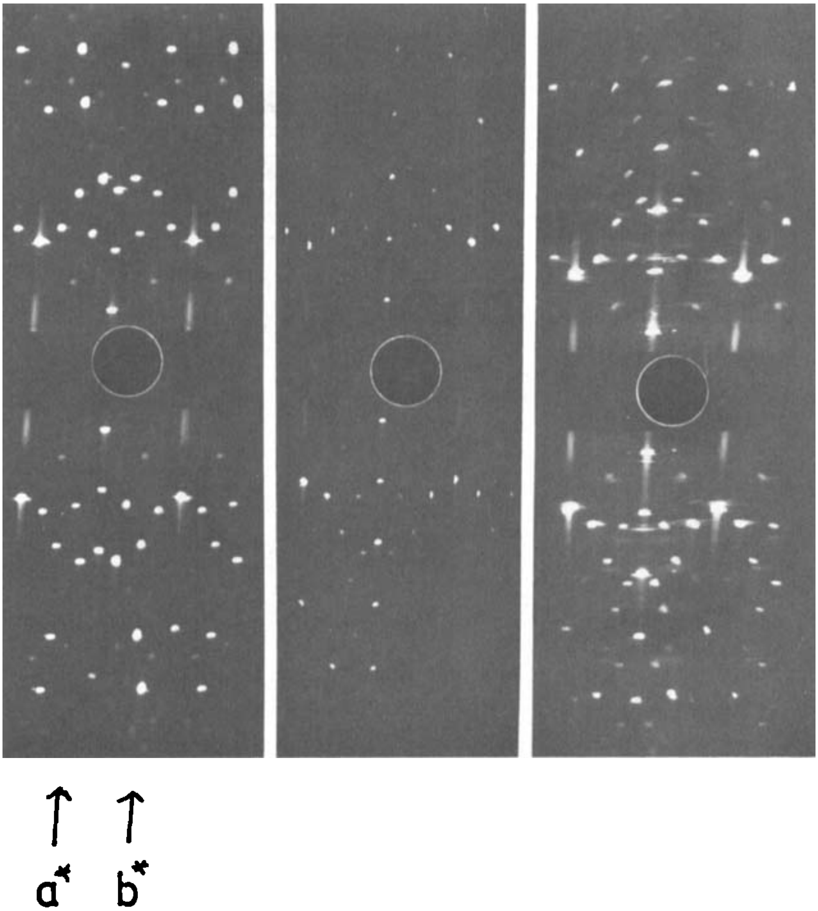

FIGURE 7. Double radius Weissenberg photographs of a) monomer and b) oligomer and c) partly polymerized crystals

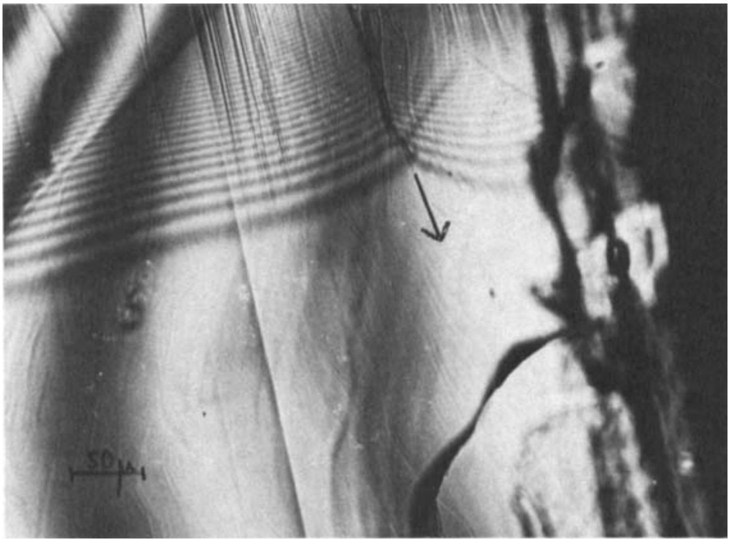

FIGURE 8. Optical, micrograph of a (365 nm) pre-irradiated oligomer crystal. The interference lines arise from a thin bent polymer sheet separating from the surface; direction of crack growth indicated by arrow.

the old oligomer and the new polymer phase. From Fig. 8 the morphological change that accompanies the polymerization is seen. The polymer separates as small thin platelike crystalline layers from the bulk oligomer crystals.

2.3. Crystal structure of DSP "as oligomerized"

The DSP crystals as oligomerized were suitable for intensity data collection on a diffractometer. The structure of the oligomer was solved by direct methods. The details of the data are to be published elsewhere (9). The carbon atoms at the cyclobutane ring as well as those at the remaining double bonds were identified in a difference fourier analysis. The positions of the phenyl side-groups at the cyclobutane ring appear to be the same as those at the terminal double bonds. Debeye-Waller factors of the side groups were relatively large. This indicates some slight disordering of the side groups. The distance between the reactive terminal double bonds of adjacent oligomer molecules is only about 3.27 Å. This is much less than in the monomer where this distance amounts to 3.94 Å (10). As far as we know this is the closest distance between reactive double bonds that has ever been found in a four-center-photoreactive compound. Fig. 9 shows an ORTEP plot of both monomer and oligomer such that the plane of the cyclobutane ring is within the plane of the image. The large increase of the b-lattice parameter is caused by a tilting of the pyrazine rings. The movement of the molecules in the reaction does not follow a simple shear mechanism as it is found for the polymerization of certain diacetylenes (11). In these systems the configuration of the monomers which are linked upon polymerization does not change much from educt to product. This is

TABLE 2 Characteristics of the synthesized polydiacetylenes

	λ_{max}/nm	ε_{max}/ (l·mol^{-1}·cm^{-1})	[η]/(ml·g^{-1})	$\bar{M}_n$	$\bar{P}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\sqrt{\bar{r}^2}$/Å
Poly (2c)	470	17300	1150	240000	510	800000	3.33	1100
Poly (2e)	473	18000	970	340000	600	1340000	3.94	1310
Poly (2i)	475	17300	520	320000	480	1200000	3.75	1260

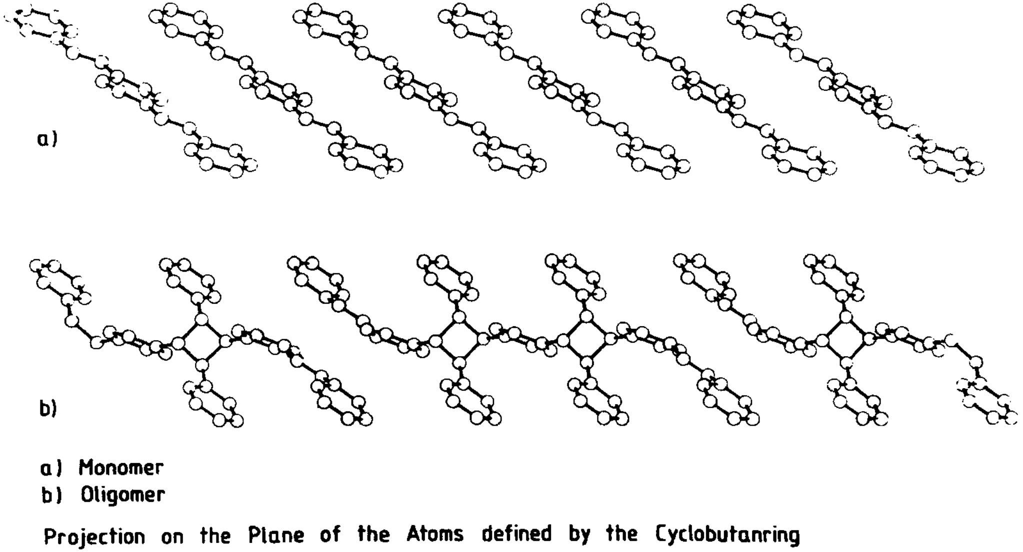

FIGURE 9. ORTEP plot of the oligomer on the plane defined by the cyclobutane ring units.

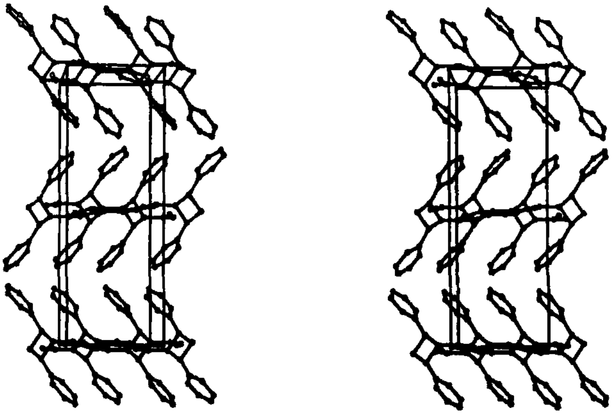

FIGURE 10. Stereoplot of the oligomer "as oligomerized".

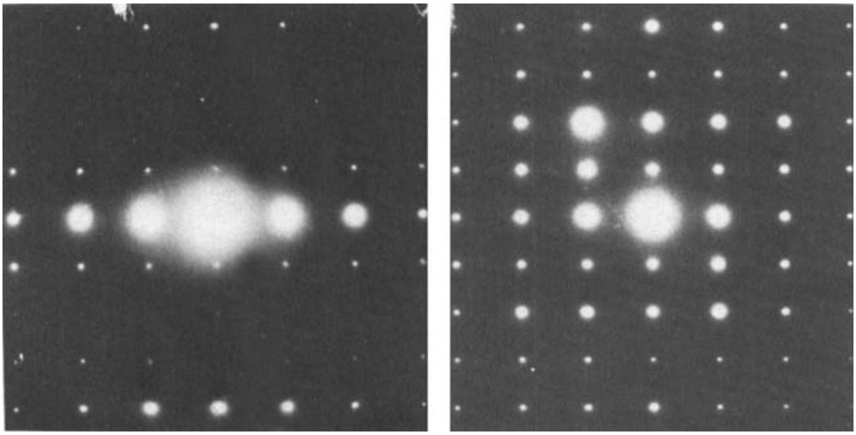

FIGURE 11. a) Oligomer and b) polymer electron diffraction pattern of the |100| zone.

2.4 Gelpermeation chromatography (GPC)

Single crystals as well as crystalline powders of DPS "as oligomerized" were dissolved in chloroform and were analyzed by GPC. Experimental details are given elsewhere. A typical chromatogram obtained for 100 % conversion is depicted in fig. 12a. The molecular weight for this sample was independently determined by vapour pressure osmometry. The degree of polymerization was found to be 3.2 ± 2. This result differs significantly from data published by Hasegawa (4). The lowest molecular weight that is to be expected for a pure homogeneous reaction can be calculated with the reactand isolation model described by Flory (12). A pure homogeneous reaction is defined by a random bond formation within the proper lattice direction. Further on it is assumed that the photoreactivity of a monomer is the same toward another monomer as to an adjacent oligomer. While Flory's model is only valid for the dimerisation we did a Monte-Carlo calculation for a pure homogeneous reaction considering also higher degrees of oligomerization. The result of these calculations is shown in fig. 12b. The graph shows the change in oligomer distribution with increasing conversion. Comparing the data for 100 % conversion with that of the experimental data in Fig.12a we see a significant difference in the distribution of the oligomers. The experimental molecular weight is higher than that expected for a pure homogeneous mechanism. The amount of dimers calculated is much higher and that of trimers and higher oligomers much lower than in the experiment. This is possibly due to an influence of lattice strains produced by the product on the further reactivity of residual monomer in the stress field. The experimental determination of the change in molecular weight distribution with increasing conversion is in progress.

3. CONCLUSIONS

Discussing the homogeneity or heterogeneity of a solid state photoreaction one has to carefully consider the irradiation conditions applied to the crystals. The strong absorption of light at the surface regions of the crystal favours an inhomogeneity in the experimental conditions. The philosophy of topochemical reactions assumes that the mechanism is dictated by the intrinsic structure of the crystal. An experiment that is to give information about the solid state photoreaction mechanism has to guarantee a homogeneous distribution of light inside the crystal. Only if this condition is fullfilled the experiment allows for an unambiguous evaluation of the mechanisms. Otherwise product formation which usually disturbs the lattice locally will start preferently in the parts of the crystal reached by most of the incoming light.

Perturbation of the lattice by product formation does not necessarily increase the number of dislocations. Each isolated product molecule itself

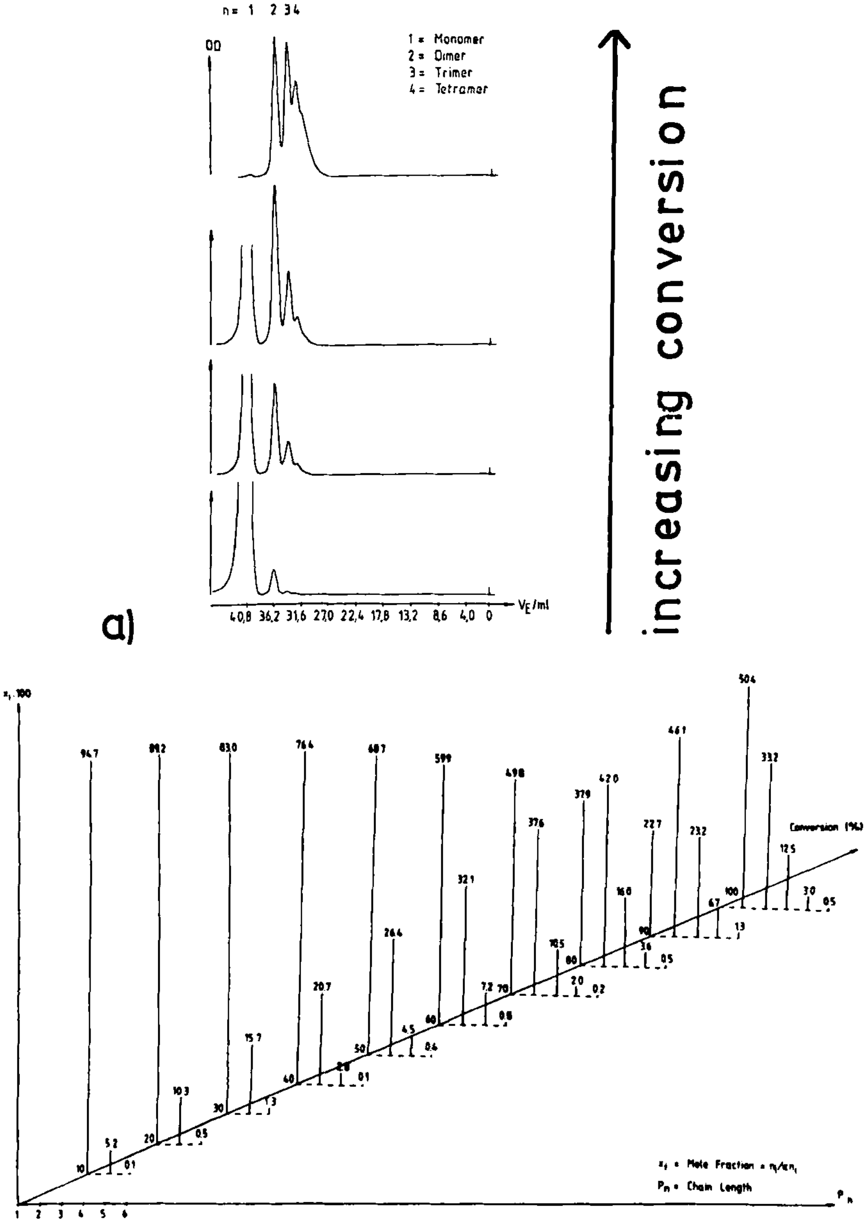

FIGURE 12. a) GPC diagram at 100 % conversion after exhaustive irradiation at 478 nm. b) calculated molecular weight distributions for increasing conversion assuming a pure homogeneous reaction.

is a center of internal stress in the lattice. It can therefore probably influence the reactivity in its neighbourhood. The occurence of cracks and dislocations due to product formation is only the answer of the crystal on the magnitude and distribution of internal stresses produced by each individual molecule. One should not only discuss the increase or decrease of reactivity at cracks, dislocations and other topological defect sites but also in the stress field of each product molecule. To calculate the response of the crystal on such internal stresses more information about the mechanical properties of photoreactive organic materials should be available.

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