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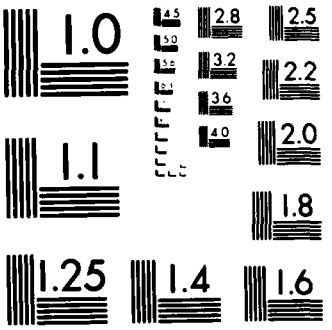

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Several monomer/polymer systems which exhibit the ability to undergo a solid state polymerization were studied as to their abilities to undergo epitaxial growth followed by such polymerization (i.e., epitaxial polymerization). The materials studied included disulfur-dinitride/polythiazyl $(SN)_x$, hexamethyl-cyclotriphosphazene/polydichloro-phosphazene $(NPCL_2)_x$, alcohol and phenylurethane substituted diacetylenes/polydiacetylenes, $R-(C-C\equiv C-C)_x-R$, and p-terphenyl/poly(p-phenylene) $(C_6H_4)_x$.

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Final Technical Report

Contract DAAG29-80-C-0099

Army Research Office

by

Jerome B. Lando and Eric Baer, Department of Macromolecular Science, CWRU

EPITAXIAL POLYMERIZATION AS A MOLECULAR ENGINEERING TECHNIQUE

Several monomer/polymer systems which exhibit the ability to undergo a solid state polymerization were studied as to their abilities to undergo epitaxial growth followed by such polymerization (i.e., epitaxial polymerization). The materials studied included disulfur-dinitride/polythiazyl $(SN)_x$, hexamethylcyclotriphosphazene/polydichloro-phosphazene $(NPCL_2)_x$, alcohol and phenylurethane substituted diacetylenes/polydiacetylenes, $R\text{-}(\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-C}\equiv\text{C-}\overset{\text{O}}{\overset{\|}{\text{C}}})_x\text{-R}$, and p-terphenyl/poly(p-phenylene) $(C_6H_4)_x$.

The following research assistants and associates worked on this project: 1) Dr. Hemi Nae, 1/81 - 10/81; 2) Mr. Steven Ching, 9/81 - 3/83 (M.S. in Macromolecular Science); 3) Mr. Lary Adams, 9/81 - 3/83; 4) Mr. Gwo-Shin Swei, 6/82 - 3/83.

The following publications were obtained from this research:

1. Epitaxial Polymerization as a Tool for Molecular Engineering, ACS Symposium Series 212/8, 89 (March 1982 ACS National Meeting), J. B. Lando, S. E. Rickert, E. Baer, H. Nae, and S. Ching.
2. Single Cyrstal Polymeric Phosphazenes by Epitaxial Polymerization, Bulletin of the American Physical Society, 27 (3), (1982) 360, H. Nae, J. B. Lando, E. Baer, and S. E. Rickert.
3. Epitaxial Polymerization of Diacetylene Monomers, Bulletin of the American Physical Society, 27 (3) (1982) 298, S. Ching, J. B. Lando, E. Baer, and S. E. Rickert.

4. The Formation of Single Crystal Films of Polydiacetylenes, Polymer Preprints, 23 (2), (1982) 139. S. Ching, J. B. Lando, E. Baer, and S. E. Rickert.
5. Epitaxial Growth of Polydiacetylenes, submitted April 1983 to the ACS Symposium Series, S. E. Rickert, J. B. Lando, and S. Ching.
6. Epitaxial Polymerization to Synthesize Conjugated Polymers in Single Crystal Films, Case Western Reserve University, M. S. Thesis, 1983, S. Ching.

Substantial progress was made during the course of this grant in our understanding of the processes which control the adsorption of reactive monomers on alkali halide surfaces, from dilute solution, the melt, and from condensation from the vapor phase. It was found that the orientation, structure and size of the crystals comprising the epitaxial film depended upon the nature of the solvent, temperature, and the defects in the substrate.

Unidirectional growth of diacetylene and p-terphenyl monomers on monovalent alkali halides were seen under most deposition conditions, whereas, both polythiazyl and polyphosphazenes exhibited the traditional bidirectional growth. In addition, crystals which were several tens of microns in size accompanied unidirectional growth, whereas bidirectional growth was typified by crystals in the micron size. This is to be expected, as unidirectional growth occurs when nucleation in the rate limiting step in film formation, whereas bidirectional growth occurs when nucleation and growth have about the same rate.

Deposition of the monomer from the vapor phase, followed by

polymerization via radiation or thermal treatment seems most likely to be the feasible route to commercial production of such films.

Several new structures were seen when bidirectional growth occurred, but only the normal structures were observed when unidirectional growth took place. This can be explained due to the fact that metastable structures need more time to form, in general, than the conventional structures, and only bidirectional growth has a slow enough growth rate to allow these unusual phases to appear.

Attachments (6)
(abstracts)

EPITAXIAL POLYMERIZATION AS A TOOL FOR MOLECULAR ENGINEERING.

Jerome B. Lando, Eric Baer, Scott E. Rickert, Hemi Nae and Stephen Ching. Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

Epitaxial crystallization is the oriented overgrowth of a substance on a crystalline substrate. The interaction between the two is usually highly specific and has profound effects on the morphology and structure of the crystallizing material. Epitaxial polymerization is a new phenomenon in the field of macromolecular science. It combines the epitaxial crystallization of a monomer on a crystalline substrate, followed by solid-state polymerization, which is controlled by the epitaxial crystallization of the monomer. A study of the vapor phase epitaxial polymerization of disulfurnitride to polythiazyl, $(SN)_x$, resulted in three new crystalline phases of $(SN)_x$ and a new appreciation of the catastrophic effect of water on this polymer. The epitaxial polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene), $(NPCl_2)_x$ has been investigated. Deposition from both the vapor phase and solution has been studied. The polymer structure and morphology depend upon the monomer epitaxial crystals. The actual monomer morphology and structure have been found to be dependent on the geometry of the substrate. The application of this method to the epitaxial polymerization of diacetylenes will also be discussed.

A topochemical effect in a solid state reaction is any effect on the structure and properties of the product or the kinetics of the reaction that can be directly attributed to the geometric arrangement of the reacting groups or the distance between those groups. The degree of topochemical control in a solid state reaction can vary greatly depending upon the particular system investigated.(1) Reactions to be discussed here, in which there is a crystallographic correlation between the reactant and the resulting product, can occur in solid solution or with the nucleation and growth of a product phase.

Systematic investigation of solid state polymerization reactions began with the discovery that crystalline acrylamide polymerizes when exposed to ionizing radiation. (2,3) Since that

Abstract Submitted

for the March 1982 Meeting of the

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October 27, 1981

High Polymer Physics
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Polymer Crystallization

Single Crystal Polymeric Phosphazenes by Epitaxial Polymerization. H. NAE, J. B. LANDO, E. BAER, and S. E. RICKERT, Case Western Reserve U.--For the first time, single crystals of polyphosphazenes have been formed by epitaxial polymerization, a technique developed in our laboratory. Epitaxial crystallization is the overgrowth of a substance on a crystalline substrate. Epitaxial polymerization is a new phenomenon in the field of macromolecular science. It combines the epitaxial crystallization of a monomer on a crystalline substrate, followed by solid state polymerization which is controlled by the epitaxial crystallization of the monomer. The epitaxial polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazine), $(NPCl_2)_x$ has been investigated. Deposition on alkali halide substrates from the vapor phase, solution and the melt has been studied. The polymer structure and morphology depend upon the monomer epitaxial crystals. The actual monomer morphology and structure have been found to be dependent on the geometry of the substrate. As a consequence, previously unobserved structures of both monomer and polymer were obtained.

Scott E. Rickert

Prefer Poster Session

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for the March 1982 Meeting of the

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Polymer Crystallization

Epitaxial Polymerization of Diacetylene Monomers. S. CHING, J. B. LANDO, E. BAER, and S. E. RICKERT, Case Western Reserve U.--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.

Scott E Rickert

Prefer Standard Session

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THE FORMATION OF SINGLE CRYSTAL FILMS OF POLYDIACETYLENES

SCOTT E. RICKERT, JEROME B. LANDO AND STEPHEN CHING
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

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≡C-CR⟩ or a butatriene

EPITAXIAL GROWTH OF POLYDIACETYLENES

SCOTT E. RICKERT, JEROME B. LANDO AND STEPHEN CHING
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EPITAXIAL POLYMERIZATION TO SYNTHESIZE CONJUGATED POLYMERS IN SINGLE CRYSTAL FILMS

Abstract

by

STEPHEN KWONG-KAI CHING

Epitaxial polymerization, a novel concept in molecular engineering, was applied to the synthesis of conjugated polymers and the design of polymer morphology suitable for applications. It consists of the oriented crystallization of a monomer on a single crystal substrate followed by topochemical solid-state polymerization. It simplifies the fabrication of intractable polymers by processing the monomers. The result is a highly oriented, crystalline film with extended polymer chains.

Polydiacetylene films were made from the bis-phenylurethane of 5,7-dodecadiyne-1,12-diol (TCDU) and 2,4-hexadiyne-1,6-diol. Large crystals with a unique orientation were produced on alkali halides from vapor deposition and isothermal crystallization from solution. Both monomers yielded the usual morphology of elongated platelets. Poly(TCDU) was observed exclusively in the phase 2 crystal form while a new polymer structure of 2,4-hexadiyne-1,6-diol was obtained.

Vapor phase deposition of hexachlorocyclotriphosphazene onto

NaCl, KCl, KBr and KI resulted in four new polymorphs. Post-polymerization annealing revealed only amorphous polymer on these substrates.