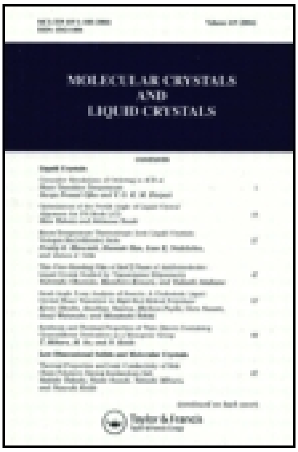

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Reactivity of Strained Configurations in Solid-state Polymerization Reactions

G. N. Gerasimov [a]

[a] Karpov Institute of Physical Chemistry, 103064, Moscow, USSR

To cite this article: G. N. Gerasimov (1990): Reactivity of Strained Configurations in Solid-state Polymerization Reactions, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 215-222

To link to this article: http://dx.doi.org/10.1080/00268949008036045

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 215–222
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

REACTIVITY OF STRAINED CONFIGURATIONS IN SOLID-STATE POLYMERIZATION REACTIONS

G.N.GERASIMOV
Karpov Institute of Physical Chemistry
103064 Moscow, USSR

Abstract Low-temperature photocyclopolymerization of crystalline DPDA and polymerization under high pressures of two crystalline diacetylenes (TS and DCH) with different lattice structure are considered. It was shown that the polymer chain growth is dependent upon strains arising during reaction in the solid phase. These strains increase with the decrease in temperature and (or) rise in pressure because of the hindering of the lattice relaxation. Structure and reactivity of the strained metastable configurations that arise are governed by the crystalline lattice structure.

INTRODUCTION

A part of the chemical energy released during a solid state chemical reaction may be transformed into the energy of mechanical strain if the time of the chemical reaction is less than that of the lattice relaxation. The reactivity of the metastable strained configurations that arise may be quite different from that of usual stable ones and depends on the crystalline lattice structure. In multi-step reactions the strains arising during a step influences the course of the subsequent one.[1]

In this contribution the low-temperature photocyclopolymerization of crystalline diethyl ester of p-phenylene diacrylic acid (DPDA)[2] and the high-pressure polymerization of two crystalline diacetylenes[3] - 1,6-bis(p-toluenesulphonate) of 2,4-hexadiynediol (TS) and 1,6-di-N-carbazolyl-2,4-hexadiyne (DCH) - are considered from this point of view.

RESULTS AND DISCUSSION

Photocyclopolymerization of DPDA

This reaction was first described by M.Hasegawa and co-

workers.[4] The monomer molecules are arranged in stacks which are the precursors of the polymer chains (Fig. 1). DPDA-photodimerization leads to formation of the substituted cyclobutane with active groups K (Fig. 1) followed by the photoaddition of monomer molecules to these groups (chain growth). The oligomer chains combine together into polymer ones by the photocombination of the groups K of the neighbouring chains in the stacks.

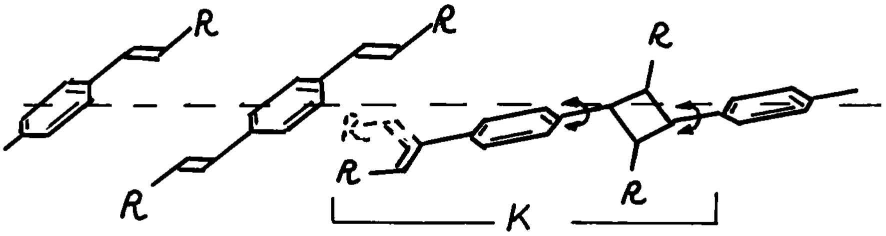

FIGURE 1 Arrangement of the monomer molecules and the growing chain in DPDA-crystal: $R = -C\begin{array}{l}\nearrow\!\!\!\nearrow O\\ \searrow OC_2H_5\end{array}$. K is the terminal active group of chain.

To study the reaction, IR-spectroscopy has been used. In the spectra of crystals are the following characteristic bands[2]: at 1640cm^{-1} relating to C=C-double bonds, at 1570 and 1600cm^{-1} relating to the asymmetrically p-substituted phenyl rings[5] in the terminal groups, K, of the chains and at 1280cm^{-1} relating to the ester groups of crystalline monomer. From spectral data the conversion of monomer, X_M, and that of double bonds, X_c, as well as relative content of groups K can be determined. The average length of chains $Pn = \frac{X_M}{X_M - X_c}$. We investigated the polymerization under the action of UV-radiation with wave-length 360 nm. Absorption of this radiation by K groups is next to nothing and, therefore, the photocombination of K groups can be neglected.[4] The chain growth proceeds only by the addition of the excited monomer molecules to the terminal groups of chains in the stacks.

X_M differs from X_c because in our experiments only short chains are formed. Figure 2 shows X_M and X_c as depending on time of irradiation. After first period of autoacceleration the low-temperature polymerization proceeds with a constant rate up to high conversions.

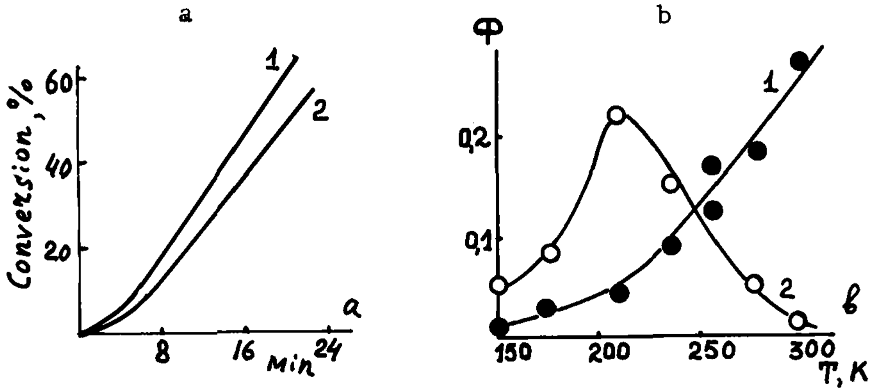

FIGURE 2 DPDA-photocyclopolymerization: a) conversion of monomer (1) and that of double bonds (2) versus time of irradiation at 125K; b) temperature dependence of quantum yelds of monomer photodimerization (1) and chain growth (2).

The rate of conversion of double bonds, W_c, and that of monomer, W_M, are related to the rates of elementary processes in the following manner:

$$W_c(N_c)_o = 2w_d + 2w_g + 2w_{co}$$

$$W_M(N_M)_o = 2w_d + w_g$$

where w_d, w_g and w_{co} are the rates of monomer photodimerization, photostimulated chain growth and photocombination of chains, resp. $(N_c)_o$ and $(N_M)_o$ are the initial number of double bonds and that of monomer molecules, resp. $(N_c)_o = 2(N_M)_o$. Considering that $w_{co} \simeq 0$, rates w_d and w_g as well as corresponding quantum yelds φ_d and φ_g can be determined from

$$w_d = \varphi_d J \simeq (N_M)_o(W_M - W_c)$$

$$w_g = \varphi_g J = (N_M)_o(2W_c - W_M)$$

where J is the radiation absorbed by monomer. As seen from Figure 2,b, φ_d rises with temperature over the full range investigated. However, φ_g reaches a maximum at 230K and than decreases rapidly, practically vanishing at about 300K (Fig. 2,b). It should be noted that the chain growth retardation occurs at a temperature of about 100 degrees below the melting point. Obviously, the difference between monomer dimerization and chain growth is due to the different disposition of reacting molecules. Unlike the photodimerization, the chain growth proceeds via the strained reactive configuration at the reaction front, in the stack (Fig. 1). This configuration is formed during monomer dimerization at low temperatures and does not change during subsequent chain growth.

To clear up the features of the chain growth, the IR-spectra of the oligomer obtained were determined in polarized light. It was shown that the dichroic ratio of the band at 1640 cm^{-1} related to the terminal double bonds, decreases with temperature over the same range in which φ_g drops (Table 1).

TABLE I Dichroic ratio K_d of 1640 cm^{-1} - the band of C=C - double bonds versus temperature

T,K	120	170	273	283	295
K_d (monomer)	1,5	1,6	1,5	1,6	1,6
K_d (oligomer)	4,5	4,3	3,4	2,0	1,9

Thus, in the course of the reaction at elevated temperatures, the reorientation of the terminal double bonds became possible (Fig. 1). This leads to the relaxation of strains and to a decrease of the reactivity of growing chains in the crystal.

Polymerization of crystalline diacetylenes under high hydrostatic pressures

Solid-state polymerization of diacetylenes was first described by G.Wegner.[6] In crystals of diacetylenes, the monomer units are arranged in stacks which resemble that of DPDA-crystal (Fig. 3). For TS-polymerization the parameter of monomer stacks (l_m) is larger than that of undeformed chains in polymer crystals (l_p). For DCH-polymerization the revers relation exists.[6] It is essential that the polymerization of the both monomers leads to the decrease of overall volume.

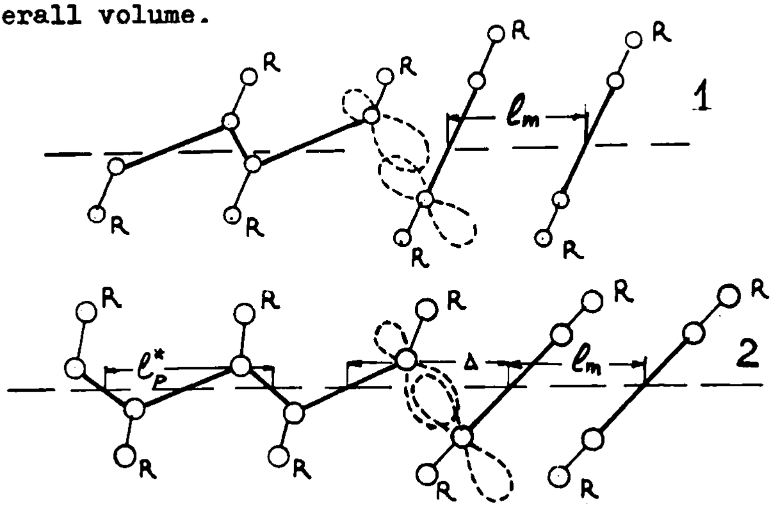

FIGURE 3 Polymer growing chain and monomer molecules in DCH (1) and TS (2). l_m and l_p* are the parameters of monomer stacks and deformed growing chains, resp. The overlapping orbitals of terminal carbenes and adjacent molecules are shown.

Polymerization was investigated up to conversions of no more than one percent.[3] In this case the chain growth occurs in the initial monomer lattice.

In TS-crystals the polymer chain is extended in the chain growth direction under the influence of monomer lattice.[7] But the parameter of the extended chain, l_p*, is less than l_m and the chain growth stops after a few steps because of geometrical restraints. As a result, at the initial stage of reaction (induction period) only short chains are formed and polymerization rate is low. Fast reaction begins at some critical monomer conversion due to the crystalline lattice change.[6] Under high hydrostatic pressures the initial rate of TS-polymerization increases and the induction period sharply decreases.[8]

To clarify the causes of the kinetical effects, we determined the spectra of polymer chains formed in TS-crystals under pressure. It was shown that energy of the exciton peak E_{ex} in these chains (Fig. 4, curve 1) increases as compared with that in ordinary polymer chains under the same conditions (Fig. 4, curve 3). This is an indication of the increase of the chain extention relative to the lattice, l_p^*/l_m, during TS-polymerization under pressure. Considering that pressure leads to lattice compression, the dependence of E_{ex} on pressure has a maximum close to 1000 bar.

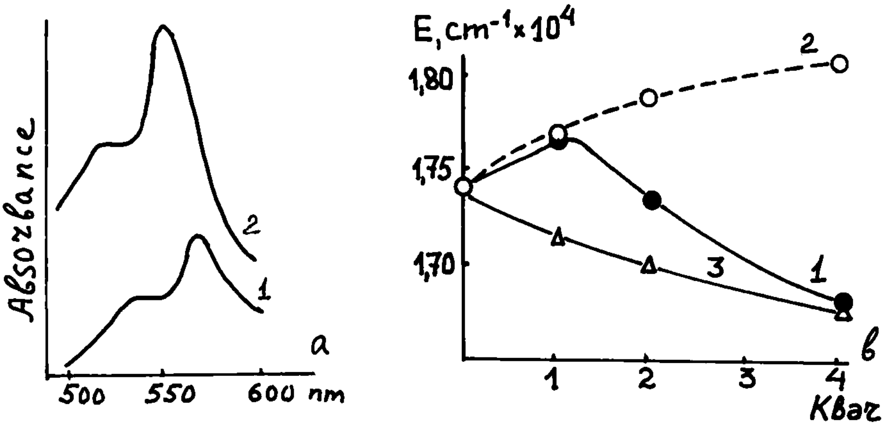

FIGURE 4 TS-polymerization at 298K: a) absorption spectra of polymer in crystals polymerized at 1 (1) and 1000 (2) bars; b) pressure dependence of energy of the polymer exciton peak in TS-crystals. 1 - crystals polimerized at various pressures and observed under polimerization conditions; 2 - the same crystals at 1 bar after pressure release; 3 - crystals polymerized at 1 bar and observed at various pressures.

We also measured E_{ex} at 1 bar after pressure release (Fig. 4, curve 2). In this case E_{ex} in crystals polymerized under various pressures increases with pressure up to a limit which corresponds to a maximum of the chain extention in monomer lattices, $l_p{}^*=l_m$. The stretching frequencies of $C=C$ - and $C\equiv C$ - bonds in the polymer chains obtained also decrease up to a limiting values (Table 2).

TABLE 2 Raman spectra of polymer chains formed in TS-crystals at various pressures (observed at 1 bar).

Pressure, bar	Stretching frequencies, cm^{-1}	
	$C=C$	$C\equiv C$
1	1450	2010
3000	1425	1950
4000	1420	1940

According to our data, the most extended chains are formed under pressures close to 4 kbar. In this case the geometrical restraints to the chain growth are absent even at the initial stage of reaction. Therefore, the induction period of TS-polymerization vanishes.[8]

Unlike TS-polymerization, the DCH-polymerization is retarded by high pressures (Fig. 5). In DCH-crystals the chains are compressed in the chain growth direction according to the crystal structure of monomer. The deformation of the chains formed in DCH under high pressures increases: the absorption band of the obtained polymer shifts to the short-wave region (Fig. 5) without noticeable change in Raman spectra.

These data are an indication that in DCH-crystals the polymerization under pressure leads to formation of slightly twisted chains and doesn't influence essentially the lengths of bonds in these chains.

In the DCH crystals the reactivity of compressed chains is reduced due to the unfavorable orientation of carbene relatively to the next molecule in the monomer stack (Fig. 3). The rearrangement of strained configurations is necessary for the reaction. The pressure hindering the rearrengement retards the reaction in this case. The strained elongated chain in TS crystals is illustrated in Fig. 3 for comparison. In this case the interaction of carbene with monomer molecule is most favorable.

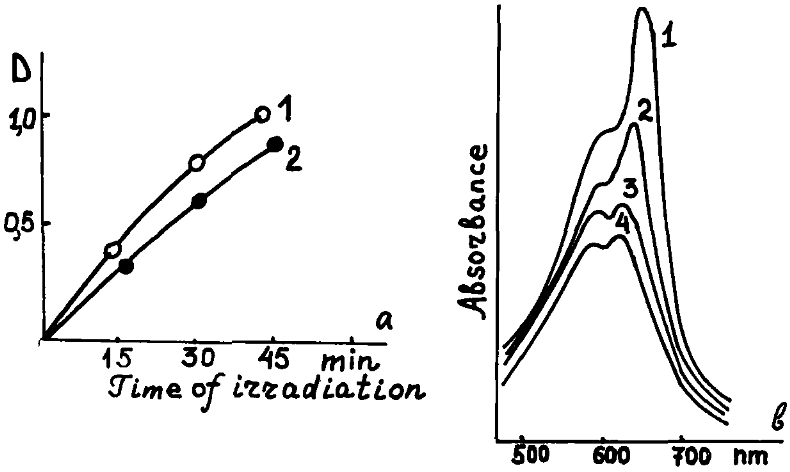

FIGURE 5 DCH-photopolymerization, 298K: a) rise of polymer absorbance in monomer crystals at 1 (1) and 1000 (2) bar; b) absorption spectra of crystals polymerized at 1 (1), 1000 (2), 2000 (3) and 3000 (4) bar. Spectra are measured at 1 bar.

REFERENCES

1. M. V. Basilevsky, G. N. Gerasimov and S. J. Petrochenko, *Zh. Fisicheskoi Khim.*, *61*, 721 (1987), in Russian.
2. G. N. Gerasimov, O. B. Mikova and A. D. Abkin, *Vysokomolekul. Soedin.*, *A27*, 1280 (1985), in Russian.
3. G. N. Gerasimov, A. N. Pankratov, A. P. Orlenko, N. V. Kozlova, E. A. Sinevitch and E. N. Teleshov, *Makromolek. Chem., Macromol. Symp.*, *26*, 131 (1989).
4. H. Nakanishi, F. Nakanishi, F. Suzaki, M. Hasegawa, *J. Polymer Sci., Polymer Chem. Ed.*, *11*, 2501 (1973).
5. F. J. Q. English, A. R. Katritsky, T. T. Tidwell and R. D. Topso, *J. Amer. Chem. Soc.*, *90*, 1767 (1968).
6. G. Wegner, *Z. Naturforsch.*, *B24*, 824 (1969); in *Molecular Metals, edited by W. E. Hatfield* (Plenum Press, New York, 1979), pp. 209-242.
7. D. Bloor, R. J. Kennedy and D. N. Batchelder, J. Polymer Sci., Polymer Phys. Ed., 17, 1355 (1979).
8. K. Löchner, H. Bässler and Th. Hinrichsen, *Ber. Bunsenges. Phys. Chem.*, *83*, 899 (1979).