argon inlet. The resulting solution was treated with triethylamine (0.034 mL, 0.24 mmol) and (+)-$\alpha$-methoxy-$\alpha$-(trifluoromethyl)phenylacetyl chloride[19] (0.018 g, 0.072 mmol) at room temperature with stirring. The reaction was quenched with dilute aqueous bicarbonate (1 mL) upon complete reaction, as determined by TLC (40% EtOAc/hexanes, followed by staining with aqueous KMnO$_4$, 1–2 h). The mixture was diluted with ether (5 mL), and the layers were separated. The organic layer was washed with dilute aqueous sodium bicarbonate (2 × 1 mL) and brine and dried (Na$_2$SO$_4$). Filtration and concentration afforded the crude esters. Analysis by $^1$H NMR (CDCl$_3$) gave several diastereotopic protons that are as follows (with integration): $\delta$ 6.98–6.95 (m, 0.50 H), 6.88–6.85 (m, 0.50 H), 5.61–5.57 (m, 0.50 H), 5.56–5.52 (m, 0.50 H), 3.779 (s, 1.48 H), 3.765 (s, 1.52 H).

The Mosher ester of hydroxy acetonide (−)-**11** (0.0005 g, 0.0022 mmol) was prepared according to the above procedure with dichloromethane (0.4 mL), DMAP (0.3 mg), pyridine (0.006 mL, 0.074 mmol), and acid chloride (0.007 g, 0.028 mmol).

Analysis by $^1$H NMR (CDCl$_3$) gave the following diastereotopic protons: $\delta$ 6.88–6.85, 5.56–5.52, 3.767. Expansions of the spectrum failed to show the characteristic peaks for the minor diastereomer.

**C. Deprotection and Acetylation of Hydroxy Acetonide 11.** The above light-brown oil was dissolved in methanol (2 mL), and *p*-toluenesulfonic acid (0.201 g, 1.06 mmol) was added with stirring at room temperature. Stirring was continued (9 h), at which time the mixture was concentrated. Residual methanol was removed under high vacuum. The flask was flushed with argon and fitted with a magnetic stir bar, septum, and argon inlet. Dichloromethane (6 mL) and 4-(dimethylamino)pyridine (0.5 mg) was added, and the resulting solution was cooled to 0 °C. Triethylamine (0.71 mL, 5.1 mmol) and acetic anhydride (0.32 mL, 3.4 mmol) were added dropwise. The bath was removed and the flask allowed to warm to room temperature. Stirring was continued (2 h), at which time the reaction mixture was diluted with ether (12 mL) and washed with dilute aqueous ammonium chloride (3 × 6 mL). The combined aqueous layers were back-extracted with ether (1 × 8 mL). The combined organic layers were washed with dilute aqueous sodium bicarbonate (3 × 6 mL) and brine and dried (Na$_2$SO$_4$). Filtration and concentration gave the crude products. Purification by PTLC (silica gel, 20% EtOAc/hexanes, two elutions, $R_f$ 0.32) afforded 0.027 g (50%) of methyl triacetyl-4-epishikimate [(−)-**12**]: $[\alpha]^{24}_{\mathrm{D}}$ −137° (*c* 1.17, MeOH); $^1$H NMR (CDCl$_3$) $\delta$ 6.78–6.76 (m, 1 H), 5.68–5.62 (m, 1 H), 5.45–5.39 (m, 1 H, 5.13 (dd, *J* = 7.4, 2.4 Hz, 1 H), 3.76 (s, 3 H), 2.78–2.57 (m, 2 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H); IR (CCl$_4$) cm$^{-1}$ 1745, 1720, 1215. *Literature*: $[\alpha]^{22}_{\mathrm{D}}$ −140° (*c* 1.2, MeOH); $^1$H NMR (60 MHz, CDCl$_3$) $\delta$ 6.73 (m, 1 H), 5.8–5.3 (m, 2 H), 5.13 (dd, *J* = 7, 2, Hz, 1 H), 3.77 (s, 3 H), 2.8–2.6 (m, 2 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H).[11,12]

**Acknowledgment.** We thank the NIH (GM 30052) for financial support. Purchase of a 400-MHz NMR spectrometer was made possible by the NIH (1 S10 RR01934) and by the NSF (PCM-83-03776).

**Registry No.** (−)-**1**, 104464-04-2; (−)-**2**, 104464-05-3; **3a** (isomer 1), 104464-06-4; **3a** (isomer 2), 104464-07-5; **3b**, 104487-42-5; 4 (isomer 1), 104530-70-3; **4** (isomer 2), 104464-21-3; (−)-**5**, 104464-08-6; (−)-**5** (diacetate), 104464-09-7; (−)-**5a**, 104464-22-4; **6** (isomer 1), 104464-10-0; **6** (R* = H, isomer 1), 104464-11-1; **6** (isomer 2), 104528-65-6; **6** (R* = H, isomer 2), 104528-64-5; **7** (isomer 1), 104464-12-2; **7** (isomer 2), 104528-63-4; **7** (mesylate, isomer 1), 104464-13-3; **7** (mesylate, isomer 2), 104528-66-7; (+)-**8**, 104464-14-4; **9** (isomer 1), 104464-15-5; **9** (isomer 2), 104464-16-6; **10** (isomer 1), 104464-17-7; **10** (isomer 2), 104528-67-8; (−)-**11**, 104464-18-8; (±)-**11**, 104528-68-9; (+)-**11** (mosher ester), 104464-19-9; (−)-**11** (mosher ester), 104464-20-2; (−)-**12**, 104528-69-0; (+)-$\alpha$-methoxy-$\alpha$-(trifluoromethyl)phenylacetyl chloride, 20445-33-4.

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# The Preparation of Low-Spin *trans*-Polyacetylene

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*Received June 19, 1986*

**Abstract:** *trans*-Polyacetylene was prepared directly at 25 °C with a modification of the standard AlEt$_3$/Ti(O-*n*-Bu)$_4$ catalyst. The product was characterized by IR, transmission electron microscopy, electron diffraction, photothermal deflection spectroscopy, and electron spin resonance. The product was identical in all respects with *trans*-polyacetylene prepared by standard routes, except that the number of neutral defects (solitons) is reduced from ~1/3000 C atoms to ~1/47000 and the line width of the signal due to these defects increased from ~1 to 5 G. The reduced defect level makes this an extremely useful material for studying the effect of solitons on the physical properties of polyacetylene.

Perhaps the most distinguishing physical property of polyacetylene is its extreme physical intractability.[1,2] Since it neither dissolves in solvents nor can be thermally processed, the physical form of this polymer is set at the time of synthesis. Thus, different synthetic routes to polyacetylene might be expected to yield polyacetylenes with different purities, morphologies, and/or microstructures. The most widely used procedure for polyacetylene synthesis was developed by Ito et al.[3] and yields silvery films with a high cis isomer content. The trans isomer can be produced by a suitable thermal treatment, which also generates numerous (~1/3000 C atoms) free spins.[4]

A more recent approach to polyacetylene synthesis was developed by Feast and Edwards.[5,6] Their route, via a precursor polymer which can later be converted to polyacetylene, has led to the development of highly ordered crystalline films of *trans*-polyacetylene.[7,8] These films also contain numerous free spins[9] (~1/2000 C atoms) and can be converted to polymeric conductors by either oxidation or reduction.[10,11]

The spins observed in *trans*-polyacetylene prepared by the Shirakawa method are distinguished from those found in other conducting polymers by their postulated mobility in the conjugated

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† Bell Communications Research.

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$\pi$ system of the polymer.[12,13] This mobility, along with an overall neutral charge, and a similarity to topological solitons, has resulted in the name "neutral soliton" for these defect sites. In addition, the unexpectedly high conductivity of *trans*-polyacetylene at low doping levels has been attributed to the intermediacy of neutral solitons.[14] Although soliton motion is widely accepted, other magnetic measurements[15-19] suggest that only a minority of the spins in *trans*-polyacetylene might actually be mobile, or that their mobility is restricted to small portions of typical polyacetylene samples. Unfortunately, there has been no suitable method available for controlling the spin density in samples of polyacetylene. This limitation has prevented an unambiguous investigation of soliton dynamics and the predicted spin-conductivity relationship.

The generation of long-lived free radicals during the thermally induced cis-trans isomerization of polyacetylene is a characteristic feature of the latter stages of the isomerization process[22,23] and has been investigated by many authors.[20-22] Presumably, these thermally generated diradicals[22,24] are stabilized by delocalization and by the steric constraints imposed by the crystal lattice. In principle, the number of such spins might be reduced by carrying out the isomerization step under milder conditions (i.e., in solution). Alternatively, a catalyst could be employed which would yield the trans isomer directly, obviating the isomerization step.

The preparation of such a material would have important implications for the study of soliton diffusion and the mechanism of conductivity in polyacetylene. In this paper, we describe the synthesis and characterization of *trans*-polyacetylene which is identical with that prepared by the Shirakawa catalyst, but which contains an order of magnitude fewer spins.

## Results and Discussion

Previously reported work has indicated the possibility of synthesizing *trans*-polyacetylene under relatively mild conditions. A procedure using $AlEt_3/TiCl_4$ as catalyst[25] yielded primarily *trans*-polyacetylene, but $TiCl_4$ and metal halides in general are known oxidizers of polyacetylene,[26] and the polymer as obtained was largely amorphous. In previous work by Shirakawa,[3] it was mentioned that the trans isomer content rose as the ratio of $AlEt_3/Ti(O\text{-}n\text{-}Bu)_4$ in their catalyst system was lowered, but the characterization of the products was not described. In each of these examples, the catalyst is preformed and then the monomer is added to the reactor to initiate the polymerization.

In our recent papers on the synthesis of graft copolymers of polyacetylene,[27-29] we described an alternate method for generating the active acetylene polymerization catalyst. In this procedure, the catalyst was prepared in situ, by adding triethylaluminum to a solution containing the remaining reagents for the graft polymerization. This ensured that the catalyst was dilute at all times, and the solubilized polyacetylene products obtained by this method contained only the trans isomer. We have subsequently found that the same synthetic procedure can be modified to consistently yield homopolyacetylene with a ~95% trans isomer content in the *absence* of a carrier polymer. This material is obtained as a fine suspension and can be deposited onto substrates by solvent evaporation to yield thin, silvery films of *trans*-polyacetylene.

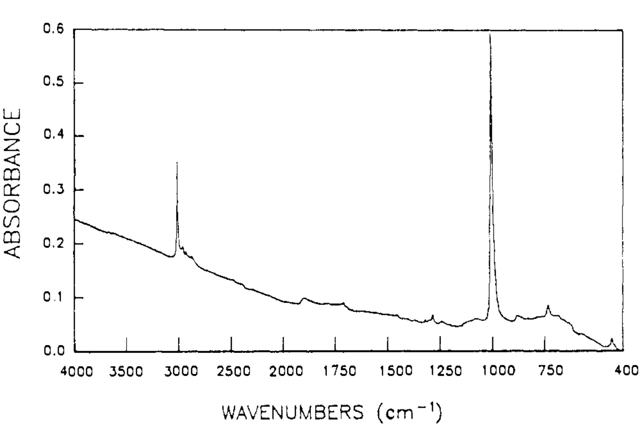

**Figure 1.** infrared spectrum of a 0.8-$\mu$m film of low-spin *trans*-polyacetylene prepared by solvent evaporation. The measured[32] trans isomer content is ~95%.

In a separate mechanistic study of the $AlEt_3/Ti(O\text{-}n\text{-}Bu)_4$ catalyst system,[30] we have also found that the trans isomer content is relatively insensitive to variations in catalyst concentration and to the ratio of monomer to catalyst employed. Decreases in temperature or the ratio of aluminum alkyl to titanium alkoxide lead to increases in the cis isomer content of the polymer. From these results, we have concluded that a trans-selective catalyst species dominates the polymerization. Since a cis-trans isomerization step need not take place in the solid state, the formation of most of the neutral defects is avoided.

Several requirements must be satisfied in order for this preparation of polyacetylene to be useful as an alternate preparation of Shirakawa polyacetylene and as a model system for the infinite polyene. Among these are high chemical purity, appropriate isomeric content (cis/trans), an identical crystal structure and morphology, similar conjugation lengths, and an enumeration of the charged and neutral defects in the polymer. We have considered each of these points by the appropriate experimental technique, and we conclude that the polyacetylene prepared by our revised synthetic method is identical with that prepared by the Shirakawa technique *except for the density of neutral defects.*

The infrared spectra of dried films (Figure 1) are identical with those obtained from *trans*-polyacetylene films prepared by the Shirakawa route.[3] Residual absorptions at 745 and 450 cm$^{-1}$ are attributable to small amounts (~5%) of *cis*-polyacetylene.[24] By subjecting the sample to a thermal treatment commonly used to convert *cis*-polyacetylene to the trans isomer[15] (180 °C, 5 min) the intensities of these peaks are slightly reduced.

The transmission electron microscopy results (Figure 2) are characteristic of polyacetylene prepared by the Shirakawa route; a fibrous microstructure[3] is observed with typical fiber diameters of 30-60 nm. Diffraction patterns from these samples were indistinguishable from those reported for Shirakawa preparations of *trans*-polyacetylene,[32] both in the position of the diffraction lines and in their intensities.

The most critical test for similarities in conjugation lengths and charged defect levels between these two polymers is an examination of the low energy absorption edge by photothermal deflection spectroscopy (PDS).[33] The advantage of this method over transmission spectroscopy is that it is a calorimetric technique,

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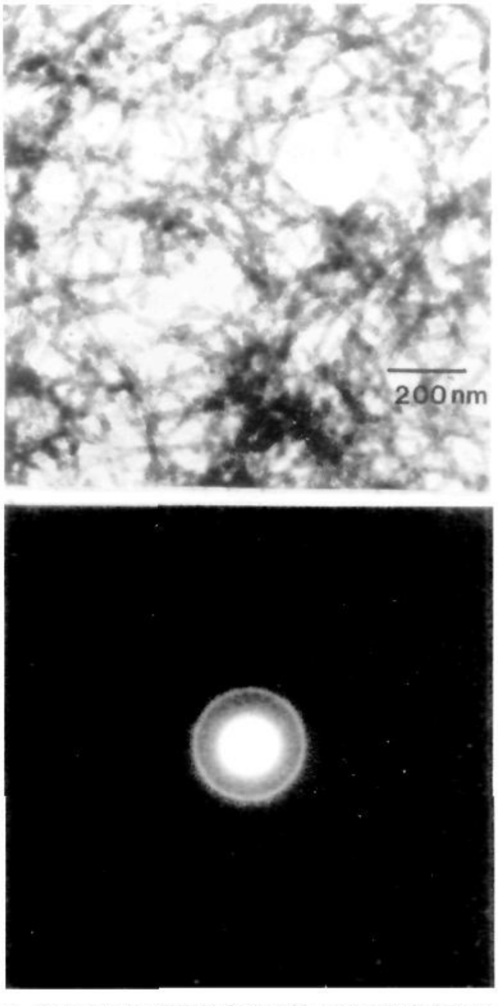

**Figure 2.** Upper photo: TEM of low-spin *trans*-polyacetylene. Lower: electron diffraction pattern from the same sample. Both the morphology and the diffraction pattern are indistinguishable from those obtained from standard Shirakawa preparations of *trans*-polyacetylene.

and thus it is insensitive to light scattering and pinholes in the sample. This technique allows the measurement of the optical properties of thin films at very low levels of absorption, and thus it is ideal for examining the impurity levels in polyacetylene. These impurities are usually masked by intense scattering in optical transmission experiments. Two films, one prepared by the Shirakawa method and a second and slightly thicker film prepared by our revised method, are compared in Figure 3. The materials have identical absorptions in the range from 1.35 to 1.00 eV, but at lower energies, the Shirakawa material appears to have nearly an order of magnitude more charged defects.[34] Total absorption of the probe beam occurs at 1.35 eV for the low-spin sample and at 1.5 eV for the thinner Shirakawa sample, preventing meaningful comparisons to be made above these energies. Inadvertent oxidation of the low-spin sample would be manifest by an increase in absorption at ~0.9 eV and a shift of the band edge to higher energies. Obviously this is not the case.

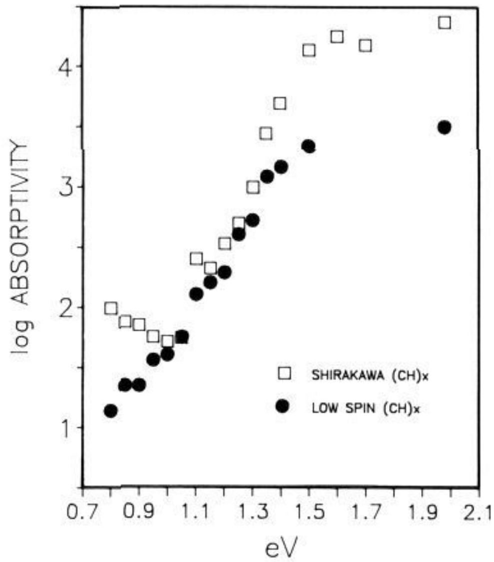

**Figure 3.** Photothermal deflection spectroscopy of a 0.5-μm film of *trans*-polyacetylene prepared by the Shirakawa method and a 5-μm film synthesized by the revised procedure of this report.

As anticipated, the magnetic properties of the products of polymerizations which yielded the trans isomer directly differed considerably from the *trans*-polyacetylene samples which had been prepared by thermal isomerization of the cis isomer. Previously, we had noted that preparations of solubilized polyacetylene contained very few spins[29] (<1/300000 C atoms) and that the line width of the ESR signal was nearly 5 G, a value more typical of *cis*-polyacetylene.[20] A typical sample of *trans*-polyacetylene prepared at 25 °C (95% trans) also contained few spins (1/47000 C atoms) and had a broad 5-G resonance. As a result of a thermal treatment (180 °C, 5 min) to eliminate the residual cis isomer content, the spin density increased by a factor of 3, and the line width had decreased to 3.8 G. A further heat treatment of the sample at 180 °C for 2 h produced no effect on the line width, although the number of spins decreased by one-half .

Within the soliton description for these defects, a broad line width would indicate fixed[4] and not mobile spins. This can be the result of trapping by oxygen[36] or by some other defect. The PDS results and the excellent elemental analyses argue against trapping by oxygen. In addition, samples of Shirakawa polyacetylene handled under identical conditions had much narrower line widths (~1 G). Alternatively, the broad line width could be interpreted as a decrease in spin–spin exchange as a result of the decreased spin density in the low-spin samples. More sophisticated magnetic resonance experiments will be required to differentiate between these two possibilities.[37]

Clearly this alternative synthesis of polyacetylene yields materials that are identical in all respects with those prepared by the traditional route, except of course for the level of magnetic defects. It is important to note that this material will not replace other methods of polyacetylene synthesis but rather is complementary to existing methods. Although the product is obtained as a suspension which can easily be dried to give a high-quality film, dried films are not mechanically robust. Further work is in progress to extend this procedure to the synthesis of free-standing films suitable for conductivity studies. In its current form, we anticipate that the questions of mobility of neutral solitons in polyacetylene can finally be answered through magnetic studies on this new material.

## Experimental Section

In a typical polymerization, $1 \times 10^{-2}$ mol of purified acetylene was transferred into a 300-mL flask connected to a vacuum manifold. Under air-free conditions, 14.9 mL of a 0.134 M solution of titanium tetrabutoxide in toluene and 14.4 mL of dry deoxygenated toluene were added. With the reactor maintained at 25 °C, 10.8 mL of a solution of triethylaluminum in toluene (0.188 M) were added under vigorous stirring

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to form the catalyst and initiate the polymerization. After 30 min, the product was transferred into a helium-filled drybox. The product was loaded into centrifuge tubes and extracted exhaustively with dry deoxygenated hexane. Typical yields of dried, purified product were 70–80%. The bulk densities of dried films were calculated by evaporating 3-$cm^2$ films onto silica plates. The thickness of the films was measured with a Dektak profiler, and from the measured weight of the film, the bulk density was calculated to be 0.4 $g/cm^3$.

The trans isomer content was assayed[38] by allowing a portion of the fine suspension to evaporate to dryness on a silicon plate, thus forming a thin film which could then be analyzed by infrared spectroscopy. The validity of the IR method for determination of the isomeric content of deposited films was confirmed by measuring the absorption coefficients for the bands at 1013 $cm^{-1}$ and 3010 $cm^{-1}$. They were found to have the identical ratio and had the same magnitude as had been previously determined for *trans*-polyacetylene.[29] In addition, polyacetylene suspensions prepared with the Shirakawa catalyst and dried to give similar films were found to have identical trans isomer contents as pinhole-free free-standing Shirakawa films. Similarly prepared films were used for PDS spectroscopy. ESR spectra were obtained on a Varian X-band spectrometer, and spin densities were calculated relative to a strong pitch standard. Analyses were performed by Galbraith Laboratories, Knoxville TN. Anal. Calcd for $(CH)_n$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.69.

**Acknowledgment.** We thank M. Sargent, and D. V. Lang for the electron spin resonance measurements, S. Etemad for help with the PDS work, and F. Padden for help with the microscopy work.

**Registry No.** $AlEt_3$, 97-93-8; $Ti(OBu)_4$, 5593-70-4; *trans*-polyacetylene, 25768-71-2.

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