

SOLID-STATE POLYMERIZATION MECHANISMS

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Abstract - Mechanisms of topochemical polymerizations are described using the four-center-type photopolymerization of diolefins and the polymerization of diacetylenes as actual examples. Solid-state polymerizations can be treated as a special case of phase change which may proceed homogeneously or heterogeneously. Special consequences of the mechanism of phase change are described. The scope of the four-center-type and of diacetylene polymerization is discussed and some rules relating molecular shape and packing into a reactive modification are discussed. Photoresponse curves for diacetylenes are reported and the relation between molecular structure and photosensitivity is discussed. Finally, the nature of chain growth is considered. Four-center-type photopolymerization proceeds in a stepwise manner along the same mechanism which is also true for dimerization of cinnamic acids and derivatives. Diacetylene polymerization proceeds via carbenoid intermediates which add to polymer chain ends with carbene character.

INTRODUCTION

A number of different classes of organic compounds undergo photopolymerization if irradiated by uv-light as bulk crystalline material. The preparative and technical aspects of such solid-state polymerizations have received much attention and have been reviewed by different authors in the past. Some more recent reviews are cited in Ref. 1-6.

Among the many different reactions known, only two systems have been studied to greater depth because they belong to the class of the so-called topochemical reactions and provide a means of direct synthesis of highly crystalline polymers. In some cases nearly defect free macroscopic crystals of macromolecules can be easily synthesized and there seems to be a direct relation between the packing of the monomer molecules in the starting crystal, the reaction path and the crystal and molecular structure of the final product.

These two reactions are:

the "Four-Center-Type" photopolymerization of diolefins which has been studied in detail by M. Hasegawa, H. Nakanishi and coworkers (7) and leads to polymers with a cyclobutane ring in the base unit and

the topochemical polymerization of monomers with conjugated triple bonds. The latter reaction has been found and studied by G. Wegner and coworkers (8,9) and was also investigated in the groups of R. H. Baughman (10,11) and more recently D. Bloor (12,13).

In the following some mechanistic aspects of these two photoinduced polymerizations will be considered and compared with the main emphasis on the following subjects: i) Scope of the reactions, i.e. relating molecular structure of the monomers to the necessary requirements for packing in a photoreactive crystal structure, ii) Wave-length-dependence of polymerization (photoresponse of the monomers), iii) Consideration of the photopolymerization as a special kind of phase transition and iii) Nature of chain propagation.

DEFINITIONS AND CLASSIFICATIONS

The expression "Topochemical Polymerization" is sometimes regarded as synonymous with "Solid-state-polymerization" or "Topotactic Polymerization". This has led to some serious misinterpretations of experimental results because each of the three terms implies a well defined but different picture of the reaction mechanism.

The most general term is solid-state polymerization. It implies that a polymerization proceeds starting from the bulk of the solid crystalline monomer or complex of the monomer with host molecules. Solid-state polymerization is thus a more or less concise description of the experimental technic similar as "bulk-polymerization" or "solution-polymerization". Solid-

state polymerizations can be considered as examples for the more general case of an organic solid-state reaction (e.g. Ref. 1,3).

The following picture is very helpful in order to classify various phenomena and has been widely accepted. Organic crystals are build up by packing molecules into a three dimensionally regular lattice. Individual molecules are separated from each other by van der Waal's distances which are much too large as to allow the formation of the transition state of a chemical reaction. Reactivity can only come about if the molecules are mobile enough to approach each other to a distance to less than approximately 3 Å. In many cases reaction proceeds by diffusion of the reactants to centers of reactivity or by nucleation of the new phase at certain centers of disorder and, therefore, increased mobility under complete destruction of the parent crystal. Transport of the reactants may also occur through the gas phase and precipitation of the reaction products at the surface of the parent crystal. If the product is able to crystallize it is highly probable that nucleation of the crystalline product phase at the surface of the parent crystal leads to an oriented growth under the influence of the surface tension with the result that one finds coincidence between certain crystallographic axes of mother and daughter phase. This phenomenon is called topotaxy and will be defined more precisely below.

In some cases rotational diffusion is sufficient to allow the necessary contacts between reactive groups of neighbouring molecules. In such cases ideally the centers of gravity of the molecules do not move from their proper lattice site and the reaction proceeds homogeneously inside the parent crystal. The reaction is said to proceed under topochemical control. Such a reaction is schematically shown in Fig. 1 a and the corresponding scheme for topochemical polymerization of diacetylenes in Fig. 1 b.

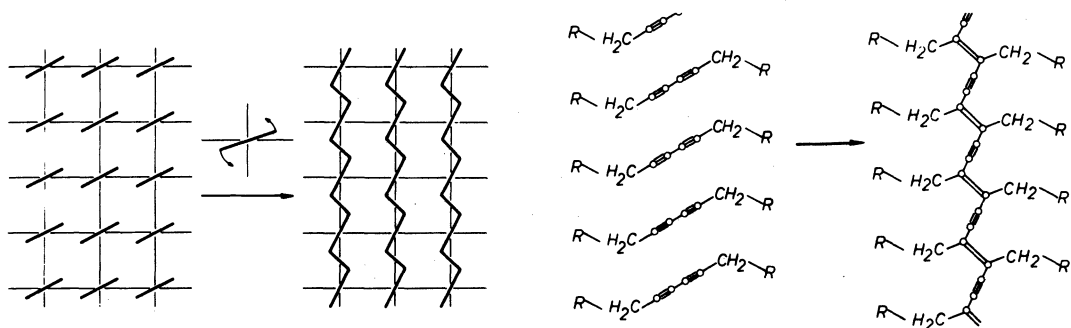


Fig. 1 a) Schematic representation of a topochemical polymerization;
b) Polymerization of diacetylenes

Following J. M. Thomas (14) the distinction between topotactic and topochemical reactions is best clarified by bearing in mind that topotaxy is concerned with three dimensional orientational relations between the crystallography of the product and the reactant phases in much the same way as epitaxy and epitactic reactions refer to the two-dimensional orientational relations that exist when a new phase forms on the surface of another. A reaction is said to be topotactic, if

1. the lattice of the solid product shows one or a small number of crystallographically equivalent, definite orientations relative to the lattice of the parent crystal and, if
2. the reaction has proceeded throughout the bulk of the reactant.

Topochemical reactions are those in which the properties, including the nature of the products are governed by the fact that the chemical changes proceed within an ordered structure, so that the geometries and space symmetries relating neighbouring molecules and the possible types of intermolecular approaches and contacts are strictly limited and well defined. It thus follows that topochemical control may often lead naturally to topotaxy, but topotaxy is in principal a phenomenon completely independent from the occurrence of a topochemical reaction.

A topochemical reaction may thus proceed

1. inside a perfect crystal where the structure and symmetry of the reaction product is defined by the packing of the monomer molecules in the lattice,
2. at well defined defect sites of crystals such as stacking sequences, stacking faults and

partial dislocations where the structure of the reaction product is predefined by the arrangement of the molecules around the particular defect (e.g. Ref. 15),

3. inside a composite structure of host and guest molecules such as chanel inclusion compounds or intercalates where the guest molecules are still mobile but mobility is so severely restricted that the number and sites of contacts between the neighbouring molecules allow but one type of reaction (e.g. Ref. 16),
4. along an array of molecules attached or adsorbed in a spatially well defined manner at a rigid molecule in solution. This type of reaction is normally called "matrix-polymerization" because of the implication that some information held by the template molecules such as molecular weight, molecular weight distribution, type and degree of stereoregularity etc. may be transferred to the reaction product.

Relation between morphology and reaction mechanism

Experimentally it is sometimes quite difficult to distinguish between a topochemical and a topotactic reaction. For example, solid-state polymerization of some oxacyclic compounds such as trioxane, tetraoxane, β -popiolactone and 3,3'-disubstituted oxacyclobutanes were regarded as typical examples of topochemical reactions for a long time until it was demonstrated that these reactions in reality are topotactic and there is no evidence for lattice control (17). Unique morphologies are to be expected whenever a new crystalline phase is formed within other crystals or at the surface of a crystalline matrix, because of the impact of surface free energy onto the shape of the nucleus. There is a separate equilibrium form for every possible relative orientation of the two sets of axes. Most relative orientations will give high-angle boundaries, hence relatively spherical equilibrium forms. A few orientations, however, will involve some very low energy boundaries and will give highly nonspherical equilibrium forms such as fibrils or elongated ribbons as they are observed in trioxane and other solid-state polymerizations (17).

This leads to the concept that solid-state polymerizations including topochemical polymerizations can be regarded as phase transitions from the crystalline phase of the monomer to the phase of the growing polymer. Topochemical polymerizations bear many similarities with the well investigated martensitic or "military" transformations of certain alloys (18) whereas topotactic and other solid-state polymerizations resemble displacive phase transformations. It is therefore important to know to what extent and by what mechanism the three dimensional order of the crystalline monomer is transferred to the resulting polymer. Thus, the knowledge of the crystal structure of the monomer as well as the molecular structure and morphology of the polymer as polymerized is necessary in order to decide whether a particular reaction is topochemical or topotactic in nature. The topochemical polymerization implies a direct transition from the monomer molecules to polymer chains without destruction of the crystal lattice and without formation of non-crystalline intermediates. As the three dimensional order of the monomer lattice is transferred without loss of periodicity, the resulting polymer must possess a three-dimensional well oriented, extended chain morphology. This idea was first expressed by H. Morawetz in 1966 (19) and was experimentally verified with the topochemical polymerization of diacetylenes in 1969 (8). A lamellar morphology, as it is often observed in solution or melt-crystallized polymers cannot be formed by a truly topochemical polymerization because the process of chain folding is not compatible with the three-dimensional periodicity of the solid monomer.

Homogeneous and heterogeneous topochemical reactions

Topochemical polymerizations may proceed as homogeneous or heterogeneous reactions (20) as schematically shown in Fig. 2 a, b.

In homogeneous reactions the polymer is formed as a solid solution of extended chain molecules which grow from points distributed at random throughout the parent crystal. The product is isomorphous with the units of the monomer crystal. We deal, however, with a kinetically forced isomorphism since the polymer because of its different molecular structure in general has packing properties different from the monomer and, therefore, would tend to crystallize in a different lattice provided it will find the chance to do so. Within the domain of the forced isomorphism time-conversion curves can be obviously related to the individual chemical events during chain growth. This is not so if the polymerization proceeds in a heterogeneous manner (comp. Fig. 2 a), e.g. if polymerization starts preferentially at defect sites of the mother crystal with nucleation of the daughter phase. Further chain growth will occur with a much higher probability at the surface of an already formed nucleus than elsewhere in the crystal. The parent crystal will decompose into a polycrystalline aggregate with increasing degree of conversion as actually observed, for instance, in the four-center-type solid-state photopolymerization. Time conversion curves contain information about the frequency of nucleation, the geometry of the growing polymer phase and/or the rate of diffusion of the monomer molecules across the interphase between monomer and polymer but do NOT bear direct information on the growth of the isolated chain. These generalizations have to be kept in mind in order to appreciate the following discussion of scope and mechanism of the four-center-type photopolymerization and the polymerization of diacetylenes.

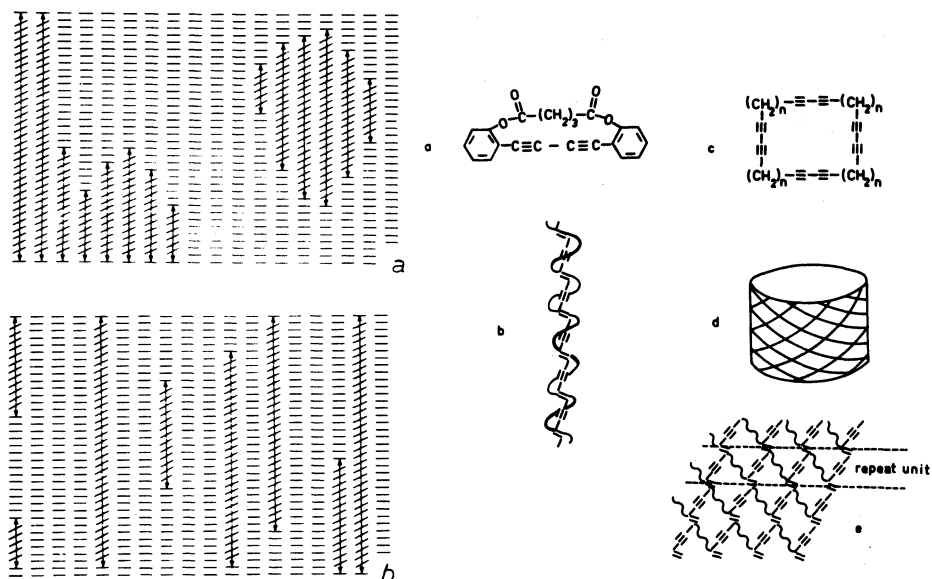


Fig. 2 Mechanism of phase change in the course of a topochemical polymerization. a) heterogeneous, b) homogeneous reaction

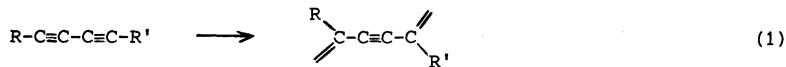
Fig. 3 Polymer structures obtained from cyclic diacetylenes a) compounds with one diacetylene group per cycle give rise to b) quasi-helical structures (25) and c) compounds with more than one diacetylene groups per cycle give rise to d) molecules resembling a hollow cylinder whose chemical structure is best clarified if the cylinder surface is d) thought to be cut and put into a plane

SCOPE OF THE TOPOCHEMICAL PHOTOPOLYMERIZATIONS

Both types of photopolymerizations are of general importance from the synthetic point of view because they provide methods to produce stereoregular polymers of particular chain structure with a wide variety of substituents. The intimate relation between molecular structure of the monomer its packing properties and the chemical reactivity in the lattice makes it worthwhile to look for the scope of reaction with regard to the geometrical details of the monomer molecules.

Molecular structure and reactivity in diacetylene polymerization

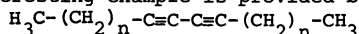
The solid-state polymerization of diacetylenes proceeds in a sense as a 1,4-addition to the conjugated triple bonds according to



and gives rise to polymers with a fully conjugated backbone. Irradiation of the monomer crystals with uv-light is just one way to bring polymerization about. In most cases the individual monomers are also polymerized to the same polymer structure by annealing at elevated temperature but well below the melting point or under the action of high-energy radiation. Some examples for allowable structures of R and R' are compiled in Tab. 1 and additional information is contained in Fig. 3. The structure and stereoregularity of the polymers is well established by a number of x-ray structure analyses (comp. Ref. 9) and by Raman-spectroscopy (10,21,22). A number of these polymers can be obtained as nearly defect free single crystals and have been recognized to belong to the class of so-called one-dimensional metals exhibiting a number of quite interesting optical and electrical properties (12,23,24). The structure of the polymer backbone as defined in (1) is only one resonance formula. In reality the single bond contains some double bond character.

With regard to the question of relation between molecular structure and reactivity some rules can be derived from experience based on successful polymerization of more than a 100 different diacetylene derivatives. These rules are: a) mesomeric or inductive effects of substituents on polymerization behaviour have never been observed; b) substituents which prevent the mutual approach of neighbouring molecules in the lattice to a distance less than 0.40 nm simply by action of their van-der-Waals-radii do also prevent polymerization. Thus, compounds with secondary aliphatic carbons in the side chain show poor performance and a tertiary carbon prevents polymerization at all; c) aromatic rings do not interfere with reacti-

vity because they allow close contact in directions perpendicular to the plane of the ring; d) the same argument applies to compounds where the diacetylene group is part of a ring itself such as the ones shown in Fig. 3. e) side groups with ability to form hydrogen-bridges are favourable in order to bring about reactivity although such features are not a necessary prerequisite for reactivity nor bring about reactivity in all cases. The arrangement of neighbouring molecules in the lattice absolutely necessary for polymerization was derived in more mathematical terms by R. H. Baughman (11) and is based on x-ray crystallographical evidences. As depicted in Fig. 4, polymerization is described as translational direction invariant motion of the structural units (comp. also Fig. 1 b). Spacing of the reactive rod-like triple bonds along the growth direction is defined by the translational period d_1 along the lattice vector a and the angle γ_1 , between rod direction and a . Consequently, the distance S_1 between adjacent triple-bond systems is defined by $S_1 = d_1 \sin \gamma_1$. Experience demonstrates that S_1 has to be smaller than 0.40 nm with the lowest limit at $S_1 = 0.34$ nm. Thus γ_1 in reactive arrangements is of the order of 45° or in other words in such structures carbon 4 of one molecule is very close to carbon 1' of the next molecule in the same stack. The parameters S_1 , γ_1 and d_1 are changed to S_2 , γ_2 and d_2 on polymerization and from experience it is known, that highly perfect polymer crystals or, more generally speaking, high conversion is reached only when $(d_2 - d_1)$ is very small or preferably zero. Although Fig. 4 provides a nice rationale of the relation between molecular structure and reactivity, it is useless for quantitative predictions. This is easily recognized from the fact, that most diacetylenes crystallize in different modifications with completely different reactivity. Thus, a given diacetylene can be completely inactive or very reactive, depending on the modification. An interesting example is provided by the behaviour of the pure hydrocarbons



with $3 < n < 15$. All these hydrocarbons can be photopolymerized (24) but only in form of their low temperature (instable) modification. The high temperature modifications which are obtained by normal crystallization from the melt are in most cases completely and in some more complicated cases (e.g. below) - almost inactive. Additionally, all compounds where n is an odd number do polymerize considerably slower than the corresponding monomers where n is even. Quite clearly, our theoretical understanding of the packing properties of organic molecules is not yet sufficiently developed in order to predict such behaviour nor to devise a theory under what circumstances a given compound will form an active or an inactive modification.

Translational direction invariant motion

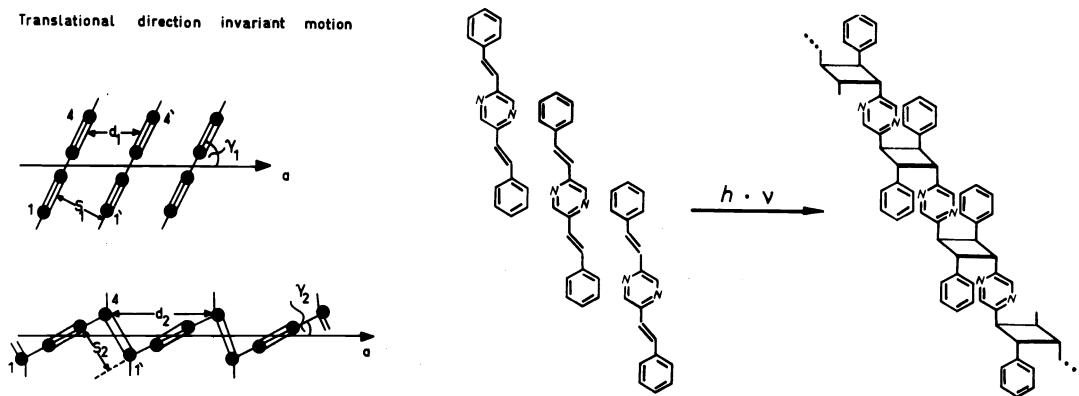



Fig. 4 Explanation of the topochemistry of diacetylene polymerization according to Ref. 11 applying the least motion principle

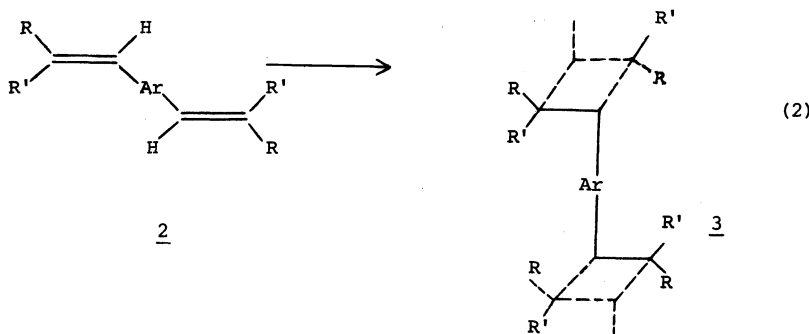
Fig. 5 Scheme of the four-center-type photopolymerization of DSP

Molecular structure and reactivity in four-center-type photopolymerization

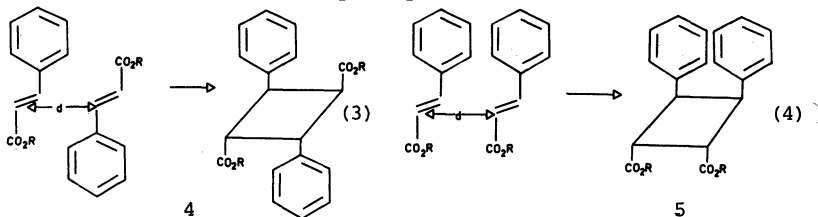
The four-center-type photopolymerization is shown by crystalline diolefins of general structure 2 and gives rise to polymers 3 which contain a cyclobutane ring per base unit and an arrangement of the substituents like in α -truxillic acid, the corresponding photodimer of cinnamic acid. This polymerization was mainly investigated by the group of M. Hasegawa in Japan and has - unlike diacetylene polymerization - a counterpart in low molecular weight organic chemistry. It seems, in fact, that this photopolymerization is just a special case of the more general topochemical photodimerization of olefins which was so brilliantly elucidated by the late G. M. J. Schmidt and his coworkers (e.g. Ref. 1,3,26) and which has served as the basis for development of organic topochemistry. For the sake of completeness his findings are repeated once more: trans-cinnamic acid, substituted trans-cinnamic acids and their derivatives and similar compounds are found to crystallize in three different structural types, designated α , β and γ on the basis of the shortest axis of the unit cell of the crystalline monomer. The shortest axes found in the β -type are 0.39 ± 0.02 nm, in the γ -type they are 0.49 ± 0.2 nm and in the α -type they are greater than 0.51 nm. The α -type crystals yield α -truxillic acid derivatives 4 (3) that is a dimer of symmetry $\bar{1}$, and the β -type crystals

Table 1 Examples of photoreactive diacetylenes $R-C\equiv C-C\equiv C-R'$

a) symmetrical (R=R')	b) unsymmetrical	
R	R	R'
$-(CH_2)_n-CH_3$	$-CH_2OH$	$-C\equiv C-CH_2OH$
$-(CH_2)_n-OH$	$-CH_2-O-CO-NH-Ph$	$-C\equiv C-CH_2-O-CO-NH-Ph$
$-(CH_2)_n-CO_2H$ and salts	$-(CH_2)_n-OH$	$-(CH_2)_m-CH_3$
$-(CH_2)_n-O-CO-NH-Ph$	$-(CH_2)_n-CO_2H$	$-(CH_2)_m-CH_3$
$-(CH_2)_n-O-SO_2-$ $-CH_3$		
 (o-, m-, <u>not</u> p-)		
NH-Ac		










yield dimers 5 (4) with symmetry m . The γ -crystals are not photoreactive. There are cases, where the same compound forms three different modifications belonging to these three different classes of crystal structure and consequently two different dimers are obtained by solid-

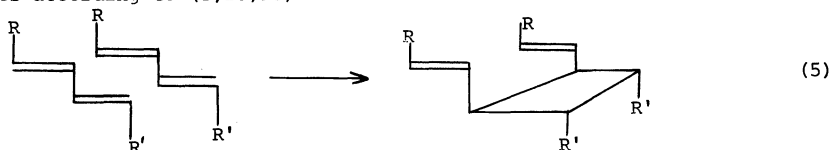


state reaction. Now coming back to the case considered by Hasegawa it turns out that at least in those cases which have been crystallographically studied the α -type packing is found and the corresponding polymers, therefore, have the molecular symmetry $\bar{1}$ (7,27). The overall relation between monomer packing and reactivity bears some similarity with diacetylene polymerization as shown in Fig. 5 in so far as the center of gravity of each molecule ideally does not move but each molecule is only tilted from its starting position such that adjacent double bonds can meet to form a cyclobutane ring. Similarly, the space group does not change and the total volume change during polymerization is very small. These topochemical similarities should not be overestimated because the two reactions are completely different from other point of views.

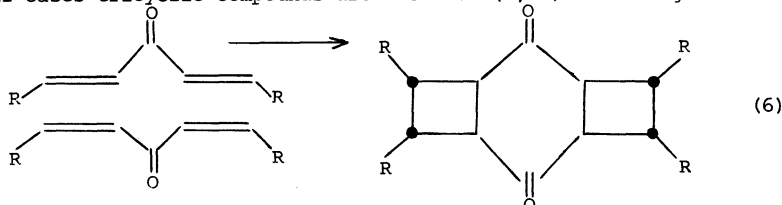
Table 2 Examples of diolefins which undergo four-center-photopolymerization (7) according to eqn. 2

A_r	R	R'	Abbreviation
		H	DSP
		H	P2VB
	$-CO_2H$	H	pPDA
	$-CO_2Et$	H	pPDAEt
	$-COCH_3$	CN	pCPAMe

It is interesting to note, that a polymerization along the second mode, namely between monomers related by symmetry m has not been observed. Crystals of diolefins, in which the molecules are arranged in such a way are photoreactive but in many cases only one of the two double bonds reacts according to (1,26,28)



and in some special cases tricyclic compounds are obtained (1,29) according to



It thus seems to be a necessary requirement in order to get an arrangement of molecules in the crystal which is favourable for polymerization, that the two olefinic double bonds are separated by an aromatic ring preferably in 1,4-position and that the molecules packed along a stack are related by symmetry 1 .

WAVE LENGTH DEPENDENCE OF POLYMERIZATION AND PHOTO-RESPONSE

From the photochemical point of view it is interesting to ask in what spectral range does the photoexcitation to reactive states occur and what is the mechanism of excitation transfer from that primary excited part of the molecule or crystal to the actual reaction center? In diacetylene polymerization this is by no means a trivial question, since it was quite early observed, that polymerization does take place readily, even if a given compound is not irradiated inside the range of the absorption of the triple-bond but elsewhere in the absorption bands of side groups. Other wave-length dependent features such as oligomerization and depolymerization are observed in four-center-type photopolymerization. These observations will be discussed below.

Action spectra of diacetylenes

When a colorless single crystal of a diacetylene is irradiated by uv-light a series of color changes in the visible-range of the spectrum is observed due to the formation of the polymer with and without living chain ends. The whole process can be most easily studied using small single crystals which can be irradiated on the stage of a uv-microscope photometer by monochromatic light, so that a number of irradiation experiments can be performed on the same specimen and the change in optical density can be simultaneously recorded. The spectral changes which are typically observed in most diacetylenes are shown in Fig. 6. Here, in the case of N,N' -Diacetyl- m,m' -diaminodiphenyldiacetylene we deal with the fortuitous case that the diacetylene chromophore and consequently the polymer backbone are strongly inclined with respect to the surfaces of the crystal so that we are able to observe the full absorption spectrum. In most crystals these chromophores are parallel to the most developed surface. Since both the extinction coefficient of the monomer in the triple-bond area around 250-300 nm and of the polymer in the 480-600 nm area are of the order of 10^4 - 10^5 cm^{-1} it is difficult to prepare crystals thin enough such that the full shape of the monomer absorption band can be measured. Consequently, since also the final polymer exhibits strong absorption in this area thick crystals generally cannot be photopolymerized to high yield because light does not penetrate beyond the first few microns into the crystal.

Coming back to Fig. 6 it is seen, that the spectrum of the polymerizing crystal exhibits two peaks at 630 nm and 580 nm resp. which change their relative intensities with increasing irradiation time. If a crystal exhibiting these features is treated with solvent for the monomer these peaks disappear and the absorption of the pure polymer at around 530 nm is observed. The two peaks are ascribed to chains with carbene-like chain ends (see below) and are infinitely stable if the crystal is not further irradiated nor treated with solvents. Photopolymerization, however, does not proceed, unless the crystal is irradiated in the uv-range, that is in the present case between 250 and 360 nm. There is no self-sensitization by the polymer chromophores.

The rate of photopolymerization can now be measured as change in optical density in the visible as a function of exposure time in the uv. The photoresponse is defined as $R = \lim_{t \rightarrow 0} \Delta OD / \Delta t$ and the action spectrum is obtained by plotting R vs. wave length of irradiation at constant quantum flux. A number of such action spectra together with solution absorption spectra of the same monomers are shown in Fig. 7 a-c. As generalization one takes from these spectra that the action spectrum resembles approximately to a distorted version of the

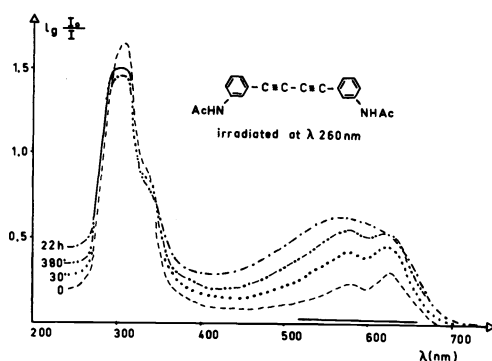


Fig. 6 Changes in crystal spectrum upon monochromatic irradiation for different times (single crystal) — pure monomer: —

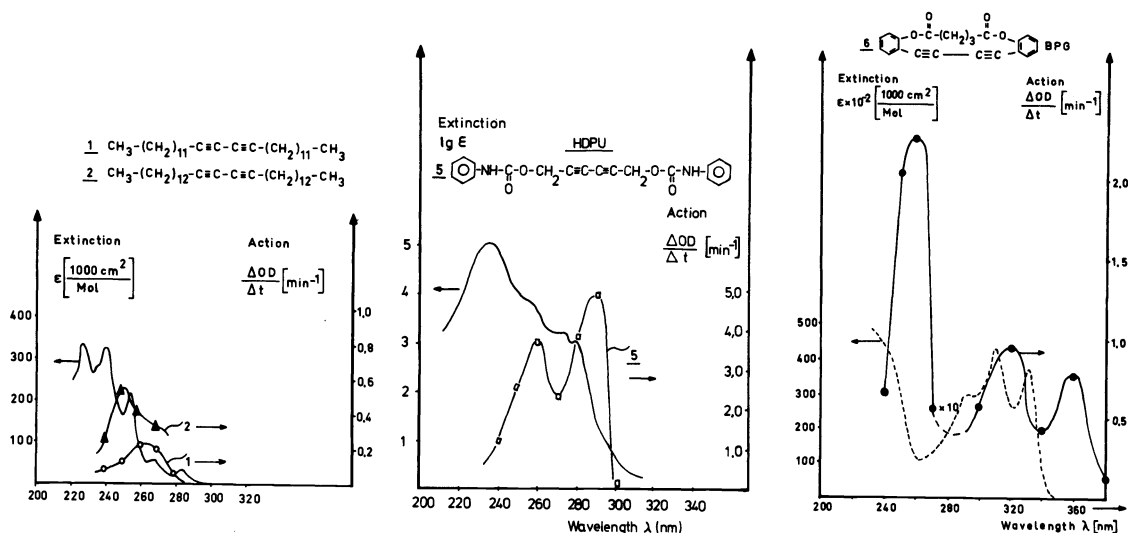


Fig. 7 Photoresponse of diacetylenes together with solution absorption spectra

absorption spectrum of a given compound, but there is well defined photoresponse upon irradiation into the bands of side groups as is most clearly seen in Fig. 7 b. It is still an open question how the excitation energy is transferred from the side groups to the triple bond system. The question becomes still more complicated if one remembers that the same spectral features as indicated in Fig. 6 and the same polymers are generally formed upon annealing in the dark or upon high-energy irradiation.

Photochemical observations in four-center-type photopolymerization

Unlike as in diacetylene polymerization where the product exhibits absorption in the wavelength range necessary for photopolymerization, diolefin four-center-type reaction produces cyclobutane rings which do absorb at much shorter wavelength. At the other hand, if such a polymer is irradiated within its absorption band (~ 250 nm) it is photodepolymerized whereas polydiacetylenes do not repolymerize. A most interesting observation was made by Hasegawa and coworkers (7) which sheds light onto the mechanism of polymerization. If monomer crystals are irradiated just in the long wave-length tail of absorption oligomers such as dimers and trimers are formed only. If these oligomer crystals are irradiated further at shorter wavelength the same high-polymer is produced which can be obtained directly by short wavelength irradiation. For pPDAEt (comp. Table 2) this is sketched in Fig. 8. The reason for this behaviour simply is, that dimers and trimers absorb at considerably shorter wavelength than the monomer so that these intermediates cannot be further excited when the system is irradiated in the long wave-length tail of monomer absorption. There is, however a topochemical restriction such that only oligomer crystals formed in situ are further reactive but, if the oligomers are recrystallized, inactive modifications are obtained.

Hasegawa and coworkers did also try to determine the quantum yield ϕ of oligomerization and polymerization using polycrystalline samples in KBr as dispersant (7). In DSP ϕ was 1.2 for oligomerization at $\lambda = 436$ nm and 1.6 for polymerization at $\lambda = 365$ nm. Contrary to that, P2VB showed a ϕ of 0.04 if irradiated at $\lambda = 405$ nm, the proper wavelength for oligomerization. The meaning of these apparent ϕ values is not quite clear, because reaction rates and light absorption are vectors in anisotropic media and, more over, four-center-type photopoly-

merization is a typical heterogeneous reaction and only that part of the molecules can be reactive which is situated near a defect site or in the immediate neighbourhood of the phase boundary between monomer and polymer. Fig. 9 and Fig. 10 explain some of the inherent difficulties one will encounter when one tries to evaluate the quantum yield of a crystal photoreaction. First of all, part of the incident light is always reflected and the light penetrating into the crystal is partially polarized according to Brewster's law. The reflectivity of the crystal increases many fold inside an absorption band, where one always observes anomalous dispersion of the refractive index (comp. Fig. 9). Since both the direction of the wave fronts and the polarization direction depends on the shape and position of the indicatrix whose main axes are the refractive indices n_x , n_y and n_z it becomes extremely important to use highly monochromatic light in order to avoid dispersion of the indicatrix in the real space, since n varies rapidly with wave-length inside an absorption band. Finally, all the light entering the crystal will be split into two rays polarized perpendicular to each other. For an optically two-axial crystal as are most of the monomers under consideration here, the situation is very complex and only for planes of symmetry of the indicatrix the two rays will travel in one crystallographical plane. Because of the polarization both rays will be absorbed differently by the molecules and thus, photoreaction depends on the angle between the incident light and the crystallographical axes. For further details the book of Wahlström (30) may be consulted.

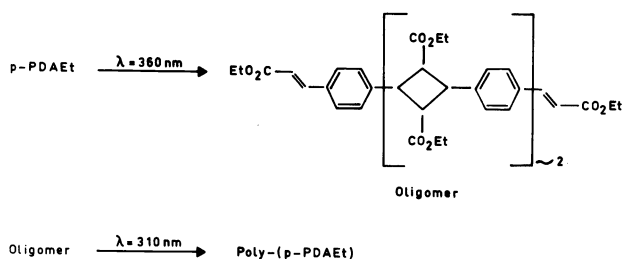


Fig. 8 Wave-length dependence of oligomerization and polymerization

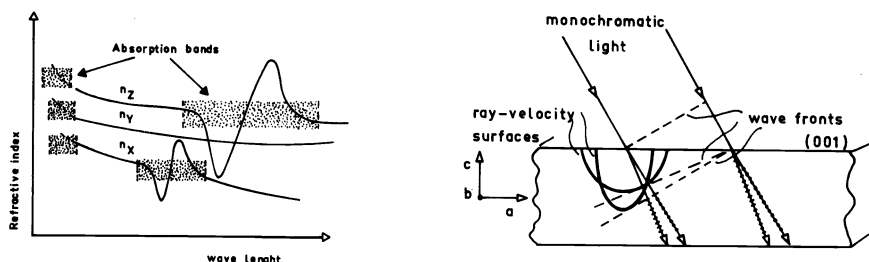


Fig. 9 Dispersion of the refractive indices (schematically)

Fig. 10 Huygenian construction for an orthorombic crystal in a plane of symmetry; \dashv — \dashv — wave vibrating normal to drawing \dashv — \dashv — wave vibrating in plane of drawing (according to Ref. 30)

TIME-CONVERSION CURVES

Four-center-type and diacetylene polymerization show considerable differences with regard to conversion-time dependence. Hasegawa and coworkers have published a number of detailed investigations. Their results can be summarized into a typical shape of a time conversion curve as shown in Fig. 11 a, curve b. There is an induction period and an autocatalytic type of increase of reaction rate in the very beginning. Contrary to that, diacetylenes do start to polymerize as soon as the light reaches the crystal. Reaction rate decreases with increasing conversion for reasons already explained. Both reactions do not show post-polymerization effects but reaction starts and stops when the light is switched on and off. The dependence of the molecular weight or reduced viscosity on conversion demonstrates some further characteristics. In diacetylene polymerization there are only very limited data available due to the poor solubility of most polymers. In the photopolymerization of the p-toluene sulfonate of hexadienediol a linear dependence of η_{sp}/c on conversion was observed with a finite value for extrapolation to zero-conversion indicating that the first photoproduct is already of some higher degree of polymerization (31).

In four-center-type polymerization the first photoproducts are dimers and trimers and the reaction proceeds in a stepwise manner. Nevertheless η_{sp}/c depends typically on conversion as shown in curve b, Fig. 11 b. Very high molecular weights are reached, if the polycrystalline

polymer which does not contain any residual monomer is further irradiated.

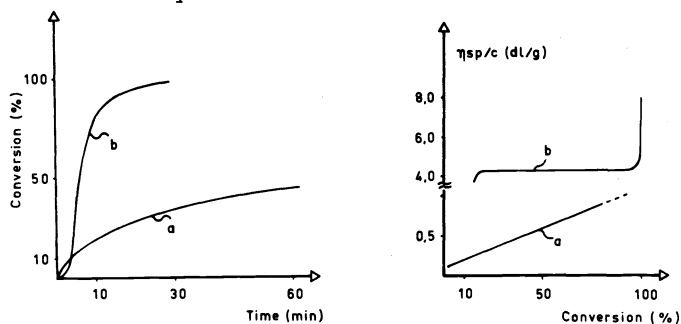


Fig. 11 a) Time-conversion curves for polycrystalline samples of (curve a) a diacetylene according to Ref. 31 and (curve b) for DSP according to Ref. 32; b) Reduced viscosity vs. conversion for (curve a) polydiacetylene (Ref. 31) and (curve b) Poly-DSP (Ref. 32)

CHANGES IN MORPHOLOGY DURING POLYMERIZATION

If a single crystal of a diacetylene is irradiated by uv-light, polymerization occurs throughout the irradiated area. The reaction is thought to proceed inside the perfect lattice in a homogeneous manner as sketched in Fig. 2 b. In the case of the bis-p-toluene sulfonate of hexadienediol defects have been characterized first by etching methods. Subsequent irradiation showed, that the photopolymerization does not start or stop at such defects. Contrary to that, thermal polymerization does start preferentially at such defects (33) although the polymer does never grow as an isolated phase but always in the sense of a solid solution with residual monomer. This has been checked by several authors and was found to be a unique feature for more or less all diacetylenes (11,13,20,34).

Sometimes, when a given compound is able to pack in different modifications, some complicated situations can arise. Cases have been described, where an inactive or almost inactive modification under the action of light is first transformed to a very reactive one which subsequently polymerizes rapidly. In such cases (20,24) the polymerization seemingly is accompanied by a phase change although the polymer chains again grow inside the newly formed monomer phase. Phase change is obviously brought about by mechanical strain which is imposed on a crystal upon polymerization which is not so well suited to form a solid solution with the newly formed polymer. An interesting case of that type was recently observed (24) in the polymerization of n-octacosadiene-13.15 where an inactive modification M-II transforms by a martensitic type of phase change into the reactive modification with simultaneous polymerization, so that large polymer single crystals are obtained despite the occurrence of a phase change. Four-center-type photopolymerization proceeds in a heterogeneous manner. If, for instance, a crystal of DSP is irradiated on a microscope stage the polymerization is always seen to start preferentially at defect sites such as cracks or edges. As polymerization proceeds more cracks and fissures are produced. In a polarizing microscope it is clearly recognized that the polymerization does not proceed in the perfect crystal but the perfect crystal is first broken down into tiny crystallites under the influence of mechanical strain exerted onto the crystal from areas which have just started to polymerize. Once the crystal is broken down, polymerization rapidly converts these crystallites into polymer starting from the edges. Surprisingly enough a crystal of DSP does not fibrillize as one would expect from the known crystal structure. In order to get a better impression of the mechanism of phase change a series of electron micrographs of the growing polymer or oligomer phase resp. was prepared. For that purpose thin monomer crystals were irradiated at $\lambda \geq 431$ for oligomerization and $\lambda \geq 340$ for polymerization. After different exposure times unconverted monomer was sublimed off and the electron micrographs shown in Fig. 12 a-c were taken. The polymer is seen to grow in layers which extend in crystallographical a-direction over only one to three unit cells. These flakes grow both in crystallographical b and c (chain) direction until the preformed microcrystal is converted into polymer. The final appearance of the sample which seems to consist of a thin foil with large fissures extending along chain direction and areas of collapsed folds extending perpendicular to it, is not a consequence of chain growth but rather of the mechanical stress onto the monomer crystal prior to polymerization. Polymer and oligomer do not differ much in morphology and the axes are easily assigned based on electron diffraction data. These also show (Fig. 12 c) that the polymerized area is of single crystal like character.

At present, it is difficult to see how these findings that rather perfect polymer or oligomer crystallites are formed do correlate to Hasegawa's observation that there is still an increase in degree of polymerization on further irradiation.

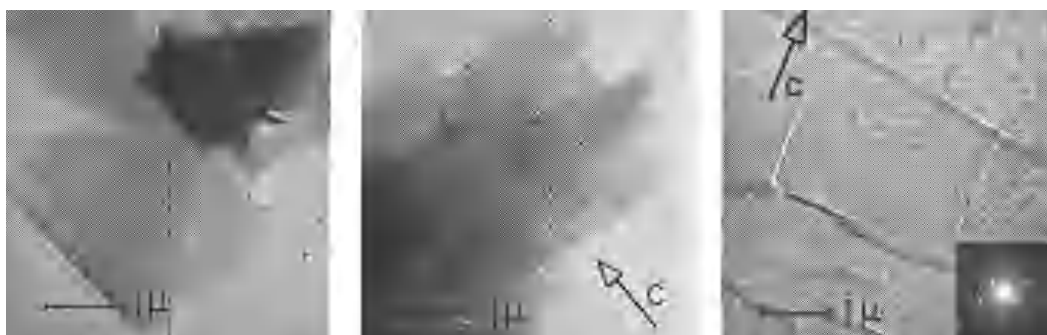


Fig. 12 Electron micrographs of the growing polymer phase in DSP-crystals, exposure times at $\lambda > 340$ nm a) 1 min; b) 16 min; c) 36 min.

NATURE OF CHAIN PROPAGATION IN DIACETYLENE POLYMERIZATION

Two possible mechanisms have been suggested for the growth of the polymer chains during topochemical polymerization of diacetylenes (35). First a radical type polymerization with a subsequent indirect change in bond structure and alternatively as a second possibility a carbene centre at a bent monomer terminal carbon bond involving a direct change from monomer to polymer without subsequent bond isomerization was proposed. The latter proposal was favoured by Wegner in the recent years (4,9) and was originally based on the spectroscopic observations already mentioned. If a monomer single crystal is irradiated one observes in almost all cases a series of colour changes corresponding to spectral changes in the visible spectrum such as shown in Fig. 6 or in Fig. 13 for the case of the hydrocarbon octacos-13,15-diene. There is always an absorption maximum obtained at $\lambda > 600$ nm upon short irradiation times which gradually changes into a very intense absorption centered around 560 nm upon further exposure to the light source. Finally with increasing irradiation time a rather broad absorption with maximum at about 490 nm is recorded. The latter is due to the "dead" polymer and is the only absorption remaining if a partially polymerized crystal at any stage of conversion is treated with solvent for the residual monomer. Additionally, it should be mentioned that oligomers or side-products of the reaction have never been detected despite many efforts. Since the absorptions at 600 and 560 nm show the same dichroic behavior as the 490 nm absorption with ϵ_{\max} parallel to fibre direction it is inferred, that these are due to different forms of "living" chain ends trapped within the monomer lattice.

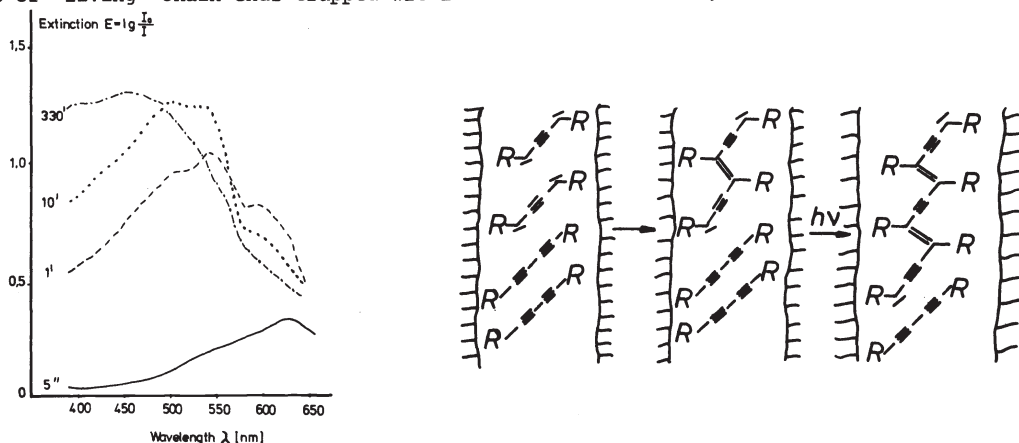


Fig. 13 Transient spectra of a single crystal of octacos-13,15-diene irradiated at $\lambda = 250$ nm after different exposure times as indicated at the curves (comp. also Fig. 6)

Fig. 14 Excitation of the triple bond system to dicarbenes, growth of the polymer chains via carbene mechanism

The following mechanism of chain growth as indicated in Fig. 14 was therefore proposed. Ex-monomers excited either directly by irradiation into the triple-bond chromophor or by excitonphonon coupling, if irradiation occurs such, that side groups are excited which are not linked directly to the triple-bond system. The reactive species is a dicarbene which reacts with an adjacent dicarbene such that two monomer units are linked by a double bond to a species which can add to further dicarbenes within the same stack of molecules. It is probable

that we deal with a cooperative process so that always a number of molecules adds together at once. At the other hand, the stability of the trapped chain ends in the crystal and the lack of post-polymerization effects indicates that the reaction is not of the type of a pure chain-reaction but contains some elements of a step-reaction such that only excited molecules add to reactive chain ends. The decay of one chain end at surfaces or defects would then create a new species with different absorption spectrum so that the occurrence of three peaks in the visible spectrum could be explained as due to chains growing at both ends, chains growing at one end and dead chains.

Recent work of D. Bloor and coworkers has completely vindicated this proposal (36) in so far as they were able to observe two different types of carbenoid species during polymerization of bis (p-toluene sulfonate) of hexadienediol by ESR-spectroscopy. As they point out, in carbenes the unpaired spins can be parallel or antiparallel giving states of total spin $S = 1$ or 0 . When the polymerization was carried out inside the cavity of the spectrometer a number of signals were obtained, but there was no evidence of a singlet ($S = 1/2$) radical species associated with polymerization. In single crystal experiments several lines could be observed characteristic of triplet species and associated to the active centers of polymerization. Analysis of the angular dependence of the signal form showed that one center has large values of the fine structure tensor and maximum intensity at maximum polymerization rate. The other has small fine structure values and anneals out slowly after the polymerization is over thus corresponding quite well to the picture given in Fig. 14.

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