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THE FORMATION OF SINGLE CRYSTAL FILMS OF POLYDIACETYLENES

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Abstract The two-step process of epitaxial polymerization has been applied to symmetrically substituted diacetylenes. First, the monomers have been crystallized epitaxially on alkali halides substrates from solution and the vapor phase. The oriented monomer crystals are then polymerized under the substrate's influence by gamma-irradiation. The diacetylenes in this study are 2,4-hexadiyn-1,6-diol (HD) and the bis-phenylurethane of 5,7-dodecadiyn-1,12-diol (TCDU). The polydiacetylene crystal structures and morphologies have been examined with the electron microscope. Reactivity and polymorphism are found to be controlled by the substrate.

INTRODUCTION

Epitaxial polymerization is a general process applicable to monomers that may be polymerized in the solid state. The study of disulfurnitride vapor phase crystallization on alkali halides with thermal polymerization to polythiazl, $(SN)_x$, has shown that substrate controlled reaction led to three new crystal phases of $(SN)_x$.[1-2] Diacetylenes are monomers that can be polymerized from the monomer crystals to varying degrees of conversion and crystallinity depending on the nature of the substituents and their packing within the monomer lattice.[3] Furthermore, the polymer backbone may adopt either an acetylenic $\{RC-C\equiv C-CR\}$ or a butatriene

$\{RC{=}C{=}C{=}CR\}$ bonding.

The urethane-substituted polydiacetylenes exhibit thermo-chromic transition with low and high temperature crystal phases favoring acetylenic and butatriene backbone, respectively.[4-6] Our interest in the application of epitaxial polymerization to diacetylenes has been the possibility of substrate control over orientation, structure, and the single crystal nature of thin films.

EXPERIMENTAL

2,4-hexadiyne-1,6-diol (DMDA) from Farchan Laboratories was recrystallized from toluene. Solutions up to 1 wt. % in toluene were prepared for epitaxial crystallization. Bis-phenylurethane of 5,7-dodecadiyne-1,12-diol (TCDU) was supplied by Allied Chemical Co. The monomer was extracted from the partially polymerized lattice with acetone. The monomer was dissolved in ethyl acetate to make a 0.4 wt. % solution.

TABLE I TCDU

	Phase 1	Phase 2
Monomer	a = 0.708 nm	a = 1.160 nm
	b = 3.397 nm	b = 1.897 nm
	c = 0.523 nm	c = 0.519 nm
	β = 115.85°	γ = 91.0°
Polymer	a = 0.623 nm	a = 1.184 nm
	b = 3.903 nm	b = 1.987 nm
	c = 0.491 nm	c = 0.495 nm
	β = 106.85°	γ = 94.94°

Epitaxial crystallization was accomplished by the immersion of a preheated substrate (the substrates for epitaxial crystallization were single crystals of alkali halides from Harshaw Chemical Co.) into the monomer solution followed by its in-situ cleavage to expose two fresh (100) surfaces.

TABLE II Diol unit cell parameters

	a	b	c	β
Monomer	.409	1.60	.477	106.3
Polymer	.411	1.61	.482	106.1
Polymer/KBr	.421	1.02		

units in nm

The isothermally crystallized monomers were polymerized with 2·4 Mrad γ-irradiation. The polymer film was removed from the substrate after C , Pt coating by dissolving the salt. A Jeol JEM 100B electron microscope was used to examine the samples.

RESULTS AND DISCUSSION

Large domains of oriented single crystals of poly(TCDU) and poly(DMDA) were produced on the alkali halide surface. Figures 1 and 2 show the typical elongated platelet morphology. Selected area electron diffraction from such domains gave single crystalline pattern as in Figures 3 and 4. The unit cell parameters are given in Tables 1 and 2.

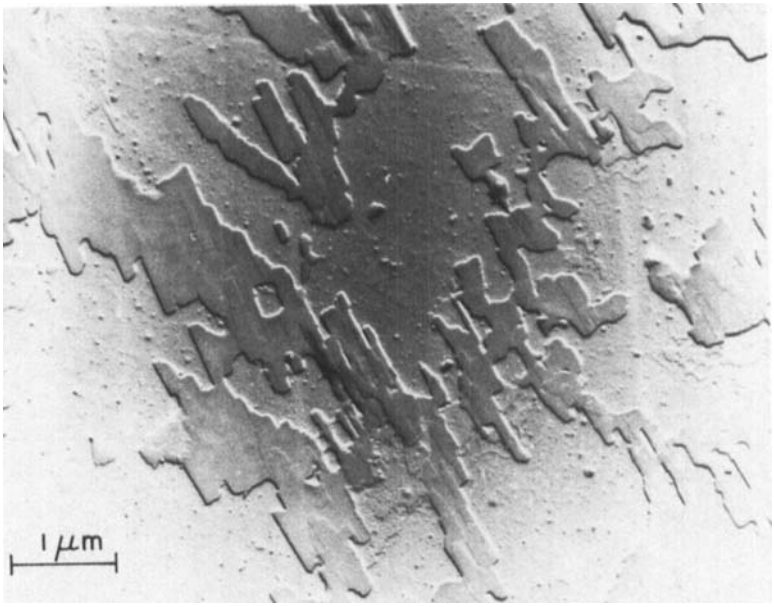

FIGURE 1. Poly(TCDU) polymerized on KCl and deposited from a 0.4 wt. % ethyl acetate solution at 30°C.

Poly(TCDU) in thin film exists in the acetylenic phase 2, as opposed to the butatriene phase 1 found in bulk crystals polymerized from macroscopic monomer crystals.[7] Polymerization to completion in thin film, thereby removing the constraint of the monomer lattice, could account for the acetylenic phase.

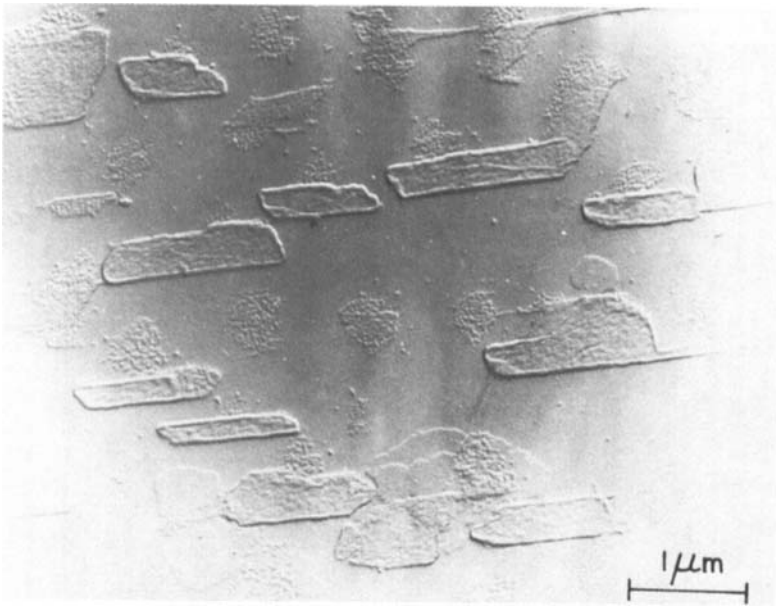

FIGURE 2. DMDA polymerized on KBr and deposited from a 1 wt. % toluene solution at 78°C.

The orthogonal projection of the epitaxial poly(DMDA) could not be indexed using the unit cell data for the bulk polymerized crystal.[8] However, poly(DMDA) cannot usually be polymerized to completion or to high crystallinity in the bulk due to crosslinking. The use of an epitaxial substrate may have controlled the polymerization process that led to oriented single crystals.

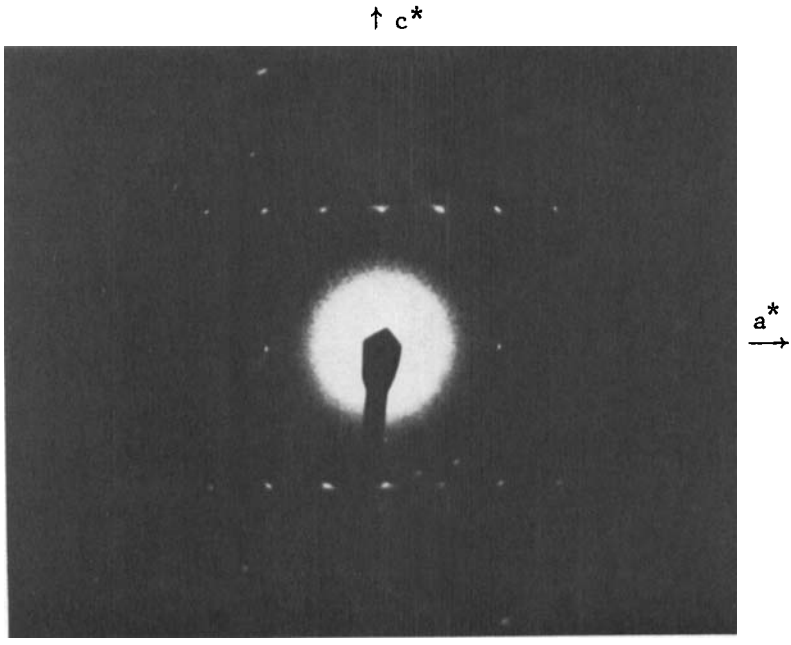

FIGURE 3. Electron diffraction of Poly(DCDU) formed under conditions specified in Figure 1.

CONCLUSION

Two diacetylenes have been epitaxially polymerized as thin films in contact with alkali halide substrates. These films consisted of highly oriented single crystals aligned along both <110> directions of the substrate. The structures of both poly(TCDU) and poly(DMDA) were modified by this technique and, in all cases, highly crystalline near-perfect films were achieved.

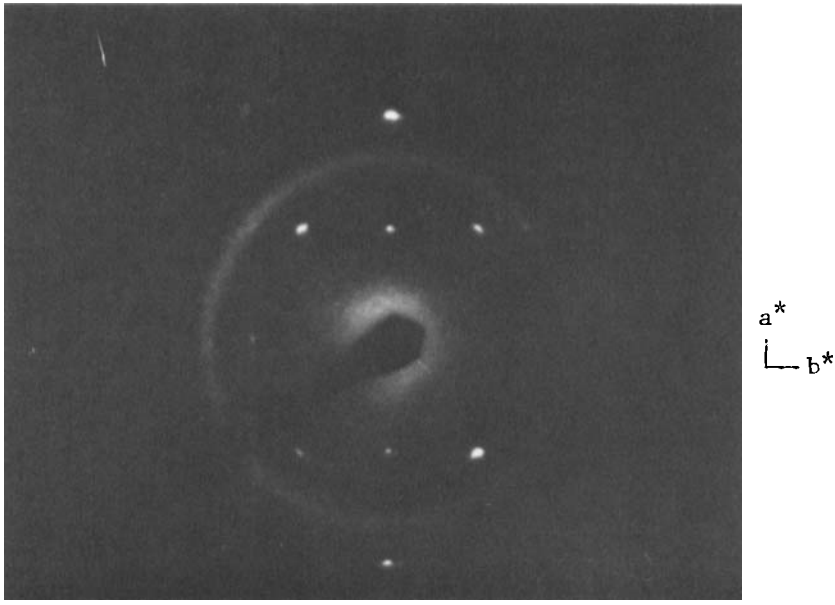

FIGURE 4. Electron diffraction of poly (DMDA) from Figure 2.

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