C_2H_4 arising from a trace amount of water. The flask was cooled at −78 °C and CH_3CHO (0.053 mol) added. The temperature was raised until evolution of propene was observed. Propene was passed through the reflux condenser at −30 °C and collected in a trap cooled at liquid-nitrogen temperature. Reaction was continued 4 h by warming at reflux temperature while stirring and stripping with a helium stream. The yield of [1-^{13}C]propene was 35% (based on $^{13}CH_3I$).

Enriched [3-^{13}C]propene (90%) was prepared as previously described.[10]

The ^{13}C-enriched monomers, after isotopic dilution, were purified by fractional distillation and subsequent treatment with $Al(C_2H_5)_3$. The monomer's purity which was checked by GLC on a Poropak Q column at 100 °C was higher than 99.9%.

Polymerization Runs. Soluble catalytic systems were prepared by mixing reagents (VCl_4, 5×10^{-4} mol; anisole, 5×10^{-4} mol; $Al(CH_3)_2Cl$,[18] 5×10^{-3} mol in 15 mL of toluene at −78 °C under nitrogen atmosphere). Reaction vessels were then cooled at liquid nitrogen temperature and evacuated at 10^{-4} mmHg. Subsequently, the proper amount of 10% enriched [1-^{13}C]propene or 30% enriched [3-^{13}C]propene was admitted and the temperature raised to −78 °C. After 24 h, the polymerizations were stopped by adding dropwise, under nitrogen atmosphere, HCl-acidified methanol. Care was taken to exclude air in order to prevent oxidation of reactive metal–carbon bonds from occurring instead of hydrolysis. The reaction mixture was left to stand at room temperature for 3 h. Finally, polymers were precipitated with excess methanol, purified by being dissolved in hot toluene and reprecipitated with methanol, and dried in high vacuum at 70 °C. The polymer yield was 0.4 g.

NMR Analysis of Polymers. Samples were prepared by dissolving the polymers in 1,2,4-trichlorobenzene and by adding 1% of hexamethyldisiloxane (HMDS) as an internal reference. Samples were placed in 10-mm o.d. tubes containing a coaxial capillary of deuterated dimethyl sulfoxide for field-frequency stabilization. Spectra were measured with an HX270 Bruker spectrometer operating at 67.88 MHz in the PFT mode. The temperature of the probe was 100 °C. A dwell time of 66 s was used with 16K of computer memory for the interferogram, corresponding to an acquisition time of 1.081 s and to a digital resolution of 0.0136 ppm/point. The pulse width was 10 s (the pulse width for a 90° pulse for the nucleus being examined is 30 s).

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Epitaxial Polymerization of $(SN)_x$. 1. Structure and Morphology of Single Crystals on Alkali Halide Substrates

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ABSTRACT: S_2N_2 vapor was epitaxially crystallized on a variety of alkali halide substrates. The resulting platelet crystals were allowed to polymerize in the solid state while on the substrates to form $(SN)_x$ single crystals. The polymer chains were always parallel to the $\langle 110 \rangle$ directions on the surface, but only one chain direction was observed from each monomer crystal. While the usual α form of $(SN)_x$ was the structure obtained on KCl, a novel γ form was discovered from growth on NaF and KI. Lattice matching between the polymer chains and the $\langle 110 \rangle$ substrate spacings can explain these structures. Two projections of each structure were observed and explained by proposing two independent nucleation mechanisms.

Much interest has been generated in the past several years regarding the inorganic polymer, polythiazyl (better known as poly(sulfur nitride) or $(SN)_x$). Burt first reported synthesizing this polymer in 1910,[1] but for many years it was relatively ignored. In 1956, Goehring reported that the polymer could conduct electricity,[2] and the work was further developed by Kronick et al.[3] in 1962. Kronick also reported that S_2N_2, the cyclic dimer of sulfur nitride which is the reactive species, was highly unstable in its crystalline form. There the studies remained until intense work was initiated into the electrical conductivity of the polymer by groups at IBM,[4,5] the University of Pennsylvania,[6,7,11] Temple University,[8,9] and others.[10] Concurrently, various groups in France[12] and at Allied Chemical[13-15] studied the poly(sulfur nitride) crystal structure and polymerization mechanism of the solid state reaction.

We became interested in polythiazyl when it became apparent that increased crystal perfection in $(SN)_x$ would be necessary to significantly improve its conductivity. Perfect single crystals of poly(sulfur nitride) are unobtainable because the normal bulk polymerization process allows twin boundaries to form during the final stages of reaction. This twinning is characteristic of a nonunique topochemical reaction. Our group has been interested for many years in improving the crystallinity and orientation of polymers through epitaxial crystallization. We hoped epitaxial crystallization of $(SN)_x$ would reduce the number of twinning defects.

Epitaxy is the oriented overgrowth of a crystalline substance on a substrate which is also crystalline. The interaction between depositing material and the surface is usually highly specific and has pronounced effects on the morphology and structure of the crystallizing substance. Willems[16] and Fischer[17] first reported epitaxially crystallizing a polymer in 1957. They investigated the crystallization of polyethylene from a dilute xylene solution on the surfaces of large single crystals of NaCl. Rodlike, anisotropic crystals grew preferentially oriented along rows of like charges (i.e. ⟨110⟩ directions) in the substrate surface. They proposed that a lattice matching between the polyethylene chain repeat and the substrate's [110] spacing was responsible for the interaction. Koutsky, Walton, and Baer[18] later found that this rodlike morphology was obtained when polyethylene was crystallized on a variety of alkali halide crystals with substantially different interatomic spacings, thus proving that lattice matching in the chain direction was not a necessary criterion for obtaining polymer epitaxial crystals.

However, Wellinghoff, Rybnikar, and Baer[19] found in 1974 that lattice matching could induce the growth of the unusual monoclinic form of polyethylene in thin growth regions on NaCl. An intermolecular spacing was the most important factor in controlling polyethylene's polymorphism. The authors previously showed in a series of papers from 1976 through 1978 that polymorphism could be controlled for other polymers and substrates by various phenomena: lattice matching with poly(oxymethylene),[20] crystallization kinetics with isotactic polypropylene,[21] and dipolar alignment with a series of linear polyesters.[22] These studies involved crystallization from dilute solution or crystallization from the melt of commercially produced polymers on the substrates. The morphology was always anisotropic, rodlike crystals strictly aligned according to the substrate's geometry.

Epitaxial polymerization includes the combination of epitaxial crystallization with solid state polymerization. Epitaxial polymerization is a general technique, applicable to a wide variety of monomers and substrates. The choice of alkali halides as the substrates for this study of S_2N_2 was based on our previous experience using these salts, coupled with the recent theoretical predictions of Mauritz and Hopfinger[23] concerning interactions between disulfur dinitride molecules and the surfaces of alkali halides.

Experimental Section

Polythiazyl was produced through the thermally initiated solid state reaction of the dimer S_2N_2, which is produced by a vapor phase catalytic reaction of S_4N_4 with silver sulfide.[24,25]

Tetrasulfur tetranitride was synthesized by the reaction of sulfur dichloride with ammonia, as outlined by Villena-Blanco and Jolly.[26] Several recrystallizations of the final product from benzene assured near complete removal of residual sulfur byproduct. Long thin needles of S_4N_4 crystallized from the benzene solution, and these needles were used in all subsequent experiments.

The S_4N_4 sublimed under a vacuum of 10^{-5} torr at 100 °C and passed through Ag_2S wool at 210 °C.[32] The resulting hot S_2N_2 vapor was condensed on a cold finger kept at −78 °C (dry ice–isopropyl alcohol mixture). The cold finger was specifically designed to provide maximum heat flux through its bottom and a minimum through its sides. The sides of the finger are a double walled evacuated Dewar-like container, merging into a single-walled bottom. Most of the S_2N_2 was condensed on the alkali halide substrate attached to the bottom of the cold finger. The single-crystal salts were placed in a steel holder which was held to the bottom by magnets inserted into the finger. The entire apparatus is shown in Figure 1.

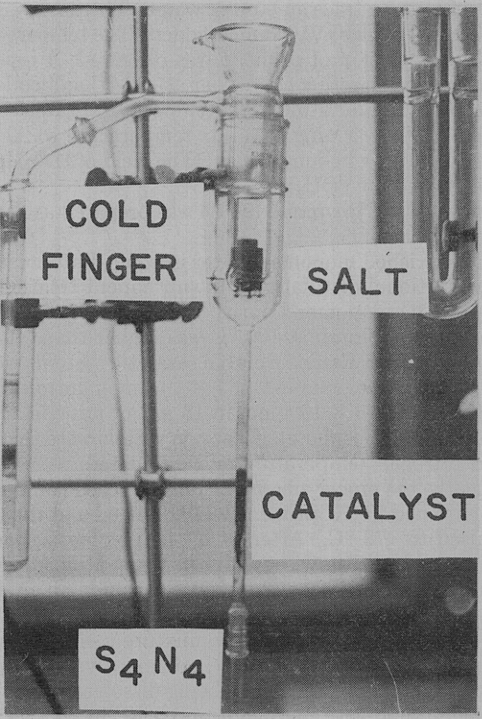

Figure 1. The glass sublimation–condensation vessel is shown here, with labels on the important sections. The hot S_4N_4 is sublimed and reacted with the catalyst, yielding S_2N_2 as product. This dimer vapor is targeted toward the salt substrate, held inverted on the bottom of the cold finger.

The time of sublimation determined the resulting film thickness. Twenty minutes was optimum to produce final thicknesses near 10 nm. This thickness was preferred to minimize dynamical scattering effects in the electron microscope.

The solid state polymerization was thermally initiated by allowing the cold finger to warm slowly to room temperature (25 °C) over the course of several hours. The film was annealed at 25 °C for 18–24 h to complete the polymerization. Since this study deals only with very thin films of $(SN)_x$, no further treatments were necessary to complete the reaction. During the annealing, a small quantity of unreacted S_2N_2 resublimed into the evacuated chamber surrounding the cold finger.

Sodium fluoride (NaF), potassium chloride (KCl), and potassium iodide (KI) were used as substrates. These three salts cover a large range of interatomic spacings (0.327–0.498 nm) in the alkali halide series. The single crystals were cleaved into rectangular parallelopipeds with approximate dimensions of 1 × 1 × 0.5 cm. The rough salts were supplied by the Harshaw Chemical Co. Each crystal was cleaved just before it was placed in the vacuum system to ensure a fresh (100) surface. Trace amounts of adsorbed water were removed by annealing the surface of the salt at 25 °C for 24 h at 10^{-5} torr.[27]

Initially, the salt was dissolved in water to remove the $(SN)_x$ film from its surface. This technique was first used by Koutsky et al.[18] and has become a standard method used to remove the substrate without distorting the film. But, as Boudelle described in her thesis,[12] poly(sulfur nitride) rapidly decomposes on contact with liquid water and more slowly in atmospheric humidity. (The kinetics of this decomposition are currently disputed.)

Because of this sensitivity, a collodion stripping technique was developed. The polythiazyl film was first platinum shadowed or gold decorated and then carbon coated. A 7% solution of collodion

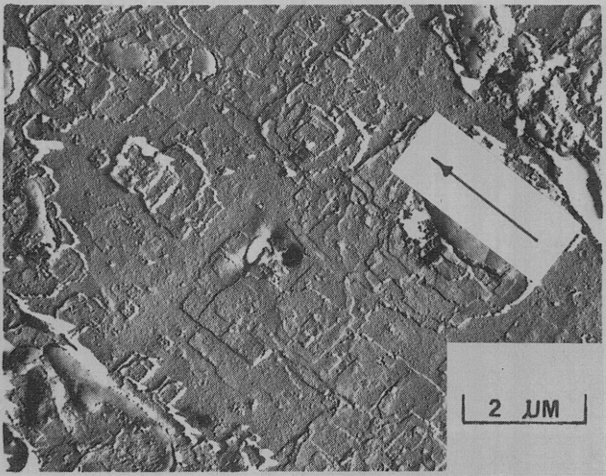

Figure 2. Electron micrograph of single crystals of poly(sulfur nitride) polymerized epitaxially on NaF. The arrow indicates the substrate's [110] direction. The sharp rectangular shape of these crystals is readily apparent.

in amyl acetate was applied to the surface and left to dry, and the resulting film was sliced into square pieces while still on the surface. The pieces were peeled off the substrate and placed on top of electron microscope grids that were sitting on amyl acetate soaked filter paper. The collodion dissolved slowly over an 18-h period, leaving the poly(sulfur nitride) film on top of the grids, with virtually no distortion. These grids were examined in a Jeol JEM 100B electron microscope in both bright field and diffraction modes.

Results and Discussion

A. Morphology of $(SN)_x$ Epitaxial Crystals. Poly(sulfur nitride) crystals usually appear as "bundles" of crystalline fibers. The bundles are about 20 nm in diameter and lie along the polymer chain axis. The cause of this fibrous morphology is unknown, but it is possibly due to (100) twinning during the final stages of the polymerization.[13]

Although we cannot directly examine the S_2N_2 epitaxial crystals formed on various alkali halides, it is assumed that they do not change shape during the solid state reaction that forms the polymer crystals. This assumption is correct in the vast majority of similar reactions.[28]

The first substrate examined was NaF, which has a small characteristic ⟨110⟩ spacing of 0.327 nm. The observed morphology was a relatively dense growth of rectangular platelet crystals with edges aligned along the surface's ⟨110⟩ direction (Figure 2). This alignment contradicts the predicted ⟨100⟩ orientation made recently by Mauritz and Hopfinger.[23] Crystal thicknesses varied with deposition times, although lateral growth rates were very much faster than thickening rates. Because of this, the crystals reached a limiting height of 100 nm before merging into a uniformly thick, featureless film on the NaF surface.

If the normal bulk polymerization had occurred, one should observe about 100 parallel fibers, approximately 20 nm in diameter, spanning the 2-μm width of each crystal. The absence of this morphology indicates a more prefect structure is present in epitaxially polymerized crystals. This perfection is confirmed by substantially reduced diffraction line widths in epitaxially polymerized samples compared with normal bulk samples.

The next substrate tried, KCl, has a medium ⟨110⟩ spacing of 0.444 nm (Figure 3). The crystals seen on this substrate appeared rough on the surface and rounded on the edges. This morphology can be explained by a surface resublimation of S_2N_2 molecules from each crystal before complete polymerization. This correlates with the experimentally observed resublimation during the annealing process. The relatively large amount of S_2N_2 resublimation from KCl suggests that the reaction is nucleated uniformly at the substrate surface and that the reaction is much slower on KCl compared with NaF.

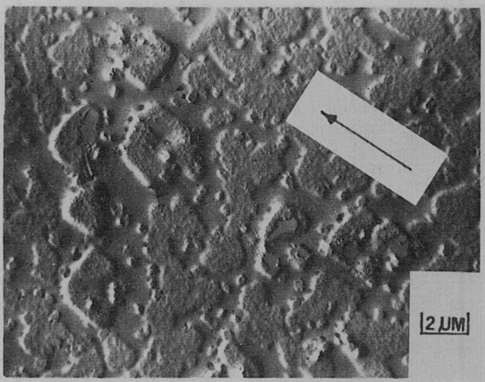

Figure 3. Polythiazyl crystals grown on KCl are seen in this electron micrograph. Even though the crystals show rough surfaces and rounded edges, the general rectangular nature is observable. The [110] orientation, as indicated by the arrow, is also readily apparent. Note that in certain regions, many crystals have grown together in the precursor of a uniformly thick film.

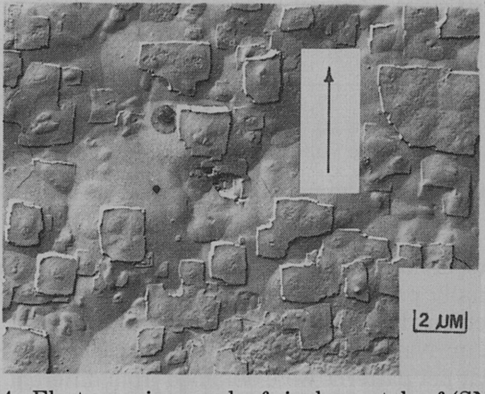

Figure 4. Electron micrograph of single crystals of $(SN)_x$ epitaxially polymerized on KI. These rectangular platelets are aligned in the surface's [110] direction. The best morphology was observed from growth and polymerization on this substrate.

$(SN)_x$ crystals on KI again exhibited the rectangular platelet morphology, in which the crystals are aligned in KI's ⟨110⟩ directions (0.498 nm) (Figure 4). The crystals are sharply defined here like those grown on NaF. Thus, although three widely differing cubic substrates were used, a similar morphology of rectangular platelet crystals was observed. The sharp crystal definitions on NaF and KI suggest, however, that the reactions are faster on these substrates than on KCl. One must examine the structure of these crystals in order to understand differences in reaction rates.

B. Structure of $(SN)_x$ Single Crystals. Selected area electron diffraction from poly(sulfur nitride) epitaxial crystals was excellent and allowed structures to be identified on all three alkali halides. Only one pattern was obtained per polymer crystal, indicative of one chain direction in each single crystal. The patterns obtained from crystals grown on KCl were rectangular nets of the a^*–c^* plane of the normal α form of polythiazyl. Superimposed on some of these nets was another, involving $(1\bar{2}0)$ and c^* directions. The c^* axes of these two nets were coiincident (Figure 5). Such a superposition pattern was recently reported by Stejny and Keller[29] as being caused by a new $(1\bar{1}0)$ twin plane. There was no evidence of the usual (100) twinning assumed responsible for the fibrous nature of bulk polymerized $(SN)_x$ crystals. This absence confirms

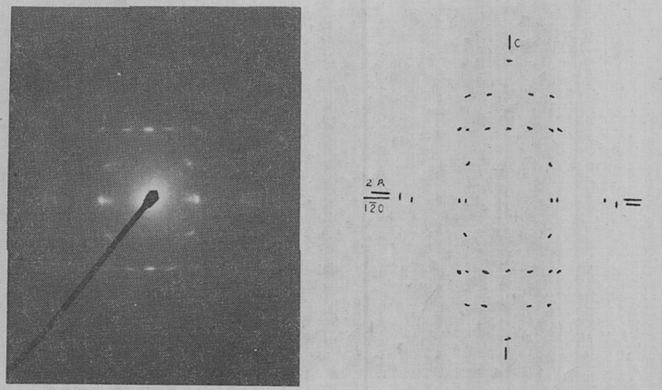

Figure 5. A twinned electron diffraction pattern taken from crystals of $(SN)_x$ grown on KCl. This twinning has recently been reported by normal polymerization by Stejny and Keller.[29] The *a* axis of the α polymer must be doubled to index all reflections.

Table I
Crystal Forms of $(SN)_x$[a]

form	class	*a*	*b*	*c*	γ	space group
α	monoclinic	0.415	0.764	0.444	110	$P2_1/a$
β	orthorhombic	0.481	0.625	0.443		$P2_12_12_1$
γ	orthorhombic	0.920	1.072	0.493		$P2_12_12_1$

[a] Units are in nanometers and degrees. *c* is the chain axis.

the morphological evidence of the nonfibrous character of epitaxially polymerized $(SN)_x$.

Electron diffraction patterns obtained from crystals grown on NaF and KI were identical. Two distinct rectangular net patterns were obtained from different polymer crystals on both salts, which could not be indexed by the usual α or sheared β phases of poly(sulfur nitride). Note that the α phase designated here is the Cohen et al.[11] phase I and the β phase is the Baughman et al.[15] phase II. If one assigns each net to a structure projection (i.e., a^*–c^* and b^*–c^*), a new unit cell can be derived which will index all reflections (Figure 6). The common axis to both nets was assigned as c^* because it was observed from growth on KCl that the polymer chain is always parallel to the surface. It should be emphasized that there are some doubts that these two diffraction patterns are truly structure projections.

The new structure has been tentatively designated as the γ form of poly(sulfur nitride). It is compared with the two previously known phases in Table I. Another phase of $(SN)_x$ has also recently been reported by Love et al.[31] It should be noted that since the β form of $(SN)_x$ is merely a sheared form of the bulk polymerized α form, no real change in the polymer molecular structure has been previously observed. The space group of the γ form, based on the available data, would be $P2_12_12_1$. The chain repeat which is constant in the α and β unit cells of polythiazyl is increased by 0.05 nm in the new structure.[14]

C. Lattice Matching. As applied to epitaxy, lattice matching usually means that the substrate exerts a strong influence over the lateral spacings of depositing molecules or molecular segments and forces the spacing to correspond to a characteristic substrate dimension. If the induced spacing is at or near an energetically favorable intermolecular spacing for the adsorbing material, it will be incorporated into the crystal's unit cell. The new packing geometry of the crystal can induce a new polymorphic form to be observed, even at relatively large distances from the substrate surface. If the spacing induced by the substrate is not energetically favorable, the adsorbed molecules will resume their usual spacings as the crystals grow away from the surface. No lattice matching effect will then be observable. These lattice matching forces are probably acting upon depositing S_2N_2 molecules in the following manner.

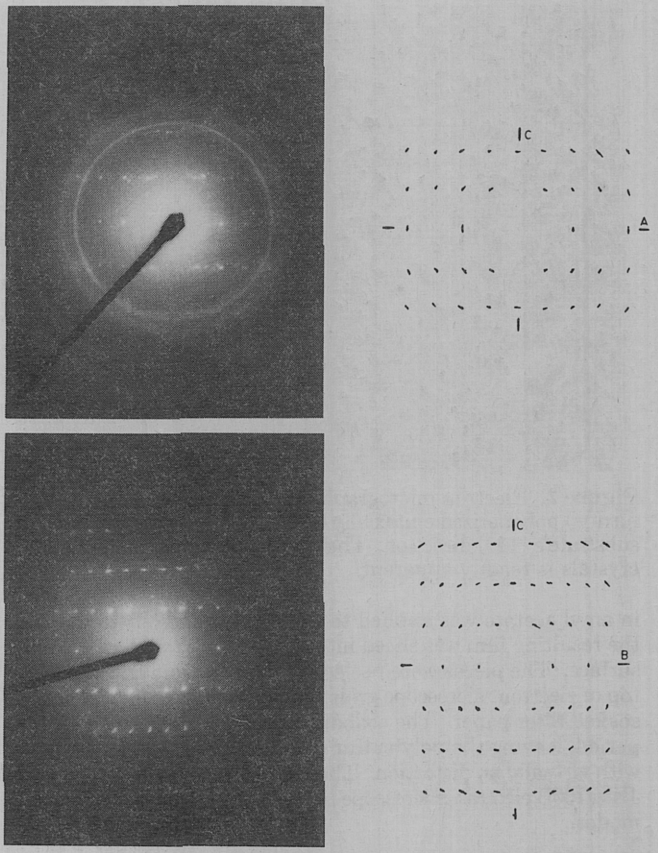

Figure 6. The two unique electron diffraction patterns observed on both NaF and KI are shown here. Each can be assigned to a structure projection of a new unit cell of polythiazyl. The common axis has been assigned as the c^* axis for reasons mentioned in the text.

Table II
Lattice Matching Comparison[a]

substrate	[110] substrate spacing	*c* polymer spacing	% difference
NaF	3 × 0.327 nm	2 × 0.493 nm	0.5
KCl	0.444 nm	0.444 nm	0.0
KI	0.498 nm	0.493 nm	1.2

[a] Comparisons within 5% are considered very favorable.

The only dimension of polythiazyl which is constantly parallel to the substrate is the *c* axis, or the chain axis. In dilute solution polymer epitaxy, this dimension does not seem to be critically important. In epitaxial polymerization, however, the polymer chain spacing was initially an intermolecular spacing of the cyclic dimer. This spacing must be the one which actually matches with that of the substrate. It is experimentally unobtainable, but assuming it does not differ greatly from the final polymer chain axis, the polymer chain dimension can be compared with the characteristic ⟨110⟩ spacings of the substrates (Table II). This assumption finds support in the least motion principle in solid state polymerization espoused by Cohen and Schmidt[30] and more recently by Baughman, Chance, and Cohen[13] and the strong influence of the substrate. Thus, the appearance of a new form on both NaF and KI and the formation of the usual α form on KCl are predictable on the basis of lattice matching.

D. Primary and Secondary Nucleation. The two independent diffraction patterns of the γ form can be

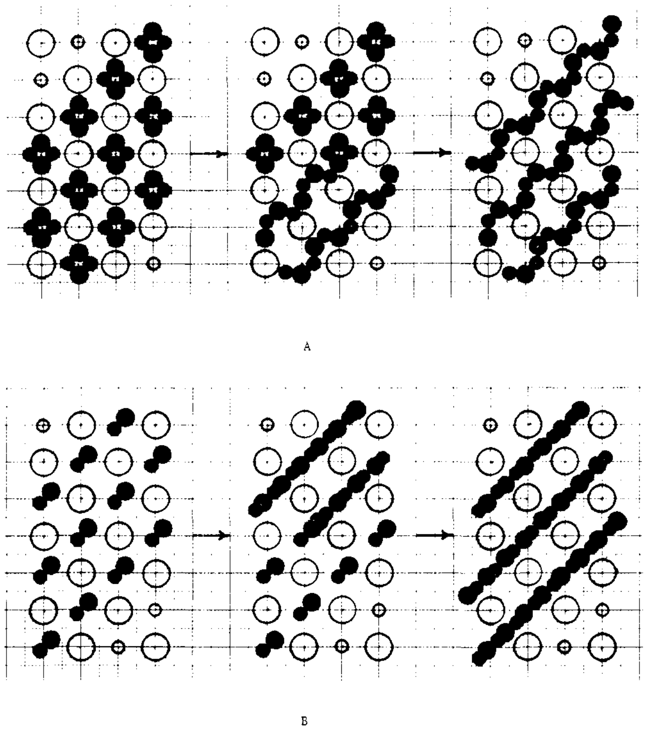

Figure 7. The presence of two distinct patterns of the same structure can be explained by two independent nucleation mechanisms, as schematically shown here: (a) secondary nucleation of individual dimer molecules; (b) primary nucleation of a group of dimer molecules, followed by secondary nucleation on the initial homogenous nucleus. The surface initiated polymerization on a (100) alkali halide surface is indicated as well.

explained by two independent nucleation mechanisms. The expected secondary nucleation assumes the S_2N_2 molecules are individually adsorbed with the squares parallel to the surface (Figure 7A). An unusual primary nucleation presupposes that nuclei are formed by the condensation of several dimer molecules prior to surface adsorption. Those nuclei laying edgewise on the surface would cause other dimers to align with them as deposition continues (Figure 7b). This type of nucleation is not observed in polymer epitaxial crystallization from solution or the melt and is allowed by the unique method of vapor phase condensation–polymerization.

Conclusions

A new γ form as well as the usual α form of poly(sulfur nitride) have been produced by epitaxial polymerization on lattice matching alkali halide substrates. Rectangular platelets aligned along the $\langle 110 \rangle$ directions of the surface were observed on all three substrates examined. Only one chain orientation was observed per crystal, but both $\langle 110 \rangle$ directions were equally represented in the total field of crystals examined. Two distinct nucleation mechanisms must exist to account for the two structure projections of the α and γ phases of $(SN)_x$, although the morphology of these two crystal types was similar. The technique of epitaxial polymerization is general and should be amenable for use with a wide variety of monomer–substrate systems.

The detailed structure of the γ form, as well as continued microscopic and new spectroscopic studies of these epitaxially formed crystals, will be reported in future papers.

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