model gave an upward-convex curve and was not fully satisfactory. The plot of log σ vs. $T^{-1/3}$ was also not satisfactory. On the other hand, as shown in Figure 3b, the plot of log σ against $T^{-1/2}$ gives a straight line over a relatively wide range of T below 270 K. This satisfies a requirement for the one-dimensional variable-range hopping model.[14] The departures at high temperatures are also expected from the theory.[14]

Figure 4 shows the dependence of the conductivities on the degree of orientation f for the stretched films with $Y = 0.1$ and 0.4. Unfortunately, the films with the widely varied stretch ratio λ all resulted in a degree of orientation f between 0.40 and 0.45, as mentioned above. Nevertheless, comparing with the data for the unstretched film, we notice that the $\sigma_{\parallel}$ value appears to increase rather rapidly but the $\sigma_{\perp}$ less rapidly with increasing f. As a result, the $\sigma_{\parallel}/\sigma_{\perp}$ value tends to increase with f. The $\sigma_{\parallel}$ may become larger with increasing f due to the conduction along the conjugated chains, while the $\sigma_{\perp}$ is not appreciably affected by the chain orientation, since it may occur mostly through hopping. This conclusion is only tentative since it is derived from data over a limited range of f. More elaborate experiments will be needed before a final conclsuion can be reached.

An increase in $\sigma_{\parallel}$ by stretching was also reported for stretch-oriented films of other conductive polymers,[6–8] while the change in $\sigma_{\perp}$ was somewhat contradictory among them. Park, Shirakawa, and Ikeda[6] reported that the $\sigma_{\perp}$ for polyacetylene films decreases with stretch ratio λ. For poly(p-phenylenevinylene), Gagnon et al.[7] observed a decrease in $\sigma_{\perp}$ with λ, while Murase et al.[8] reported the opposite result. These discrepancies may be attributed to the difference in the morphology and in the crystallinity of the films used in these studies.

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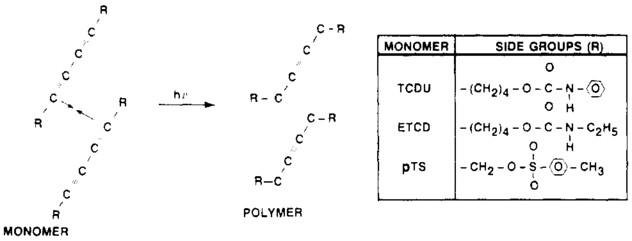
Growth of Large-Area Thin-Film Single Crystals of Poly(diacetylenes)

Poly(diacetylenes) are distinguished from traditional polymeric systems by virtue of their superior crystalline properties. Poly(diacetylenes) are the only known conjugated systems that can be obtained as macroscopic single crystals. As nonlinear optical materials poly(diacetylenes) are competitive with select inorganic systems such as GaAs for many important future applications.[1] Recently, extensive attention has been paid to this unique class of one-dimensional system from the fundamental as well as the technological standpoint,[2–4] and a variety of optical and optoelectronic applications have been proposed.[1,2,5] Specifically for pTS-poly(diacetylene) (see Figure 1), the nonlinear response time in the nonabsorptive region has been estimated to be in the subpicosecond domain, which may have major importance in the emerging ultrafast optical signal processing technologies.[2,6] One critical obstacle in the way of materializing the proposed applications has been the poor quality of the available crystals. The bulk crystals of poly(diacetylenes) that are obtained in the conventional crystallization procedure (such as slow cooling or evaporation from solution) are full of defects such as cracks, grain boundaries, uneven surfaces, stacking faults, etc. and are also produced with uncontrollable dimensions (see Figure 2). In the interest of detailed fundamental optical characterizations as well as practical applications, it is required that the crystals not only are optical quality but also possess some specific desired forms. The most versatile form that would be compatible with the silicon planar technology and also facilitate experimental characterization is the form of a thin-film single crystal with optically flat surfaces. Such thin films on suitable substrates form planar wave guides, which would be ideal for optical signal processing involving nonlinear interactions. Many other important applications would also become amenable if such wave guide structures are fabricated. Additionally, some of the crucial experimental measurements such as the time scale of nonlinear optical response, time-resolved carrier mobility measurements, etc. could be carried out with a great deal of accuracy and facility if good-quality thin-film single crystals were available. Thus, the thin-film crystal growth of diacetylenes is a much longed for research area which may have significant implications in fundamental understanding as well as practical applications of these materials.

At present, thin-film crystal growth of inorganic metal and semiconducting materials (Au, GaAs, Si, etc.) is a very demanding and mature field of research.[7] The basic operational method therein relies on "epitaxy" or lattice matching. Accordingly, a material crystallizes from a mobile phase (melt, solution, or vapor) onto a solid crys-



MONOMER	SIDE GROUPS (R)
TCDU	$-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{\|}{N}}-C_6H_5$
ETCD	$-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{\|}{N}}-C_2H_5$
pTS	$-CH_2-O-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-C_6H_4-CH_3$

Figure 1. Diacetylene monomers and their polymerization. In the box three well-known diacetylene monomers have been defined in terms of their respective substituents.

talline substrate provided the lattice spacings of the substrate and the crystallizing material are well matched. This time-worn and useful method, however, is not effective in the case of large organic molecular systems primarily because appropriate substrates that satisfy the condition of lattice matching are not available. Specifically, diacetylene crystals containing more than 60 atoms in each molecule (see Figure 1) have lattice spacings that exceed 20 Å along the molecular axes. No known organic or inorganic crystalline materials of sufficient crystal quality have large enough lattice spacing to match such repeat distances. Consequently, the epitaxial method has not been successful in producing large-area thin single-crystal films of poly(diacetylenes) or any other polymer.[8,9] Clearly, thin-film organic crystal growth is a relatively unexplored and difficult field of research that does not lend itself to the standard growth techniques.

Recently, we investigated a conceptually novel approach to the organic crystal growth that appears to be particularly well suited to rodlike molecules such as diacetylenes. The diacetylene monomer molecules, specifically, the ones that are relatively easier to crystallize in the macroscopic form (Figure 1), have a few very special attributes. They have the diacetylenic rods at the centers, flexible methylene linkages on the sides, and some polar chemical moieties on the ends. In addition, these cylindrical molecules are fairly long (≃25 Å) in the axial direction with diameters of approximately 5 Å. Thus, in a mobile phase such as melt or concentrated solution, these molecules are expected to have very small diffusion coefficients because of their size and shape as well as intermolecular interactions. The diffusion coefficients are further reduced if the mobile phase is trapped within an interface of two opposing flat surfaces so that the polar ends interact with and adsorb to the surfaces. In such a constrained mobile phase of molecular assembly, the orientational memory would tend to have a very long persistence. The corresponding retention time can be further prolonged if the molecular mobility is gradually reduced via slow cooling or evaporation of the solvent. A continuation of such slow cooling or solvent evaporation would eventually lead to oriented thin films with the long molecular axes approximately perpendicularly oriented to the interface. These are the basic points that underlie the thin-film crystal growth method which we discuss below with specific examples. Interestingly, this simple concept, very well suited for rodlike molecular systems, may not be very useful for small molecular systems such as inorganic, semiconducting materials.

The principal steps that were involved in our approach for the thin-film crystal growth of diacetylenes are as follows: (1) the selected monomer was placed in the interface between two optically flat opposing surfaces, (2) the monomer was brought to a mobile phase by melting or dissolution with a suitable solvent, (3) an appropriate magnitude of pressure was applied to the substrate/monomer/substrate assembly, (4) the mobile phase under a constant pressure was subsequently subjected to a shear via a linear slow translation of one of the substrates with respect to the other, and (5) finally the mobility of the diacetylene molecules was slowly reduced by a gradual reduction of the temperature in the case of a melt and a slow solvent evaporation in the case of a solution. We have applied this method to three different diacetylene monomers, namely, TCDU (5,7-dodecadiyne-1,12-diol bis(phenylurethane)), ETCD (5,7-dodecadiyne-1,12-diol bis(ethylurethane)), and pTS (2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate)), which were synthesized and purified by established methods.[4] In the case of TCDU and ETCD, we have used the melt phase while for pTS the solution phase was used since the pTS monomers polymerize very rapidly at higher temperatures and thus create unwanted nucleation centers. The uniaxial shear introduces a preferred orientation of the long molecules in a direction approximately perpendicular to the dual substrate interface. The details of the effect of shear and its interrelation to the various interactions in the interface are presently under investigation. The partial orientating characteristic of a shear, however, was reported earlier.[10] A schematic diagram of our melt-shear apparatus is shown in Figure 3. In the case of TCDU and ETCD a pressure of approximately 200 lb/in.^{2} and a shear rate of ≃1 mm/s were used. A dc drive was utilized for introduction of the shear and the rate of cooling was less than 0.5 °C/h for TCDU and slightly higher for ETCD. In the case of pTS, acetone was used as the solvent and the solute concentration was approximately 0.08 g/mL. The schematic of the solution-shear apparatus was similar to the melt-shear apparatus except a thermoelectric cooler replaced the bottom base (B) and a transparent window on top (A). The pressure utilized in the solution-shear growth was less than 0.5 lb/in.^{2} and the evaporation was continued for more than a week at 20 °C subsequent to initial seeding (few hours) at 0 °C. Both the melt- and the solution-shear growth were carried out under an inert atmosphere and in a darkroom condition since diacetylene monomers tend to become more reactive in the oxygen atmosphere and even visible light is sufficient to induce polymerization. Specific attention was paid to the cleanliness of the whole environment (class 100 clean room condition) and the optical flatness of the substrates. Expectedly, the hydrophilic substrates were more effective than the hydrophobic ones since the former enhanced the interaction of the polar side groups of the monomers with the substrate surfaces.

The thin-film single crystals of TCDU and ETCD that we have obtained following the above method were approximately 1 cm^2 in area and 1 μm in thickness. By varying the magnitude of pressure (≃25–300 lb/in.^{2}) we could vary the thickness of the films from 0.4 to 2.0 μ. The solution-shear-grown pTS monomer crystals were approximately 50 mm^2 in area and 1 μm in thickness. Optical micrographs (×120) of some of the thin-film single crystals subsequent to polymerization are shown in Figure 4. The polymerization was effected by using established means such as UV radiation or heat.[4] The optical quality of these shear-grown crystals was far superior to conventionally grown bulk crystals (compare Figures 2 and 4). Specifically, the solution-shear-grown pTS crystals have been found to be the best in terms of surface quality and lack of bulk defects. The optical absorption spectra of poly(TCDU) at two different orientations of the incident polarization are presented in Figure 5, which demonstrates the optical anisotropy, typical of poly(diacetylene) single

Figure 2. Optical micrograph (×120) of the surface of a bulk PTS single crystal, grown by slow evaporation from acetone solution.

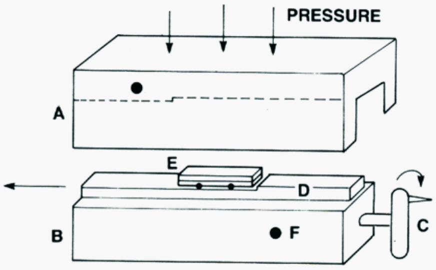


Figure 3. Schematic of the melt-shear growth apparatus: (A) top heating plate; (B) base heating plate having a proper mold design for holding the substrates in place; (C) dc drive attached to movable platen D; (D) platen that introduces shear by moving the bottom substrate with respect to the top; (E) substrates carrying the monomer in the interface; (F) thermocople probes of the temperature control unit. The whole assembly is covered with a heat-reflecting boundary wall to ensure temperature stability. A laboratory hydraulic press was used to apply the pressure on AB.

crystals.[11] X-ray, electron diffraction, FTIR, and Raman spectroscopy have been used for crystallographic and chemical characterization of these thin films. The poly(TCDU) and poly(ETCD) thin films have been found to have unit cell parameters slightly different from those of the respective bulk crystals at room temperature. However, the PTS (polymerized) thin films that were grown by solution shear had the same unit cell parameters and optical absorption properties as the bulk PTS crystals. The change of crystal unit cells as observed in case of poly(TCDU) and poly(ETCD) thin films was attributed to the high pressure ($\simeq$200 lb/in.^{2} and more severe growth conditions compared to the solution-shear growth of pTS (pressure $\simeq$0.5 lb/in.^{2}). The X-ray diffractometer tracing of the PTS thin film is shown in Figure 6. The details of the structure and optical properties of the melt-shear-grown crystal phases of poly(TCDU) and poly(ETCD) will be reported separately. As the diffraction results have shown, the long side groups were approximately perpendicularly oriented to the substrate surface in all three cases. Thus, the surface orientations were (100) for pTS and (010) for poly(TCDU) and poly(ETCD).

Recently, a degenerate four-wave mixing experiment on the thin-film PTS crystals has been completed and the results will be published shortly. These measurements were facilitated by the excellent quality of these thin sample crystals.[6] Negligible scatter (Rayleigh) of the laser beams and very small surface roughness factor ($\simeq$100 Å) as measured by a Dektak clearly attested to the excellent optical quality of the thin-film PTS crystals.

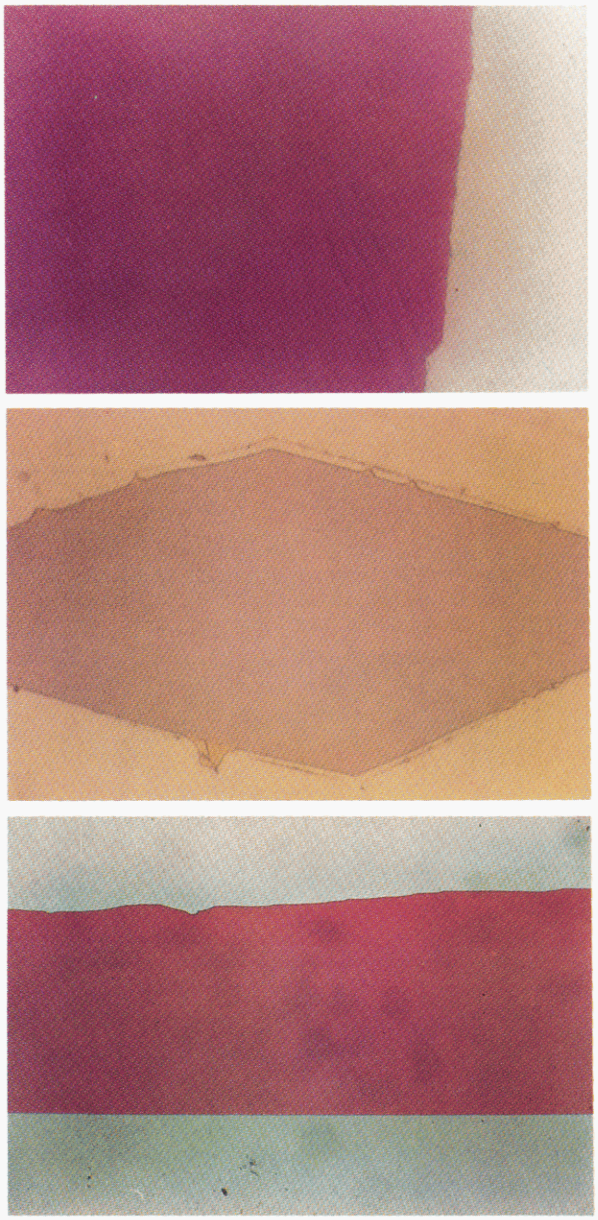


Figure 4. (a, top) Optical micrograph (×120) of a thin-film single crystal of poly(TCDU) (approx 1 cm^2 in area). This was grown by melt shear. (b, middle) Optical micrograph (×120) of a thin-film single crystal of pTS-poly(diacetylene) (approximately 5 mm^2 in area) grown by solution shear. (c, bottom) Optical micrograph (×30) of another thin-film pTS single crystal (approximately 50 mm^2 in area) that was grown by solution shear on a prestructured (having a valley) substrate surface.

In summary, we have established a novel, conceptually simple thin-film crystal growth technique that is particularly suitable to large rodlike molecules such as diacetylenes. As we have demonstrated, the application of this technique has resulted in thin-film poly(diacetylene) single crystals that are 4 orders of magnitude larger in area than what is reported in the literature.[9] In addition, we believe this is the first time that the single crystal of a polymer is obtained with excellent optical quality. A complete optimization of the growth conditions for best results is presently under way. The detailed investigation of the growth kinetics in the light of the structure and interaction of such large molecules has not been pursued before and is definitely a subject of fundamental interest.

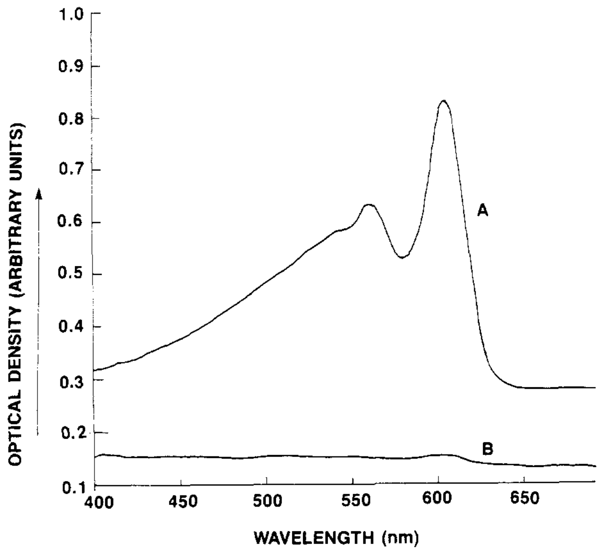


Figure 5. Optical absorption spectra of poly(TCDU) thin film for two orthogonal orientations of the incident polarization: (A) polarization parallel to the chain axis; (B) polarization perpendicular to the chain axis.

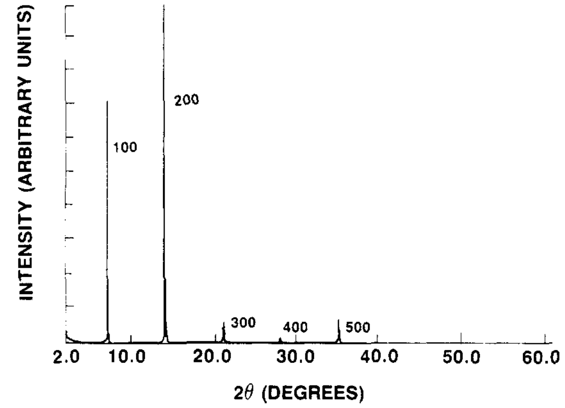


Figure 6. X-ray diffractometer tracing of a thin-film single crystal of pTS-poly(diacetylene). The surface orientation was (100).

It is hoped that the availability of optical-quality thin single-crystal films of unique molecular systems such as poly(diacetylenes) will inspire many novel and hitherto unattempted experiments in fundamental and applied macromolecular condensed matter physics. Finally, our results indicate that while established techniques for the well-ordered crystal growth of inorganic materials is not expected to be tenable for large organic molecules, novel parallel approaches leading to a similar level of perfection can be identified that take advantage of the characteristic molecular features of the system.

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Registry No. TCDU (homopolymer), 59418-25-6; ETCD (homopolymer), 63809-82-5; pTS (homopolymer), 32535-60-7; TCDU (SRU), 62300-45-2; ETCD (SRU), 83441-81-0; pTS (SRU), 61614-97-9.

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