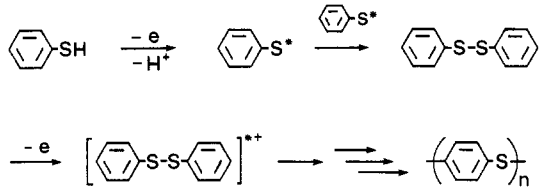
**Scheme I**



active species of this polymerization.

**Acknowledgment.** This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of Macromolecular Complexes from the Ministry of Education, Science and Culture, Japan.

**Registry No.** Thiophenol, 108-98-5; thiophenol (homopolymer), 33411-63-1; thiophenol (SRU), 25212-74-2.

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(7) Poly(*p*-phenylene sulfide): IR (KBr) ($cm^{-1}$) 3000, 3050 ($\nu_{C-H}$); 1380, 1460, 1560 ($\nu_{C=C}$); 820 ($\delta_{C-H}$); 480, 550, 700, 740, 1050, 1080, 1090. The absorption attributed to 1,4-substituted phenylene indicates a linear or 1,4-conjugated phenylene sulfide structure. No typical absorption in the range between 800 and 900 $cm^{-1}$ excludes a branching and cross-linking structure.
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## Photoinitiated Anionic Coordination Polymerization of Epoxides, a Novel Polymerization Process[1]

Much attention has recently been paid to the photoinitiated cationic polymerization of epoxides for its potential application in industry.[2] However, no works on the anionic counterpart appear to have been reported. Strohmeier and Barbeau[3] previously described the polymerization of propylene oxide with dimanganese decacarbonyl under UV irradiation, but the polymerization mechanism remains equivocal. We wish to report herein the first unambiguous example of photoinduced anionic coordination polymerization of epoxides.

Quite recently we have communicated a new catalyst system comprised of titanium tetraisopropoxide and phenol or its derivatives, which is highly effective for the anionic coordination polymerization of cyclohexene oxide.[1]

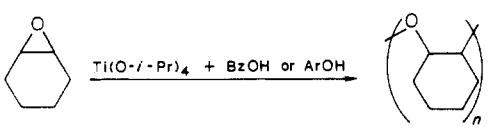
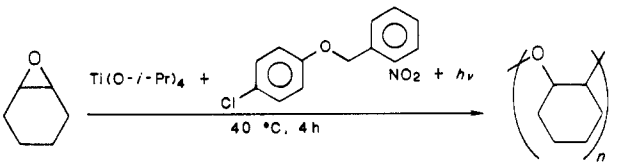


**Table I**
**Photoinitiated Polymerization[a]**

| no. | catalyst | UV | ratio | yield |
|---|---|---|---|---|
| 1 | $Ti(O\text{-}i\text{-}Pr)_4$ + CNE | + | 1:1 | 19 |
| 2 | $Ti(O\text{-}i\text{-}Pr)_4$ + CNE | + | 1:2 | 35 |
| 3 | $Ti(O\text{-}i\text{-}Pr)_4$ + CNE | + | 1:4 | 54 |
| 4 | $Ti(O\text{-}i\text{-}Pr)_4$ + CNE | + | 1:6 | 57 |
| 5 | $Ti(O\text{-}i\text{-}Pr)_4$ + CNE | − | 1:2 | 1 |
| ref | $Ti(O\text{-}i\text{-}Pr)_4$ + *p*-Cl-C$_6$H$_4$-OH | − | 1:2 | 88 |

[a] CNE = *p*-chlorophenyl *o*-nitrobenzyl ether; cyclohexene oxide, 20 mmol; $Ti(O\text{-}i\text{-}Pr)_4$ 0.02 mmol; UV irradiation, 4 h; temperature 40 °C; time, 4 h.

It was noticed that, while the ring-opening reaction itself is initiated by an isopropoxy group, the addition of phenolic derivatives is a prerequisite to control the electronic state of the titanium center for the coordination of epoxides. This fact prompted us to design those compounds that can generate phenol or its derivatives under UV irradiation. Photogeneration of alcohol[4] or silanol[2o,p] from *o*-nitrobenzyl derivatives was reported, so that *p*-chlorophenyl *o*-nitrobenzyl ether was prepared, which afforded *p*-chlorophenol quantitatively after irradiation of UV light for 4 h at 40 °C.



A representative procedure for the photoinitiated polymerization is as follows. To a mixture of titanium tetraisopropoxide (5.7 mg, 0.02 mmol) and *o*-nitrobenzyl *p*-chlorophenyl ether (21.1 mg, 0.08 mmol) was added cyclohexene oxide (1.96 g, 20 mmol) at room temperature. The mixture was stirred for 4 h at 40 °C under irradiation of ultraviolet rays. (500-W USHIO high-pressure mercury lamp, USH-500D, without filter). The polymer was obtained in 54% yield after removal of unreacted monomer. Without UV irradiation no polymer was obtained.

The yield increased with increase of the ratio of *p*-chlorophenyl *o*-nitrobenzyl ether to titanium tetraisopropoxide, but no further significant increase in the yield was observed at the ratio higher than 4 (6:1, 57%) as shown in Table I. These results are inconsistent with the fact that the yield was as high as 83% at the 2:1 ratio of *p*-chlorophenol to titanium tetraisopropoxide under the same conditions without UV lights. This is not only because an excess of *p*-chlorophenol formed during the reaction occupies the coordination sphere of the titanium metal center to inhibit the access of cyclohexene oxide to it but because the by-products formed concomitant with *p*-chlorophenol in the photodecomposition reaction may somehow retard the polymerization. In fact, the yield of polymer decreased when an excess of phenol was added to the system. Furthermore, the use of a photodegradated mixture of *o*-nitrobenzyl *p*-chlorophenyl ether in cyclohexane oxide involving *p*-chlorophenol and other components, in place of the pure *p*-chlorophenol, gave a polymer in a low yield under similar conditions (the ratio of *p*-chlorophenol formed to titanium was 4:1). Further investigations are now in progress to elucidate these factors and to explore new catalyst systems using other transition metals for photoinitiated anionic polymerization of epoxides.

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**Registry No.** $Ti(OPr\text{-}i)_4$, 546-68-9; CNE, 109669-56-9; cyclohexene oxide (homopolymer), 25702-20-9; cyclohexene oxide (SRU), 32146-09-1.

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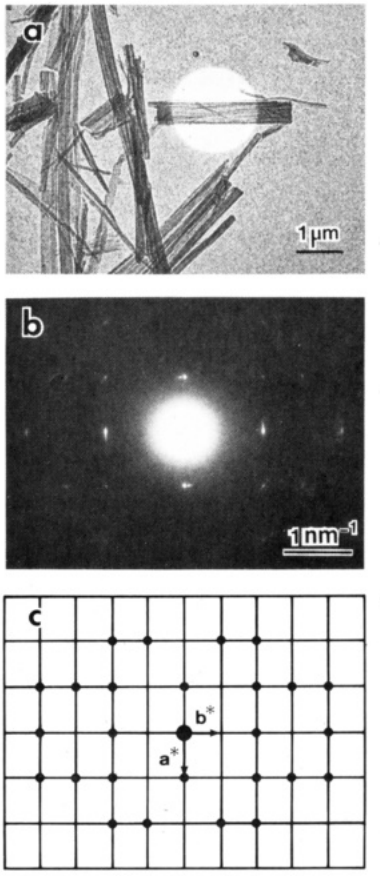


**Figure 1.** (a) Single crystal of cellulose tripropionate grown at 205 °C from a mixture of dibenzyl ether and tetradecane (20/80 v/v). Crystallization time, 4 h; polymer concentration 0.01%. (b) Corresponding electron diffraction diagram from the circled area. (c) Schematic drawing of the reciprocal lattice of the diffraction diagram. The dots show the diffraction spots actually observed.

## Single Crystals of Cellulose Tripropionate

The properties of aliphatic cellulose esters were reported more than 30 years ago by Malm et al.,[1] but very little progress has been achieved in our knowledge of the structures of cellulose derivatives, and the heterogeneously and homogeneously acetylated celluloses, the so-called cellulose triacetate I[2] and triacetate II,[3] are the only extensively studied cellulose derivatives whose structures have been determined. Recently, Zugenmaier reported that cellulose tripropionate crystallized in an orthorhombic unit cell with $a$ = 3.16 nm, $b$ = 2.21 nm, and $c$ (fiber axis) = 1.50 nm, which contained eight chains.[4]

We wish to report ribbonlike lamellar single crystals of cellulose tripropionate grown from a mixture of dibenzyl ether and *n*-tetradecane at 205 °C. On the basis of the electron diffraction spots, we propose new orthogonal lattice parameters and the two-dimensional space group.

The cellulose tripropionate (CTP) was prepared by acylating an Avicel cellulose powder in the mixture of trifluoroacetic anhydride and propionic acid. The acylation was repeated to obtain trisubstituted cellulose propionate. The DS of the CTP was 3.0 from $^1H$ NMR spectrum and the weight-average molecular weight was 66 000 $g \cdot mol^{-1}$ from GPC data in which polystyrene was used as the standard.

The growth procedure followed the method reported in Chanzy and Roche.[5] The crystallization was achieved by cooling dilute CTP solutions (0.01 g/100 mL) in various mixtures of dibenzyl ether (poor solvent) and *n*-tetradecane (precipitant) at elevated temperatures. The best results were obtained when the CTP sample was dissolved in a mixture of 20% dibenzyl ether and 80% *n*-tetradecane at 205 °C, crystallized for 4 h, and slowly cooled. The crystals were recovered by repeated centrifugation and washing with ethyl alcohol and stored in ethyl alcohol.

Drops of the crystal suspension in ethyl alcohol were evaporated on carbon-coated grids. A JEM-2000ES electron microscope was used at 200 kV both for imaging and for diffraction. The electron diffraction diagrams were calibrated with the (111) plane of platinum ($d_{111}$ = 0.2266 nm).

A typical electron micrograph of the CTP single crystal is shown in Figure 1a. The ribbonlike lamellar crystals are seen in this micrograph. Either increasing the volume ratio of dibenzyl ether against *n*-tetradecane or lowering the crystallization temperature resulted in smaller single crystals. The lamella is composed of finer rodlike crystals. Figure 1b shows a selected-area electron diffraction diagram obtained from the crystal shown in Figure 1a (see the encircled area), and Figure 1c shows an indexed schematic display of the diffraction diagram. The diagram contains all the ($hk$0) reflections of the CTP X-ray fiber patterns[4,6] which confirms that the diagram is a projection along the $c$ axis: i.e., the polymer chains are perpendicular to the lamellar base of the crystal.

All the reflection spots can be indexed in terms of an orthogonal cell parameters, $a^*$ = 0.91 $nm^{-1}$, $b^*$ = 0.65 $nm^{-1}$, and $\gamma^*$ = 90°. The two base plane dimensions are exactly half of the unit parameters proposed by Zugenmaier,[4] and accordingly the size of base plane becomes one-quarter.

Along the $b$ axis only even-order reflections appear which suggests that the crystal possesses a *pg* two-di-

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