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Thin Film Single Crystal Growth of a Nonlinear Optical Polymer

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Over the past decade macromolecules with an extended chain geometry and conjugated backbone electronic structure have been established as novel electronic and optical materials. This includes photo-, thermo-, solvato- and electro-chromism, large electrical and photo-conductivities and unique linear and nonlinear optical properties among others. Polydiacetylenes, a class of a conjugated polymers are considered possible candidate material for all optical switching and logic applications. In the transparent regime they possess some of the largest third order nonlinear optical susceptibilities. In general, it is extremely difficult to grow bulk polymeric single crystals. Polydiacetylenes, however, can be grown to a large size in single crystal form. Single crystals of polydiacetylene can be directly grown from monomer single crystals through solid-state polymerization by heat, UV, or ν^2 radiation. This solid-state polymerization of diacetylene monomer produces a conjugated polymer back bone structure shown in Figure 1. Polydiacetylenes have large nonresonant ultrafast third order nonlinear susceptibilities which may compete with the inorganic nonlinear optical materials as shown in Table 1.						
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THIN FILM SINGLE CRYSTAL GROWTH OF A NONLINEAR OPTICAL POLYMER

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INTRODUCTION

Polydiacetylenes(PDA) have been extensively studied and proposed as nonlinear optical material (NLO).⁽¹⁻⁵⁾ They have large nonresonant ultrafast third order nonlinear susceptibilities^(2,6-8) ($\chi^{(3)} \approx 10^{-9}$ - 10^{-10} esu). PDAs are available in single crystal form by solid-state polymerization (topochemical polymerization) in the diacetylene monomer single crystal by UV, γ -ray radiation or heat. Solid-state polymerization produces a conjugated polymer structure⁽⁹⁾, leading to large third order nonlinearity. Side group with high π electron density directly bound to the backbone has been proposed to increase nonlinear susceptibilities.⁽¹⁰⁾ 1-(N-carbazolyl)-penta1,3-diyne-5-ol,CPDO, has a carbazole group directly attached to the diacetylene stem.⁽¹⁰⁾

Third order nonlinearity is inversely proportional to a high power in the band gap energy, E_g , that is, a small reduction in E_g can lead to a significantly larger $\chi^{(3)}$ value. It is reported⁽¹⁰⁾ that the band gap energy of poly(CPDO) is 1.6 eV compared to 2.1 eV for poly(PTS).

Third order nonlinear susceptibilities of several polydiacetylenes are shown in Table 1.

Table 1. Third order nonlinear susceptibilities.⁽¹¹⁾

polymer	thickness (μm)	$\chi^{(3)} \times 10^{10}$ (esu)		
		pumping wavelength(μm)		
		1.83	1.94	2.10
poly(PTS)	0.90	2.3	0.91	0.40
poly(BTFP)	0.27	6.4	3.2	2.0
poly(DFMP)	1.09	0.80	0.69	0.56

Thin film single crystals of diacetylenes have been grown from solution and melt by confining the liquid in a growth cell and subsequently allowing the melt to cool or solvent to evaporate.⁽¹²⁾ PTS monomer crystals have been extensively studied in the authors' and other laboratories. However, many cracks were observed during the solid-state polymerization of poly(PTS), which is due to a decrease in the volume of the unit cell during polymerization and resulting

strain in the system. If the interface between the monomer single crystal and crystal growth cell(quartz plates) is lubricated, strain developed during lattice contraction may be released.

In this paper, modifications to thin film polymer single crystal growth technique for poly(PTS) are discussed and poly(CPDO) single crystals are grown from confined solution single crystal growth technique. Growth morphology of poly(CPDO) are compared with poly(PTS).

EXPERIMENT

Poly(PTS) single crystals were grown using the following steps. <1>. Monomer single crystals were grown from concentrated solution confined between two optically flat quartz plates.⁽¹²⁾ <2>. Monomer crystals were floated off from the plates and placed on plates lubricated by a mineral oil(Nujol). <3>. The monomer crystal was covered with another lubricated plate and pressure was applied to the plate/monomer crystal/plate assembly to prevent the crystals from bending or coiling during polymerization. <4>. Polymerization was initiated by UV irradiation for a short time and completed by thermal polymerization in water bath at 70-80° C for 2-5 hours.

Monomer CPDO single crystals were grown by the same technique and polymerization was carried out without using any lubricants.

RESULTS AND DISCUSSION

PTS monomer crystals are grown as thin film single crystals(thickness less than a micron) as shown in Fig. 1. The monomer single crystals polymerized using lubrication results in few or no cracks. A further advantage of this growth technique is that the polymer single crystals may be easily removed as free standing film. Fig. 1a and 1b are transmission optical micrographs with different incident polarization. The chains are oriented along the long axis of the crystal.

While PTS grows in a platelet morphology, CPDO crystals are grown with ribbonlike morphology. Crystals with width of ~ 1 mm and several centimeter of length are easily grown. Fig. 2 and 3 are transmission optical micrographs of a section of a CPDO ribbon magnified a few times. Again excellent chain alignment is easily seen. In this preliminary experiment no lubricants were used and yet polymerization does not lead to cracks. Upon polymerization there is a slight expansion of the CPDO lattice. The lattice volume expands from 1280.4 to 1296 Å³.⁽¹⁰⁾

The polymerized CPDO sample appears dark grey. The absorption edge is significantly red shifted compared to PTS. Fig. 3 shows a single fiber of CPDO

polymer that is many centimeters long. Propagation experiments through this fiber are presently underway.

CONCLUSIONS

Poly(PTS) single crystal is grown as thin film without cracks by applying a lubricant at the interface between the monomer crystal and the quartz plates. Poly(PTS) single crystals grown from this method are several mm wide and over a centimeter long.

Poly(CPDO) single crystal with a few mm width and several centimeter length can be grown from solution confined between two plates. Poly(CPDO) crystal is grown to a fiber-like morphology which may be best for waveguide application. CPDO crystals grown by this method show few or no cracks even when no lubricant is used. Optical and spectroscopic properties of these systems will be presented and compared.

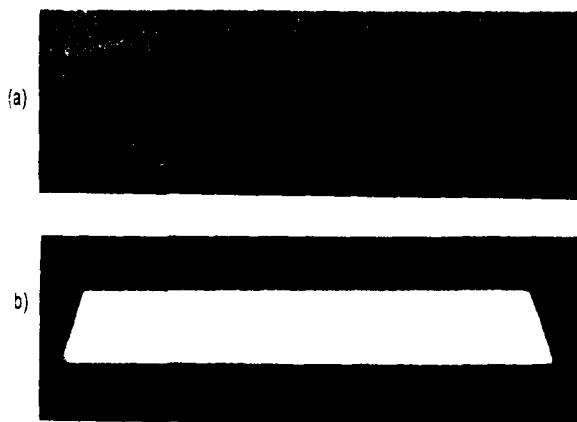


Fig. 1. Micrographs of PTS monomer single crystal with different incident polarization.

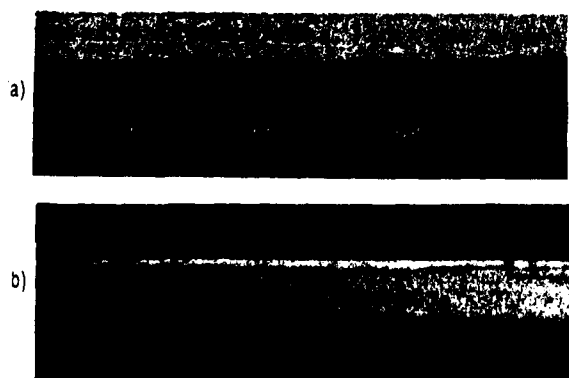


Fig. 2. Micrographs of a section of poly(CPDO) single crystal with 1 mm width with different incident polarization.

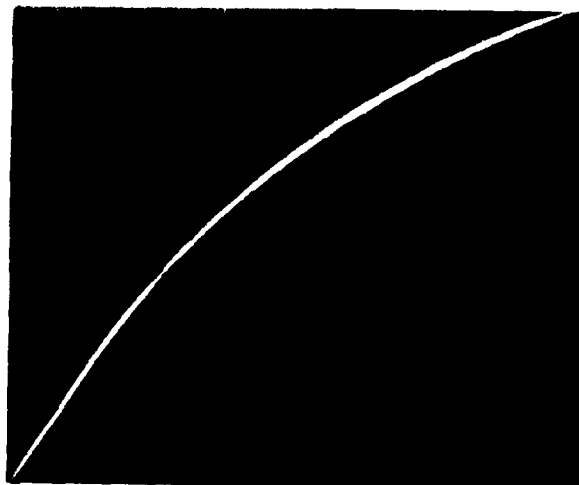


Fig. 3. Micrograph of a section of poly(CPDO) single fiber crystal.

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