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# Epitaxial polymerization of $(SN)_x$ : Lattice effects on structures and topochemistry

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Disulfur dinitride was epitaxially crystallized from the vapor phase on freshly cleaved (100) faces of monovalent alkali halide single crystals. Subsequently, the dimer was polymerized in the solid state, while still on the substrates. This epitaxial polymerization leads to highly oriented crystalline polythiazyl  $[(SN)_x]$  which shows no evidence of the usual fibrillar morphology. Fibrils of  $(SN)_x$  have been produced by epitaxial polymerization of a second layer of dimer on a previously polymerized layer. Three new structures of polythiazyl have been observed from crystals grown on NaCl, KBr, and KI. The structures differ significantly from the usual  $\alpha$  phase of  $(SN)_x$ . Because of such large differences in the polymer chain spacing in these forms when compared to the normal form, a new polymerization mode and direction may be involved. The diagnosis of the true effect of water on  $(SN)_x$  using Fourier-transform infrared spectroscopy (FT-ir) aided in discovering why structural studies from samples exposed to water are impossible.

PACS numbers: 82.35. + t

## I. INTRODUCTION

Polythiazyl was the first example of a metalliclike conductor which was also a linear macromolecule. Its unusual one-dimensional optical and electronic properties have been the subject of many studies,<sup>1-6</sup> as have its structure and polymerization mechanism.<sup>7-10</sup> Since the authors are well versed in the technique of epitaxial crystallization and its application to improvement of orientation and modification of structure,<sup>11-15</sup> we have continued to pursue the application of epitaxial polymerization to this unique inorganic polymer.

The phenomenon of an epitaxial crystallization of a monomeric species followed by a substrate-controlled solid-state polymerization was initially investigated in a previous paper.<sup>16</sup> The substrate also controlled the dimer crystal structure, and indirectly controlled the nature of the polymerization in this way. In that work, it became clear that the alkali halide (100) face would shape-oriented single crystals of polythiazyl being more perfect than the normal fibrous polymer. Furthermore, it was found that a new structure of polythiazyl could be produced on certain alkali halides (NaF and KI), with the polymer chain spacing matching the [110] dimension of each salt. Because of the novelty of this phenomenon, a more complete study was undertaken to investigate all possible interactions between  $(SN)_x$  and alkali halides.

## II. EXPERIMENTAL

The sample preparation for microscopic examination has been previously described in detail,<sup>16</sup> and will only be briefly reviewed here. Tetrasulfur tetranitride was sublimed at 100 °C and  $10^{-5}$  Torr. The vapor was passed through hot  $Ag_2S$  wool at 210 °C, forming SN monomer radicals. A small fraction of these monomers deposited on the vessel walls above the catalyst and formed a blue film of polythiazyl immediately. The rest of the radicals underwent dimerization to form  $S_2N_2$ . The hot  $S_2N_2$  vapor condensed and crystal-

lized on a single-crystal alkali halide kept at -78 °C.

After polymerizing at room temperature for 24 h, the sample was removed from the vacuum system. Following



FIG. 1. Polythiazyl epitaxially polymerized on a (100) surface of KCl. The rectangular platelets are oriented in the  $\langle 100 \rangle$  directions of the substrate (direction of arrow on micrographs). (a) Large individual crystals shadowed at a 45° angle. (b) Crystals merging into uniform film (shadowed at a 45° angle)

suitable shadowing of the sample, a collodion stripping technique was used to place the coated polymer film on electron microscope grids. A Jeol JEM 100B transmission electron microscope was employed in both bright-field and diffraction modes for examination of the polymer samples. Some samples were examined while still on the alkali halide single-crystal substrate using Fourier-transform infrared spectroscopy (FT-ir). The instrument was a Digilab FTS-14 Spectrophotometer.

### III. RESULTS AND DISCUSSION

#### A. Morphology and structure

Eventually, dimer crystals grow together, forming a uniformly thick featureless film when deposited on the (100) face of an alkali halide. At this stage it is impossible to examine any orientational effect of the substrate. But by carefully controlling the decomposition process, one may stop growth of these epitaxial crystals prior to complete film formation. These nucleated crystals are usually rectangular platelets, which are 1–2  $\mu\text{m}$  thick in lateral dimensions but only 100 nm or less in thickness. In addition, the crystals are highly oriented along the two  $\langle 110 \rangle$  directions of the substrate (Fig. 1).

When  $(\text{SN})_x$  was polymerized on potassium chloride (KC1), electron diffraction indicated that the usual  $\alpha$  form



FIG. 2. Electron diffraction from above rectangular crystals. The rectangular net cannot be indexed as the  $\alpha$  or  $\beta$  phases of  $(\text{SN})_x$ . The new  $\gamma$  indexing is shown in the illustration below.

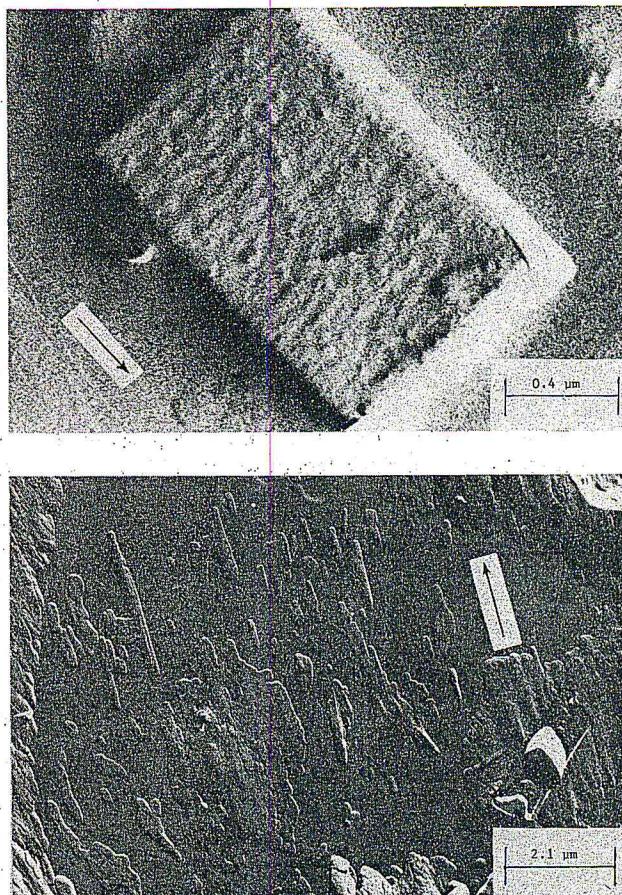


FIG. 3. (a) Electron micrograph of  $(\text{SN})_x$  single crystal grown in NaCl. The arrow is in the substrate's  $[110]$  direction. Shadow angle is  $45^\circ$ . (b) Elongated platelet morphology dominates in epitaxially polymerized polymer on NaCl. Note the diffuse ridges in the crystals which align along the  $[110]$  spacings in the surface (arrow direction).

was present.<sup>16</sup> However, when potassium iodide (KI) or sodium fluoride (NaF) were used as substrates, a new diffraction pattern was obtained which could not be indexed by the known  $\alpha$  or  $\beta$  structures of polythiazyl. It was termed the  $\gamma$  structure,<sup>16</sup> and its typical electron diffraction shows very sharp spots (Fig. 2). This sharpness indicates large crystal sizes and a high degree of lattice perfection induced by the epitaxial substrate.

We have since examined several new alkali halides [i.e., sodium chloride (NaCl), potassium bromide (KBr), potassium fluoride (KF), and rubidium iodide (RbI)] as potential substrates influencing an epitaxial polymerization of  $(\text{SN})_x$ . We found that the last two substrates, KF and RbI, are so hygroscopic that their potential to orient the dimer is not realized. Their (100) surfaces rapidly became wet when freshly cleaved in air, and when the water was removed in the vacuum system, recrystallization caused microcrystals to form on the surface. The polycrystalline topology eliminates any orientation possibility in the  $(\text{SN})_x$  crystals polymerized on KF or RbI. Additionally, no structural information could be obtained from these crystals due to the large water concentration present after removal from the vacuum

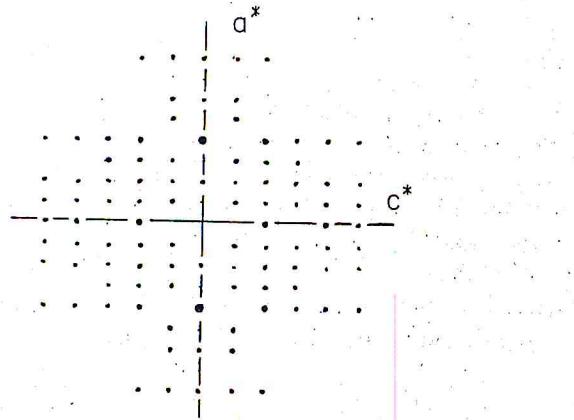
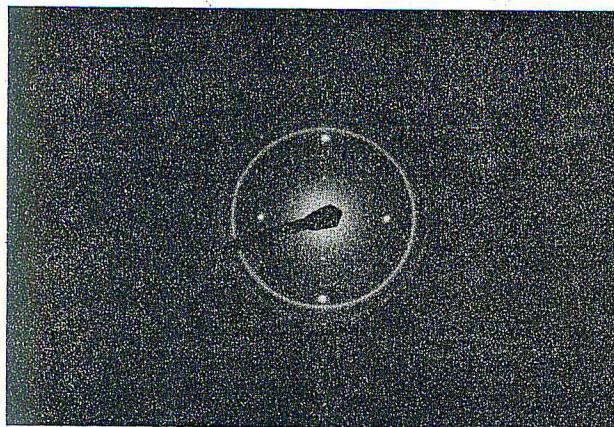


FIG. 4. Electron diffraction taken from the rectangular platelets on NaCl. The net is indexed as a new  $\delta$  phase projection as illustrated.

system. The FT-ir study of the  $(SN)_x$  on these substrates indicates a high degree of degradation by water.<sup>18</sup>

In contrast, sodium chloride proved an excellent substrate for the epitaxial polymerization of  $(SN)_x$ . Two different morphologies were observed in thin films on NaCl. A small amount of the observed growth was the usual rectangular platelet morphology (RPM) observed on NaF, KI, and KC1 [Fig. 3(a)]. These platelets were also oriented in the substrates'  $\langle 110 \rangle$  directions. More of the substrate, however, was covered with an elongated platelet morphology (EPM) [Fig. 3(b)]. EPM is characterized by very thin crystals with irregular edges and diffuse ridges present in their interior. These ridges are aligned with the long edges of the crystal in the  $\langle 110 \rangle$  directions of NaCl.

No electron diffraction was obtained from the RPM regions on sodium chloride, but excellent rectangular net patterns were obtained from the EPM domains (Fig. 4). As we previously observed when diffraction was obtained from the RPM on KI, only one pattern was available per crystal, and there was no evidence of twinning or other defects in the pattern. The absence of diffraction from the RPM regions can be explained by the low probability of observing such areas in any particular sample examined.

Potassium bromide also yielded more EPM than RPM for epitaxially polymerized polythiazyl (Fig. 5). The elongated crystals were highly oriented along the  $\langle 110 \rangle$  direc-

tions of KBr. Electron diffraction from the EPM regions was excellent and yielded rectangular net diffraction patterns, indicating large crystal sizes and a high degree of lattice perfection as before (Fig. 6).

All patterns obtained from electron diffraction of  $(SN)_x$  formed on KC1, KI, KBr, and NaCl are similar in shape. These nets, however, cannot be superimposed.

### B. The structures of $(SN)_x$

In the case of the epitaxial polymerization of  $(SN)_x$  on KI and NaF, it was seen that a new unit cell had to be conceived in order to index the two different diffraction patterns obtained.<sup>16</sup> By analogy to the observed  $\alpha$  form of  $(SN)_x$  on KC1, it was assumed that the polymer chain axis was always in the plane of the substrate. The new  $\gamma$  unit cell had a chain axis close to the  $[110]$  spacing of KI and also matched on a 2 : 3 basis with the  $[110]$  spacing of NaF. Such multiple lattice matchings have been a frequent epitaxial phenomenon.<sup>17</sup>

If unit-cell axes are assigned in a similar manner to the diffraction patterns of  $(SN)_x$  formed on NaCl and KBr, two new structures of  $(SN)_x$  are found (Table I). Since only one projection of the reciprocal lattice of the  $\delta$  and  $\epsilon$  forms was observed, only a partial space group can be assigned to each. More symmetry is possible in these structures.

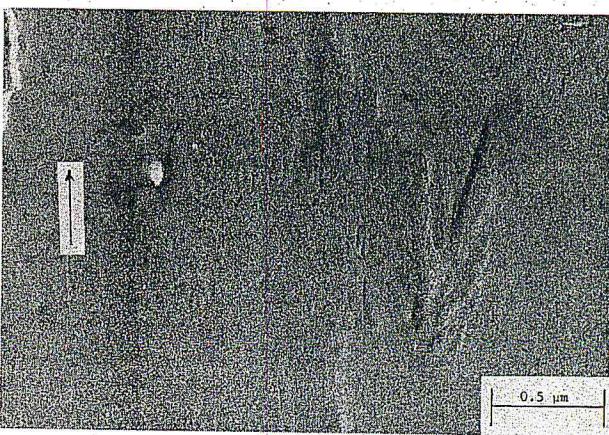
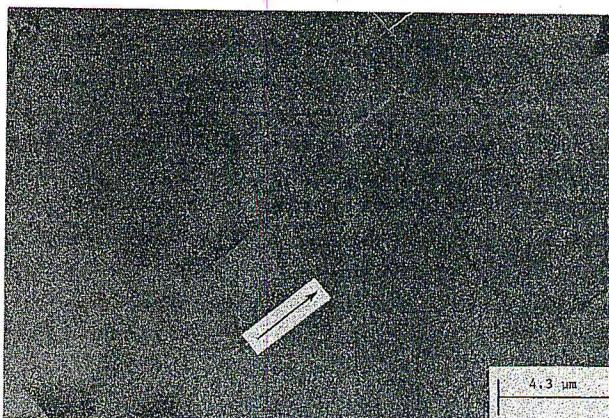


FIG. 5 (a) Rectangular platelets of  $(SN)_x$  on the  $(100)$  surface of KBr. These crystals are aligned in the  $\langle 110 \rangle$  direction as well. (b) Elongated platelets on KBr are shown oriented in the  $\langle 110 \rangle$  direction. Shadow angle is  $45^\circ$ .

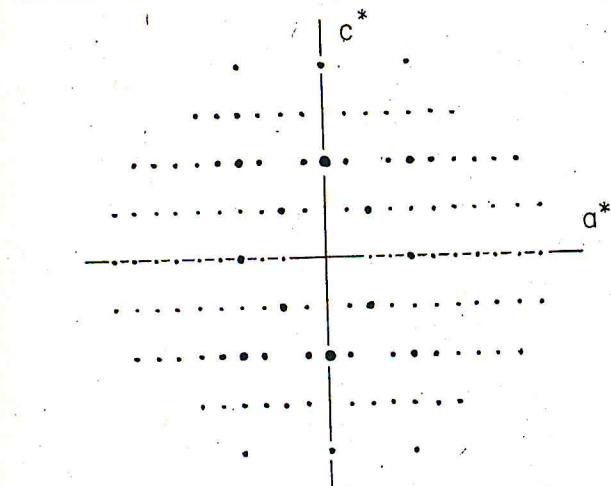


FIG. 6. Diffraction from these platelets is yet another rectangular net. A new  $\epsilon$  indexing is used to index the pattern and is illustrated below.

It is interesting to investigate the possibility of lattice matching in the  $\delta$  and  $\epsilon$  structures, as was done for the  $\alpha$  and  $\gamma$  unit cells.<sup>16</sup> The chain axes do match with the  $\langle 110 \rangle$  spacings of the substrates (Table II). In all cases the  $\delta$  factor, or percent mismatch, is well below the 5% considered acceptable for basal plane pseudomorphism.<sup>17</sup> It also became clear during this matching exercise that the intermolecular spacings in the four epitaxially produced  $(SN)_x$  phases match with the substrates'  $\langle 110 \rangle$  spacings quite exactly.

The intensities (and structure factors) of diffraction reflections were measured using a Joyce-Loebl Densitometer (Tables III-V). We are continuing to refine the structure projections of the three new phases of polythiazyl. However, at this point no definitive structures can be presented.

By examining Table I, it is obvious that the probable polymer chain axis is much larger in the  $\delta$  and  $\epsilon$  structures than in the normal  $\alpha$  or even in the  $\gamma$  phases. This can easily be explained if one accepts the possibility of an alternate polymerization direction in  $S_2N_2$  crystals. It must be emphasized that the dimer crystal structure is most probably quite different than the normal arrangement. In both the  $\alpha$  and  $\gamma$  phases of  $(SN)_x$ , it was observed that the square dimers could align flat or edgewise on the alkali halide (100) surface.<sup>16</sup> If the edgewise alignment yields EPM on NaCl and KBr, it opens the possibility of a new topotactic direction for polymerization along the dimer  $C$  axis (Fig. 7). Such a polymerization mode was considered when the polymerization mechanism of  $(SN)_x$  was first solved.<sup>9</sup> The substrate may change the least motion criteria in the dimer crystal, thus favoring a  $c$  axis polymerization.

The polymer chain resulting from a  $c$  axis polymerization would exhibit  $2_1$  symmetry. In order to determine if such a polymer chain was sterically possible, a list of sulfur-sulfur contact distances was prepared for the three new structures and compared to that of the  $\alpha$  phase (Table VI). All distances are within 7% of the  $\alpha$  phase. The new polymer chains postulated do not violate the minimum S-S contact distance and are therefore conformationally reasonable.

### C. Polymer stability and chemical defects

Throughout the course of the investigation, it was apparent that  $(SN)_x$  was susceptible to water attack. The exact nature of this reaction was elucidated in the preceding paper (hereafter referred to as paper I).<sup>18</sup> It is important to note for this discussion that the ability to observe electron diffraction from samples of  $(SN)_x$  is determined by the number of chemical defects present along the polymer backbone.

Fourier-transform infrared spectroscopy was used because of our initial feeling that a correlation between band position and structure could exist. Although a firm correlation was not found, this technique did permit the study of the ongoing chemical reaction in polythiazyl. A detailed description of this reaction is described in paper I.<sup>18</sup> It was thus determined that the color of the sample is not a sufficient criteria to judge the purity of the polymer sample. We have prepared lustrous golden-colored crystalline films of  $(SN)_x$  which contained a large quantity of chemical defects. These defects increase in number rapidly upon exposure of a film to humidity or liquid water. This explains our inability to obtain electron diffraction from epitaxial films of  $(SN)_x$ , which

TABLE I. Crystal forms of  $(SN)_x$  produced by epitaxial polymerization.<sup>a</sup>

Form	Crystal class	<i>a</i>	<i>b</i>	<i>c</i>	$\gamma$	Space group
$\alpha$	Monoclinic	0.415	0.764	0.444	110	$P2_1/a$
$\gamma$	Orthorhombic	0.920	1.072	0.493		$P2_12_12_1$
$\delta$	...	0.680	...	0.524		$P2_1^3$
$\epsilon$	...	1.392	...	0.581		$P2_1^1$

<sup>a</sup>Units are in nanometers and degrees, and *c* is the chain axis.

<sup>b</sup>Full space group unknown.

TABLE II. Lattice matching comparison.<sup>a</sup>

Substrate	[110] spacing (nm)	c polymer spacing (nm)	Difference (%)
NaCl	4×0.398	3×0.524	3.3
KBr	5×0.465	4×0.581	0.4

<sup>a</sup>Comparisons within 5% are considered very favorable.

were removed from the substrates by dissolution of the salts in water.

The difference between polythiazyl macroscopic crystals and thin films is significant because the secondary attack of water is diffusion limited. Since electron diffraction examines thin films, whereas x-ray diffraction examines larger crystals, the chemical defects affect electron diffraction more than x-ray diffraction due to differences in surface to volume ratios of the  $(SN)_x$  samples. It is to be expected that short exposure of each to water will have different degrees of effectiveness in reducing crystallinity.

TABLE III. The  $\gamma$  phase of  $(SN)_x$ .

hkl	d spacing (nm)	F (observed) (0-100 scale)	Reflection number
011	0.448	100	1
021	0.336	83	2
012	0.240	81	3
040	0.268	79	4
032	0.203	78	5
033	0.149	76	6
023	0.157	75	7
101	0.435	71	8
022	0.224	63	9
041	0.235	59	10
031	0.289	57	11
002	0.247	57	12
102	0.238	56	13
043	0.140	53	14
051	0.197	50	15
200	0.460	50	16
202	0.217	49	17
042	0.181	48	18
201	0.336	40	19
014	0.122	37	20
052	0.162	34	21
013	0.162	34	22
053	0.130	34	23
302	0.192	33	24
044	0.112	28	25
061	0.168	27	26
024	0.120	27	27
301	0.260	25	28
062	0.145	23	29
034	0.117	23	30
081	0.129	23	31
071	0.146	22	32
004	0.123	22	33
054	0.107	16	34
020	0.537	15	35
100	0.920	0	36
300	0.307	0	37
010	1.072	0	38
030	0.357	0	39
001	0.493	0	40
003	0.164	0	41

#### D. Fibrous $(SN)_x$ and double depositions

One of the more interesting morphological features of epitaxially polymerized polythiazyl is the lack of any fibrous nature to the single crystals. A rough calculation indicated there should be 100–200 such fibers spanning the width of each crystalline platelet,<sup>16</sup> if normal  $(SN)_x$  had been produced. The substrate evidently hinders the normal twinning mechanism responsible for these fibers.

The substrate effect can be removed if a double-deposition procedure is followed. A thin film of  $S_2N_2$  is deposited and allowed to polymerize completely. Another layer of the dimer is now deposited on top of the  $(SN)_x$  film and also allowed to polymerize. This second polymer layer, preferen-

TABLE IV. The  $\delta$  phase of  $(SN)_x$ .

hkl	d spacing (nm)	F(observed) (0-100 scale)	Reflection number
002	0.262	100	1
200	0.340	74	2
400	0.170	49	3
402	0.143	45	4
202	0.208	41	5
204	0.122	41	6
004	0.131	40	7
302	0.171	38	8
502	0.121	31	9
602	0.104	31	10
201	0.285	25	11
404	0.104	25	12
104	0.129	22	13
103	0.169	21	14
303	0.138	21	15
500	0.136	20	16
603	0.095	20	17
600	0.113	18	18
304	0.113	18	19
105	0.104	17	20
005	0.136	16	21
501	0.132	16	22
503	0.107	15	23
401	0.162	14	24
203	0.155	13	25
205	0.100	13	26
006	0.087	10	27
101	0.415	7	28
301	0.208	7	29
305	0.095	7	30
403	0.122	7	31
601	0.111	7	32
102	0.244	5	33
100	0.680	0	34
300	0.255	0	35
001	0.524	0	36
003	0.175	0	37

TABLE V. The  $\epsilon$  phase of (SN).

hkl	d spacing (nm)	F(observed) (0–100 scale)	Reflection number
002	0.291	100	1
400	0.348	62	2
402	0.223	56	3
201	0.446	55	4
004	0.145	55	5
601	0.215	51	6
600	0.232	38	7
303	0.179	34	8
102	0.284	33	9
404	0.134	27	10
302	0.246	25	11
301	0.363	23	12
401	0.299	22	13
203	0.187	22	14
801	0.167	21	15
702	0.164	21	16
701	0.188	20	17
502	0.201	20	18
802	0.149	19	19
602	0.181	17	20
1201	0.114	16	21
104	0.144	16	22
500	0.278	15	23
101	0.536	14	24
103	0.192	14	25
501	0.251	13	26
1001	0.135	13	27
100	1.392	10	28
200	0.696	10	29
300	0.464	9	30
700	0.199	8	31
800	0.174	7	32
202	0.291	7	33
204	0.145	6	34
304	0.139	5	35
001	0.581	0	36
003	0.194	0	37

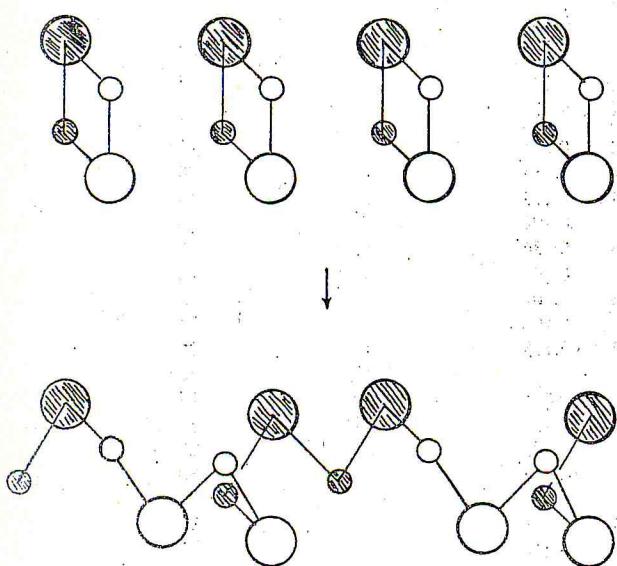
FIG. 7. Schematic illustration of a possible  $c$  direction of the polymerization of  $S_2N_2$  squares. The resulting chain could have a  $2_1$  symmetry. (Sulfur—large circles, nitrogen—small circles).

TABLE VI. Intramolecular sulfur-sulfur contact distances.

Crystal phase	Polymer chain spacing (nm)	S-S distance (nm)
$\alpha$	0.444	0.279
$\gamma$	0.493	0.295
$\delta$	0.524	0.262
$\epsilon$	0.581	0.291

tially deposited on top of the first-layer crystals, takes on a heavily fibrous nature (Fig. 8). The fibers align along the  $\langle 110 \rangle$  directions of the substrate and the polymer chain directions of the first layer. While the double layer is too thick for electron diffraction, one can reasonably expect the second layer to be the normal  $\alpha$  phase of polythiazyl which is oriented by the first crystalline layer. The significant substrate effect on the epitaxial polymerization process is well documented in this sample.

## CONCLUSIONS

We have shown that a lattice matching between molecules of  $S_2N_2$  and the (100) surface of various alkali halides,

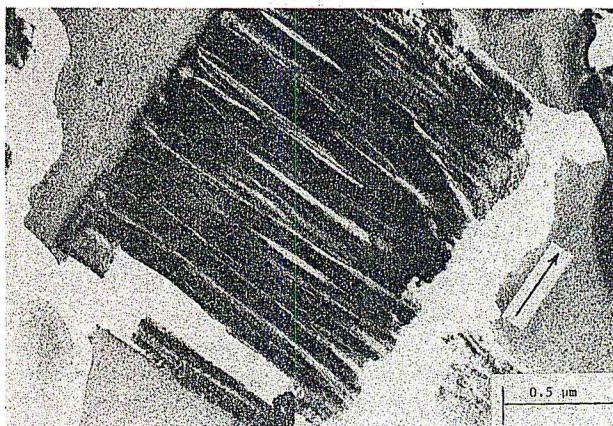


FIG. 8. (a) Double-layer morphology of polythiazyl deposited in KI. The second layer preferentially grows on top of the first layer, and clearly shows a fibrous nature. (b) Electron micrograph as above, indicating the orientation of the chain is along both  $\langle 110 \rangle$  directions of the substrate, but with only one direction per crystal. Some of the second deposit grows on previously unoccupied regions on the substrate as normal rectangular platelets (arrow points to one of three in micrograph).

coupled with substrate-controlled dimer structure modification and solid-state polymerization, produces novel structures and morphologies of  $(SN)_x$ . The polymer crystals are free from any fibrosis or the common twinning of normal  $\alpha$ -phase polythiazyl. Two new structures and one new type of morphology have been observed from polymer formation on NaCl and KBr. The novel chain repeat spacings assumed can be explained by postulating a new *c*-axis polymerization direction caused by the dramatic change in the dimer crystal intermolecular spacings. Such a polymer chain would not violate any minimum atomic contact distances.

The absence of electron diffraction from thin films immersed in water for a short time is explained by the diffusion-limited attack of water along the polymer chain. Color alone is not sufficient to determine the state of purity of polythiazyl because the small concentration of such impurities would not necessarily disrupt the degree of chain conjugation necessary for the appearance of the color.

By depositing a second layer of dimer on top of previously polymerized  $(SN)_x$  crystals, it was possible to epitaxially prepare the common fibrillar morphology of polythiazyl. Even that morphology, however, showed strong orientational behavior of the fibers along the  $\langle 110 \rangle$  rows of the substrate. The second layer reveals the strong orientation of the first-layer polymer chains. This is the strongest evidence for substrate nucleated and controlled solid-state polymerization in  $(SN)_x$ .

Epitaxial polymerization has been shown to be a useful technique in preparing near-perfect single crystals of an extended-chain polymer. In addition, the substrate has been shown to direct and orchestrate the entire polymerization process. The results, therefore, indicate a strong potential for applying this basic technique to a wide variety of polymers and substrates.

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