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On the Polymerization of Crystalline 1,4-Diethynylnaphthalene, 2[a]

The Reaction Mechanism

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SUMMARY:

Crystalline 1,4-diethynylnaphthalene (**1**) is photochemically polymerized in the solid state by a radical mechanism. Only the chain initiation step is induced by light, whereas chain propagation also occurs in the dark. The polymerization is controlled by diffusion processes within partially melted domains of the crystal, ultimately leading to a completely disordered system. The reaction rate, however, also depends on the packing of the monomer in the crystal lattice and—in the beginning of the reaction—the polymer chains have a preferential orientation with regard to the crystal axes of the monomer. Radical polymerization in solution indicates that—due to the lack of effective chain termination steps—**1** can be polymerized rather effectively as compared to other acetylenes. The photochemically induced polymerization is approximately of second order with regard to monomer concentration.

Introduction

Since 1958[1)] when 1,4-diethynylnaphthalene (**1**) was first prepared by Ried et al., this compound has been known to be highly light sensitive in the crystalline state[2–5)]. In a recent paper[6)] we have shown that upon irradiation with UV light crystalline **1** forms a purple polymer which has a polyene structure and an average length of about 50 monomeric units. Only one ethynyl group participates in the polymerization process, whereas the second ethynyl group of the monomer remains unreacted.

This reaction seems to resemble very much other light induced polymerizations like the topochemical reactions of diacetylenes[7,8)] and the four-center-type photopolymerization of diolefines in the solid state[9–11)].

In comparison to other aromatic acetylenes such as **2–8** which are described in Tab. 1 and which all are quite unreactive in this respect, the photoreaction of **1** appears to be rather unique.

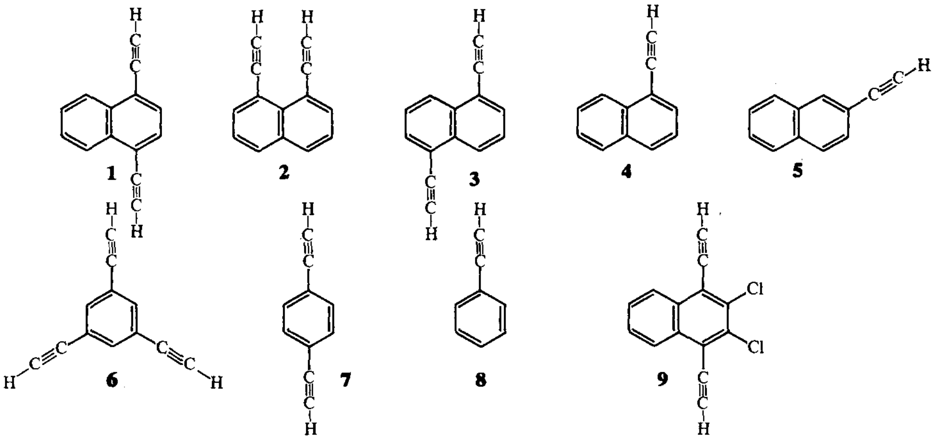
In this paper we want to report on the mechanism by which **1** is polymerized photochemically in the solid state. We also want to compare **1** to other aromatic acetylenes, and discuss the properties of further 1,4-diethynyl substituted aromatic compounds like 2,3-dichloro-1,4-diethynylnaphthalene (**9**) which were described by Ried to be light and heat sensitive, too.

[a)] Part 1: cf.[6)], preceding publication.

Tab. 1. Structure and properties of various ethynyl substituted aromatic compounds in comparison to 1,4-diethynylnaphthalene (**1**)

Compound[a]	mp/°C	Properties
1,4-Diethynylnaphthalene (**1**)	63,0	highly light sensitive; rapidly turns purple upon irradiation
1,8-Diethynylnaphthalene (**2**)	73,5	turns greyish upon storing and upon prolongued irradiation with UV light
1,5-Diethynylnaphthalene (**3**)	150,5	turns red upon prolongued storing at room temperature
1-Ethynylnaphthalene (**4**)	3,0	turns yellow upon prolongued irradiation with UV light
2-Ethynylnaphthalene (**5**)	41,5	unreactive in comparison to the other compounds listed
1,3,6-Triethynylbenzene (**6**)	107	slowly becomes orange when irradiated with UV light
1,4-Diethynylbenzene (**7**)	96,5	slowly turns yellow upon irradiation and storing at room temperature
Ethynylbenzene (**8**)	−44,8	unreactive in comparison to the other compounds listed
2,3-Dichloro-1,4-diethynylnaphthalene (**9**)	135	rapidly turns violet at room temperature in the dark, forms brownish products upon irradiation, melts under fire

[a] Formulae



Results and Discussion

1. *The photoreactivity of crystalline 1,4-diethynylnaphthalene* (**1**) *at room temperature*

The photopolymerization of **1** is characterized by the fact that it proceeds within the monomer crystal well below its melting point (63 °C). Although the photopolymerization of 2,3-dichloro-1,4-

diethynylnaphthalene (**9**) is somewhat slower than that of **1**, crystals of **9** can be photopolymerized at 25 °C, that is 110°C below the melting point of this compound.

Selecting **1** for the analysis of this type of photoreaction we have been able to prepare and characterize single crystals of three different modifications (α, β, and γ), the crystallographic data of which are listed in Tab. 2 together with the appearance of the respective polymers formed upon irradiation.

Tab. 2. Crystallographic data of the three different modifications of **1** together with the appearance of the polymer formed upon irradiation

Modification	Space-group	$\frac{a}{Å}$	$\frac{b}{Å}$	$\frac{c}{Å}$	β	Colour of polymer
α	$Pca2_1$	31,065	4,024	15,638	90°	dark red
β	$P2_1/c$	34,600	4,000	15,100	112°	orange red
γ	$P2_1/c$	28,200	4,000	19,000	117°	orange red

Using DSC analysis, modification α was shown to be the "high temperature" modification, mp 63,0°C. The modifications β and γ can be converted into α shortly below the melting point (β converts to γ at 60,7°C and γ is transformed to α between 61,0 and 61,2°C[12]). Modification α is obtained by crystallization either from the melt or from solution (e.g. methanol/water), whereas modifications β and γ are obtained under special conditions as described in the Exptl. Part.

In all three cases the colourless monomer crystals of **1** appear as needles with a maximum length of 15 to 20 mm and a cross section of about 0,2 mm^2 which upon irradiation with UV light (<370 nm) turn deeply coloured. The light sensitivity of **1** can be characterized by the "action spectrum[13,14] shown in Fig. 1. It was obtained in the following way: A melted and recrystallized colourless film of **1** on a glass slide (mod. α) was irradiated with monochromatic light and the appearance of optical density OD of the polymer at 550 nm was monitored as a function of irradiation times t. The slope of the curve thus obtained at zero conversion, namely lim $\Delta OD/\Delta t$, was taken as a measure of the light sensitivity at the given wavelength. The values obtained at various wavelengths corrected for constant light flux are plotted in Fig. 1 vs. the wavelength of initiating light.

Comparing the photoreactivity of the modifications α, β, and γ we find that modification α is clearly more reactive than the other two. Also, the polymer formed from modification α at room temperature has a higher molecular weight. Comparing the action spectrum to the absorption spectrum of the monomer in solution, one can clearly see that the threshold at 370 nm is an image of the aromatic absorptions of the compound between 300 and 340 nm, shifted to longer wavelengths by about 30 nm. Similar effects have been observed earlier with the action spectra of diacetylenes which upon irradiation readily polymerize in the solid state[14].

When viewed under the polarizing microscope, partially polymerized crystals exhibit strong dichroic absorption parallel to the needle axis (which is the crystalline b-axis in all the three cases). The polyene chains, therefore, must have a pronounced preferential orientation along this axis, which is known to be parallel to the stacks of aromatic rings[15–16].

A strong dependence of the photoreactivity on the molecular packing in the crystalline state is characteristic of topochemical reactions[17]. This was shown for a variety of systems

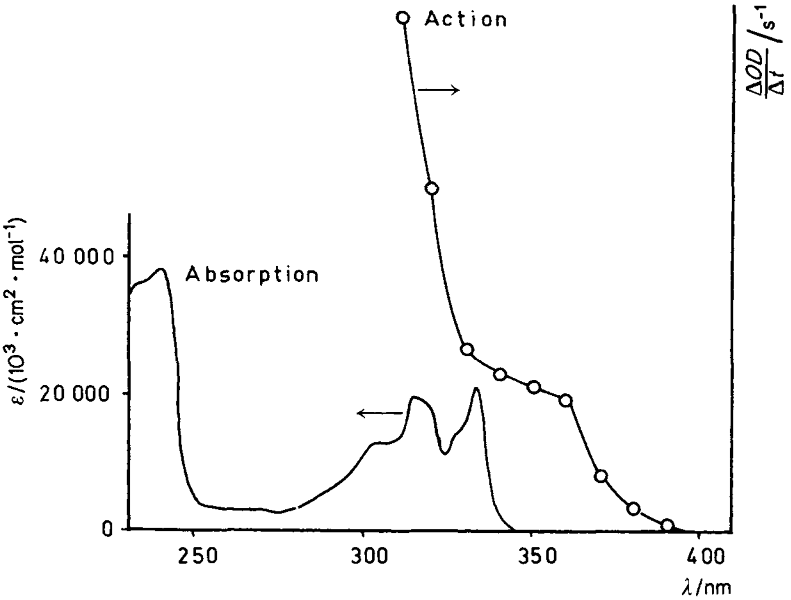


Fig. 1. Action spectrum of a melted and recrystallized film of **1** (modification α), together with the absorption spectrum of **1** in solution

like the diacetylenes[7,8], the derivatives of cinnamic acid[18], and a number of diolefines[9-11]. Many examples have been given where photoreactivity is observed only with those crystal modifications of the monomer which allow for specific interactions between neighbouring molecules[19]. Strong dichroic absorption upon polymerization also is typical of topochemical reactions. Particularly, strong dichroism is observed with polymer single crystals of diacetylenes in which the long-chain chromophores are perfectly aligned along certain crystallographic axes[7].

We have therefore analyzed, whether there is a topochemical control of the polymerization process by which **1** is photochemically polymerized in the solid state. A full structural analysis of modification α, which is the most reactive one, has been made and is published elsewhere[20]. A stereographic picture of modification α as viewed along the crystalline *b*-axis is given in Fig. 2.

Note that the spacegroup $Pca2_1$ does allow only for 4 asymmetric units per unit cell, so that there must be two molecules per asymmetric unit, as outlined in Fig. 3. Two molecules per asymmetric unit, which are not equivalent, have been observed in very few crystal structures only. One is therefore tempted to look for specific forces which determine this unusual molecular packing. Analysis of the structure, however, reveals that there is nothing like pairing of molecules, for instance. In no place atoms come closer to each other than one should expect from standard van der Waals radii.

From the fact that 1,4-dibromonaphthalene also crystallizes with two independent molecules per asymmetric unit[21] it seems that the unique molecular packing is a consequence of the molecular geometry and that it does not bear any importance for the topology of the reaction

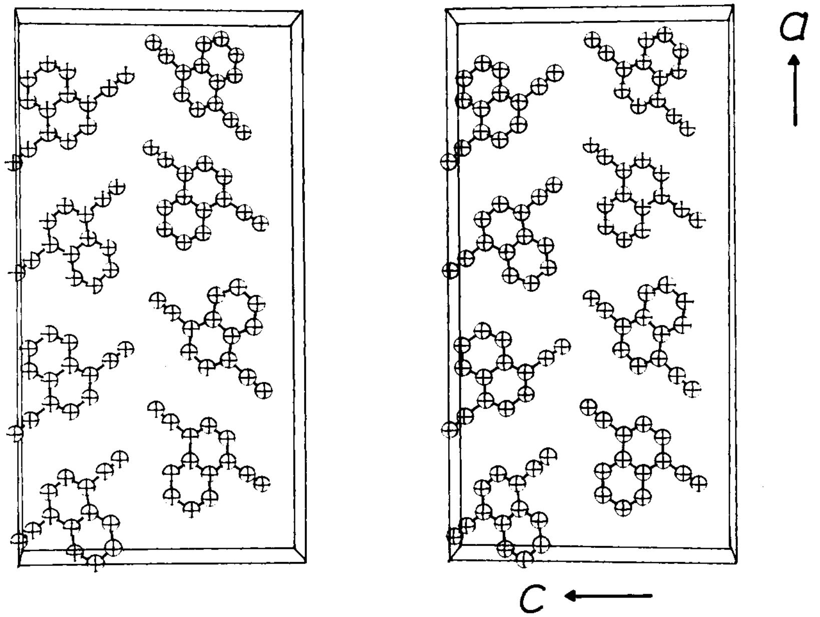


Fig. 2. Stereographic picture of modification α of **1** as viewed along the *b*-axis

product. Figs. 2 and 3 further show that neither chain initiation nor chain propagation of the polymerization process are favoured by the arrangement of molecules in space. Obviously, the reaction proceeds via diffusion processes which take place within partially melted and

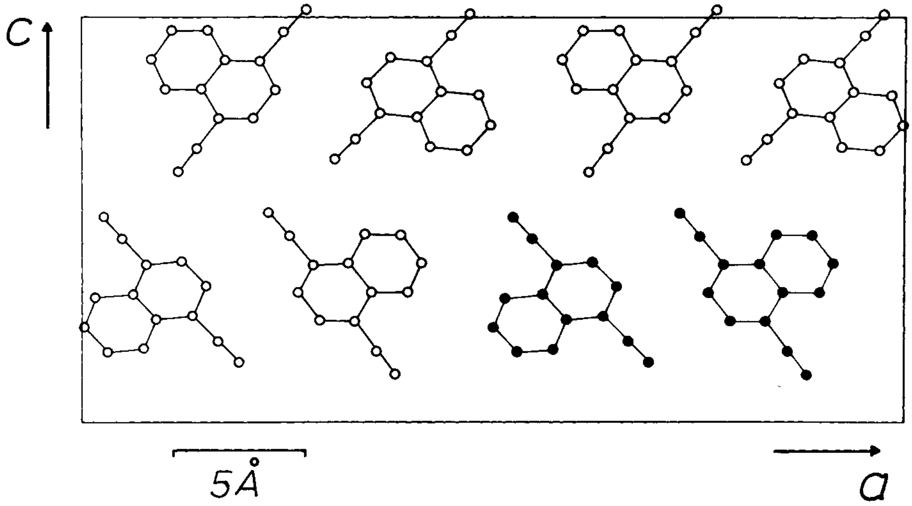


Fig. 3. Projection of the unit cell onto the *a*, *c* plane with an outline of the asymmetric unit (two symmetrically nonequivalent molecules)

disordered domains of the crystal. Therefore, the pronounced photoreactivity of **1** is due to the molecular structure of the monomer molecule itself, and not to the packing behaviour of the compound in the crystalline state.

The differences in reactivity between the three modifications then might be explained by an additional activation energy which has to be afforded when going from modifications β or γ to the melt, rather than going from modification α to the melt directly. Nevertheless, the strong dichroic absorption along the *b*-axis of partially polymerized monomer single crystals indicates that, at least in the beginning, polymerization preferentially proceeds along the stacks of aromatic rings resulting in uniaxially oriented polyenic chains. However, as the polymerization proceeds, the monomer crystals become more and more amorphous ending up in a completely disordered system, as evidenced by X-ray analysis. When fully polymerized, the single crystals have turned completely amorphous, and become grossly disrupted. In the case of 2,3-dichloro-1,4-diethynylnaphthalene (**9**), however, the original shape of the crystals is retained in all its features, but the crystalline structure is lost.

2. *Thermal polymerization of crystalline* **1** *and* **9**

At room temperature **1** seems fairly stable in the dark. Upon standing for more than 24 h, however, polymerization can be observed even without irradiation. At temperatures between 30 and 60 °C thermal polymerization becomes quite rapid. Thermal polymerization of **9**, however, appears to be very rapid. Pure crystals turn violet after standing at room temperature for one hour only. At higher temperatures polymerization becomes so fast that melting (around 140 °C) cannot be observed, unless the compound is put on a preheated hot stage. When quickly heated to about 140 °C **9** melts with ignition.

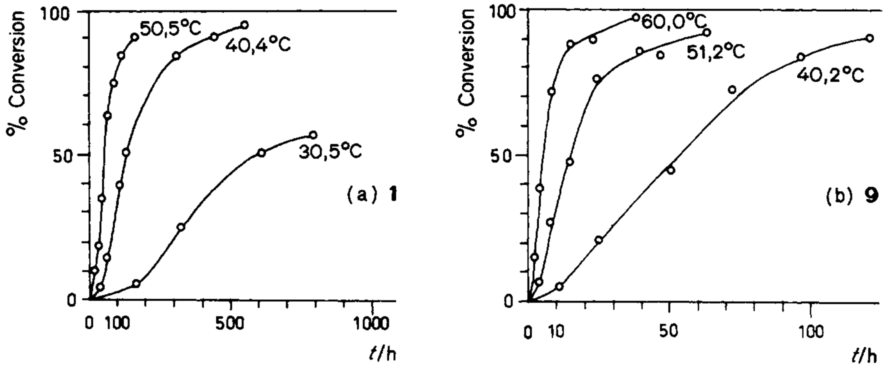


Fig. 4. Time-conversion curves during thermal polymerization of (a) 1,4-diethynylnaphthalene (**1**), modification α and (b) 2,3-dichloro-1,4-diethynylnaphthalene (**9**), both as obtained by crystallization from petroleum ether

Time-conversion curves are given in Fig. 4. These curves[22] were obtained by gravimetric methods using the fact that the polymers formed upon thermal polymerization are insoluble to more than 98%, in contrast to the photopolymers of **1** and **9**.

The IR spectra of the thermal polymers are essentially the same as the spectra of the photopolymers. However, there is some broadening and weakening of the band at 3300 cm^{-1} which indicates some crosslinking of the polymer chains via the pendant ethynyl groups.

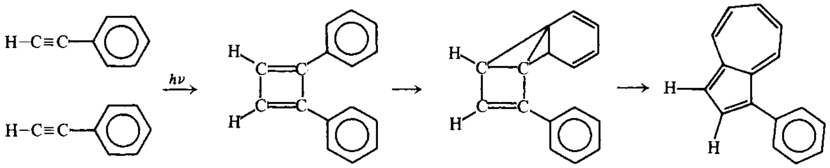
Estimating the activation enthalpy from the maximum slope of these time-conversion curves we obtain 100 ± 20 kJ/mol for both monomers.

Comparing the reactivity of modifications α and β of **1** in their thermal polymerization at 40°C, we found that modification β had only reached 8% conversion when modification α had already reached 40%.

This shows that there are pronounced differences between the reactivities of the different crystal modifications. However, these differences are relatively small when compared to the effects that are observed with different modifications of diacetylenes, the reactivity of which, for example, strongly depends on the molecular packing in the solid state.

3. *Polymerization of solution and melt*

The photochemistry of acetylenes seems quite complicated and there has been a series of publications on the photodimerization of aromatic acetylenes in solution. A recent review of this field has been given by Sauerbier[23)]. Many of these investigations initially aimed at preparing stable derivatives of cyclobutadiene by photodimerization of the respective acetylenes. Dimerization always occurred slowly and in very low yield, and the products isolated were azulene derivatives[24)], which might formally be derived from a cyclobutadiene by rearrangement of the carbon skeleton, as outlined in the scheme below.



Derivatives of cyclobutadiene were never observed and large quantities of polymers were described to form as undesired side products.

We find that in solution **1** behaves very similar to these other aromatic acetylenes described earlier. Upon irradiation of monomer solutions of **1**, polymer as well as dimers are formed. The IR spectrum of the polymer formed in solution is essentially the same as the spectrum obtained from the polymer formed upon irradiation of single crystals. The melt of **1** is very light sensitive, too, and the same polymer is formed as from crystalline monomer.

The kinetics of polymer and dimer formation in solution was analyzed in the following way: Using cyclohexane as solvent polymer and dimers (a mixture of different isomers[25)]) can be separated easily by making use of their different solubility properties. Upon storing, the red polymer precipitates quantitatively, whereas the green dimers and a fraction of yellow oligomers stay in solution. The respective absorption spectra, as obtained starting from a 0,2 molar solution of **1** in cyclohexane, are shown in Fig. 5. As gravimetric determination of the polymer and dimer fractions is rather difficult under these circumstances, the respective molar absorption coefficients (in CH_2Cl_2) were taken to be $\varepsilon_{550} = 1800$ l·mol^{-1}·cm^{-1} for the polymer and $\varepsilon_{700} = 250$ l·mol^{-1}·cm^{-1} for the dimers[25)]. These values have been measured

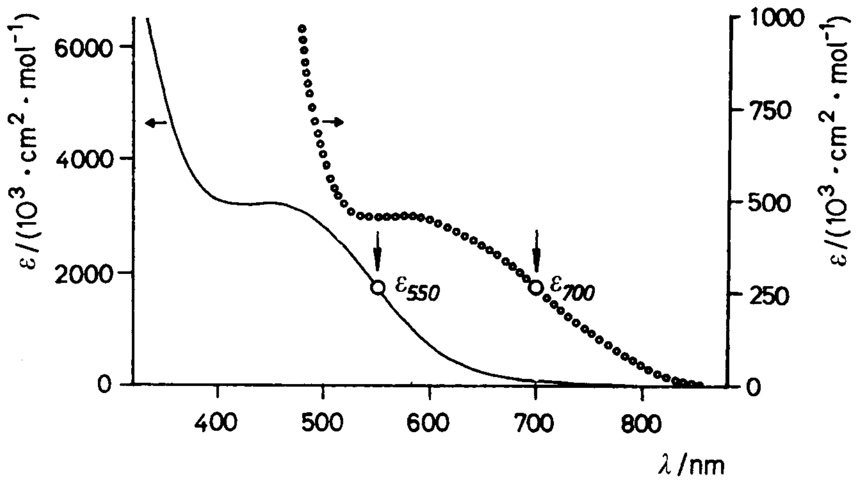


Fig. 5. Absorption spectra of the dimer and polymer fractions as isolated from irradiated monomer **1** solutions (conc.: 0,2 mol/dm^3 in cyclohexane). (----): polymer; (ooooo): dimers + oligomers

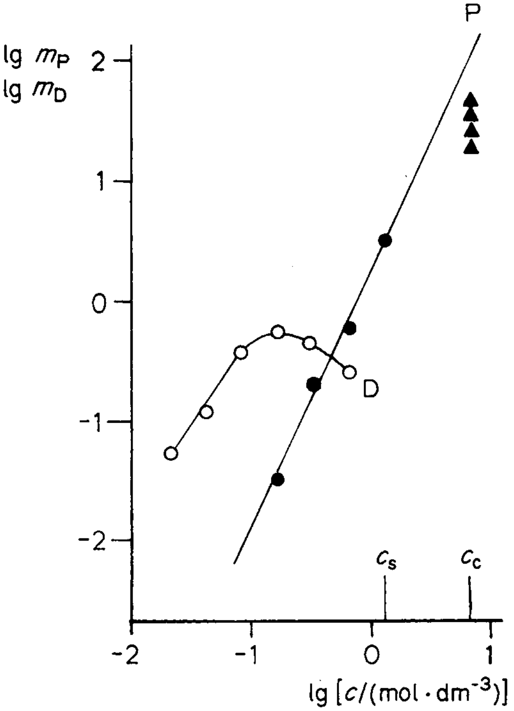


Fig. 6. Yield of polymer (m_P) (●) and dimer (m_D) (○) per time unit of irradiation as a function of monomer **1** concentration (in mol/l). Unit of m_P; m_D: μg per 15 s irradiation; c_s: saturated solution in cyclohexane at 20 °C (1,33 mol/l); c_c: theoretical monomer concentration in the crystalline state; (▲): yield of polymer from single crystals

for the isolated polymer, as described by us[6] earlier, and for the azulene bodies, as analyzed by Ried and Sauerbier[25,26], respectively.

Fig. 6 then shows the yields of polymer and dimers per time unit as obtained by irradiating solutions with varying concentration of **1** at 20 °C.

At concentrations below 0,3 mol/dm^3 mainly dimerisation is observed and the yield of dimers per time unit (m_D) goes through a maximum at a concentration of 0,8 mol/dm^3.

Polymerization can by completely neglected at low concentration. But there is a sharp increase of polymer yield per time unit (m_P) with increasing monomer concentration, which shows that the reaction is approximately of the second order.

Regarding monomer single crystals as extremely concentrated solutions (6,8 mol/dm^3) we find the reaction rates drawn above c_c. These data all fall below the line extrapolated from the yields per time unit found from the solutions. However, there is still some agreement from which we conclude: The photochemical polymerization of **1** follows the same path in solution as in monomer single crystals. The reaction rate increases approximately with the square of the monomer concentration. In the crystalline state, however, there is no additional acceleration of the reaction caused by the molecular packing. It is the second order of this photoreaction which accounts for the fact that monomer crystals are much more readily polymerized than monomer solutions. This in turn is responsible for the unusual behaviour of this compound.

4. *Photopolymerization of crystalline* **1** *at low temperatures*

By irradiating single crystals of **1** at low temperatures the polymerization process can be broken down into different steps. One can clearly distinguish:

a) A light induced initiation step
b) A propagation step which also proceeds in the dark

Experiments were conducted in the following way: Melted and recrystallized films of **1** on glass slides were cooled to 77 K and irradiated with a strong UV light source (> 330 nm). No change of the samples could be observed at these temperatures. After warming to about −15 °C rapid colouring of the samples occurred without further irradiation. Within 30 s the colour of a sample would change from white over bright yellow to dark red.

Using CH_2Cl_2 as solvent at a temperature of −30 °C the reaction was stopped at different times and the absorption spectra of the respective reaction products were determined. Thus subsequent stages 1: yellow, 2: orange, 3: orange-red, and 4: dark red of the polymerization process could be isolated as demonstrated in Fig. 7. Absorptions at longer wave lengths clearly arise from longer polyene chains. Thus the photochemical polymerization of **1** is initiated by light, whereas chain propagation also occurs in the dark. Chain growth is governed by the mobility of the monomer molecules within the crystal lattice and therefore is strongly dependent on the temperature. The reactive chain ends of the polymer appear to be quite stable so that at low temperatures they can be trapped over a period of seconds or minutes.

5. *ESR spectra*

The stability of the reactive chain end strongly indicates that the polymerization of **1** proceeds via a radical mechanism. Indeed, structured ESR spectra can be obtained from irradiated single crystals of **1** and **9**.

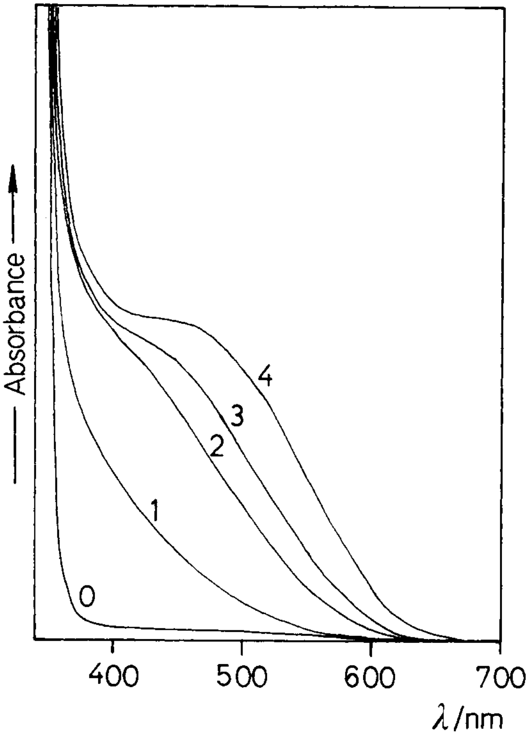
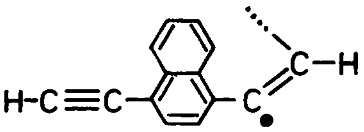


Fig. 7. Absorption spectra of the polymer of **1** at different stages of the polymerization process (chain growth in the dark at −15 °C). Spectra measured after dissolution in CH_2Cl_2. 0: monomer, 1–4: cf. text

Recently, Gordon et al. described the formation of radicals, which were formed upon irradiation of 1,4-diethynylbenzene (**7**) with γ-rays[27–29]. The ESR spectra of partially polymerized **1** and **9** are shown in Fig. 8. Powdered **1** (Fig. 8a) shows a very weak ESR signal at $g=2$, which is due to impurities. Upon irradiation (under N_2-atmosphere, $\lambda=365$ nm, $T=20$°C) a characteristic ESR signal appears at $g=2$ with a line width of 15 G and carrying shoulders with a splitting of 40 G. The main line remains stable, whereas the two shoulders disappear after ca. 1 min. Further irradiation only increases the intensity of the main signal. The number of unpaired spins is estimated to be $10^{15}-10^{18}$ spins per gram.

Fig. 8e shows the ESR spectrum of powdered, 2,3-dichloro-1,4-diethynylnaphthalene (**9**) which was slightly violet in colour due to thermal polymerization.

In this case the shoulder peaks with a splitting of 28 G were stable at room temperature. We believe that the shoulder peaks in the ESR spectra of **9** are due to a vinyl radical structure:



in which the *cis* proton gives rise to a splitting of about 32 G[30,31]. However, it is also known that polyene structures like polyphenylacetylene [poly(1-phenylvinylene)] exhibit radical activity,

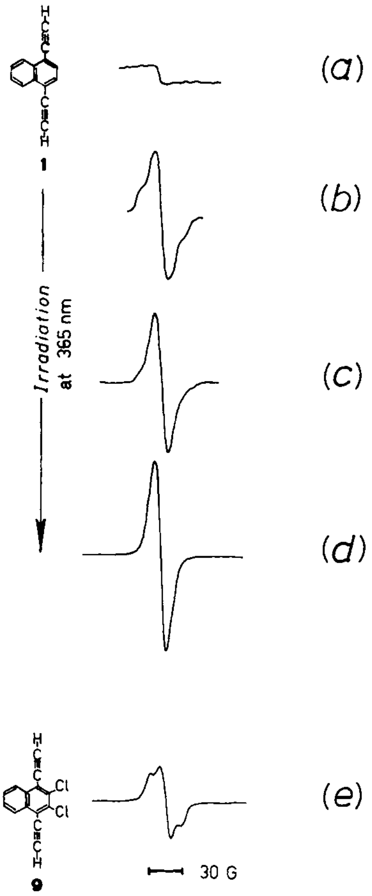


Fig. 8. ESR spectra of powdered samples of **1** and **9**; (a) pure monomeric **1**, (b) monomer after irradiation with UV light of 365 nm for 30 s, (c) the same sample as under (b), but 3 min later, (d) signal after further irradiation (power amplification reduced by a factor of 8), (e) powdered crystals of **9** containing a very small amount of thermally created polymer (violet colour). (SI-unit: 1 G = 10^{-4} T)

by themselves[32,33]. It seems difficult to distinguish these unpaired electrons forming the growing chain-end from those unpaired electrons which are due to excitations of the polyene chain. Nevertheless, together with the other evidence presented, the structured spectra of Fig. 8b) and e) make clear that the polymerization of **1** proceeds via a radical mechanism.

6. *Polymerization in solution with radical initiators and inhibitors*

As the photopolymer obtained by irradiation of single crystals and the polymer prepared by photopolymerization in solution yield IR spectra which are practically indistinguishable, we may conduct experiments in solution ot study the process which take place upon irradiation of monomer single crystals.

In fact, **1** is readily polymerized in concentrated solutions using radical donators like AIBN and $BrCCl_3$. Oxygen inhibits the polymerization. For example, using a 0,6 molar solution of **1** in toluene, together with 0,02 mol/dm^3 AIBN, a dark red polymer rapidly forms at

63 °C. As measured from the absorbance at 550 nm, however, the conversion of monomer to long chain polymer does not exceed 1% after complete decomposition of the initiator.

Adding $BrCCl_3$ as a photoinitiator to concentrated solutions of **1**, the yield of photopolymer is greatly enhanced. A maximum enhancement of 20 was found with a toluene solution containing 0,37 mol/dm^3 of **1** and 22 mmol/dm^3 of $BrCCl_3$.

Thus, it is clear that **1** can be polymerized to a polyene structure via a radical mechanism. As the above experiments show, however, the quantum yield of this photochemically initiated radical polymerization is quite low in solution and the polymer yield also greatly depends on the concentration of the monomer.

The concentration of monomer being as high as in monomer single crystals (6,8 mol/dm^3) this photopolymerization becomes quite effective.

Nevertheless, from experiments in solution one can clearly demonstrate that **1** can be polymerized rather effectively as compared to all other aromatic acetylenes.

Subjecting the compounds listed in Tab. 1 to a radical polymerization under exactly the same conditions as already described above (toluene as solvent, monomer concentration = 0,6 mol/dm^3, AIBN concentration = 0,02 mol/dm^3, $T = 63$ °C, reaction time = 1 h), we find the following results: Only **1** does form a purple polymer at a reasonable rate. All other monomers only yield yellowish or brownish products[34,35], the absorption spectra of which are drawn in Fig. 9. The polymer of **1** shows a smooth absorption curve from 400 to 600 nm which is characteristic of a polydisperse system of long-chain polyenes. The products of all the other monomers absorb at much shorter wavelengths and some of the absorption curves are structured. We believe that in all these cases efficient chain termination accounts for the fact that only very short oligomeric structures are formed, and that the structures in the absorption spectra even might be assigned to some well defined sideproducts formed

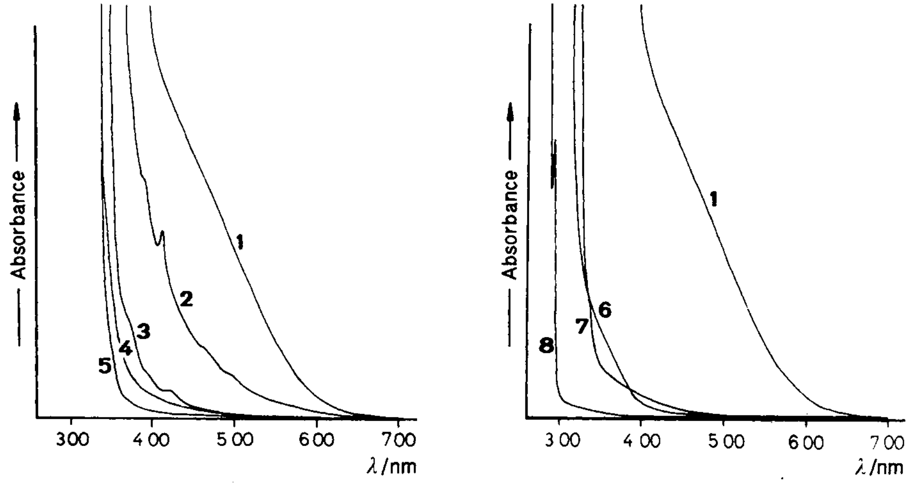


Fig. 9. Absorption spectra of the reaction products formed during radical polymerization of a variety of ethynyl substituted aromatic compounds

during the reaction. Chain termination during the catalytical polymerization of phenylacetylene has been observed by Ferguson et al.[36)] earlier.

However, comparing **1** to its isomers like 1,8-diethynylnaphthalene (**2**), 1,5-diethynylnaphthalene (**3**) and to 1-ethynylnaphthalene (**4**), it is still hard to see, why only this compound does polymerize rather effectively by a radical mechanism and this question has to be the subject of further investigations.

Experimental Part

1. *Preparation of the monomers*

1.1. *1,4-Diethynylnaphthalene* (**1**)

The synthesis and purification of **1** has been described earlier[6)].

1.2. *1,8-Diethynylnaphthalene* (**2**)

2 was prepared in a 7 step synthesis from naphthalic anhydride[*)] following the procedures described by Sondheimer[37)] and Staab[38)].

a) *1,8-Bis(hydroxymethyl)naphthalene*[**)]*:* 0,4 mol of naphthalic anhydride were reacted with 1 mol of lithium aluminium hydride according to the procedure given by Beyler and Sarett[39)]. Yield: 44 g (59%), (lit.[37)]: 66%).

b) *1,8-Divinylnaphthalene:* Following the procedure of Sondheimer[37)], 1,8-bis(hydroxymethyl)naphthalene was converted to 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide[***)] in an overall yield of 68,8%. Combining the procedures of Sondheimer[37)] and Staab[38)] the phosphonium salt then was reacted with butyllithium in diethyl ether, and subsequently with gaseous formaldehyde obtained by pyrolysis of paraformaldehyde.

Thus, 20 g (24 mmol) 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide were suspended in 1000 cm^3 anhydrous diethyl ether and reacted with 30 cm^3 (60 mmol) of butyllithium in hexane (15%). In a horizontal glass thoroughly dried paraformaldehyde was heated up to 200°C, and by means of a gentle stream of nitrogen the monomeric formaldehyde was driven over the reaction surface via a short bridge. After the red colour of the ylide had disappeared, the mixture was refluxed for 15 more minutes. Water was added and the ether phase was separated. After removing the ether, the organic residue was extracted with pentane from which 3,5 g of yellowish crystals were obtained. Yield after recrystallization from pentane: 3,2 g (74%) (lit.[37)]: 87%), mp. 44–45°C (lit.[37)]: 44–46°C).

c) *1,8-Diethynylnaphthalene* (**2**): Following the procedure given by Sondheimer[37)], 1,8-divinylnaphthalene subsequently was brominated in CS$_2$ solution yielding 1,8-bis(1,2-dibromoethyl)naphthalene which was then trated with potassium *tert*-butoxide in THF. Overall yield after sublimation of the product in high vacuo: 57,5%. mp. 71–73°C (lit.[37)]: 71–72°C, lit.[38)]: 73–73,5).

1.3. *1,5-Diethynylnaphthalene* (**3**)

1,5-Diethynylnaphthalene was prepared by reacting 1,5-diacetylnaphthalene with PCl$_5$ in methylene dichloride and by eliminating the reaction products with sodium amide in liquid ammonia.

a) *1,5-Diacetylnaphthalene* was obtained in 11% yield following the procedure of Stephan[40)].

b) *1,5-Diethynylnaphthalene:* 1 g (4,7 mmol) of 1,5-diacetylnaphthalene and 3 g (10,6 mmol) of PCl$_5$ were dissolved in 100 cm^3 of methylene dichloride and refluxed for 6 h. Isolation of the product was achieved by evaporating the solvent, taking up into diethyl ether, and adding a diluted aqueous solution

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[*)] Systematic name: 1,8-Naphthalenedicarboxylic anhydride.

[**)] Systematic name: 1,8-Naphthalenedimethanol.

[***)] Systematic name: Naphthalene-1,8-diyldimethylbis(triphenylphosphonium) dibromide.

of sodium hydroxide in order to neutralize the $POCl_3$ formed. According to ^1H NMR the product isolated showed the following composition:

8%: $\delta = 2,74$ (s; unreacted acetyl groups)
46%: $\delta = 2,88$ (s; $—CCl_2—CH_3$ groups)
46%: $\delta = 5,78$ (q; $—CCl{=}CH_2$)

The reaction products then were dissolved in 20 cm^3 of anhydrous ether and added dropwise to a suspension of sodium amide in liquid ammonia (100 cm^3 ammonia and 60 mmol sodium amide from 1,4 g sodium). After reacting for 5 h, the mixture was neutralized with 6 g ammonium chloride, the ammonia was eavporated and replaced by ether. 345 mg of crude product were obtained, which then were sulbimed in a high vacuum analogous to the purification procedure described for 1,4-diethynylnaphthalene (**1**) earlier (10^{-3} to 10^{-4} mbar, temperature gradient from +50°C to −50°C, 3 d). Thus 250 mg (30%) of pure **3** were isolated, mp 150,5 °C.

$C_{14}H_8$ (176,2)	Calc.	C 95,42	H 4,58
	Found	C 95,31	H 4,70

^1H NMR (acetone-d_6): $\delta = 7,05–8,58$ (m: aromatic, protons); $\delta = 4,10$ (s: ethynyl proton, 1-position).

1.4. *1-Ethynylnaphthalen* (**4**)

The synthesis of **4** has been described earlier[6].

1.5. *2-Ethynylnaphthalene* (**5**)

A sample of **5** was prepared according to the procedure described by Bodendorf and Mayer[41][*].

1.6. *1,3,5-Triethynylbenzene* (**6**)

According to the method of Hübel and Merenyi[43] **6** was obtained by reacting 1,3,5-triacetylbenzene with PCl_5 in methylene dichloride and by subsequently eliminating the reaction products formed with sodium amide in liquid ammonia. Overall yield: 31% (lit.[43]: 39%).

1.7. *1,4-Diethynylbenzene* (**7**)

Following the method worked out by Hay[42] **7** was obtained by brominating a mixture of isomeric divinyl benzenes in chloroform and separating the *para* isomer of the products formed. Elimination with potassium *tert*-butoxide readily yielded **7** in an overall yield of 66,3% (lit.[42]: 71%; lit.[25]: 12%, Ried's method). For the synthesis of **7** this route appears to be much more efficient than the rather laboureous method given by Ried.

1.8. *Phenylacetylene* (**8**)

8 was synthesized by standard methods.

1.9. *2,3-Dichloro-1,4-diethynylnaphthalene* (**9**)

a) *2,3-Dichloro-1,4-diethynyl-1,4-dihydroxy-1,4-dihydronaphthalene:* The synthesis was conducted exactly in the same way as the synthesis of 1,4-diethynyl-1,4-dihydroxy-1,4-dihydronaphthalene[6]. Thus, 4 mol of lithium amide were prepared from 28 g lithium in 3 dm^3 of liquid ammonia and reacted with acetylene gas to yield lithium acetylide as described earlier. The lithium acetylide formed then was reacted with 305 g (1,34 mol) of 2,3-dichloro-1,4-naphthoquinone for 2 d. The product was isolated as described before and recrystallized from boiling toluene. Yield: 204 g (60%) of large crystals, mp 184,5 °C (lit.[1,3]: 184,5 °C).

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[*] Kindly supplied by Dipl. Chem. H.-J. Graf, Freiburg.

b) 2,3-Dichloro-1,4-diethynylnaphthalene (**9**): At 55°C a saturated solution of 15 g (0,054 mol) of 2,3-dichloro-1,4-diethynyl-1,4-dihydroxy-1,4-dihydronapthalene in methanol was added dropwise to a solution of 27,5 (0,12 mol) $SnCl_2 \cdot 2H_2O$ in 80 cm^3 acetic acid (50%). After reacting for 25 min, 1,5 dm^3 toluene, 100 cm^3 acetone, and 1 dm^3 of hydrochloric acid (2 M) were added. The organic phase then was washed with aqueous sodium hydroxide (2 M) and water. After evaporation of the solvent the organic residue was taken up into 300 cm^3 of methanol. Upon adding boiling water to the hot methanol solution and cooling, 4,8 g of crude product precipitated. For purification the compound was recrystallized repeatedly from petroleum ether (bp 80–110°C). 3,2 g (24,2%), (lit.[2–4]: 23%) of white needles were obtained which rapidly turned violet in the dark. mp 135°C (explosive). The compound polymerizes very rapidly at elevated temperatures so that melting could only be observed when the crystals were given on a preheated hot stage.

$C_{14}H_{10}Cl_2$ (145,2)	Calc.	C 68,80	H 2,47	Cl 28,93
Monomer:	Found	C 68,88	H 2,72	Cl 28,19
Thermal polymer:	Found	C 68,46	H 3,02	Cl 29,59

2. *Thermal polymerization of* **1** and **9**

For thermal polymerization of **1** and **9** quantities of 50 to 100 mg of the respective monomer were sealed in glass vessels under an atmosphere of argon gas and annealed in a thermostat. After the required time the samples were finely powdered and the unreacted monomer was extracted with boiling acetone in the case of **1**, and with hot diethyl ether in the case of **9**, respectively. The polymerization yield then was determined gravimetrically.

3. *Photopolymerization of* **1** *in solution*

All photoreactions were performed in cyclohexane. For quantitative measurements with small samples 60 MHz NMR sample tubes were used as reaction vessels. All samples were thoroughly purged with high grade nitrogen, sealed, and irradiated with a strong mercury UV lamp (Hanau, model S 500). As the walls of the sample tubes absorbed all radiation below 330 nm, no additional filters were used. After irradiation the sample tubes were stored at 20°C for seven days in order to allow the polymer to precipitate quantitatively. Separation of polymer and dimers was then achieved by filtration and a quantitative measure for the amount of the respective product formed was obtained from the absorptions at 550 nm and 700 nm, respectively.

For comparative measurements irradiation was performed in such a way that all sample tubes were exposed to the same light intensity, whereby the size of the irradiated surface and the quantity of the irradiated volume were kept constant. Depending on the experiment the irradiation time varied between 30 s and 12 h. The experimental values, depicted in Fig. 6, partially were obtained at different irradiation times and were then expressed in µg polymer formed per 15 s irradiation time.

As measurements of the time dependence of the polymer yield indicated, there is no strictly linear relationship between the irradiation time and the quantity of polymer formed. The rate of polymerization rather decreases with increasing irradiation time. However, as extrapolation to zero time for all the concentrations is rather tedious, this error has been neglected. As it turns out, the error made by assuming the relationsship between time and polymer yield to be linear is by more than one magnitude smaller than the concentration dependent effects depicted in Fig. 6.

4. *Preparation of different modifications of* **1**

Modification α, mp 63,0°C, is obtained either by recrystallizing melted monomer or by dissolving the compound in boiling methanol, adding boiling water, and allowing to cool to 0°C. By sublimation modification β is formed together with modification α. The following conditions were used: temperature gradient: +50°C to −50°C over 20 mm, pressure: 20 mbar. Small amounts of modification β developed as bushels of long needles, well distinguishable from the smaller crystals of modification α. Modification γ was obtained once by crystallization from methanol, but could not be reproduced.

5. *Instrumentation*

Action spectra: The technique of measuring action spectra has been described earlier[13,14]. Measurements were performed on a Leitz Microscop-Photometer MPV using melted and recrystallized films of **1** on glass slides.

ESR spectra were recorded on a Varian E-10 ESR spectrometer.

IR spectra were recorded on a Unicam IR spectrometer (model SP 1000).

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1) W. Ried, H.-J. Schmidt, A. Urschel, Chem. Ber. **91**, 2472 (1958)

2) W. Ried, Angew. Chem. **76**, 973 (1964)

3) W. Ried, Äthinierungsreaktionen, in "Neuere Methoden der präparativen organischen Chemie", Verlag Chemie, Weinheim/Bergstr., 1966, Vol. 4, p. 88ff.

4) K.-H. Wesselborg, Dissertation, Universität Frankfurt/M. 1959

5) W. Ried, K.-H. Wesselborg, J. Prakt. Chem. **12**, 306 (1961)

6) O. Rohde, G. Wegner, Makromol. Chem. **179**, 1999 (1978), preceding publication

7) G. Wegner, Chimia **28**, 475 (1974)

8) G. Wegner, Makromol. Chem. **154**, 35 (1972)

9) M. Hasegawa, Y. Suzuki, H. Nakanishi, F. Nakanishi, Prog. Polym. Sci., Jpn. **5**, 143 (1973)

10) H. Nakanishi, F. Nakanishi, Y. Suzuki, M. Hasegawa, J. Polym. Sci., Part A-1, **11**, 2501 (1973)

11) H. Nakanishi, M. Hasegawa, Y. Sasada, J. Polym. Sci., Part A-2, **10**, 1537 (1972)

12) O. Rohde, Dissertation, Universität Freiburg 1977

13) K. Takeda, G. Wegner, Makromol. Chem. **160**, 349 (1972)

14) G. Wegner, G. Arndt, H.-H. Graf, M. Steinbach in "Reactivity of Solids", edited by F. Wood, O. Lindquist, C. Helgesson, and N.-G. Vannerberg, Plenum Press, 1977, p. 487–492

15) A. I. Kitaigorodsky, "Organic Chemical Crystallography", Consultants Bureau, New York, 1961, p. 94

16) N. A. Ahmed, A. I. Kitaigorodsky, M. I. Sirota, Acta Crystallogr., Sect. B, **28**, 2875 (1972)

17) M. D. Cohen, G. M. J. Schmidt, J. Chem. Soc. **1964**, 1996

18) G. M. J. Schmidt, The Photochemistry of the Solid State in "Reactivity of the Photoexcited Molecule", Interscience Publ., London, 1967, p. 227

19) A. W. Hanson, Acta Crystallogr., Sect. B **31**, 831 (1975)

20) V. Enkelmann, O. Rohde, Acta Crystallogr., Sect. B **33**, 3531 (1977)

21) J. Trotter, Can. J. Chem. **39**, 1574 (1961)

22) G. Wegner, Habilitationsschrift, Universität Mainz 1970

23) M. Sauerbier, "Photochemische Reaktionen der C≡C-Dreifachbindung", in Houben-Weyl, Methoden der Organischen Chemie, IV/5a, Photochemie, Teil 1, Georg Thieme Verlag, Stuttgart, 1975, p. 461

24) E. Müller, J. Heiß, M. Sauerbier, Justus Liebigs Ann. Chem. **723**, 61 (1969)

25) G. Clauß, W. Ried, Chem. Ber. **108**, 528 (1975)

26) E. Müller, M. Sauerbier, D. Streichfuß, R. Thomas, W. Winter, G. Zountsas, J. Heiß, Justus Liebigs Ann. Chem. **735**, 99 (1970)

27) V. L. Broude, V. I. Goldanski, D. A. Gordon, Vysokomol. Soedin., Ser. B, **9**, 864 (1967)

28) D. A. Gordon, I. I. Migunova, A. I. Mikhailov, Dokl. Akad. Nauk. SSSR **213**, 368 (1973)

29) D. S. Gordon, A. I. Mikhailov, Vysokomol. Soedin., Ser. A, **17**, 1663 (1975)

30) E. L. Cochran, F. J. Adrian, V. A. Bowers, J. Chem. Phys. **40**, 213 (1964)

31) A. Carrington, A. O. McLachlan in "Introduction to Magnetic Resonanz", Harper and Row, New York, 1967, p. 80

32) P. Ehrlich, E. C. Metzluft, J. Polym. Sci., Part B, **12**, 125 (1974)

(33) G. M. Holob, P. Ehrlich, R. D. Allendorfer, Macromolecules **5**, 569 (1972)
(34) T. F. Rudledge, "Acetylenic Compounds", Reinhold Book Corp., New York, 1969
(35) Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellmann, W. Brenner, Chem. Ind. (London) **1961**, 2004
(36) J. Ferguson, A. W.-H. Mau, Mol. Phys. **27**, 377 (1973)
(37) R. H. Mitchell, A. Sondheimer, Tetrahedron **24**, 1397 (1968)
(38) H. A. Staab, J. Ipatschki, A. Nissen, Chem. Ber. **104**, 1182 (1971)
(39) R. E. Beyler, L. H. Sarett, J. Am. Chem. Soc. **74**, 1406 (1952)
(40) R. Stephan, Chem. Ber. **90**, 296 (1957)
(41) K. Bodendorf, R. Mayer, Chem. Ber. **98**, 3554 (1965)
(42) A. S. Hay, J. Org. Chem. **25**, 637 (1960)
(43) W. Hübel, R. Merenyi, Angew. Chem. **74**, 781 (1962)