# Single Orientation in Poly(diacetylene) Films for Nonlinear Optics. Molecular Epitaxy of 1,6-Bis(9-carbazolyl)-2,4-hexadiyne on Organic Crystals

**J. Le Moigne,*,† F. Kajzar,‡ and A. Thierry†**

*IPCMS, Groupe des Matériaux Organiques, Institut C. Sadron, 6, Rue Boussingault, 67083 Strasbourg-Cedex, France, and Laboratoire de Physique Electronique des Matériaux-DEIN, CEA, Saclay, 91191 Gif sur Yvette, France*

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ABSTRACT: Oriented thin films of a diacetylene derivative with carbazolyl substituents (DCH) have been prepared under vacuum by epitaxial nucleation on an organic single crystal. Polymerization performed by thermal heating preserves the anisotropic orientation of the diacetylene crystals. A good alignment of the poly(diacetylene) chains (pDCH) has been obtained on large-area single crystals of a series of acid phthalate salts used as substrates. In optical studies, the dichroism observed by UV-visible spectroscopy confirms a long-range organization established mainly by electron microscopy. The uniaxially oriented film is constituted of an arrangement of microcrystals oriented along a privileged direction of the potassium acid phthalate single crystal (KAP). The pDCH chain axis, $b_{\mathrm{pDCH}}$, is parallel to $c_{\mathrm{KAP}}$ and we propose a new type of epitaxy, "*molecular epitaxy*", based on the insertion of the DCH molecule on the KAP surface. Third-order harmonic generation has been measured on these highly oriented poly(diacetylene) films. Experimental values of $\chi^{(3)}$ measured at two wavelengths, 1.064 and 1.907 μm, confirm the three-photon resonance to the exciton in poly(diacetylene) at 650 nm (1.91 eV). A high value of the cubic susceptibility $\chi^{(3)} = 6 \times 10^{-10}$ esu is observed at 1.907 μm (0.65 eV).

## Introduction

In long π-conjugated molecules, electron delocalization and π-orbital overlap give materials that exhibit high nonlinear optical response. For π-conjugated polymers $\chi^{(3)}$ is proportional to the fifth power of the number of double bonds.[1a,b] Conjugated polymers such as poly(acetylenes), poly(diacetylenes), poly(*p*-phenylenevinylene), ladder polymers [poly(*p*-phenylene-2,6-benzobisthiazole) (PBT) or poly(*p*-phenylene-2,6-benzobisoxazole) (PBO)] present large nonresonant third-order susceptibilities, typically in the range $10^{-10}$–$10^{-12}$ esu.[2] Poly(diacetylene) (PDA) is one of the most π-delocalized of the family of conjugated backbone polymers, exhibiting particularly high cubic susceptibility values.[3a,b] New materials, such as charge-transfer complexes or radical salts have also been investigated. The organic metal complex α-[bis(ethylenedithio)-tetrathiofulvalene]$_2$I$_3$ shows the highest cubic nonlinearity, as observed by four-wave mixing[4a,b] and it appears to be a very promising material if the crystal growth process can be controlled to yield large crystals of good optical quality. However, PDAs are still considered interesting materials for their high $\chi^{(3)}$ values in relation to their large range of optical transparency. Therefore, it is very important to be able to orient the conjugated chain in order to maximize the third-order nonlinear optical response.

The topotactic polymerization of some substituted diacetylenes seems an attractive method to prepare single crystals of long conjugated polymer chains. In such crystals, perfect orientation of the polymeric backbone should result in higher cubic susceptibilities. However, many problems arise for optical applications. First, crystallogenesis of large defect-free single crystals of monomer is very difficult. Second, polymerization of diacetylenes induces large defects due to the modification of the crystalline lattice.[5a,b] Finally, as for all methods of preparation yielding polycrystalline or amorphous films, high $\chi^{(3)}$ values are strongly dependent on the polymer chain orientation and packing.

Preparations of oriented thin films for nonlinear optical applications, such as wave guides, have been reported and the various alignment techniques produce varying degrees of orientation of the polymer chains.[6] The films are generally cast from a polymer solution, the method used to prepare optical films with low optical losses. The conjugated polymer most often used is a poly(diacetylene) with urethane substituents: the latter are known to give a good solubilization and stabilize the planar configuration of the backbone. In the first method, the orientation is achieved by rubbing the poly(diacetylene) layers obtained by vacuum deposition of the monomer followed by UV polymerization. Generally this tedious method produces films of poor optical quality; the measurements of third-order nonlinear susceptibility parallel to the polymer chain, in a series of PDA urethane side groups, give $\chi^{(3)}$ values in the range of $10^{-10}$ esu. A more interesting method is the deposition of a poly(diacetylene) solution on an anisotropic polymer surface with a subsequent thermal treatment to induce the orientation of the chains.[7] Poly(4BCMU) films have been deposited by spin casting from a solution on a preoriented polymer such as poly(1,4-butylene terephthalate) (PBT). A thermal cycling treatment enhances the orientational order of the film. The increase of the film birefringence on the pair p4BCMU/PBT during the thermal treatment is, in our opinion, a weak proof of the orientation of the conjugated chain; the value of the optical dichroism may be a more convincing evidence of the monoorientation.

To produce highly oriented thin films, our approach is to synthesize highly polymerizable diacetylenes with lateral substituents perfectly adapted for an epitaxial growth. In previous work we reported some results on epitaxial growth and polymerization of 1,6-bis(9-carbazolyl)-2,4-hexadiyne (DCH) on alkali halide single crystals.[8a,b] However, the double orientation obtained in this case is not the most favorable one from an application viewpoint.

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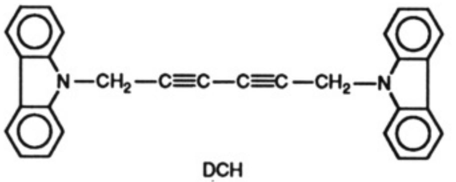
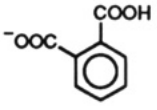
† Institut C. Sadron.

‡ Laboratoire de Physique Electronique des Matériaux-DEIN.

In this paper, we report a significant step further in the preparation of oriented thin films with enhanced nonlinear optical properties. We have prepared large-scale, thin poly(diacetylene) films with a well-characterized single orientation. The films are obtained by epitaxial growth of the same monomer (DCH) on appropriate organic crystals: *alkali acid salts of phthalate* (sodium, potassium, rubidium acid phthalates, respectively abbreviated NaAP, KAP, RbAP), which have a lower degree of symmetry than alkali halides:



DCH



acid phthalate anion

We note that KAP has already been used as an epitaxial substrate for polyolefins.[9a,b]

## Experimental Section

Experimental conditions have been described in some detail in reference 8a. DCH is produced in our laboratory. The monocrystalline substrates are prepared for microscopic observations by evaporation of an aqueous solution of substrates (KAP, NaAP, RbAP). The NaAP, KAP, and RbAP macroscopic organic crystals are supplied by Quartz et Silice (Nemours, France). In both microscopic and macroscopic preparations, the surface plane of the crystals is the natural cleavage plane (perpendicular to the *b* axis). Only freshly cleaved surfaces are used as substrates for preparation of the DCH films.

The thin films are prepared by a flash sublimation of the DCH monomer under high vacuum. The DCH vapors condense at room temperature on the freshly cleaved phthalate crystals. The samples are subsequently polymerized up to 99% by heating at 150 °C for 24 h.

The optical microscopy is performed on a K. Zeiss photomicroscope II equipped with polarizer and light phase contrast optics. Electron microscopy studies are performed with either a Hitachi HU 11CS or a Philips CM12 microscope. The optical spectroscopy experiments are performed with polarized beams on a Cary 2300 spectrophotometer (Varian).

The molecular crystalline packing has been represented by computer graphics. The simulation, using the structure data of Okaya[10a,b] corrected by Smith,[11] is performed with Sybyl 5.3 software (Evans and Sutherland), run on a DEC Vax unit linked with a graphics unit from Evans and Sutherland.

Third harmonic generation (THG) measurements have been performed at two wavelengths, 1.064 and 1.907 μm, using the apparatus previously described.[12] The light source is a neodymium-doped yttrium–aluminum garnet laser operating at 1.064-μm fundamental wavelength with 10 pulses/s repetition rate and 13-ns pulse duration. The 1.907-μm wavelength was obtained by Raman shift (first Stokes radiation) in a high-pressure hydrogen cell (56 bar). The pDCH thin film (thickness 800 Å) was mounted on a rotation stage on the laser source side. The polymer film was rotated along an axis coinciding with the beam propagation direction.

## Results and Discussion

**Optical Microscopic and Macroscopic Observations.** For optical microscopic observation the DCH monomer is deposited on thin crystals and then polymerized: viewed in natural light the polymer film is blue (see Figure 1a and b). The crystalline texture depends on the nature of the substrate. The polymer texture is rather fine around the crystal on the glass slide and it becomes smooth on the organic substrate.

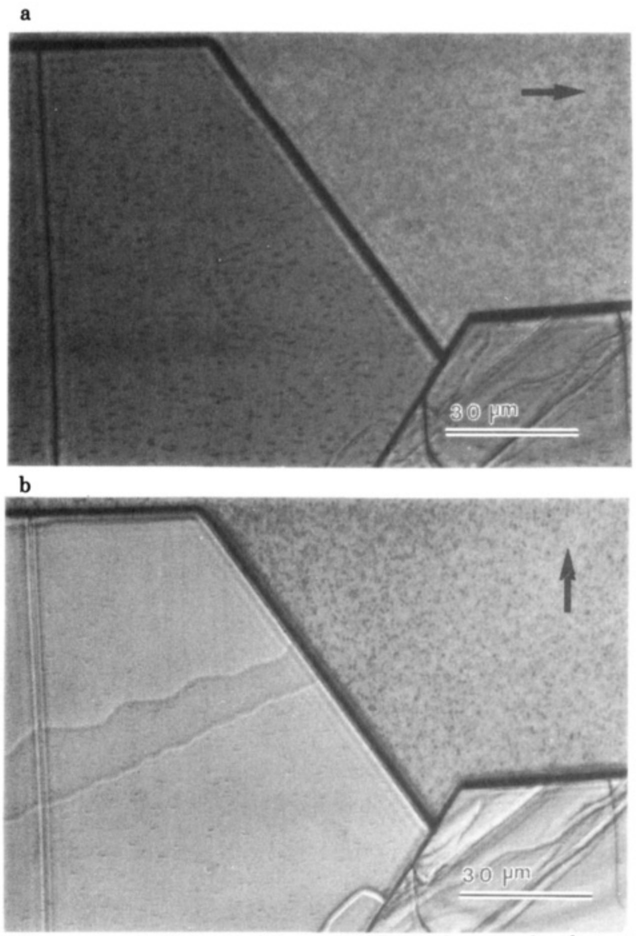


**Figure 1.** pDCH thin film on KAP single-crystal substrate observed by optical microscopy. The dichroism of the poly(diacetylene) film is observed in polarized light. The polarization direction is given by the black arrows. It can be noted that the background on the glass side is uniform. When some long needles are seen on the crystal surface, they all have the same single orientation. The crystalline faces of KAP are indexes from the reported morphology in ref 23. pDCH film thickness 20 nm.

On the thin crystals, observation in polarized light reveals the dichroism of the pDCH film due to the single orientation of the polymer chains. The intensity of the blue color depends on the relative orientation of the polymer chains with respect to the polarization plane. At the minimum absorption, the film becomes perfectly transparent and the absorption reaches its maximum when it is exactly orthogonal.

A macroscopic crystal of 9–10-cm length has also been used to realize large surfaces of monoriented pDCH.[13] An example of this preparation is presented in Figure 2a and b with the polarization axis of incident light at 90° to each other. The blue color appears with the polarization direction perpendicular to the *a* axis of the KAP crystal and transparency with the polarization direction parallel to the *a* axis of the single-crystal substrate.

**Spectroscopic Properties.** Measurements of linear optical dichroism have been performed on thin films on KAP substrates with polarized incident light beam. The results are given in Figure 3. The polarization axis of incident light is successively parallel and perpendicular to the *a* axis of the single-crystal support. The first measurement (curve a) corresponds to the polarization direction parallel to the polymer chain axis. The high

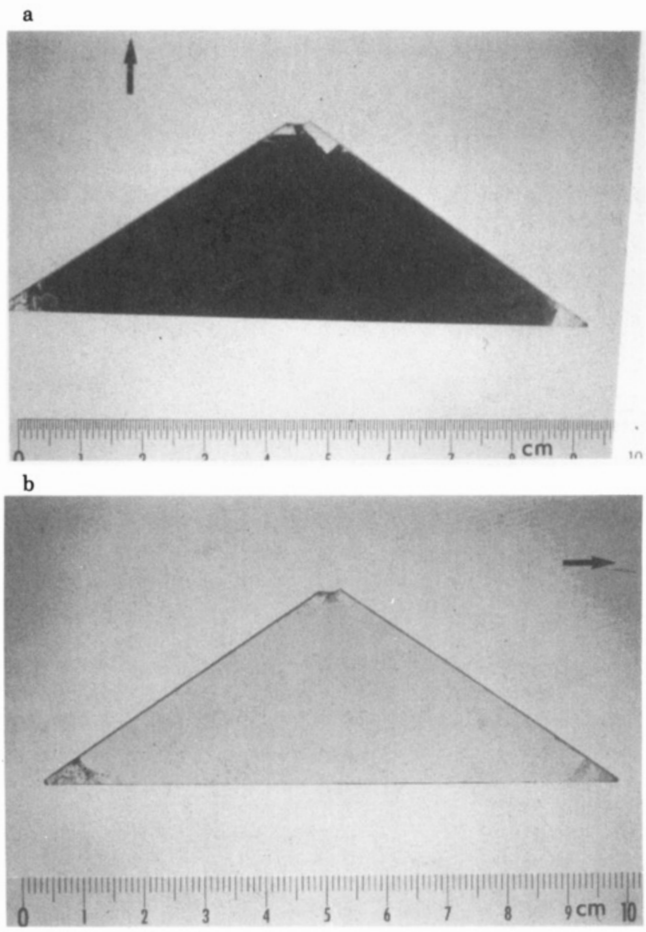


**Figure 2.** Orientation of pDCH at macroscopic scale. The dichroism of the pDCH thin film extends over the entire surface of the single KAP crystal. The polarization direction is given by the black arrows. The film appears blue when the polarization direction is parallel to the polymer chain axis (color not shown). pDCH film thickness 130 nm.

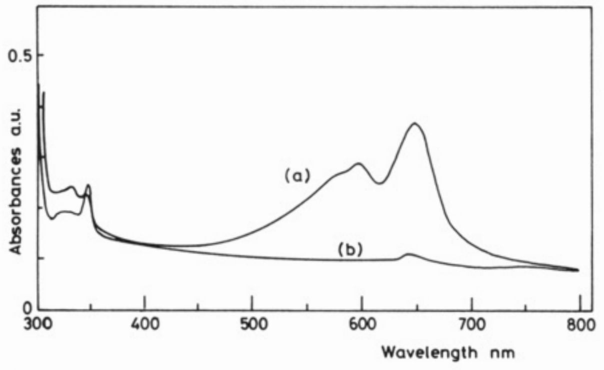


**Figure 3.** pDCH absorption spectra of a thin film grown by epitaxy on KAP substrate. Curve a is the absorption spectrum with the polarization parallel to the *c* axis of the KAP crystal; curve b is with polarization perpendicular to the same axis. pDCH thickness 30 nm.

absorption is due to the absorption by the polymeric backbone in the range from 450 to 750 nm related to the $\pi \rightarrow \pi^*$ transition. The two peaks at 650 and 596 nm correspond respectively to the exciton transition and to its vibronic side-group absorption, found in the single crystal.[12] At lower wavelengths, from 320 to 360 nm, the absorption is mainly due to the carbazolyl lateral substituent. The second curve (b) corresponds to the polarization direction perpendicular to the chain axis. The main absorption peak at lower energy vanishes. The residual low absorption at 640 nm may arise from a lack of precision in the orientation of the crystal in the experimental setting.

**Discussion of the Optical and Spectroscopic Results.** First, the absorption spectra observed with the two perpendicular polarization directions show that the polymer chain axis lies along the KAP surface. Second, from the experimental absorption in the low-wavelength range, one may expect to infer the contact plane of the DCH crystal, which should be one of the natural growth faces [(100), (102), ($\bar{1}$02)].[14] As the electronic transitions of the poly(diacetylene) bonds are quite weak in this energy range,[15] the observed absorptions must be correlated to the orientation of the carbazolyl group in the crystal. The main transitions of the carbazolyl absorption[16] have strongly different components in the natural faces. The 331- and 347-nm peaks, assigned to the carbazol short axis,[17] have been observed (Figure 3). However, the peak at 301 nm, assigned to the carbazol long axis, is masked by the intense absorption of the KAP substrate. The projection of the short-axis transition (331 and 347 nm) on the natural faces does not differ enough with the polarization direction to give any information on the epitaxial contact face. These limiting experimental conditions prevent the exact assignment of the natural face indices.

**Morphology and Structure.** The monomer DCH and the polymer pDCH crystal structures have been determined by X-ray diffraction.[18a,b] The two species are isomorphous and have monoclinic cells (space group $P2_1/c$) with the following parameters:

| | monomer | polymer |
|---|---|---|
| *a*, Å | 13.60 | 12.89 |
| *b*, Å | 4.55 | 4.90 |
| *c*, Å | 17.60 | 17.39 |
| $\beta$, deg | 94.0 | 108 |

Modification of the lattice parameters during polymerization is essentially the result of a shearing of the carbazolyl planes that maintains a constant distance (3.36 Å). The numerous defects observed in large polymer crystals have in large part their origin in the strains induced by the parameter modifications.

The needle-like morphology of the DCH crystals[14] is preserved by our experimental conditions. The electron microscopy results (described later) show that one of the lateral growth faces ($\bar{1}$02) plays a special role in the growing process of the film. The structure of the DCH monomer in this face is represented in the computer drawing of Figure 4a. The DCH molecule looks like a dumbbell, the rigid diacetylenic core linking the two carbazolyl moieties. The aromatic atoms rising from the carbazolyl group, seen edge on, line the surface plane, whereas the rigid diacetylenic cores lie down in valleys. The known structures of phthalate salts[10,11] are rather similar. The variations in the orthorhombic lattice parameters with the cation size are small, ranging from 9.31 to 10.81 Å for the first axis and from 6.40 to 6.76 Å for the second axis:

| M | crystalline parameters, Å | | | space gp |
|---|---|---|---|---|
| $Na^+$ | *a* = 9.314, | *b* = 26.42, | *c* = 6.76 | *Aba*2[11] |
| $K^+$ | *a* = 9.609, | *b* = 13.315, | *c* = 6.466 | $Pca2_1$ |
| $NH_4^+$ | *a* = 10.23, | *c* = 26.14, | *b* = 6.40 | *Pbca* |
| $Rb^+$ | *a* = 10.064, | *b* = 13.068, | *c* = 6.561 | $Pca2_1$ |
| $Tl^+$ | *b* = 10.54, | *c* = 12.95, | *a* = 6.63 | $P2_12_12$ |
| $Cs^+$ | *b* = 10.81, | *c* = 12.84, | *a* = 6.58 | $P2_12_12$ |

As an example, the KAP is built-up of alternate layers of potassium and phthalate ions stacked along the *b* axis. The cleavage plane is the (010) one. Rows of aromatic rings, standing nearly edgewise, line the cleavage contact plane (Figure 4b).

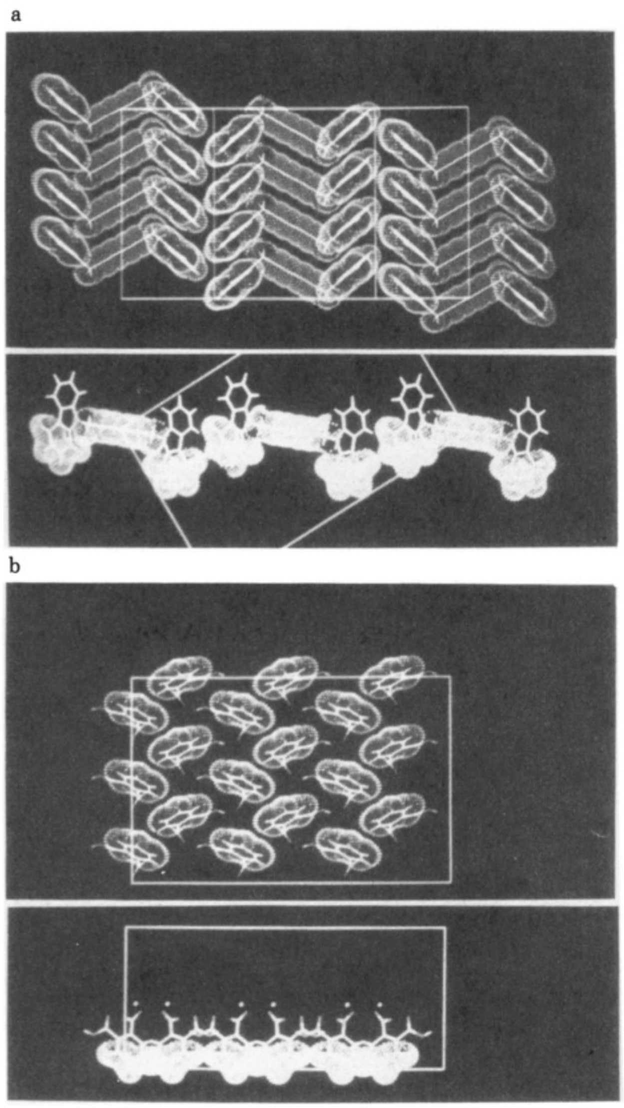


**Figure 4.** Molecular simulation of the crystal surfaces. (a) $(\bar{1}02)$ face of the DCH monomer and its orthogonal view; (b) (010) face of the KAP and its orthogonal view.

The following description is divided into two parts: first, the description of the morphology of the film observed in the three cases, KAP, NaAP, and RbAP; and second, the description and detailed discussion of the geometric interactions involved in the epitaxial growth on KAP substrate.

**Electron Microscopy.** Bright-field observations indicate an excellent quality of the pDCH films on KAP (Figure 5). Although polycrystalline, the texture is extremely fine and homogeneous. Compared for instance to the films prepared under the same conditions on KBr,[8] the width of the crystallites is $^1/_3$ to $^1/_5$ smaller and they tend to lie down in a single direction. On both macroscopic and microscopic substrates, crystals are produced with the same single orientation, as shown by selected area diffraction (inset in Figure 5). The reflections are organized in the classical layered structure, which clearly arises from the single orientation of the pDCH crystals. They are slightly arced with a half-width of ±8°, thus confirming the narrow distribution of the crystal orientations around the main direction. Some long needles are misoriented; the number of such defects is extremely small.

Two other acid phthalate salts can be grown into large macroscopic monocrystals (RbAP, NaAP). We have determined that both salts used as substrates also induce a single orientation of DCH monomer and hence of the resulting DCH polymer (Figure 6).

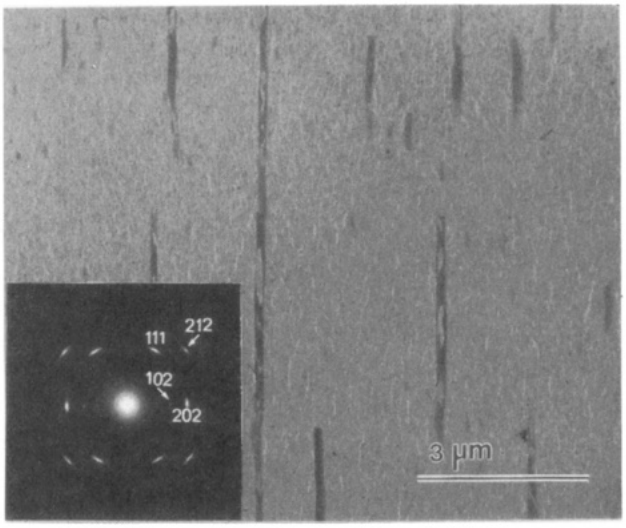


**Figure 5.** Bright-field microscopy of a pDCH film grown on KAP. The polymerized film is constituted of fine and long needles on a background of elongated crystals; all of them are parallel. pDCH film thickness 30 nm. Inset, the corresponding electron diffraction pattern.

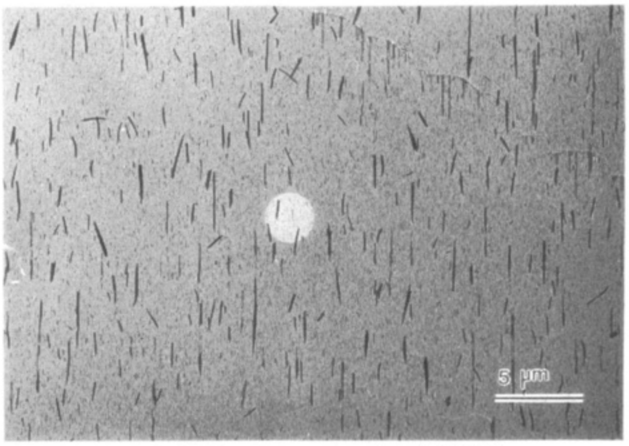


**Figure 6.** Bright-field microscopy of a pDCH film grown on RbAP. pDCH film thickness 32 nm.

**Geometric Interactions and Epitaxy.** The crystallographic relationship between the monomer crystal and the substrate crystal cannot be determined directly from the composite diffraction pattern, since the monomer polymerizes quasi-instantaneously under the electron beam. During this polymerization a crystalline-phase transition takes place that induces a change in the crystalline parameters (vide supra). However, a realistic characterization of the epitaxial monomer–substrate relationship may be inferred from that of the polymer–substrate one, as determined with the aid of a *composite diffraction pattern*.

For these particularly complex diffraction patterns, we have prepared extremely thin crystals of the substrate (less than 30 or 40 nm) on which the pDCH films are grown by epitaxy using the above-mentioned method. We can thus obtain in a single exposure a composite diffraction pattern of the two types of crystals (substrates and pDCH) and determine the relative orientation of the two materials. These composite diffraction patterns are shown in Figure 7a for KAP and 7b for NaAP.

As in every case studied so far (present work and ref 8), the pDCH contact plane is $(\bar{2}03)$. We also observe on the diffraction pattern the $(\bar{1}01)$ and $(\bar{1}02)$ dense planes, which

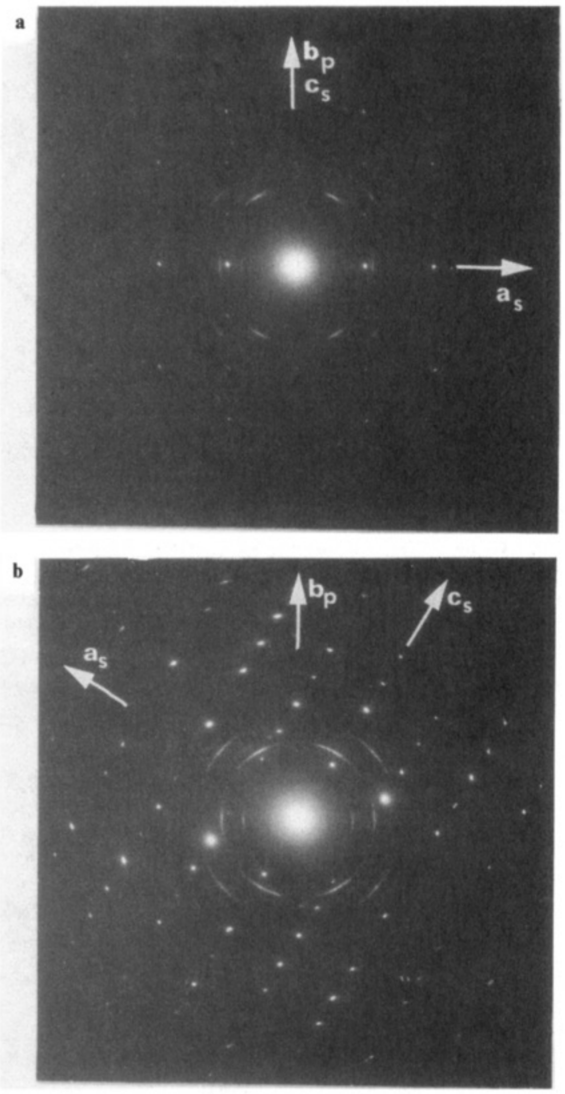


**Figure 7.** Composite diffraction pattern of pDCH. The arrows indicates the main cristallographic directions: *p* subscript for the polymer; *s* subscript for the substrate. Film thickness 21 nm; (a) on KAP, (b) on NaAP.

lie within 15° of ($\bar{2}03$). ($\bar{2}03$) comes from the original ($\bar{1}02$) plane of the monomer crystal; if we assume that during the phase transformation of the DCH monomer crystal into the polymer the *b* direction remains constant and that transformation proceeds by shearing in the (010) plane parallel to the [001] direction (see Figure 8a,b and ref 18a).

**Discussion of the Relative Orientations.** The relationships derived from composite electron diffraction patterns *of pDCH on KAP* are the following: contact planes, $(\bar{2}03)_{\mathrm{pDCH}}//(010)_{\mathrm{KAP}}$; directions, $b_{\mathrm{pDCH}}//c_{\mathrm{KAP}}$, $[101]_{\mathrm{pDCH}}//a_{\mathrm{KAP}}$.

These observations are consistent with optical macroscopic observations under polarized light, which indicate that the polymer chain axis lies in the direction of the *c* axis of the KAP substrate.

Therefore, the initial orientation of the *DCH monomer on KAP* can be traced back and is most probably as follows: contact planes, $(\bar{1}02)_{\mathrm{monomer}}//(010)_{\mathrm{KAP}}$, with $b_{\mathrm{monomer}}//c_{\mathrm{KAP}}$.

The epitaxial relationships turn out to be different for the two substrates (KAP and NaAP). For NaAP the two patterns are tilted relative to each other by 32°, *b* of pDCH differs by 32° from the *c* direction of NaAP, and $[101]_{\mathrm{pDCH}}$ makes the same 32° angle with the $a_{\mathrm{NaAP}}$ direction. This will be further discussed.

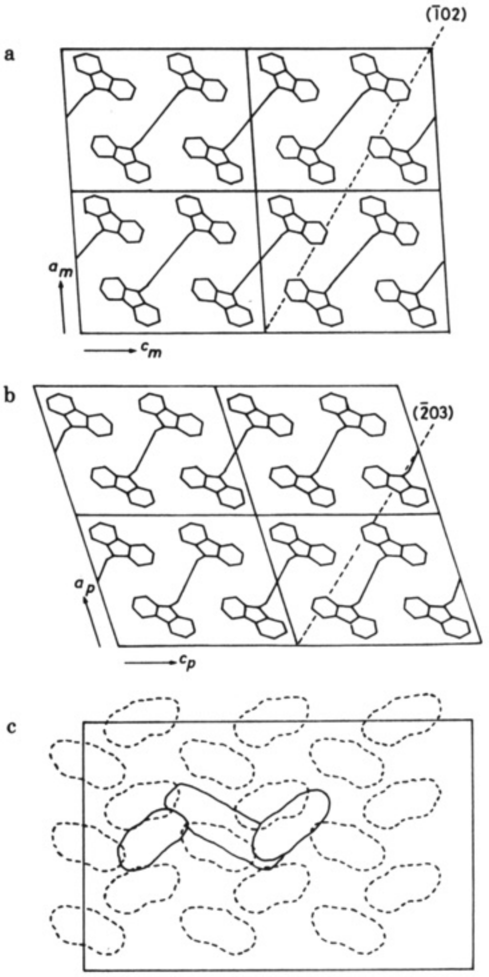


**Figure 8.** Schematic drawing of the geometric relation between $(\bar{1}02)_{\mathrm{DCH}}$ and $(\bar{2}03)_{\mathrm{pDCH}}$. (a) (010) monomer face; (b) (010) polymer face; (c) schematic drawing of the orientation of the first DCH molecule on the (010) KAP face.

The geometric crystallographic relations are clearly established through the analysis of the composite diffraction pattern. However, these relations, in the case of KAP, are nontypical for epitaxy. It is usually accepted that there must be a direct matching between the crystallographic parameters or between rows of molecules. Here the matching is obtained between $3b_{\mathrm{DCH}} = 13.65$ Å and $2c_{\mathrm{KAP}} = 12.92$ Å in one direction (with a mismatch of 5.6%) and between 2[101] = 31.35 Å and $3a_{\mathrm{KAP}} = 28.83$ Å in the other direction.

In spite of this rather weak matching, the molecular orientation of the DCH monomer on KAP crystals has always been obtained in numerous experiments either on microscopic crystals or on very large crystals of KAP.

The concept of mutual orientation of crystals, named epitaxy by Royer,[19a] was based on the structural matching of crystallographic directions in the contact plane. It was nevertheless admitted that a mismatch of lattice parameters does not prohibit the oriented overgrowth of crystals: actually it was observed experimentally that the mismatch should not exceed 15% disregistry.[19b] When a more complex lattice matching is described,[19c,d] the authors do consider a close matching between the rows of molecules (or atoms) in the contact planes of crystal/substrate.

Considering these results, the oriented overgrowth of DCH on phthalate salts is rather peculiar. We believe that the orientation of DCH is driven by the molecular insertion of the carbazolyl group between KAP phenyl rings. Hence we propose the name of "*molecular epi-*

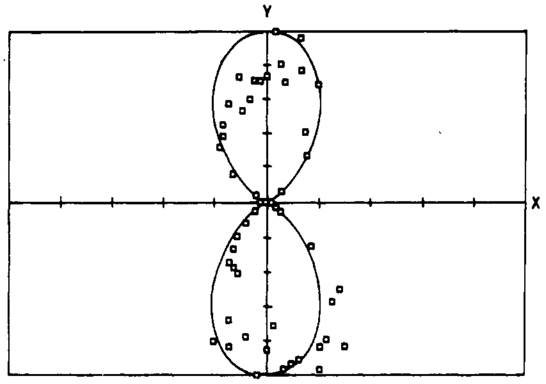


**Figure 9.** Third-harmonic intensity versus the rotation angle $\theta$ of the film around an axis normal to the substrate. PDCH monooriented film of 80-nm thickness on a KAP crystal. Solid line is the least-squares fit of eq 6 to experimental values. The incident wavelength is 1.907 $\mu$m.

*taxy*". Moreover, a careful examination of the geometric relations shows that, in the contact plane, DCH/KAP, the aromatic planes have nearly the same orientation within 10°. The angles formed between the phenyl planes and the contact plane for DCH and KAP are, respectively, 41.8 and 32.8°. The spacing between the two carbazolyl groups in the DCH monomer is nearly equal to the spacing between two of the deepest wells surrounded by the aromatic rings of the stacked rows along the KAP *c* axis (see Figure 8c). Therefore, a molecule of monomer, coming from the vapor phase, can easily lie down in the valley between these phenyl groups. As the rigid core of the DCH monomer is thinner than the carbazolyl group, there is no steric hindrance between the rigid core and the phenyl groups located in the intercalated row. Once this first molecule has settled onto the KAP crystal, the DCH crystal, which has a preferrential growth direction along the *b* axis (needle-like morphology), can then easily grow. If we now consider the other row of phenyl groups stacked along the $c_{\mathrm{KAP}}$ axis, a DCH molecule with its carbazolyl groups inserted in the corresponding wells maintains the $b_{\mathrm{DCH}}$ direction.

This nucleation and orientation process of DCH on the acid phthalate salts is quite original; it is based upon the insertion of the first deposited molecule on the substrate. The position of this first molecule is probably stabilized through $\pi$ interactions between the phenyl groups of the DCH molecule and those of the substrate. One cannot rule out completely the occurrence of $\pi$ interactions between the rigid core of DCH and the so-called intercalated row of KAP, which may also take part in the stabilization of the first molecule on the substrate.

**Nonlinear Optical Properties: Third Harmonic Generation (THG) Studies.** Figure 9 shows angular dependence of third-harmonic intensity for a full-angle scan. A strong dependence on rotation angle is seen with two maxima corresponding to parallel and antiparallel orientation of electric field with respect to polymer chains (0 and 180°, respectively).

For the present experimental situation, and neglecting harmonic field generated in the substrate, the harmonic intensity from a thin film with thickness $l$ is given by[20]

$$I_{3\omega} = \frac{64\pi^4}{c^2}(e^{i\varphi^{\mathrm{p}}_{\mathrm{H}}})^2\left(\frac{\chi^{(3)}}{\Delta\epsilon}\right)^2 |A(e^{i\Delta\varphi} - 1)|^2 (t_\omega{}^{\mathrm{op}})^6 (t_{3\omega}{}^{\mathrm{so}})^2 I^3_\omega \qquad (1)$$

where $\Delta\epsilon = (n^{\mathrm{p}}_\omega)^2 - (n^{\mathrm{p}}_{3\omega})^2$ is the dielectric constant dispersion between fundamental (F) and harmonic (H) frequency, $I_\omega$ is the fundamental beam intensity, and $\Delta\varphi$ is the corresponding phase mismatch in polymer film. For the normal incidence

$$\Delta\varphi = \frac{6\pi l}{\lambda_{\mathrm{F}}}(n^{\mathrm{p}}_\omega - n^{\mathrm{p}}_{3\omega}) = \varphi_\omega - \varphi_{3\omega} \qquad (2)$$

$A$ is a factor arising from boundary conditions[21]

$$A = (n^{\mathrm{p}}_{3\omega} + n^{\mathrm{p}}_\omega)/(n^{\mathrm{s}}_{3\omega} + n^{\mathrm{p}}_\omega) \qquad (3)$$

and $t^{ij}_{\omega(3\omega)}$ are corresponding transmission factors between $i$ and $j$ media:

$$t^{ij}_{\omega(3\omega)} = 2n^i_{\omega(3\omega)}/(n^i_{\omega(3\omega)} + n^j_{\omega(3\omega)}) \qquad (4)$$

the subscripts o, p, and s referring to air (vacuum), polymer film, and substrate, respectively.

Due to the fact that polymer film is absorbing at harmonic frequency, the corresponding refractive index is complex:

$$n^{\mathrm{p}}_{3\omega} = n^{\mathrm{r}}_{3\omega} + ix_{3\omega} \qquad (5)$$

For the experimental situation described here and 1D-enhanced cubic susceptibility tensor $\chi^{(3)}{}_{xxxx}$, the harmonic intensity should depend to the eight power of cosine of the rotation angle:

$$I_{3\omega} = A\cos^8(\theta + \theta_0) \qquad (6)$$

where $\theta_0$ is the reference angle. The solid line in Figure 9 shows results of least-squares fit of eq 6 to the experimental data. An excellent agreement is seen ($A$ = 140 mV and $\theta_0$ = 90°) showing the one-dimensional orientation of polymers chains.

Using an isotropic pDCH with a thickness of 3270 Å deposited on a silica substrate as standard and measured under the same conditions, we have determined the relative value of $\chi^{(3)}{}_{xxxx}$ with respect to that of $\langle\chi^{(3)}{}_{xxxx}\rangle$ for isotropic film. The absolute value of $\chi^{(3)}{}_{xxxx}$ for monooriented film was then obtained by measuring the relative value of $\langle\chi^{(3)}{}_{xxxx}\rangle$ for isotropic film with respect to that of silica in vacuum. Using for silica the value for $\chi^{(3)}{}_{xxxx} = 2.8 \times 10^{-14}$ esu as determined by Meredith et al.,[22] one obtains

$$\chi^{(3)}{}_{xxxx} = (1.04 \pm 0.1) \times 10^{-10} \text{ esu at } 1.064\ \mu\text{m}$$

and

$$\chi^{(3)}{}_{xxxx} = (6 \pm 0.6) \times 10^{-10} \text{ esu at } 1.907\ \mu\text{m}$$

The $\chi^{(3)}{}_{xxxx}$ value at 1.907 $\mu$m is resonantly enhanced by a factor of 6 with respect to that at 1.064 $\mu$m (three-photon resonance[8a,12]). We note here an excellent agreement with the value reported by Sauteret et al.[3a] for a PTS single crystal at 1.907 $\mu$m [$\chi^{(3)}{}_{xxxx} = (8.5 \pm 5) \times 10^{-10}$ esu]. The values reported are larger than those previously deduced by us from THG measurements on an isotropic film.[8a] The reason probably lies in a different polymerization yield of this sample and a larger conjugation in the monooriented films. The previous methods used to prepare oriented films, such as rubbing of a polymerized layer obtained by vacuum deposition followed by polymerization,[6] give a lower calculated value of the susceptibility along the polymer chain than our measurements. A large enhancement is also observed for the three-photon resonance. However, a fine comparison of $\chi^{(3)}$ is difficult, as the mesure of $\chi^{(3)}$ is strongly dependent on the thickness of the layer. Due to removal of material during the rubbing preparation, the calculated cubic susceptibility value must be estimated with a large error. The anisotropy ratio $\chi^{(3)}_{\mathrm{parall}}$ to $\chi^{(3)}_{\mathrm{perpend}}$ is a excellent indication of the degree of polymer chain orientation, and we found a higher value than that found in the rubbing films. These measurements give a value for the nonlinear anisotropy equal to or greater than 140 for our epitaxial samples whereas the average anisotropy of the rubbing samples is approximately 20, with an exceptional value of 96 in the best preparation.

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## References and Notes

(1) (a) Hermann, J.P.; Ducuing, J. *J. Appl. Phys.* **1974**, *45*, 5100. (b) Rustagi K. C.; Ducuing, J. *Opt. Commun.* **1974**, *10*, 258.

(2) Dalton, L. R.; Thomson, J.; Nalwa, H. S. *Polymer* **1987**, *28*, 543.

(3) (a) Sauteret, C.; Hermann, J. P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R.; Chance R. R. *Phys. Rev. Lett.* **1976**, *36*, 956. (b) Carter, G. M.; Thakur, M. K.; Chen, Y. J.; Hrynievicz, J. V. *Appl. Phys. Lett.* **1985**, *47*, 457.

(4) (a) Huggard, P. G.; Blau, W.; Schweitzer, D. *Appl. Phys. Lett.* **1987**, *51*, 2183. (b) Sipp, B.; Klein, G.; Lavoine, J. P.; Penicaud, A.; Batail, P. *Chem. Phys.* **1990**, *144*, 299.

(5) (a) Young, R. J.; Read, R. T.; Bloor, D.; Ando, D. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 509. (b) Young, R. J.; Read, R. T.; Petermann, J. *J. Mater. Sci.* **1981**, *16*, 1835.

(6) Kanetake, T.; Ishikawa, K.; Hasegawa, T.; Koda, T.; Takeda, K.; Hasegawa, M.; Kubodera, K.; Kobayashi, H. *Appl. Phys. Lett.* **1989**, *54*, 2287.

(7) Patel, J. S.; Sin-Doo Lee; Baker, G. L.; Shelburne, J. A., III *Appl. Phys. Lett.* **1980**, *56*, 131.

(8) (a) Le Moigne, J.; Thierry, A.; Chollet, P. A.; Kajzar, F.; Messier, J. *J. Chem. Phys.* **1988**, *88*, 6647. (b) Le Moigne, J.; Thierry, A.; Chollet, P. A.; Kajzar, F.; Messier, J. *SPIE's 32nd Int. Tech. Symp. Opt. Opto-Electron. Appl. Sci. Eng.* **1988**, *971*, 173.

(9) (a) Walton, A. G.; Carr, S. H.; Baer, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 603. (b) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1837.

(10) (a) Okaya, Y.; Pepinsky, R. *Acta Crystallogr.* **1957**, *10*, 324. (b) Okaya Y. *Acta Crystallogr.* **1965**, *19*, 879.

(11) (a) Smith, R. A. *Acta Crystallogr.* **1975**, *B31*, 1773 (b) **1975**, *B31*, 2345. Note: the nonstandard space group of *NaAP*, *B2ab*, given by Smith is erroneous and is inconsistent with the standard group *Aba*2. The space group corresponding to the given parameters must be *B2cb*.

(12) Kajzar, F.; Messier, J. *Thin Solid Films* **1985**, *132*, 11.

(13) Le Moigne, J.; Thierry, A.; Guerder, P. Eur. Pat. *89 403 536.9*, 1989.

(14) Enkelmann, V.; Leyrer, R. J.; Schleier, G.; Wegner, G. *J. Mater. Sci.* **1980**, *15*, 168.

(15) Kawaoka, K. *Chem. Phys. Lett.* **1976**, *37*, 561.

(16) Johnson, G. E. *J. Phys. Chem.* **1974**, *78*, 1512.

(17) Hood, R. J.; Müller, H.; Eckhardt, C. J.; Chance, R. R.; Yee, K. G. *Chem. Phys. Lett.* **1978**, *54*, 295.

(18) (a) Enkelmann, V.; Schleier, G.; Wegner, G.; Eichele, H.; Schwoerer, M. *Chem. Phys. Lett.* **1977**, *52*, 314. (b) Apgar, P. A.; Yee, K. C. *Acta Crystallogr.* **1978**, *B34*, 957.

(19) (a) Royer, L.; *Bull. Soc. Fr. Mineral. Crystallogr.* **1928**, *51*, 7. (b) Mauritz, K. A.; Baer, E.; Hopfinger, A. J. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 1. (c) Fisher, E. W.; Willems, J. *Makromol. Chem.* **1966**, *99*, 85. Wittmann, J. C.; Lotz, B. *Polymer* **1989**, *30*, 33.

(20) Kajzar, F.; Messier, J.; Rosilio, C. *J. Appl. Phys.* **1986**, *60*, 3040.

(21) Kajzar, F.; Messier, J. *Phys. Rev.* **1985**, *A32*, 2352.

(22) Meredith, G. R.; Buchalter, B.; Hanzlik, C. *J. Chem. Phys.* **1983**, *78*, 1533.

(23) Hottenhuis, M. H. J.; Lucasius, C. B. *J. Cryst. Growth* **1989**, *94*, 708.