Photopolymerization of Diacetylenes

H. Bässler
Fachbereich Physikalische Chemie, Philipps-Universität, Hans-Meerwein-Straße,
D-3550 Marburg, FRG

This article reviews the current state of art of photopolymerization of crystalline diacetylenes, although complementary information on thermal and γ-polymerization is also included whenever felt appropriate. Priority is given to an outline of recent achievements regarding reaction kinetics and energetics as well as to model considerations for both initiation and propagation of the polymer chain. It will be shown that at least for diacetylene-bis(p-toluenesulfonate) (TS) existing experimental data allow establishing a consistent picture of the polymerization process. After discussing recent works on photopolymerization in Langmuir-Blodgett-multilayer assemblies, including sensitization and self-sensitization effects, potential applications of the unusual optical, electrical, and reaction properties of diacetylenes are outlined.

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1 Introduction

Although it has been known since more than a century that certain crystalline diacetylenes undergo a dramatic color change upon prolonged storage under ambient conditions, it was not until Wegner’s interpretation of the effect that these materials became popular objects of chemical and physical research. Based upon the principles of topochemical reactions developed by G. M. L. Schmidt and co-workers he concluded that the color change must be the result of a polymerization process in course of which the C1 and C4 carbon atoms of adjacent diacetylene moieties in a molecular stack are linked together. According to the following scheme elongated polymer chains are formed under preservation of the single crystalline phase structure provided that the molecular motions accompanying the chemical transformation compensate each other in a way as to minimize the overall changes of the crystallographic parameters. It is also obvious that the reaction must be encumbered by an energy barrier. No matter what the total energy of the polymeric reaction product relative to the monomer is, mutual approach of the reaction centers must involve a molecular rotation which has to act against the repulsive forces exerted by the adjacent C1 and C4 atoms before bond formation. This explains why the reaction usually requires excess energy supplied by UV-photons, X-ray or γ-quanta to get started. In some cases phonons generated thermally are sufficient to trigger the polymerization process.

Not only does the solid state polymerization of crystalline diacetylenes offer a unique tool for studying topochemical reactions, it also affords fascinating, if specialized model systems for polymerization reactions in general. Of particular advantage is the absence of disorder, always present in homogeneous solution reactions and often obscuring analysis of the individual reaction steps. One can therefore apply high resolution optical and magnetic resonance techniques to elucidate the reaction mechanism. Such studies have yielded an unprecedented wealth of information about the individual reaction steps and the reaction intermediates which may be of relevance for other systems as well.
The reaction scheme shown above also allows prediction of some of the prominent properties of polydiacetylenes. Increasing the conjugation length of a molecule lowers the energy of elementary excitations of a conjugated chain \(^{26,27}\). Therefore, the highest filled molecular \(\pi\)-orbitals, i.e., the valence band of the chain, must experience an upward and the lowest empty \(\pi\)-orbitals, i.e., the conduction band, a downward shift in energy upon polymerization and the energy of the optical transition must decrease. As a consequence, one can expect that it is the electronic structure of the chain rather than that of the substituents which controls the electronic properties of the polymer, quite in contrast to the situation encountered with conventional polymers having \(\sigma\)-bonded backbones where the substituents play the dominant role. In particular, the large degree of anisotropy brought about by the different types of bonding parallel and perpendicular to the chain should be revealed in electronic transport properties. In fact, crystalline diacetylenes have been shown to provide the closest approach to one-dimensional systems known so far and are therefore widely used as model systems to study effects of reduced dimensionality on both electrical \(^{28-36}\) and optical \(^{35-40}\) properties. For a more detailed survey of the properties of polydiacetylenes the reader is referred to several review articles \(^{41-47}\).

The aim of this article is to provide an overview of the polymerization of diacetylenes. The focus will be on optical excitation, although some results on thermal reactivity will also be quoted to illustrate analogies. Comprehensiveness is not intended, instead, emphasis will be placed on model considerations. Structural aspects of the polymerization process, as well as the low temperature spectroscopy of reaction intermediates will only briefly be addressed since they are treated in detail in the contributions of V. Enkelmann and H. Sixl in this volume.

2 Phenomenological Aspects of the Polymerization Process

Upon exposure to heat, UV- or \(\gamma\)-radiation diacetylenes are converted from a soluble monomer crystal which is transparent if pure, i.e., free of residual polymer, to a deeply colored polymer crystal. With a few exceptions, the latter is insoluble in all common solvents. The color arises from the lowest \(n\)-electron transition of the conjugated polymer backbone, which has its maximum near 600 nm. It is of excitonic origin \(^{29,48-50}\) and carries an oscillator strength of the order unity. Both insolubility and optical absorption can be used to monitor the degree of conversion as a function of reaction time. In the first case the crystal is dispersed mechanically and the amount of polymer is determined gravimetrically from the weight fraction of insoluble material. Because of the high absorption coefficient of the polymer crystal, which is in the order \(10^6\) \(\text{cm}^{-1}\) for light propagation perpendicular to the polymer chain and polarized parallel to the chain, and \(\sim 2 \cdot 10^4\) \(\text{cm}^{-1}\) for perpendicular polarization \(^{36,37}\), direct absorption spectroscopy is limited to ultra-thin samples or to very low conversions. However, Chance and Sowa \(^{51}\) have demonstrated that at least for TS (for compound symbols see Table 1) reliable conversion studies do not require single crystals but can be performed with microcrystalline samples. This allows application of the diffusive reflectance technique for optical detection of the polymer content.
Table 1. List of symbols and structure formula of the substituents for the diacetylenes treated in the text

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Substituent(s)</th>
</tr>
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<tbody>
<tr>
<td>TS-6 (or TS)</td>
<td>(-\text{CH}_2\text{-O-SO}_2\text{-CH}_3)</td>
</tr>
<tr>
<td>TS-12</td>
<td>(-\text{(CH}_2\text{)}_2\text{-O-SO}_2\text{-CH}_3)</td>
</tr>
<tr>
<td>MBS</td>
<td>(-\text{(CH}_2\text{)}_4\text{-O-SO}_2\text{-OCH}_3)</td>
</tr>
<tr>
<td>TCDU</td>
<td>(-\text{(CH}_2\text{)}_4\text{-O-CO-NH-})</td>
</tr>
<tr>
<td>EUHD</td>
<td>(-\text{(CH}_2\text{)}_4\text{-O-CO-NH-CH}_3)</td>
</tr>
<tr>
<td>HDU</td>
<td>(-\text{(CH}_2\text{)}_4\text{-O-CO-NH-})</td>
</tr>
<tr>
<td>MCD</td>
<td>(-\text{(CH}_2\text{)}_4\text{-O-CO-NH-CH}_3)</td>
</tr>
<tr>
<td>n-BCMU</td>
<td>(-\text{(CH}_2\text{)}_n\text{-O-CO-NH-CH}_2\text{-CO-O-(C}_6\text{H}_9\text{)})</td>
</tr>
<tr>
<td>DCH</td>
<td>(-\text{CH}_2\text{-N-})</td>
</tr>
<tr>
<td>TCDA</td>
<td>(R_1:\ -\text{(CH}_2\text{)}_9\text{-CH}_3) (R_2:\ -\text{(CH}_2\text{)}_8\text{-COOH})</td>
</tr>
</tbody>
</table>

It is generally agreed that polymerization of diacetylenes is a multistep process. Initially a reactive center is created which subsequently grows by addition of monomer molecules. Formally the reaction can be described by a first order rate equation \(^{(52)}\):

\[
\frac{dX}{dt} = K(1 - X) \tag{1}
\]

where \(1 - X\) and \(X\) are the fractional monomer and polymer content, respectively. The rate constant \(K\) is the probability \(\gamma\) that a reaction center is created per unit time multiplied by the number of monomers, \(n\), that react per initiation event. In case of thermal polymerization:

\[
K = n\gamma_0 \exp\left(-\frac{E_{\text{therm}}^\ast}{kT}\right) \tag{2}
\]
$E_{\text{a} \text{therm}}$ being the thermal activation energy. In case of optical generation of the reaction center, $\gamma$ is the probability that a monomer molecule absorbs a photon, multiplied by the probability $q$ that excitation will lead to chain initiation. If the thickness ($d$) of the absorbing crystal is small compared to the penetration depth ($\alpha^{-1}$) of the exciting radiation:

$$K = \left( \frac{I_0 \alpha}{N_0} \right) nq$$

where $I_0$ is the incident photon flux (photons/cm$^2$ s) and $N_0$ is the number of molecules per unit volume. If $d > \alpha^{-1}$, the factor $\exp (-\alpha x)$ has to be incorporated in Eq. (3) where $x$ is the direction perpendicular to the irradiated surface located at $x = 0$. Then both $K$ and $X$ depend on the position of the absorbing molecule inside the absorber and the reaction becomes spatially inhomogeneous.

Eqs. (1) to (3) indicate that conversion studies under conditions where thermal polymerization prevails can only yield $E_{\text{a} \text{therm}}$ and the product $nT_0$, whereas the photon-induced reaction provides information on the product $nq$. To disentangle chain initiation and chain propagation effects an independent determination of the kinetic chain length is required.

![Diagram](image)

Fig. 1. Lower part: Rate constant for thermal and $\gamma$-polymerization of TS-6 as a function of conversion normalized to the rate constant at $X \to 0$. Curves are calculated from published time-conversion curves according to $K = (1 - X)^{-1} \frac{dX}{dt}$ where $X$ is the relative polymer content. $\gamma$-Polymerization data are from Ref. 53), thermal dates represent an average of literature dates, see e.g., 52). Upper portion: $K^\gamma/K_{\text{therm}}$ vs. conversion. The dashed curve is calculated on the basis of the energy transfer model of Ref. 66) for a quenching constant $k_q = k_c \tau_0 = 35$.
Representative for systems exhibiting sigmoidal conversion curves Fig. 1 shows experimental results for the rate constant of the reaction of TS, evaluated from thermal and γ-polymerization data according to $K = \frac{1}{(1 - X)} \frac{dX(t)}{dt}$, and normalized to the rate constant in the low conversion limit. It is obvious, that at low conversion $K$ depends on $X$, contrary to what is to be expected for a simple first order reaction. The functional form of $K(X)$ is different for the two modes of polymerization. The overall increase of $K$ with increasing $X$ reveals an autocatalytic reaction enhancement. A measure for its efficiency is the ratio $K(X = 0.5)/K(X = 0)$ which turns out to be about 200 for TS under thermal polymerization conditions. This effect is often observed with disubstituted diacetylenes, albeit with different kinetic parameters, and indicates that the conditions for the reaction to proceed are improved as more polymer is formed. This point will be further elaborated in the following chapters. There are, however, systems that do not exhibit autocatalytic reaction enhancement. Among these are TCDU, MBS, urethane substituted diacetylenes, notably 3-BCMU and 4-BCMU, and multilayer systems.

There is an early report in the literature claiming absence of the autocatalytic reaction enhancement in TS if the reaction is induced by UV-excitation of the monomer crystal. The implication would be that thermal and UV-polymerization involve different mechanisms. Later on, however, Chance and Patel found this to be an artifact caused by the neglect of spatially inhomogeneous absorption by polymer molecules which effectively competes with monomer excitation at increasing conversion and prematurely terminates the reaction. Although it is difficult to correct $X(t)$-curves obtained under UV-excitation for polymer absorption quantitatively, particularly if irradiation is done with unpolarized non-monochromatic light, it turns out that there is a qualitative agreement between $X(t)$-curves obtained under γ- and UV-irradiation. Application of this correction, however, does not solve the puzzle why in case of γ- or UV-polymerization of TS, the reaction rate increases less dramatically with conversion, than observed upon thermal conversion.

The latter effect can be explained by taking into account that a partially polymerized diacetylene crystal is a molecular crystal containing dopant molecules with lower lying optical transition acting as traps for monomer excitations. Take $k_r$ as the rate constant for non-radiative energy transfer from a donor to a trap, $\tau_0$ as the intrinsic donor lifetime, and $c_t$ as the relative trap concentration, then the lifetime of a donor in presence of traps would be $\tau = (\tau_0^{-1} + k_r c_t)^{-1}$. Since the probability that an excited donor can initiate a chain is proportional to its lifetime, we arrive at:

$$q(X)/q(X = 0) = \left[1 + (k_r \tau_0) X\right]^{-1}$$

for the relative chain initiation probability in presence of a relative polymer content $X$. This concept, originally proposed to explain the decrease in the photopolymerization yield in a system where spectral sensitization is effective, has been applied by Prock et al. to 4-BCMU. The advantage of this material is the absence of autocatalytic reaction enhancement. Therefore, the only concentration effect acting on the rate constant $K$ in course of a UV-photopolymerization experiment should be quenching of the excited monomer state by the polymer provided that the sample thickness is small enough to render effects of inhomogeneous sample absorption negligible. In fact, Fig. 2 demonstrates that excited state quenching accounts very...
well for the decrease of the conversion rate with increasing conversions. The fit parameter, $k_{tr} \tau_0$, turns out to be 20. Inserting $\tau_0^{-1} = 10^8 \ldots 10^9 \text{s}^{-1}$ gives $k_{tr} \sim 10^9 \ldots 10^{10} \text{s}^{-1}$. This is a surprisingly low value for a molecular crystal where energy transfer normally occurs via rapid exciton hopping \cite{64}, and suggests that single step Förster transfer is the dominant transfer mechanism. This conclusion concurs with Niederwald et al.'s \cite{67} observation that in a chemically pure TS crystal no energy transfer to physical defects is detectable. Apparently the $S_1$ state of the diacetylene moiety is rapidly localized involving structural relaxation.

The energy transfer concept can also be applied to explain why $K^\gamma(X)$ rises more slowly with conversion than $K^\theta(X)$ does. In Fig. 1 the ratio $K^\gamma(X)/K^\theta(X)$ is plotted versus $X$ and compared with the prediction of the energy transfer concept assuming a quenching parameter $k_{tr} \tau_0 = 35$. The agreement is very satisfactory. The implication would be that thermal, UV-, and $\gamma$-polymerization only differ with respect to the chain initiation mechanism, the chain propagation mechanism being essentially the same. However, this conclusion may not be of general validity. Based on the strain dependence of the frequencies of backbone vibrations, Galiotis et al. \cite{69} concluded that in a thermally polymerized ethylurethane diacetylene (EUHD), the chains are considerably longer than in X-ray polymerized samples. Conceivably, high energy radiation produces defects which interfere chain propagation. The importance of such an effect should decrease as additional chain limiting factors become dominant, e.g., lattice mismatch between monomer and polymer.

Unless proper account is taken for excited state quenching meaningful data regarding the quantum yield of photopolymerization can only be extracted from measurements under low conversion conditions, say $X < 0.03$. Owing to difficulties in

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\footnote{Recently Niederwald et al. \cite{67} observed strong fluorescence emitted from a TS crystal, the time decay following the profile of a 10 ns excitation pulse. Combining their statement of high fluorescence yield with the fact that the singlet transitions of diacetylenes have low oscillator strength \cite{68} suggests that $10^{-9} \lesssim \tau_0 \lesssim 10^{-8} \text{s}$.}
measuring absolute photon doses, quantitative experimental information is contradictory. Whereas Chance and Patel \( ^{53} \) derived \( n_q = 1.5 \) from continuous irradiation experiments with an uncertainty of a factor of 5, Bhattacharjee and Patel \( ^{70} \) reported \( n_q = 0.06 \pm 0.03 \). The yield was found to be thermally activated with an activation energy \( E_{\text{opt}} = 0.13 \text{ eV} \). From the change in optical density following excitation by a 308 nm pulse of an excimer laser Niederwald et al. \( ^{71} \) derived \( n_q = 0.07 \pm 0.02 \) at room temperature and a negative temperature coefficient. Recent work in this laboratory \( ^{72} \) gave \( n_q = 0.15 \pm 0.05 \) at \( \lambda_{\text{ex}} = 308 \text{ nm} \) with a tendency to increase upon lowering \( \lambda_{\text{ex}} \) (see Fig. 3). In summary, it seems fair to conclude that \( n_q \sim 0.1 \) represents a reasonable order of magnitude estimate for TS-6 in the low conversion limit.

For 4-BCMU, both photoacoustic \( ^{73} \) and thin film absorption \( ^{66} \) studies consistently show that \( n_q \) must be of order 100 at 295 K. The most accurate value appears to be \( n_q = 60 \), associated with an activation energy of 0.3 eV, which has been determined calorimetrically \( ^ {74} \). For mixed crystals of HD and Phenazine (HD-Ph) \( n_q = 0.5 \) and \( E_{\text{opt}} = 0.17 \text{ eV} \) has been reported under excitation of the diacetylene moiety \( ^ {65} \).

It is generally agreed that chain initiation is a statistical process occurring at random within the bulk of the monomer matrix and leading to a solid solution of polymer within the parent crystal \( ^{3,51,75} \). Recent neutron scattering experiments on TS by Grimm et al. \( ^{76} \) did not show any indication of inhomogeneous polymer growth which might have delineated existence of specific nucleation sites. Chain interaction was only noted near 50 percent conversion. Polymerization may, however, give rise to a phase transition at high conversions. An example is DCH where Enkelmann et al. \( ^{55} \) observed a reaction-induced phase transition associated with a shearing of the monomer lattice. It improves molecular packing and consequently gives rise to autocatalytic reaction acceleration. A phase transition that nucleates at defects and destroys the macrocrystalline order of the matrix thereby rendering the reaction inhomogeneous was detected in TCDA above 50 percent conversion \( ^{59} \).
3 The Chain Length Problem

3.1 Experimental Results

Determining the length of the polymer product is of key importance for understanding the polymerization process and received considerable attention ever since the reaction was discovered. On the experimental side direct determination is impeded by the insolubility of most polydiacetylenes — exceptions will be mentioned below — which precludes application of standard methods for measuring the molecular weight.

Of particular interest are changes in the chain length occurring in connection with the autocatalytic reaction acceleration in TS-6. Numerous thermal polymerization studies showed that the activation energy is \( E_a^{th} = 1.00 \pm 0.02 \text{ eV} \), independent of conversion. Consequently the autocatalytic reaction enhancement cannot be the result of an increase of the Boltzmann factor. Instead, an increase in the number of monomers consumed per primary chain initiation event has been postulated. Experimentally \( n(X = 0.5)/n(X = 0) \approx 200 \) is found \(^{51}\).

An early estimate, based upon the position of the optical absorption of TS-polymer at low conversion gave \( n(X = 0) \approx 24 \) repeat units \(^{51}\). Although the conclusiveness of the procedure to derive this number is questionable — for \( n \gtrsim 10 \) the position of the lowest absorption band of the polymer backbone is almost independent of \( n \) \(^{17}\) yet sensitive to chain expansion, known to be important at low \( X \) \(^{77,78}\) — this number has turned out to be essentially correct. Analysing diffusive features in the X-ray diffraction pattern of partially polymerized TS crystals Albouy et al. \(^{79}\) recently concluded that at room temperature \( n \) increases smoothly from \( n = 18 \) at \( X \approx 0 \) to \( n = 30 \) at \( X \approx 0.1 \) (see Fig. 4). Brillouin scattering experiments by Enkelmann et al. \(^{80}\) gave \( n \gtrsim 5 \) for \( X \lesssim 0.1 \).

![Fig. 4. Average number of repeat units contained in a TS-6 polymer chain as a function of conversion. Data points are experimental (Ref. \(^{79}\)), the full curve is calculated from Eq. (9) in Section 6.1](image)
Both ESR experiments \(^{81}\) as well as viscosity measurements \(^{2}\) are consistent with the existence of long polymer chains in high conversion TS. In an attempt to find a way for determining the chain length that does not require sample solubility, Mondong and Bässler \(^{82}\) applied the technique of photopolymerization under spatially intermittent irradiation. This work was stimulated by Avakain and Merrifield's classic experiment on triplet exciton diffusion in crystalline anthracene. In this experiment the decrease of the triplet concentration caused by exciton diffusion into unirradiated crystal areas was inferred from changes in the intensity of the delayed fluorescence \(^{83}\). Adapting their set-up to the study of photopolymerization of TS a micro-mesh with square holes of typically 50 \(\mu\)m edge length and a bar width ranging from 7 to 30 \(\mu\)m was put on top of the (100)-face of a TS crystal which had been subjected to thermal polymerization up to a certain degree of conversion \((X \leq 0.15)\). The crystal was irradiated with a continuous UV light source and subsequently etched to remove unreacted monomer from the surface. The etch profile was recorded with a scanning electron microscope. Figure 5 presents an etch pattern obtained with a crystal originally containing \(X = 0.15\) polymer, sufficient to establish autocatalytic reaction conditions for the subsequent photoreaction. The asymmetry

![Etch profile of TS-6 crystals](image)

**Fig. 5a and b.** Etch profile of TS-6 crystals after thermal polymerization for 4 h (a) and 20 h (b), respectively at 60 °C, and subsequent photopolymerization for 2 h (a) and 30 min (b), respectively, at 20 °C. The width of the grid bars of the irradiation mesh was 20 \(\mu\)m. The polymer content at the beginning of irradiation was approximately 2 percent in case (a) and 15 percent in case (b).
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of the etch pattern is in accord with the accepted view that UV-initiated polymer chains grow along [0 1 0]. Therefore, their heads can only penetrate into the unirradiated zones running along [0 0 1] and cause smearing out of the etch profile. Sharp profiles were only observed if the initial polymer content was well below the autocatalytic threshold concentrations. This experiment demonstrated that the autocatalytic reaction enhancement does involve an increase of the number of monomers converted per chain initiation event and suggested an ultimate average chain length of order 4 μm, equivalent to 8000 repeat units.

There is, however, serious doubt that 4 μm is the kinetic length of an individual chain. Consider a monomer crystal that contains a fraction X₀ of short chains consisting of n₀ repeat units. The average number of monomers enclosed between the ends of two polymer chains in a row and available for subsequent photopolymerization is:

\[ \langle n \rangle = n₀(X₀^{-1} - 1) \]  

(5)

Inserting \( n₀ = 30 \), \( X₀ = 0.1 \) gives \( \langle n \rangle = 270 \). \( \langle n \rangle \) should be an upper limit for the average chain length in the autocatalytic reaction regime, if for reasons to be discussed below any further limitation of the kinetic chain length is suspended and if dead chain ends are not revived by recombination with a running chain.

Progress in this field has been aided by the discovery of soluble diacetylenes allowing a chromatographic study of the molecular weight distribution \(^{84-86} \). The results of the most recent work by Wenz and Wegner \(^{87} \) on TS-12 are in accord with the above reasoning. TS-12 is a soluble analog to TS-6, differing only with respect to the number of CH₂-units in the substituents and likely to mimic the behavior of TS-6 reasonably well. Figure 6 shows that at low conversions, \( X < 0.05 \), only short chains with

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**Fig. 6.** Distribution of the average number of repeat units (P) contained in the polymer of TS-12 at various conversions. (b: \( X = 0.01 \), d: 0.025, f: 0.06, g: 0.12, h: 0.17, i: 0.35, j: 0.50, k: 0.64) (from Ref. \(^{86} \))
\[ \langle n_0 \rangle = 60 \] are formed. \( X \approx 0.05 \) is the critical concentration at which in TS-12 autocatalytic reaction enhancement becomes important. With increasing \( X \) a second component appears in the molecular weight distribution displaying a peak near \( \langle n \rangle = 2000 \), virtually independent of conversion. It is readily verified that the data set \( n_0 = 60 \), \( \langle n \rangle = 2000 \), and \( X_0 = 0.05 \) is compatible with Eq. (5). Several important conclusions follow from this work: (i) The short chains formed during the initial stage of the reaction remain intact up to conversions of 70 percent indicating that they cannot be incorporated into longer chains; (ii) a simple statistical model seems to reproduce the basic features of the distribution of chain lengths \( 88^\dagger \); (iii) the average maximum chain length is determined by the number of short chains produced during the induction period, and (iv) the autocatalytic behavior arises from the increase in the chain length rather than an increase of the number of chain initiation events as evidenced by the linear relationship between the number of chains formed and the irradiation dose.

There is no direct evidence that in TS-6 individual chains formed in the autocatalytic reaction regime are only a few hundred repeat units long, contrary to what is to be expected from the 200-fold increase of the reaction rate. However, there is a recent estimate based on polarization currents measured during thermal polymerization. Following earlier work on the pyroelectric response of TS \( 89,90 \), Bertault et al. \( 91 \) attributed the electric signal to an alignment of non-compensated dipolar defects associated with the chain ends. From the average value of the polarization they concluded that one chain can at most comprise a couple of hundred monomer units.

Knowledge of the chain length \( n \) and the overall yield \( nq \) allows evaluating the primary quantum yield \( q \) for optical chain initiation. Unfortunately, data are available for few systems only. Based on \( \lim_{X \to 0} n \approx 20^{79} \) and \( nq \approx 10^{-1} \) (see above), \( q \approx 5 \cdot 10^{-3} \) follows for TS-6. For 4-BCMU, a soluble diacetylene not exhibiting an autocatalytic reaction regime, \( n = 2400^{84} \) and \( nq = 60 \) (at 295 K) \( 74 \) have been reported, giving \( q = 0.025 \). In view of the considerable difficulties encountered upon measuring absolute doses in UV required to calculate \( nq \), these data should rather be considered as order of magnitude estimates.

### 3.2 The Elastic Strain Theory

Simple statistical considerations of the above sort can provide an estimate of the maximum increase of the average kinetic chain length during the reaction, yet are unable to predict whether an individual running chain can actually grow to its ultimate length determined by the number of monomers available. A quantitative theory assessing the effects of matrix structure changes during reaction on the kinetics of the subsequent reaction has been developed by Baughman \( 52 \). Its origin was the recognition that the repeat unit of a relaxed polymer chain in TS is about 5 percent shorter than the lattice constant along the \( \overline{b}^\star \) direction in the monomer crystal, which coincides with the direction of the running chain \( 75,92 \). Because of this lattice mismatch internal strain develops inside the crystal upon chain formation. In order that monomer and polymer be in register, chains have to be expanded and/or the monomer matrix has to be compressed. Which of these effects predominates depends on conversion and on the elastic moduli of monomer and polymer. At low \( X \) the
matrix influence dominates forcing polymer chains to expand as evidenced by the blue shift of their optical absorption band. Owing to their greater elastic stiffness, the compressing effect of the polymer chains on the matrix takes over at comparatively low conversions to ultimately force the monomer lattice into register with the polymer product thereby improving the reaction conditions. At arbitrary conversion the lattice constant is a function of $X$, determined by the condition that the total free energy of the system be a minimum. By considering only the elastic energy term and ignoring structural changes perpendicular to the chain direction, Baughman derived an expression for the lattice parameter $b(X)$ which meanwhile has been verified by both direct dilatometric recording during thermal polymerization of TS-6 and X-ray analysis (Fig. 7).

![Figure 7](image)

**Fig. 7.** Relative change of the lattice parameter in TS-6 along the chain direction as a function of conversion $X$. Indices $m$ and $p$ refer to monomer and polymer, respectively. The full curve is derived from a continuous dilatometric measurement, the dashed curve is calculated according to Ref. by minimizing the elastic energy assuming a ratio $E_p/E_m = 5.0$ for the elastic constants of polymer and monomer, respectively. Open circles are X-ray data from Ref. 79, crosses represent data from optical absorption studies. The correlation between the effective strain of a polymer chain and its absorption energy, established from direct absorption measurements on stretched polymer fibres, allows an independent determination of the length of the repeat unit as a function of $X$ via optical absorption measurements. Data obtained by this method display a systematic deviation from the theoretical plot (Fig. 7) as do data derived from resonant Raman measurements. This indicates that the agreement between experimental data and predictions of the elastic strain (ES)-theory is fulfilled only...
as long as the experimental conditions reflect the premises of the theory, notably its reduction to a strictly one-dimensional problem. Since electronic states of the polymer backbone as well as its vibrational modes reacts sensitively on both length of the overall repeat unit and readjustment of bond angles and bond lengths as a result of lateral forces acting on the chain, this condition is violated when performing optical chain detection experiments. Dimensional changes occurring along $[1\;0\;0]$ and $[0\;0\;1]$ in course of monomer-polymer conversion are therefore reflected in both absorption and resonant Raman studies in a manner not predictable on the basis of the ES-theory.

The main goal for developing the ES-theory was to afford a framework for understanding the increase of the chain length within the autocatalytic reaction regime. Assuming that (i) both creation and deactivation of the active species initiating a chain is independent of conversion $X$, (ii) the probability that an active species initiates a chain is $\leq 1$ and (iii) the lifetime of reactive ends on growing chains is independent of $X$, Baughman calculated the relative chain length as a function of $X$. He found that in the conversion range $0.05 < X < 0.4$ $n$ increases by approximately one order of magnitude. The result of the calculation is shown in Fig. 8 normalized in a way as

![Graph showing number of repeat units per polymer chain as a function of conversion]

**Fig. 8.** Number of repeat units per polymer chain as a function of conversion. Dashed curves are from Ref. and were calculated on the basis of the elastic chain theory for different ratios of the elastic constants $E_m$ and $E_p$ of monomer and polymer, respectively, and normalized to fit the experimental data near $X = 0.1$. The full curve is calculated according to Eq. (9) (Sect. 6.1) ignoring chain blocking effects. Data points are experimental.

Extrapolating experimental low conversion data for $n$ employing the ES-theory would predict a chain length of not more than 100 repeat units, equivalent to 500 Å, in the high conversion regime. The autocatalytic enhancement factor would then come out to be a factor of 3 less than the
maximum enhancement factor resulting from statistical considerations. This result, if correct, would imply that in TS-6 the average length of a running chain is not determined by the number of monomer molecules available for reacting between the ends of existing chains, contrary to what has been found with TS-12.

Despite the success of the ES-theory to explain the dimensional changes occurring in TS-6 along [0 1 0] as a function of conversion it thus appears, that difficulties are encountered when it is applied to predict the increase of the chain length within the autocatalytic reaction regime in a quantitative fashion. A similar reasoning was put forward by Lochner et al. who analyzed the effect of hydrostatic pressure on the thermal reactivity of TS-6. They concluded that the decrease of the induction time with pressure occurred too fast to be explained in terms of the ES-theory alone. Further, the ES-theory implies that both chain propagation and initiation are similarly affected by a decrease of the elastic energy contribution to the total free energy change during the reaction. One would therefore expect the activation energy for thermal polymerization to decrease with increasing X, contrary to what experiments consistently show (see, e.g., Refs. 51, 96). In section 5, a simple model will be presented that avoids these shortcomings and is able to correctly predict the chain length data of Albouy et al. 79).

4 Energetics of the Polymerization Process

Although kinetically hindered by an energy barrier attachment of a monomer to a running polydiacetylene chain is an exothermic process. This has been proven by Chance et al. employing differential scanning calorimetry. These authors recorded the heat evolved during thermal reaction of TS and found that an energy of 1.6 eV is released by adding one monomer to an active chain end. Experimentally, a TS-sample is held at constant temperature in the calorimeter. Onset of the reaction after the induction time shows up as a peak in the DSC scan. Since conversion is quantitative, this experiment directly yields the reaction enthalpy per monomer addition event.

Later on, Chance and Shand studied the heat evolution during UV-photo polymerization of 4-BCMU employing the photoacoustic detection technique. This technique is based on the increase of the pressure of the gas surrounding with a sample in which heat is produced as a result of light absorption. Although highly sensitive, quantitative data analysis is not straightforward since it requires taking into account both heat diffusion inside the sample and the magnitude of the acoustic coupling between solid and gas. The information it provides is the reaction enthalpy produced per chain initiation event, i.e., nqΔH. It therefore can be used to determine nq once ΔH is known from DSC studies. Being a transient technique, PA-photocalorimetry can also monitor the time response of the sample towards a light pulse that triggers the photoreaction. For 4-BCMU it was found that chain formation must be completed within a time < 1 μs, which was the time response of the detector system.

More direct information on the energetics of the photopolymerization process is afforded by DSC measurement with UV-initiation of the reaction. Under single pulse excitation the integral heat evolved per light pulse is a measure for the product nΔH and from the ratio of the signal amplitudes at t = 0 and t → ∞, respectively,
the quantity $nq\Delta H$ can be inferred independently. Thus, if the chain length $n$ is known from measurements of the molecular weight, as it is the case with soluble diacetylenes of the BCMU-type\textsuperscript{84}, both $\Delta H$ and $q$ can be determined. Employing this technique, Eckhardt et al.\textsuperscript{74} recently showed that in 4-BCMU, $\Delta H = 0.95$ eV per repeat unit, i.e., about 0.6 eV less than in TS. They proposed an explanation involving the intramolecular hydrogen bonds between the C=O and N—H functionalities on adjacent substituents of diacetylene monomers, known to exist both in solution and in the solid state\textsuperscript{85}. Based on steric arguments it has been concluded that in 4-BCMU, where four CH$_2$ groups link the side groups to the backbone, a considerable distortion of the CH$_2$-groups and possibly also the backbone is required for preservation of the hydrogen bonds after polymerization. Therefore, polymerization goes in hand with an energetically unfavorable reorganization of the intramolecular hydrogen bond network at the expense of the total reaction enthalpy. This reasoning provides a straightforward explanation why 4-BCMU does not polymerize thermally at any measurable rate. Formation of the chain initiating dimer is an endothermic process and involves similar rearrangement in the side groups as does addition of a monomer to a running chain. Therefore, the extra energy of $\sim 0.6$ eV resulting from H-bond distortion should be added to the energy barrier for chain initiation, resulting in a drastic decrease of the thermal reaction rate.

The essence of the energetic studies on TS and 4-BCMU is contained in Fig. 9. In TS formation of the chain initiating species — a dimer — requires an energy of 1.0 eV. It can be supplied thermally or optically via monomer excitation. In the former case it is this chain initiation reaction that controls the thermal reactivity and its temperature-dependence. Chain initiation can also be produced optically at a yield of order 10$^{-2}$ per absorbed UV-quantum. In this case it is chain propagation that determines the temperature dependence of the polymerization yield. However, the activation energy $E^\text{act}$ need not be and in general is not identical with the energy

![Energy Diagram](https://example.com/energy_diagram.png)  

**Fig. 9.** Energy diagram for polymerization of diacetylenes. The solid curve is for TS-6 (Ref. 98), the dashed curve for 4-BMCU (Ref. 74).
barrier for monomer addition. It is a measure for the temperature dependence of 
$q$, or, rather, of $n$, since there is good reason to suspect that except at low tem-
peratures $q$ shows only a weak if any temperature dependence. In case that the chain 
length is not saturated, i.e., limited by the number of monomers available for reaction, 
$n$ is given by $k \tau$ where $k$ is the rate constant of the addition reaction and $\tau$ the lifetime 
of the active chain end. Even then $E_{\text{opt}}^0$ is not identical with the height of the kinetic 
barrier since $\tau$ is also temperature dependent. Comparing $E_{\text{opt}}^0$-data with the results 
of kinetic studies \cite{67} (see Sect. 5) in fact indicate, that in TS the true barrier height 
for the monomer addition reaction is $> E_{\text{opt}}^0$ and dependent on the length of the 
precursor chain.

Eckhardt et al. \cite{74} also speculated on the possible reason for the high photochemical 
yield of 4-BCMU as compared to TS. Even taking into account the much longer 
chain length in 4-BCMU, the chain initiation probability $q$ is still coming out about a 
factor of 4 larger than in TS. These authors argued that because of the upward shift 
of the energy of the chain initiating species (see above) its electronic level comes closer 
to the electronic state of the excited monomer favoring non-radiative coupling 
between those states. This suggests existence of an inverse relationship, i.e., a com-
ensation effect between optical and thermal reactivity of diacetylenes. Clearly, 
more quantitative work is needed to test this interesting hypothesis.

There has been an argument in the literature whether the intermediate acting as 
a chain initiator is a dicarbene of the type:

\[ \text{R R R} \]
\[ \text{C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C} \]

or a diradical \cite{53}:

\[ \text{R R R} \]
\[ \text{C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C \equiv C} \]

The argument in favour of the latter was that the diradical should be lower in 
energy, because its formation requires disruption of only one carbon-carbon $\pi$-bond 
instead of two in case of carbene formation. Both ESR work \cite{22} and optical spec-
troscopy \cite{17} have meanwhile confirmed the diradical mechanism for growth of oligo-
meric chains up to length of 5 repeat units. Upon further addition of monomers, the 
acyclic structure becomes energetically more stable causing a cross-over to the 
carbene mechanism. For further discussion of this topic the reader is referred to the 
article by H. Sixl in this volume.
5 Time Dependent Studies

5.1 Studies at Atmospheric Pressure

A major achievement towards understanding the kinetics of photopolymerization of diacetylenes was the application of time dependent optical spectroscopy. Monitoring the appearance of the characteristic polymer reflection Leyrer and Wegner \(100\) were the first to record the time-dependent build-up of polymer in TS-6 and MCD following flash excitation. The light source was a \(\text{N}_2\)-laser delivering 5 ns pulses which drive the lowest forbidden singlet transition (at 3.7 eV) of the diacetylene moiety \(50\). Polycrystalline powder dispersed on filter paper was used as a sample. Although in a powder sample the density of structural defects which might conceivably block chain growth, inevitably is high, the experiment revealed the essential features of polymer formation correctly. Fig. 10, which is taken from Ref. \(100\), shows that build-up of the polymer is a relatively slow process, occurring on a time scale of the order 1 ms, and does not follow simple first order kinetics. Empirically a \(X(t) \sim 1 - \exp\left[-(C(t-t_d))^{1/2}\right]\) law was obeyed with \(C = 1.3 \cdot 10^3 \text{ s}^{-1}\) and a delay time \(t_d = 300 \text{ ns}\) elapsing between laser flash and onset of polymer formation. The \(\sqrt{t}\)-law led Leyrer and Wegner to conclude that it is the diffusion of excited states within the monomer matrix towards reaction centers, possibly defects that determines the kinetics. Subsequent time resolved absorption studies by Niederwald, Eichele, and Schwoerer \(101\) performed on single crystals did not confirm this aspect of Leyrer and Wegner's interpretation but showed that the observed time dependence is the necessary consequence of the multistep character of the chain propagation process. Performing either a monochromatic or a polychromatic transient absorption experi-

![Fig. 10. Time dependent conversion of TS-6 (squares) and MCD (triangles) following one \(\text{N}_2\)-laser excitation pulse of 3 ns duration. The inset shows the MCD-data on an enlayed scale. Data are normalized to the polymer content in TS-6 reached in the \(t \to \infty\) limit (from Ref. \(100\)).](image-url)
Photopolymerization of Diacetylenes

Niederwald and Schwoerer recently succeeded in recording both absorption spectra and transient behavior of short-lived reaction intermediates appearing in a TS crystal after excitation by a 15 ns laser pulse of \( \lambda = 308 \text{ nm} \) and a pulse energy of typical 1 mJ. Figure 11 presents the transient difference absorption spectra at

Fig. 11a-d. Transient absorption spectra of reaction intermediates (a–c) and final product (d) observed upon photopolymerization of a TS-6 crystal with a 308 nm laser pulse. Parameters are the temperatures and the delay times (\( \Delta t \)) between the laser pulse and spectra recording. In b and c the time window of the detection circuit was 100 \( \mu \text{s} \). \( \Delta \text{OD} \) is the difference of the optical densities after and before the UV-flash (from Ref. 67).

180 K. Spectrum a was recorded within 100 \( \mu \text{s} \) after the UV flash, spectra b and c were recorded within a time window of 100 \( \mu \text{s} \) after a delay time of 650 \( \mu \text{s} \) and 1.9 ms, respectively. The conclusion is, that a series of five intermediates A, B, C, D, E exists, whose lifetime increases with increasing absorption wavelength. The absorption spectrum of product V closely resembles the final polymer spectrum (11d). Following Sixl et al. \(^ {14,15} \) these intermediates are identified as dimer (A), trimer (B), tetramer (C), pentamer (D), and hexamer (E)-diradical (\( \text{DR}_n \)).

Growth and disappearance of the intermediates, monitored by their characteristic transient absorption (Fig. 12) can be fitted perfectly on the basis of the kinetic scheme:

\[
A \xrightarrow{K_A, \Delta \text{EA}} B \xrightarrow{K_B, \Delta \text{EB}} C \xrightarrow{K_C, \Delta \text{EC}} D \xrightarrow{K_D, \Delta \text{ED}} E
\]
where the $K$'s are rate constants in first order rate equations and the $\Delta E$'s are activation energies. Solution of the pertinent set of coupled differential equations shows that the concentration of the $i$-th product is:

$$n_i(t) = \sum_{j=1}^{i} a_{ij} \exp \left[ -K_j(t - t_0) \right]$$

(6)
where $a_{ij} = \frac{K_{i-1}}{K_i - K_j}$, $i, j \in \{A, B, C, D, \ldots\}$, and $t_0$ is the time at which the precursor to $A$, assumed to be the photoexcited monomer, is populated. For data analysis it is further assumed that population of $A$ occurs fast on the time scale of the transient absorption experiment. Verification of the above simple reaction scheme confirms the earlier notion that each reaction step consists of the addition of one monomer unit to a linear chain. As the length of the oligomers increases beyond a certain limit ($i > 5$) their diradical character changes to dicarbenic or carbenic and the absorption bands gradually converge. Product $V$ is interpreted as a superposition of long chain oligomers which absorb at a wavelength close to the value characteristic of the infinite chain. Kinetically, $V$ is therefore regarded to be the ultimate precursor for the final polymer. It is gratifying to note that the time dependence of polymer growth measured by Leyrer and Wegner agrees with single crystal data, documenting that reaction kinetics at least towards the end of chain growth — is fairly insensitive to changes in the macroscopic perfectness of the sample. Apparently, in the low conversion limit the kinetic chain length in TS-6 is much less than both the dimension of crystallites and the mean distance between lattice defects which could block chain growth.

Interestingly, the preexponential factor of the rate constants is practically the same for all intermediates ($K_0 = 10^{11} \pm 1$ s$^{-1}$), whereas the activation energy slightly increases from $\Delta E_A = 0.25 \pm 0.03$ eV to $\Delta E_{V2} = 0.40 \pm 0.03$ eV (see Fig. 13).

![Fig. 13. Activation energy for the addition reaction $n$-oligomer + monomer $\rightarrow (n + 1)$ oligomer as a function of the number of repeat units ($n$) of the oligomer (data are taken from Ref. 67)](image)

This suggests that the addition reaction is a thermally activated process, driven by a lattice mode with frequency of the order $10^{11}$ s$^{-1}$ corresponding to an energy of about 30 cm$^{-1}$, typical for optical or acoustic lattice modes. Remarkably, Niederwald and Schwoerer quote recent neutron diffraction work by Schott and coworkers delineating existence of an optical phonon at a very low frequency ($\sim 10^{11}$ s$^{-1}$) at the boundary of the Brillouin zone.

Qualitatively, the increase in activation energy with increasing length of the oligomer can be attributed to the mismatch between monomer lattice and length of the oligomer/polymer repeat unit. As the oligomer length increases, the gap between the oligomer head and the adjacent monomer widens. Therefore, more
thermal energy is required to establish the critical distance necessary for bond formation between the adjacent molecules. This idea will be elaborated further in Section 6 taking advantage of kinetic studies under hydrostatic pressure to be discussed in section 5.2.

An interesting isotope effect on both thermal- and photopolymerization of specifically deuterated or $^{13}$C-labelled TS-6 was discovered by Kröhnke, Enkelmann, and Wegner 102). These authors found that deuteration in the CH$_2$-group and/or the phenyldiazonium side group reduces both induction time for thermal polymerization and reaction rate within the autocatalytic regime by typically a factor of 2. The largest effect was seen upon isotopic substitution at the methylene group which forms the linkage between diacetylene moiety and substituent. Verification of this effect with HDU, a phenylurethane-substituted diacetylene, suggests that it is a general feature of the polymerization of diacetylenes rather than an impurity effect 103). It reflects the influence of isotopic substitution on both lifetime of the chain propagating species and the rate constant for the monomer addition reaction 67, 102).

The lifetime $\tau$ is determined by the decay of a reactive chain end of the carbene type to a stable polymer head involving electronic rearrangement and singlet-triplet intersystem crossing, known to become less efficient upon deuteration 104). An increase of $\tau$ allows polymer chains to grow longer. In course of a thermal polymerization experiment the critical conversion above which autocatalytic reaction enhancement becomes effective is therefore reached at shorter times in the deuterated material provided the chain initiation rate remains constant, i.e. the induction time decreases. On the other hand, the reaction rate within the autocatalytic reaction regime decreases reflecting the decreased rate of the monomer addition reaction in the deuterated material. This is in accord with the experiments of Kröhnke et al. 102).

A final remark regarding the maximum kinetic chain length in the absence of any other factors limiting chain growth appears in order. In this case the rate for monomer addition should be constant throughout the chain growing process and the chain length should simply be $n = k\tau$ repeat units. Assuming $k \approx k_A = 10^6$ s$^{-1}$ and $\tau \approx 10^{-3}$ s gives $n \approx 1000$ as an order of magnitude estimate. It agrees with the average chain length measured with TS-12 86) as well as 3-BCMU and 4-BCMU 84).

On the other hand, anticipation of a lifetime in the order 1 ms is at variance with the observation made in course of photoacoustic experiments that the photoreaction is accomplished within $10^{-6}$ s 98). Clearly, additional time resolved studies are required to clarify this problem.

5.2 Pressure Studies

The motivation for conducting high pressure studies on the polymerization of TS was the desire to decide whether or not the probability for initiating a polymer chain depends on the distance of the monomers forming the dimer. Remember that the elastic strain theory predicts strain to affect both chain propagation and chain initiation in the same manner. If reduction of the average lattice distance along $\overrightarrow{b}$ accompanying the autocatalytic reaction enhancement in TS were to increase the chain initiation rate, application of hydrostatic pressure should be similarly effective. In case that
chain initiation is accomplished by photons, the relative number of chain-initiators is amenable to experimental probing by time resolved absorption spectroscopy.

The experiments were similar to those of Niederwald and Schwoerer\textsuperscript{67}, except that the crystal was mounted in a high pressure cell operated with water as pressure transmitting medium and that measurements were done at ambient temperature only\textsuperscript{72}. Figure 14 shows a series of absorption transients associated with intermediate B

(see Sect. 5.1), which is the diradical trimer, recorded at variable pressure after a single UV-pulse. Each curve was taken with a new crystal. It is obvious, that both rise and decay of intermediate B become faster with increasing pressure. This implies that within the accuracy of the experiment the rate constants $K_A$ and $K_B$ are similarly affected by pressure and their relative variation can be inferred from the pressure shift of the peak of the transient absorption signal. Figure 15 reveals an exponential increase of $K$ with pressure, $K(p) = K_0 \exp(p/p_0)$ with $p_0 = 2.8 \pm 0.2$ kbar. Despite a large scatter in absolute values, inevitably caused by changing samples in each experiment, no pressure induced increase of the signal amplitude, as a measure of the number of trimeric diradicals, is noted. This provides experimental proof that pressure does not noticeably affect chain initiation but does aid chain propagation. By analogy, one has to conclude that the rate of thermal chain initiation is also independent of internal pressure, generated, for instance, by chains already present within a polymerizing matrix. This casts doubts on the applicability of the elastic strain theory to analyze polymerization kinetics of diacetylenes quantitatively.

In the following chapter a model will be presented that relates the velocity of the
reaction to the distance between the reacting centers. It is based on the fact that a chemical reaction, in course of which a covalent bond is formed, must depend on the overlap of the electronic wavefunction of the reacting species and, concomitantly, on their mutual distance $s$. Since in organic molecules wavefunction decay at large distances from the nuclei is exponential, the overlap factor must also be an exponential function of $s$. It will be shown that the effect of structure dependent variations on the overlap factor overrides the direct effect of the strain energy changes developing as a result of lattice mismatch between monomer and polymer.

6 Model Considerations

6.1 Chain Propagation

In a TS-6 monomer crystal the distance $s$ between the Cl and C4 carbon atoms of adjacent molecules is close to 3.6 Å. After formation of an oligomer $s$ is reduced to approximately 2.5 Å (see Fig. 16), still too large to allow instantaneous reaction as evidenced by appearance of an energy barrier of typically 0.25 eV controlling the reaction $n$-oligomer + monomer $\rightarrow$ (n+1)-oligomer. It is straightforward to associate this activation energy with the excitation of librational motion of the diacetylene moiety. In its course the reaction distance is temporarily reduced to a value $s_m$ characteristic of the maximum in an energy versus reaction coordinate-diagram.

The barrier height for the reaction to proceed can be expanded into a power series on $s - s_0$. Truncation at the linear term gives $E = \frac{\delta \Delta E}{\delta s}(s - s_0)$. Support for the applicability of the linear approximation comes from the data of Ref. 67). They show that the activation energy for adding a monomer to the $i$-th oligomer rises linearly with $i$. Conversion of intermediate V into the final polymer product requires an activation energy $\Delta E_V = 0.4 \pm 0.03$ eV. Since this reaction shows a more complicated

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Fig. 15. Pressure dependence of the normalized rate constant for formation and decay of reaction intermediate B. Open and full circles refer to different series of experiments (from Ref. 72).

time behavior, it cannot a priori be identified with monomer addition to an oligomer having a length characteristic of TS-6 in the $X \to 0$ limit, which is about 18 repeat units (see above). Therefore the above value represents an upper limit for the activation energy governing the addition reaction before chain termination. Since, on the other hand, the $\Delta E$-data obtained for short oligomers tend to extrapolate to 0.4 eV at $n = 18$, one can to first order approximation identify this value with the final monomer addition step. It follows that in the low conversion limit the increase of the activation energy $\delta \Delta E$ per addition reaction is

$$\frac{\delta \Delta E}{\delta n} = (9 \pm 2) \cdot 10^{-3} \text{ eV}$$

(see Fig. 13).

The increase of $\Delta E$ with chain length must originate from the difference between the monomer lattice constant and the length of oligomer/polymer repeat unit. Anticipating proportionality between $\delta \Delta E/\delta n$ and lattice mismatch as suggested by studies under pressure (see 5.2), the variation of $\Delta E$ with $n$ can be calculated for arbitrary conversion $X$ from the low conversion value ($\delta \Delta E/\delta n)_{X=0}$:

$$\frac{\delta \Delta E(X)}{\delta n} = \left( \frac{\delta \Delta E}{\delta n} \right)_{X=0} \frac{b(X) - b_p}{b_m - b_p} \quad (7)$$

Here $b_m$ and $b_p$ are the lattice constants of monomer along $\overrightarrow{b}$ and the length of the oligomer/polymer repeat unit, respectively, and $b(X)$ is the average $b$-axis dimension at arbitrary conversion $X$.

Eq. (7) can be used to calculate the number of repeat units $n$ contained in the polymer as a function of conversion. In the low conversion range, $n$ is given by the number of addition steps occurring per lifetime $\tau$ of the reacting chain end, $\tau = \sum_{i=1}^{n} k_i^{-1}$. 
The rate constant for the i-th reaction step, $k_i$, depends upon $i$ according to:

$$k_i = k_0 \exp\left[-\frac{\Delta E_i + \frac{\delta \Delta E}{\delta n}}{kT} i\right] = k_1 \left[\exp\left(-\frac{\delta \Delta E}{\delta nkT} i\right)\right]$$  \hspace{1cm} (8)

After replacing $i$ by the continuous variable $n$ and converting $\sum_{i=1}^{n} k_i^{-1}$ into an integral, Eq. (8) yields:

$$n(X) \approx \left[\frac{\delta \Delta E(X)}{kT \delta n}\right]^{-1} \ln \left[\tau k_1 \frac{\delta \Delta E(X)}{kT \delta n}\right]$$  \hspace{1cm} (9)

Inserting experimental data for $(b(X) - b_p)/(b_m - b_p)$ from Fig. 7, $(\delta \Delta E/\delta n)_{X=0} = 9 \cdot 10^{-3}$ eV (see above), $k_1 = 10^6$ s$^{-1}$, and $\tau = 7.3 \cdot 10^{-4}$ s at 295 K \cite{67} allows calculating absolute numbers for $n(X)$. Note that no adjustable parameter enters. Figure 4, which shows the result of the calculation, demonstrates that Eq. (9) provides an excellent fit to the experimental data of Albouy et al. \cite{79}. This documents that chain propagation in TS can be consistently interpreted by taking into account the variation of the reaction rate constant with reaction distance.

Unfortunately, the above data relating activation energy $\Delta E_i$ to the number of addition events are insufficient for constructing the energy profile of the reaction as a function of reaction distance $s$. This is because both oligomers and polymers formed under low conversion conditions are not in their relaxed state but are expanded as evidenced by their blue-shifted absorption. Although an average value for the lattice parameter along $\bar{b}$ will be established there will be mismatch on a molecular level accounting for the increase of $\Delta E$ discussed above. Therefore, absolute reaction distances are not available at a level of accuracy required to render an estimate of the energy profile meaningful. The missing information can, however, be extracted from the pressure effect on the reaction constant.

As mentioned above, the rate constant for generation and decay of intermediate B varies under pressure as $k(\Delta p) = k_0 \exp(\Delta p/p_0)$ with $p_0 = 2.8 \pm 0.2$ kbar at 295 K. Since the reaction is thermally activated, the pressure effect must be due to a reduction of the activation energy. Comparing exponents gives:

$$\Delta p/p_0 = -\delta \Delta E/kT$$  \hspace{1cm} (10)

On the other hand, the pressure-induced change in the reaction distance $s$ is:

$$\Delta s = s \chi_s \Delta p$$  \hspace{1cm} (11)

where $\chi_s$ is the compressibility along the lattice vector joining the C1 and C4 positions of the reacting molecules. A reasonable estimate of $\chi_s$ can be inferred from the linear compressibility $\chi_b$ of the monomer lattice, known to be $\chi_b = 4.2 \cdot 10^{-3}$ kbar$^{-1}$ \cite{96}. Because in the monomer lattice the diacetylene moiety is at an angle of 45° with respect to $\bar{b}$ (see Fig. 16) the torque felt by the $-\text{C} = \text{C} - \text{C} = \text{C} -$ unit upon applying hydrostatic pressure is likely to cancel out and the lattice compression along $\bar{b}$ will fully be converted into a reduction of the molecular center of mass distances. From
geometrical consideration \( \chi_s = 6 \cdot 10^{-3} \text{kbar}^{-1} \) and, since \( s \approx 2.5 \text{Å} \), \( \Delta s = 1.5 \times 10^{-2} \text{kbar}^{-1} \Delta p \text{Å} \) follows. Inserting this value into Eqs. (10) and (11) predicts \( \delta \Delta E/\delta s = 0.6 \text{eV/Å} \) for the slope of the energy barrier in the range where it is linear with reaction distance. This information allows to estimate the location of the maximum of the potential barrier in an \( E(s) \)-diagram. To attach a monomer to intermediate B requires an activation energy \( \Delta E_B = 0.25 \text{eV} \) at an initial reaction distance \( s_B \approx 2.5 \text{Å} \). To reduce \( \Delta E_B \) to zero requires a reduction of \( s \) by 0.4 Å to \( s_m \approx 2.1 \text{Å} \). In order to be able to react with the active end of an oligomer an adjacent monomer has therefore to execute a thermally activated torsional motion with an amplitude allowing approach of the C1 and C4 carbon atoms to \( s_m \approx 2.1 \text{Å} \).

To a first order approximation the energy profile of the reaction must be the superposition of the vibrational energy of the monomer as a function of vibration amplitude and the electronic binding energy of the reaction product as a function of bond-distances. To be realistic it must be in accord with the following experimental data: (i) \( E(s = s_m) - E(s_0 = 3.6 \text{Å}) \leq 1.0 \text{eV} \) which is the energy required to initiate a chain, (ii) \( E(s = s_m) - E(s = 2.5 \text{Å}) = 0.25 \text{eV} \), (iii) \( \delta \Delta E/\delta s \approx 0.6 \text{eV/Å} \), and (iv) \( E(s = 2.5 \text{Å}) - E(s = 1.4 \text{Å}) = 1.6 \text{eV} \) which is the amount of energy released upon addition of one monomer unit. Figure 17 shows an energy diagram which matches the above conditions. It is constructed from a vibrational potential in harmonic approximation \( V_v(s - s_0) = V_0 + \frac{1}{2}k(s - s_0)^2 \) with \( s_0 = 3.6 \text{Å} \) and a

![Figure 17](image-url)

**Fig. 17.** Energy profile for polymerization of diacetylenes. Numerical data are for TS-6. --- : harmonic potential \( V \) for librational motion of the diacetylene moiety. ---- : electronic binding energy \( E_d \); the full curve is the sum of \( E_d \) and \( V \). The origin of the energy scale (left ordinate) is chosen so that \( E_d(s \to \infty) = 0 \). The right ordinate gives the activation energy required for a monomer addition reaction as a function of reaction distance \( s \). A and V stand for reaction intermediate A (dimer) and V (precursor to stable polymer), respectively.
force constant $k = 0.72 \text{ eV/Å}$ equivalent to $23 \text{ N/m}$ and an electronic binding energy $E_B = E_B(s \to 0) - \beta \exp (\alpha s)$ with the parameters $\beta = 177 \text{ eV}$ and $\alpha = 2.68 \text{ Å}^{-1}$. The same value for $\alpha$ has been used previously to approximate the distance dependence of the overlap integral for carbon-carbon bonds in diacetylenes\textsuperscript{105}. The force constant turns out to be about two orders of magnitude smaller than force constants characteristic for double bond stretching modes. This is in accord with the finding that it is a low frequency ($\approx 30 \text{ cm}^{-1}$) librational motion of the diacetylene moiety which drives the reaction\textsuperscript{67}. The $E(s)$-profile exhibits a linear regime over a wide range of $s$-values explaining why (i) the thermal activation energy of the addition reaction is a linear function of the relative lattice mismatch and (ii) the rate constant varies exponentially with pressure. Contrary to conventional energy diagrams where the potential energy is plotted versus a generalized reaction coordinate, $E(s)$ gives the energy required by a monomer molecule to react with one of its neighbors as a function of only the $\text{C}_1$–$\text{C}_4$ reaction distance.

The above treatment for calculating $n(X)$ is readily extended to cover the whole conversion range. To facilitate comparison with the prediction of the elastic strain theory the result of the calculation has been included in Fig. 8. It is obvious that $n(X)$ rises more slowly with increasing conversion than predicted by the ES-theory. Following the principle that it is the slowest process that dominates a reaction, it is concluded, that growth of a polydiacetylene chain is essentially governed by the reaction barrier resulting from a superposition of the vibrational potential and the electronic overlap of the reacting molecules. The effect of the elastic strain is to establish the equilibrium reaction distance entering the expression for the activation energy. It does not appear to control chain growth in a direct way. This explains why often difficulties are encountered when reaction kinetics are analyzed in terms of the ES-theory\textsuperscript{95}.

At this stage it seems appropriate to comment on the principle of least motion introduced by Baughman\textsuperscript{9} in order to establish criteria for the reactivity of diacetylenes. It says that a reaction will only take place if the root mean square displacement of the atoms does not exceed a certain critical value. This means that each displacement is counted at equal weight. The dominant effect a reduction of the $\text{C}_1$–$\text{C}_4$ distance has on the reaction rate is, therefore, ignored. On the other hand, it should be pointed out that the treatment advanced above, which relies on the dominant role of the $\text{C}_1$–$\text{C}_4$ reaction distance, does embody all atomic displacements, although in an implicit way via the vibrational energy which essentially determines the energy profile for the reaction, and which depends on the structure of the reactants.

### 6.2 Chain Initiation

The energy diagram presented in Fig. 17 is of relevance for the chain initiation process as well. It demonstrates that the $1 \text{ eV}$ barrier for chain initiation is determined by the activation energy of the reaction rather than the energy difference between dimer and monomer. Since the reaction requires reduction of the reaction distance from $3.6 \text{ Å}$ to $\sim 2 \text{ Å}$, both reacting monomers have to execute torsional motions. Otherwise the diacetylene moiety of one monomer had to be rotated by about $45^\circ$ into a position parallel to the crystallographic $b$-axis. This is incompatible with steric constraints
and explains the observation of Neumann and Sixl \cite{16} that at low temperature, where librational motion is frozen-in, photoinitiation is a two quantum process. In this case the motional energy of both monomers has to be supplied externally. Further, the parabolic shape of the potential profile near the monomer equilibrium distance indicates that lattice compression either by applying hydrostatic pressure or by polymer chains already formed, will not reduce the activation energy to any measurable extent. This resolves the paradox encountered when applying the elastic strain theory to explain both autocatalytic and pressure-induced reaction acceleration. Remember that this theory predicts a lowering of the energy barrier both for chain propagation and chain initiation, quite in contrast to all experimental reports.

It is tempting to speculate on the possibility that optical and thermal chain initiation occur via basically the same mechanism, the only difference being the way of accumulating the activation energy at the reacting pair of molecules. However, this hypothesis is readily discarded by comparing the preexponential factors for thermal chain initiation and chain propagation, respectively. Whereas, for the latter process \( k_0 = 10^{11 \pm 1} \text{ s}^{-1} \) has been reported \cite{67}, it is about four orders of magnitude lower for the former \cite{97}. Since in both cases the excess energy is supplied thermally, no significant changes in the partition function entering the equilibrium constant of the transition state are expected to occur. It therefore appears that once it has reached the top of the potential barrier a pair of monomers has a \( 10^4 \)-fold higher chance to react if one of the pair partners has been optically excited. The most likely explanation is that either orbital symmetry or spatial extent of the wavefunction are more favorable for reaction while the monomer is in an excited state.

There has been discussion in the literature \cite{53} as to whether the optically excited monomer precursor state for the dimer is of singlet or triplet character. Consider that the diacetylene \( S_{1\text{D}} \)-state undergoes intersystem crossing to the triplet manifold at a yield \( q_{\text{ISC}} \). Following Chance and Patel \cite{53} the total probability for chain initiation after excitation of the \( S_{1\text{D}} \)-state by an UV-quantum can then be written as the sum of a singlet and a triplet term, \( q^{UV} = q^S + q_{\text{ISC}}q^T \) where \( q^S \) and \( q^T \) are the chain initiation probabilities for a monomer in its singlet and triplet state, respectively. If, on the other hand, the reaction is initiated by \( \gamma \)-irradiation, the primary yield, expressed in terms of the G value (number of products per 100 eV absorbed energy), is \( G = G^S q^S + G^T q^T \) where \( G^S \) and \( G^T \) are the primary singlet and triplet yields, respectively. From the organic scintillator literature it is known \cite{106} that \( G^S \approx G^T \approx 1 \).

Experimentally one finds \cite{53}, that in TS-6 about 40 monomers are polymerized per 100 eV absorbed energy, i.e., \( G \approx 2 \) assuming a chain length of 20 repeat units. In TS-12 the G-value for chain initiation is \( 1.2 \) \cite{88}. It thus follows that \( q^S + q^T \approx 1 \). Since \( q^S < q^{UV} \approx 0.005 \), \( q^T \) must be of order unity. This estimate lends support for assigning triplet character to the optical precursor state for chain initiation and for claiming that dimer formation is the dominant channel for decay of the monomer triplet state.

Albeit direct experimental evidence for polymerization upon direct optical excitation into the triplet manifold of a diacetylene is still lacking several arguments support the above reasoning.

(i) Steric arguments require that electronic excitation of the diacetylene moiety has to be accompanied by vibrational excitation in order to promote dimer
formation. Otherwise the C1–C4 distance would be prohibitively large. This condition is met if the active state is populated via a nonradiative transition from a higher excited state. UV-photopolymerization of TS is normally done by $h\nu > 4\text{ eV}$ excitation. Since the lowest triplet state of diacetylene is located at 3.1 eV \cite{107}, about 1 eV of excess energy is available for conversion into vibrational excitation. The above estimate requires that the yield for populating the active triplet state by intersystem crossing be $q_{\text{ISC}}^{\text{eff}} \sim 4 \cdot 10^{-3}$, considerably less than expected for $S_1 \rightarrow T$ conversion across an energy gap of $< 1\text{ eV}$. From spectroscopic work it follows that in this case $q_{\text{ISC}} \geq 0.1$ \cite{108}. The ratio $q_{\text{ISC}}^{\text{eff}}/q_{\text{ISC}} \sim 0.04$ could be interpreted as the probability for funnelling the excess energy into the active librational modes. An independent indication for the importance of vibrational energy in addition to electronic excitation is the increase of the quantum yield $n_q$ with photon energy (see Fig. 3 in Sect. 2).

(ii) ESR work indicated that the carbene-type as well as the diradical intermediates have triplet character. The long lifetime $\tau$ of the active chain end, typically 1 ms, is likely to originate from a slow triplet-singlet intersystem crossing process. Since all rate constants for formation of short oligomeric species including the diradical dimer are $\gg \tau^{-1}$, typically $10^6\text{s}^{-1}$, intersystem crossing processes cannot be involved in these processes. This suggests that the optical precursor state for the dimer has already triplet character. In fact, Gross et al. \cite{17} demonstrated that kinetic data for TS-6 can consistently be interpreted if the diradical dimer is assumed to be produced via a vibrationally hot triplet state of the monomer. On the basis of time-resolved studies its lifetime is estimated to be 50 to 100 ns \cite{101} and is likely to be reaction-limited (see above).

(iii) The small preexponential factor for thermal chain initiation, could reflect the low probability for $S \rightarrow T$ conversion in course of dimer formation involving thermal excitation of a pair of monomers in their singlet ground state.

In this context it seems noteworthy that $n_q$ is about four orders of magnitude smaller for DCH \cite{109} as compared to TS-6. Since contrary to TS, in DCH both singlet and triplet levels of the carbazole substituent ($E_{S1} = 3.4\text{ eV}, E_{T1} = 2.9\text{ eV}$ \cite{110}) are below the corresponding levels of the diacetylene linkage, excitations of the latter are efficiently quenched. Therefore, UV-photopolymerization of DCH must in fact occur at a much lower yield, independent of whether the precursor state is of singlet or triplet character. Surprisingly, the G-value for $\gamma$-polymerization is only about one order of magnitude less as compared to TS \cite{109}. This could be an indication that, in addition to the triplet route, charge carriers, which are produced by $\gamma$-irradiation yet not by UV-excitations, also act as chain initiating species. Support for this notion comes from the experiments on self-sensitized and sensitized photopolymerization to be discussed in Section 8, which also draw heavily on the role of charge carriers.

In summary, it is well established that the species that initiates exothermic growth of a polydiacetylene chain is a diradical dimer. It can be generated thermally, the activation energy being determined by the energy of the librational motion required to temporarily shorten the C1–C4 reaction distance of a molecular pair to about 2 Å, or by electronic excitation of the diacetylene moiety via UV- or $\gamma$-irradiation. Upon UV-excitation the number of chains initiated is of order $10^{-2}$ per absorbed photon. The active precursor state is likely to be of triplet character. Even in case of optical
generation librational excitation of the reacting molecules is required to cross over
the potential barrier. Chain growth proceeds via consecutive first order 1,4-addition
reactions each coupling one diacetylene monomer to a reactive intermediate. In the
early stages of the reaction this intermediate is a diradical oligomer. It is converted
to a dicarbene or an asymmetric carbene as the oligomer length increases beyond
5 units. The addition reaction is a thermally activated non-photochemical process.
Its activation energy, typically 0.3 eV, is a linear function of the C1–C4 separation.
If the length of the repeat unit of oligomer/polymer is shorter than the monomer
lattice constant along $\overline{b}$, the activation energy increases with growing chain length.
In this case the reaction rate can be enhanced by polymer chains already present and
acting as springs to compress the structure of the reaction matrix thereby giving
rise to autocatalytic reaction enhancement. On the basis of existing experimental
data a diagram relating activation energy and reaction distance can be constructed
for the reaction of TS-6. In essence it is the superposition of a harmonic vibrational
potential and an electronic coupling energy and can be used to calculate the kinetic
chain length. The result is in remarkably good agreement with the experimental values
obtained in the low conversion limit ($X < 0.1, n \approx 18$ to 35 repeat units). In cases
where lattice mismatch is unimportant, i.e., within the autocatalytic reaction regime
or in materials where monomer and polymer are almost in register, the maximum
kinetic chain length $n_{\infty}$ is either limited by the length of a row of monomers confined
between the dead ends of previously formed chains or the number of addition events
occurring per lifetime of the reactive chain end. For 4-BCMU and TS-12, $n_{\infty}$ is of
order 2000. Several estimates indicate that in TS-6 the limiting chain length does not
exceed a few hundred repeat units.

7 Secondary Chain Initiation in TS-6

Reaction-independent chain initiation as well as reaction-driven increase of the chain
length by not more than one order of magnitude are incompatible with the experi-
mental observation of a 200-fold increase of the total reaction rate (see section 2)
in the autocatalytic reaction regime in TS. The discrepancy appears to be even more
dramatic if photopolymerization is carried out under hydrostatic pressure. Upon
UV-irradiation of the (1 0 0) area of TS-6 and TS-12 crystals through a silver coated
mica mesh containing radiochemically fabricated rhombic holes of 10 μm edge
length Braunschweig and Bässler 111) observed polymer growth into unirradiated
crystal zones. It was found that the size of the polymerized area increases upon
applying hydrostatic pressure. Interestingly, the effect turned out to be almost isotropic
within the (1 0 0) plane (see Fig. 18). At $p \approx 4$ kbar the whole crystal surface became
polymerized. Taking into account the area density of irradiation spots ($\sim 7 \cdot 10^3$ cm$^{-2}$)
the individual polymerization zones must ultimately reach a diameter of about
60 μm. This is equivalent to chain growth across about 25 μm into unirradiated
crystal areas, in apparent disagreement with both the single chain concept and the
commonly accepted view that chains grow only along [0 1 0].

To resolve the paradox, it has been postulated 111) that a growing chain is able
to initiate secondary chains in its neighborhood by virtue of the energy of 1.6 eV
released by the monomer addition reaction. For steric reasons it appears conceivable that the librational motion involved in this reaction couples to the motion of unreacted monomers in an adjacent stack of molecules. This concept can explain (i) why more monomer molecules are consumed per primary chain initiation event than comprised within an individual chain and (ii) why the polymerization zone also grows in a direction perpendicular to the chain. Because of the strong pressure dependence of the rate of the individual reaction step, the effect of secondary chain initiation must also be subject to enhancement by pressure in accord with the experimental result.

In principle, the concept of secondary chain growth is in conflict with the commonly accepted notion that polymer growth inside the reacting matrix is a random process not involving any nucleation effects. However, a recent estimate indicates that in practice this contradiction does not exist. Analyzing thermal conversion data, Braunschweig and Bässler concluded that the probability for initiating a new chain per monomer addition reaction is of order $10^{-2}$. Therefore, the probability that in the low conversion regime of TS-6, where $n < 30$, a secondary chain is created next to promoter chain is only 0.3. The situation changes not until the high conversion regime is reached. Here, the concept of independent chain growth becomes irrelevant, since a new chain will practically always be generated in the vicinity of an existing chain.
8 Photopolymerization of Multilayer Systems

8.1 Undoped Systems

Polymerization of diacetylenes is a lattice controlled topochemical reaction. Although guaranteeing well-ordered reaction products this fact imposes serious restrictions regarding chemical tailoring for optimizing product properties. It would, for instance, be highly desirable to prepare samples that combine the unique charge transport properties of crystalline polydiacetylenes with the large conductivity of doped polymers like polyacetylene or other conjugated systems. Since the bandgap of a neat PDA chain is close to 2.5 eV, this would either require doping by electron donors or acceptors, or, preferentially, introduction of substituents that undergo efficient charge transfer with the polymer chain either in the dark or after optical excitation. Except DCH which shows weak charge transfer from the carbazole group to the chain after optical excitation none of such systems has been prepared so far, mainly because the structural modifications introduced in the monomer lattice turn out to be prohibitive for future reaction.

A major achievement towards greater flexibility with respect to structural constraints of the reaction is the discovery of polymerization in Langmuir-Blodgett (LB)-films made by Wegner and coworkers. These systems also allow introducing dye molecules acting as sensitizers for the polymerization reaction.

The LB-technique of growing mono- or multi-molecular layers is widely known and shall not be repeated here. In general, the ability to form monolayer assemblies requires that the active molecules carry a hydrophilic head group, typically $-(CH_2)_n COOH$, and a long hydrophobic tail, normally an n-paraffine chain, $-(CH_2)_m$. A list of substituted diacetylenes synthetized by Tieke et al. with the aim of producing LB-films is presented in Table 2. It contains information regarding formation of mono- and multilayers and their ability to polymerize upon exposure to UV-irradiation. Polymerization is detected by appearance of the polymer spectrum. Figure 19 shows absorption spectra recorded after irradiation of compound 3 for various exposure times. As polymerized films appear blue, i.e., they absorb in the red like most crystalline diacetylenes do. After treatment with ethanol or chloroform or by sample annealing at 90 °C, the absorption spectrum is blue-shifted irreversibly and the layer appears red. The color change is believed to result from a phase transition involving reorganization within the side groups in course of which the grain size of the layer structure is reduced by one order of magnitude. This effect shall not be considered further.

Comparison of the monomer-absorption spectrum and the photoaction spectrum for polymerization demonstrates that it is excitation of the diacetylene moiety which drives the photoreaction, in analogy to what is known from single crystal work. Upon varying the number of layers in a multilayer assembly a strictly linear relationship between optical density obtained in the saturation limit and layer thickness is observed. This documents that the multilayer structure is preserved in course of the polymerization process. Assuming quantitative conversion an optical density $OD = 4.56 \cdot 10^{-3}$ per monolayer corresponding to an absorption coefficient $\alpha = 1.61 \cdot 10^4 \text{ cm}^{-1}$ is calculated for the red form absorbing at 500 nm. Existence of the layer structure is further verified by small-angle X-ray scattering. Although
Table 2. Spreading and polymerization behavior of long-chain-diacylenes with ability to form monomolecular films

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ability to form monomolecular films</th>
<th>Multilayer formation</th>
<th>Photopolymerization*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R--C≡C--C≡C--R'</td>
<td>On H₂O</td>
<td>On 10⁻³ M CdCl₂-sol</td>
</tr>
<tr>
<td>1</td>
<td>n--C₉H₁₉ -- (CH₂)₆--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>n--C₁₀H₂₁ -- (CH₂)₈--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>n--C₁₂H₂₅ -- (CH₂)₆--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>n--C₁₄H₂₉ -- (CH₂)₄--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>n--C₁₂H₂₅ -- (CH₂)₃--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>n--C₁₆H₃₃ -- (CH₂)₂--COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>n--C₁₆H₃₃ -- COOH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>n--C₁₃H₂₅ -- COOH</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>n--C₁₀H₂₁ -- (CH₂)₉--OH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* ++ ++ : Dark blue in less than 10 sec; ++ : dark blue in 10–30 sec; + : dark red after exposure >2 min; – : no reaction;

b 5 has two modifications with different reactivity
free of holes, the sample is assumed to consist of domains with random orientation within the substrate plane. The domain size is estimated to be within the order of microns.

At low conversion the polymerization yield $n_q$ ranges between 5 and $10^{127}$. Anticipating the primary quantum efficiency $q$ to be similar to that in crystalline TS-6, i.e., $q \sim 10^{-2}$, a chain length of order 1000 repeat units would result. No autocatalytic reaction enhancement is observed. It appears that both the high degree of flexibility of the substituents and the way the molecule pack within the multilayer assembly provide sufficient motional freedom to accommodate strain developing in course of the reaction.
In course of subsequent work Bubeck, Tieke, and Wegner \cite{128} discovered that the action spectrum for photopolymerization of undoped diacetylene multilayers extends into the visible provided some polymer formed in course of previous UV-irradiation is present. Since obviously excitation of the polymer can sensitize the reaction this effect has been termed self-sensitization. Checking the absorption spectrum of the polymer produced via self-sensitization assured that the final product is identical with the product obtained under UV excitation of the monomer. Later work by Braunschweig and Bässler \cite{111} demonstrated, that the effect is not confined to multilayer systems but is also present in partially polymerized single crystalline TS-6, albeit with lower efficiency. Interestingly, the action spectrum of self-sensitization follows the action spectrum for excitation of an electron from the valence band of the polymer backbone to the conduction band \cite{117} rather than the excitonic absorption spectrum of the polymer which is the dominant spectral feature in the visible (see Fig. 21). The quantum yield is independent of the electric field, whereas in a one-dimensional system the yield of free carriers, determined by thermal dissociation of optically produced, weakly bound geminate electron-hole pairs, is an linear function of an applied electric field \cite{29,30,32,129}. Apparently, the sensitizing action does not

![Figure 21](image)

**Fig. 21.** a. Action spectra for photopolymerization of neat (triangles) and partially polymerized (circles) multilayer systems. ΔOD is the change in optical density at a given irradiation dose; b Action spectrum of intrinsic photoconductivity of a fully polymerized multilayer assembly \cite{117} from Ref. \cite{128}
require free carriers but can be brought about by electron-hole pairs which are likely to have a high mobility along the conjugated chain \(^{130,131}\).

The diacetylene monomer provides no energy states below 3.1 eV that could be populated via a sensitizer whose excitation is only 2.5 eV. Since its highest filled and lowest empty molecular level lie below and above the corresponding polymer levels, respectively, charge transfer from polymer to monomer is excluded as well. If, on the other hand, sensitization were due to secondary chain initiation involving local heating in course of a non-radiation transition, excitation of the polymer exciton state — known to decay non-radiatively — should be similarly effective, contrary to what is observed. The obvious conclusion is that self-sensitization reactivates dead ends of preformed polymer chains for further growth rather than generates new chains (see Fig. 22). Participation of charge carriers indicates that the essential process

![Diagram](image)

**Fig. 22.** Self-sensitization mechanism proposed by Bubeck et al.\(^{128}\)

is an electronic rearrangement at the polymer head, whose structure has been suggested to be of the cyclopropene type \(^{15}\). It is conceivable that temporary lowering of the electron density by putting a positive charge of a coulombically electron-hole pair to the chain end breaks up the C1–C3 carbon bond and restores the carbene structure according to the scheme:

![Scheme](image)
8.2 Doped Systems

Because of the dramatic change in color as well as mechanical stability upon polymerization diacetylenes appear to be attractive materials for image technology and information storage. A serious constraint regarding device construction is the high photon energy required to initiate photopolymerization. To overcome this difficulty there was an intense effort for finding appropriate sensitizers that could shift the photoresponse spectrum into the visible. The first material of this sort was a mixed crystal composed of amphiphilic diacetylene monocarbonic acids and phenazine. Tieke and Wegner found that the 2:1 complex of 2,4-heptadecadiynoic acid and phenazine (HD-Ph) polymerizes upon irradiating into the phenazine first singlet absorption band near 400 nm (Fig. 23). Later on Tieke and Bloor observed that nonadeca — as well as heneicosa 2,4-diynoic acid — phenazine complexes behave similarly. Monitoring resonant Raman spectra and X-ray diffraction pattern during the reaction allowed elucidating the molecular reorganization processes accompanying the reaction. Braunschweig and Bäsßler investigated the reaction kinetics following build-up of the polymer absorption as a function of irradiation time and concluded on the active role played by the phenazine singlet state. The quantum yield (nq) turned out to be 0.5 for direct excitation of the diacetylene moiety (280 nm) and 0.1 for phenazine excitation (420 nm). On the basis of ESR-studies Bubeck et al. have meanwhile established that the reaction is triggered by charge transfer from diacetylene to the excited phenazine.

The range of potential sensitizers for photopolymerization of diacetylenes widened considerably when Wegner and coworkers discovered sensitized photopolymerization in LB-multilayer systems doped with certain dyes. It is known for long that dye molecules carrying long aliphatic substituents can easily be incorporated into LB-multilayer assemblies without destroying the sample architecture. Therefore, the topotactic requirements for the polymerization reaction to proceed are retained.

Fig. 23. Reflexion spectra of the 2:1 complex of 2,4 heptadecadiynoic acid and phenazine before (a), and after sample irradiation at 410 nm for 5 min (b), 10 min (c) and 20 min (d). Spectrum e was obtained after sample annealing at 90 °C. f is the action spectrum for photopolymerization at λ > 300 nm in arbitrary units (from Ref. 132)
Table 3. List of dyes used as sensitizers for photopolymerization of diacetylene multilayer assemblies. 
(R: $-(CH_2)_n-CH_3$; the counterion was $I^-$) and their absorption maxima.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\lambda_{\text{max}}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure I" /></td>
<td>408</td>
</tr>
<tr>
<td><img src="image2" alt="Structure II" /></td>
<td>430</td>
</tr>
<tr>
<td><img src="image3" alt="Structure III" /></td>
<td>498</td>
</tr>
<tr>
<td><img src="image4" alt="Structure IV" /></td>
<td>572</td>
</tr>
<tr>
<td><img src="image5" alt="Structure V" /></td>
<td>586</td>
</tr>
</tbody>
</table>

Fig. 24. Structural model of monomeric and polymeric multilayer assemblies doped with cyanine dyes. The black bars represent the polydiacetylene $\pi$-bond system (from Ref. 135).
Table 3 presents a list of molecules used by Bubeck et al.\textsuperscript{135} to sensitize polymerization of amphiphilic diacetylene multilayers. A model of the layer architecture is shown in Fig. 24. Upon excitation into the absorption band of the chromophore the absorption spectrum characteristic of the polymer gradually develops and concomitantly the dye fluorescence becomes quenched (Fig. 25). The final product is identical with the product obtained upon UV-excitation of the diacetylene. Although sensitization occurs with a low quantum efficiency — 1400 ± 900 photons have to be absorbed by a dye molecule to convert one monomeric diacetylene molecule into a polymer unit — its yield $Y$ expressed in total number of monomers converted to polymer per dye molecule is large. Since a sample containing only $2 \cdot 10^{-4}$ mole/mole dye molecules is fully polymerized after prolonged pumping of the singlet transition of the sensitizer, $Y$ must be $>5000$ monomers per sensitizer molecule. Since on the other hand, the total chain length is undoubtedly less than 5000 repeat units, one dye molecule must be capable of sensitizing repeatedly. This is incompatible with any irreversible changes of the dye and demonstrates that sensitization is a purely electronic phenomenon. Since its yield turns out to be highest in the low conversion limit, it must be a chain initiation rather than a chain propagation phenomenon and as such be principally different from the effect of self-sensitization described in section 8.1.

![Graph](image-url)

*Fig. 25. a: Absorption spectra of a multilayer assembly consisting of 40 monolayers doped with 1 mol.-% of dye III of table 3. Parameter is the irradiation time ($\lambda = 574.5$ nm). 1: neat layer, the absorption spectrum is that of the dye, 2: 2 s, 3: 20 s, 4: 1.5 min, 5: 4.5 min, 6: 12 min, 7: 24 min; b Action spectrum of sensitized photopolymerization (from Ref.\textsuperscript{135})*
The low excitation energy of the sensitizer as compared to the diacetylene monomer rules out energy transfer to be the rate determining step for chain initiation. Instead, either charge transfer from sensitizer to diacetylene or transfer of vibronic energy released at the sensitizer as a result of non-radiative deactivation have to be invoked. The second alternative can be discarded since Bubeck et al. found no systematic difference on the sensitizing efficiency of fluorescent and nonfluorescent dyes. Therefore, one has to postulate a charge transfer mechanism as the rate determining step for promoting sensitized chain initiation.

Sensitization by charge transfer requires that the LUMO of the diacetylene monomer be below the excited singlet level of the dye. The latter is at $I_s - E_{S1}$ where $I_s$ and $E_{S1}$ are ionization potential and energy of the first singlet state of the dye, respectively. On the basis of polarographic data $I_s - E_{S1} \sim -2.7 \ldots -3.3 \text{ eV}$ is estimated for cyanine dyes. The lowest unoccupied orbital of a previously neutral diacetylene molecule is at $A + P^-$. Since in course of a CT-process a coulombically bound electron-hole pair is generated at a pair of adjacent molecules a coulombic binding energy $E_{coul}$ of order $-1 \text{ eV}$ has to be considered in the energy balance. In view of the uncertainty of these data one can safely conclude that the energetic condition for charge transfer from sensitizer to diacetylene to occur, $A + P^- + E_{coul} < I_s - E_{S1}$, is likely to be fulfilled for the dye molecules under consideration.

In summary, the results on sensitized photopolymerization of diacetylenes are of relevance for potential application and, in addition, augment understanding of the polymerization process in general. In conjunction with what is known about chain propagation and self-sensitization, they indicate that the basic requirements for both chain initiation and propagation are presence of an unpaired electron ― in form of either a radical or a charge carrier ― on the reactive center and excitation of a librational motion of the reactant(s) in course of which the reaction distance is temporarily reduced to a critical value.

9 Application

Polymerization of crystalline diacetylenes generates an ordered array of fully extended polymer chains with conjugated backbone. The increase of the extent of the $\pi$-electron system, initially confined to the diacetylene linkage, over many polymer repeat units causes a dramatic lowering of the excitation energy manifested in a shift of the optical absorption into the red. For this reason diacetylenes appear to be attractive materials to be used as active elements in devices for optical information storage or photolithography. The basic advantages as well as disadvantages faced upon such application are easily gleaned from the available data for photochemical yield and chain length. Since the primary quantum efficiency for chain initiation is of order $10^{-2}$, a total-gain $>1$ can only be achieved if the total number of reached monomers per photon is $>100$. This requires materials in which reaction is not impeded by mismatch between monomer and polymer lattices, such as 4-BCMU, where $n \approx 2400$ and $nq \sim 60$ at room temperature. Unfortunately, the reaction requires UV light.
of $\lambda \lesssim 330$ nm to get started. Use of sensitizers, for instance, dye molecules incorporated into multilayer assemblies, which extend the spectral range into the visible, do so at a drastic loss of efficiency. Therefore, diacetylenes do not appear to be suitable materials for imaging technology that requires large efficiencies. Nevertheless, their use as photographic receptors has been reported\textsuperscript{140}. On the other hand, the moderate length of the polymer product allows image recording at a spatial resolution far beyond the resolution of conventional receptor systems, relevant, e.g., in micro-lithography. In a neat TS crystal, for example, which, if carefully grown, containing less than 0.1 percent polymer, the length of a developing polymer chain is limited to about 100 Å. In this case it would be the spatial resolution of the writing beam rather than that of the receptor material that controls the resolution of the image. It seems attractive to speculate about the use of ultra narrow electron beams for writing-in image patterns which could subsequently be stabilized against undesired secondary polymerization by etching. Preliminary experiments in this laboratory have indicated that in this case it is the spread caused by electron diffusion within the monomer crystal which limits spatial resolution.

An interesting application of the high spatial resolution power associated with photopolymerization of diacetylenes is holographic image recording recently studied by Richter, Güttrler, and Schwoerer\textsuperscript{141,142}. These authors irradiated a high quality TS-6 single crystal with two interfering plane wave beams obtained from a frequency doubled Ar-laser ($\lambda = 257$ nm) by beam splitting (see Fig. 26). In the region of constructive interference the crystal surface polymerizes up to a depth of about 1 μm which is the penetration depth of 257 nm light in the monomer crystal. The interference pattern is a grating with equidistant lines, $\Lambda = \lambda/(2 \sin \theta)$ apart, where $\theta$ is the angle between the interfering beams. Variation of $\theta$ between 3° and 16° gave line distances between 5 and 0.9 μm. An example of a grating produced after 2 s recording time at an incident power of 60 mW and viewed under the transmission microscope in white light is shown in Fig. 27. Since under low conversion conditions

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**Fig. 26.** Experimental arrangement for recording and reactions of a plane wave hologram on the surface of a TS-crystal (from Ref. 141)
Fig. 27. Holographic grating on the surface of a TS crystal. Dark areas indicate polymerized TS (from Ref. 141).

the chain length in TS is of order 100 Å, the width of the polymerized lines is determined by the spatial extent of the regions of constructive interference between the recording beams. Depending upon the wavelength of the read-out light the recorded image acts as both a phase and amplitude grating. If read-out is done with a HeNe-laser operating at 633 nm where polymer absorption is weak the diffraction effect arising from the phase hologram prevails. Diffraction efficiencies, defined as the ratio of the first order diffraction intensity to the incident intensity of the analysing light up to 35 percent were observed at a exposure light dose of about 100 mJ/cm².

Holographic gratings produced in the above manner need not be processed after recording. However, a weak hologram can be developed by gentle annealing in the dark to increase its efficiency. In this case the autocatalytic enhancement of thermal polymerization in TS once the conversion has reached about 10 percent is utilized as a stimulus for further growth of the polymeric grating lines 142.

Another potential application of fully converted polydiacetylenes is based upon their unusual non-linear optical properties. Sauteret et al. 143 found that the third order susceptibilities of TCDU and TS increases by about a factor of 600 upon polymerization and become comparable to those of inorganic semiconductors like GaAs or germanium. This is a consequence of the increase of π-electron delocalization upon polymerization. Polymeric diacetylenes can therefore be used as efficient elements for third harmonic generation. In Ref. 143 this effect has been employed for tripling the frequencies of 1.89 μm and 2.62 μm radiation.

The unusual non-linear optical properties of polymer diacetylenes opened attractive prospects for their application in three or four-wave parametric amplifiers. Sauteret et al. 143 reported that with a 1.06 μm, 1 GW/cm² pump the gain for four-wave parametric amplification in the near infrared in PTS is about ten times larger than the gain for three-wave parametric amplification in LiNbO₃. However, later work 144.
showed that usage of polydiacetylenes in three-wave mixing devices is affected by strong two-quantum absorption. Therefore, the spectral window available for application is limited by onset of intense vibrational transitions at the high wavelength side (≈ 3 μm) and onset of two- or three-quantum absorption of the primary beam at the short wavelength side.

The color change of diacetylenes upon polymerization, either thermally or UV and γ-induced, can be used in temperature-dose or radiation-dose indicators. Their advantage is their high sensitivity allowing to cover a dose range of 50 rads to 50 Mrads. In addition, some compounds undergo an abrupt color change in solution at a certain concentration.

If different diacetylenes are cocrystallized they may form reactive or unreactive phases. Which of these actually occur, can depend on the substrate on which crystallization proceeds. For instance, spraying a mixture of a phenylurethane and a p-chlorophenylurethane diacetylene into an oil-covered surface causes formation of the unreactive modification. This effect has been utilized by Miller and Patel to record latent fingerprints.

As far as their electrical properties are concerned, polydiacetylenes are mainly used as model systems for basic research on one-dimensional crystalline solids that are non-conductive under conditions of thermodynamic equilibrium, although potential technical applications have also been suggested. For instance, spraying a mixture of a phenylurethane and a p-chlorophenylurethane diacetylene into an oil-covered surface causes formation of the unreactive modification. This effect has been utilized by Miller and Patel to record latent fingerprints.

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Although being insulators in general at least one crystalline polydiacetylene DCH was found to be electrochemically dopable up to a conductivity of 10^{-3} (Ωm)^{-1} by applying an NaJ/J2 electrolytic contact. One could think of combining this technique with electron-beam polymerization in order to produce a well-defined conducting pattern at the surface of a diacetylene crystal support or LB system.

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2 In a three-wave mixing experiment, two incident beams of frequency \( w_1 \) and \( w_2 \) are focussed onto the mixing element and an outcoming beam generated at \( w_3 = 2w_1 - w_2 \) is detected.
10 Concluding Remarks

It appears that the basic mechanisms involved in polymerization and, in particular, in photopolymerization of diacetylenes are understood. Nevertheless, to date it is not possible to design a diacetylene monomer on the basis of desired reaction behavior and/or product properties. To this end more quantitative information on the reaction kinetics of diacetylenes including quantum-mechanical aspects is needed which could form the basis for developing a quantitative relationship between structure and reactivity.

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