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ELECTROCHEMICAL ISOMERIZATION OF CIS-(CH)X TO TRANS-(CH)X.(U)
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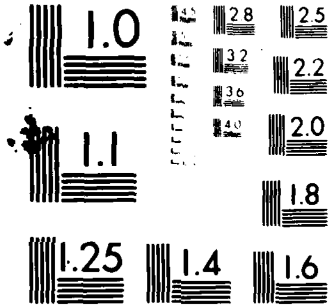
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REPORT DOCUMENTATION PAGE	**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER Technical Report No. 81-15 14 TR-	2. GOVT ACCESSION NO. AD-A110 618
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Electrochemical Isomerization of Cis-$(CH)_x$ to Trans-$(CH)_x$ ①	5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Tze-Chieng Chung, Avi Feldblum,* Alan G. MacDiarmid and Alan J. Heeger*	8. CONTRACT OR GRANT NUMBER(s) N00014-81-K-0648
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry and Department of Physics*, University of Pennsylvania, Philadelphia, Pa. 19104	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-356-602-4-13-91
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Va. 22217	12. REPORT DATE January 13, 1982
	13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) LEVEL	15. SECURITY CLASS. (of this report) unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for public release.

DTIC ELECTE FEB 8 1982 D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Journal of Polymer Science

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

electrochemical, isomerization, pure trans-$(CH)_x$, in situ, room temperature, p- or n-doping and undoping, metallic regime, visible/near ir spectrum, mid-gap peak, V_{oc} (open circuit voltage), $V_{applied}$, constant voltage power supply, sodium naphthalide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract No. N00014-81-K-0648

Task No. 356-602

TECHNICAL REPORT NO. 81-15

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by

Tze-Chieng Chung, Avi Feldblum,* Alan G. Mac-
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Prepared for publication in

Journal of Polymer Science

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Electrochemical Isomerization of *Cis*-$(CH)_x$ to *Trans*-$(CH)_x$

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Summary

Electrochemical isomerization of films of *cis*-$(CH)_x$ may be accomplished conveniently by first n-doping the $(CH)_x$ with $(Bu_4N)^+$ to the metallic regime or p-doping the $(CH)_x$ with $(ClO_4)^-$ to the metallic regime followed in each case by electrochemical undoping to yield pure *trans*-$(CH)_x$.

Cis-$(CH)_x$ is isomerized to the more thermodynamically stable trans isomer by heating briefly at 150-200°C.[1] Isomerization also takes place during chemical p- or n-doping and/or "undoping", i.e., compensation, but no agreement has been reached as to when isomerization commences or when it is complete. Furthermore, no pure trans-$(CH)_x$ has been produced by chemical isomerization methods since the final product has always been obtained in the doped state[2] or partly hydrogenated state.[2] We have shown previously, using electrical conductivity measurements, that $(CH)_x$ may be p- or n-doped electrochemically to the metallic state.[3] A conductivity in the approximate range 50-1000 $ohm^{-1}cm^{-1}$ at room temperature was used to indicate that the metallic state had been reached. The present study was performed in order to (i) show that isomerization can be attained by electrochemical doping of cis-$(CH)_x$ followed by its electrochemical undoping to parent trans -$(CH)_x$; (ii) confirm the electrochemical conversion of $(CH)_x$ to the p- or n-doped metallic state by physical measurements other than electrical conductivity; and (iii) to show that electrochemical and also chemical isomerization of cis-$(CH)_x$ to trans-$(CH)_x$ take place via the intermediate formation of chemically similar doped $(CH)_x$ species.

I. Electrochemical Studies

A very important characteristic feature of electrochemical doping is that application of a given potential to a $(CH)_x$ electrode results in a given level of p- or n-doping when equilibrium or near equilibrium conditions are established. The doped $(CH)_x$ can be undoped subsequently by applying the potential characteristic of parent $(CH)_x$ in a given electrolyte.

A pyrex electrochemical cell was constructed so that the visible/near ir spectrum of the $(CH)_x$ could be recorded throughout the electrochemical doping and/or undoping processes. A thin cis-rich $(CH)_x$ film was polymerized on a conductive glass electrode which was immersed in the electrolyte solution. When trans-$(CH)_x$ was required, the cis film was thermally isomerized in situ before adding the electrolyte. A lithium wire served as the other electrode. The "blank" spectrum of the cell and electrolyte was recorded, stored in a computer, and electronically subtracted from the spectra of the doped and undoped $(CH)_x$ as required. All potentials given are with respect to a lithium metal reference electrode. It has been found from studies of the open circuit voltage, V_{oc} (the voltage measured when no current is flowing) that a threshold exists below which charge is not injected. Thus voltages in the range between about 2.2-2.8 V are characteristic of parent $(CH)_x$.

(i) Electrochemical p-doping of Trans-$(CH)_x$ with $(ClO_4)^-$

The trans-$(CH)_x$ electrode was attached to the positive terminal of a constant voltage power supply. A 1.0M solution of $LiClO_4$ in propylene carbonate was used as the electrolyte. $V_{applied}$ potentials (measured as current was passing) were applied for ca. 30 minute periods during which time the current fell from ca. 20 μA to ca. 0.2 μA. Spectra were recorded at the following values of $V_{applied}$ (dopant levels given in parentheses): 3.46V (1.2%), 3.57V (2.5%), 3.64V (3.7%), 3.73V (6.8%). Doping levels were obtained from V_{oc} versus charge data relating V_{oc} values to percent doping.[4] The error introduced will be small since $V_{applied}$ and V_{oc} values will not differ greatly under the quasi-equilibrium conditions at the end of the 30 minute periods. As doping proceeded, the intensity of the trans peak at 2.0 ev decreased continually while at the same time the midgap soliton transition[5] at 0.7-0.8 ev increased. At 3.73V, i.e., at a composition corresponding to $[CH(ClO_4)_{0.068}]_x$ both these peaks had been replaced by the free carrier spectrum characteristic of the metallic state identical to that found in highly chemically p-doped[6] trans-$(CH)_x$.

(ii) Electrochemical Isomerization of Cis-$(CH)_x$ to Trans-$(CH)_x$

Electrochemical isomerization was carried out by either n-doping or p-doping cis-$(CH)_x$* (ca. 85% cis isomer) to the metallic regime, followed by electrochemical undoping.

N-doping was accomplished using a similar apparatus to that discussed in (i) except that the two electrodes were separated by a fine glass frit. The electrolyte was a 1.0M solution of $(Bu_4N)(ClO_4)$ in THF. Electrochemical n-doping occurs spontaneously; the constant voltage power supply was used simply to maintain the voltage applied to the cis-$(CH)_x$ at a given pre-selected fixed value which would result in a given level of doping (or undoping) when the final doping current had fallen to 1-2% of the initial value. Figure 1, spectrum 1, is that of the parent cis isomer. Spectra 2-5 were recorded at $V_{applied}$ values of 1.50V (~1%), 1.35V (~3%), 1.30V (~5%) and 1.25V (~8%), respectively, to give n-doped material of composition $(Bu_4N)_y CH_x$ (y=mole fraction of dopant, Bu_4N^+).[7] As can be seen from spectra 1-5, the peaks characteristic of cis-$(CH)_x$ at 2.1 and 2.3 ev decreased continually on doping,and the soliton mid-gap peak at(0.7-0.8 ev) characteristic of doped trans-$(CH)_x$ appeared and increased with doping. At 1.25V the spectrum characteristic of the metallic state, essentially identical to that observed in highly chemically n-doped (with Na^+) trans-$(CH)_x$[8] was obtained. The spectrum was also identical to that obtained in (i) by the electrochemical p-doping of trans-$(CH)_x$. On applying potentials of 2.0V and 2.8V, spectra 6 and 7, respectively, were obtained, the latter being essentially identical to that of pure trans-$(CH)_x$ formed by thermal isomerization of cis-$(CH)_x$. These results are consistent with isomerization occurring upon doping; the pure parent trans isomer is then obtained upon undoping.

In a further series of experiments, ca. 85% cis-$(CH)_x$ was doped electrochemically with $(Bu_4N)^+$ to ca. 1% ($V_{applied}$=1.50V) and was then undoped (at 2.7V) to parent $(CH)_x$. A small increase in the peak characteristic of the trans isomer

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*It is convenient to refer to "doping of cis-$(CH)_x$"; however, we show in these studies that as soon as cis-$(CH)_x$ is "doped" it converts spontaneously to doped trans-$(CH)_x$.

and a corresponding decrease in the peaks of the cis isomer were observed in the visible/near ir absorption spectrum. This doping-undoping cycle was repeated seven times, the extent of isomerization decreasing after each of the first three cycles. After the fourth cycle, no further isomerization occurred. In a related experiment, a cis-rich sample was first doped to a concentration y_1, then undoped to parent neutral $(CH)_x$. On subsequent doping to $y_2<y_1$, no additional isomerization occurred. These results show that doping of the trans isomer occurs preferentially to the reaction of the cis isomer with the dopant. It should be noted that that portion of the cis isomer which had undergone reaction with the dopant is apparently converted to the trans isomer at some stage during the doping-undoping cycle. Thus subsequent undoping and re-doping to the same level re-dopes only that portion of the material which was already trans.

In another study, a free standing film of cis-rich $(CH)_x$, to which a platinum wire was affixed, was n-doped to composition $[(Bu_4N)_{0.03}(CH)]_x$ by placing it in the electrolyte and short-circuiting it to a lithium wire also in the electrolyte. Spontaneous electrochemical doping occurred. It exhibited a conductivity in the metallic regime (25 $ohm^{-1}cm^{-1}$). Its thermoelectric power at room temperature (-43.5 μV/K) was characteristic of an n-type metal. Moreover, in the heavily doped regime the thermoelectric power decreased linearly with temperature, consistent with metallic behavior.

P-doping ot cis-$(CH)_x$ (ca. 85% cis isomer) was accomplished at $V_{applied}$=3.83V in the same apparatus and in the same manner as in (i). A spectrum identical to that observed by either p-doping trans-$(CH)_x$ or n-doping cis-$(CH)_x$ (Figure 1, Spectrum 5) was obtained. The sample was subsequently undoped by setting the applied voltage to 2.0V. The spectrum then showed no evidence of cis-$(CH)_x$ peaks and consisted only of the peak characteristic of undoped trans-$(CH)_x$.

(iii) Electrochemical Doping/Chemical Undoping Induced Isomerization of Cis-$(CH)_x$ to Trans-$(CH)_x$

Cis-$(CH)_x$ film (ca. 85% cis isomer; 0.01 mm thick) was polymerized on a platinum grid and was n-doped with $(Bu_4N)^+$ in a similar manner to that employed for the preparation of the sample used in the thermoelectric power studies. The film was completely opaque in the ir region, consistent with its being doped to the metallic state. It was then undoped in the ir cell by exposing it to ~0.1 Torr of AsF_5 vapor until the characteristic soliton peak at 1380 cm^{-1}[9] disappeared completely to yield a spectrum characteristic of undoped trans-$(CH)_x$ containing $(Bu_4N)^+(AsF_6)^-$ formed according to equations (1) and (2):

$$2[(Bu_4N^{+y})(CH^{-y})]_x + xyAsF_5 \rightarrow 2(CH)_x + 2xy(Bu_4N)F + xyAsF_3 \qquad (1)$$

$$xy(Bu_4N)F + xyAsF_5 \rightarrow xy(Bu_4N)(AsF_6) \qquad (2)$$

II. Chemical Isomerization

Cis-$(CH)_x$ was chemically doped with Na^+ using sodium naphthalide solution in THF. Doping and washing were carried out as previously described[8] for epr studies of Na-doped trans-$(CH)_x$ except that the epr tube was replaced by a rectangular Pyrex cell on the inside walls of which a thin film of cis-$(CH)_x$ had been polymerized. Successive doping, washing and visible/near ir spectral studies were carried out in situ. As doping proceeded, the intensity of the characteristic cis peaks at 2.1 ev and 2.3 ev decreased and the soliton mid-gap peak at 0.8 ev appeared and increased in intensity. Finally, the only absorption present was that characteristic of the free carrier metallic state. The $[Na_y(CH)]_x$ was then undoped with 0.1 Torr of AsF_5 vapor. As this compensation reaction proceeded, the 0.8 ev peak again appeared and then decreased in intensity while at the same time, the 2.0 ev peak characteristic of trans-$(CH)_x$ appeared and grew in intensity. The final spectrum obtained showed only the presence of the trans-$(CH)_x$ absorption indicating complete isomerization.

A similar experiment was carried out except that undoping was accomplished by the use of iodine vapor and that the doping and undoping was constantly monitored by observing changes in the ir spectrum. The NaI formed in the reaction with iodine was removed by washing with water. The ir spectrum of the resulting film showed it consisted of pure trans-$(CH)_x$.

All methods of isomerization, including thermal isomerization, give trans-$(CH)_x$ containing approximately the same number of unpaired spins and an epr signal of the same g value and line width.

Cis/trans isomerization of $(CH)_x$ has been shown to occur in these studies as proceeding via a doping-undoping cycle involving the metallic state of $(CH)_x$ regardless of whether the cycles are completely electrochemical in nature, completely chemical or partly electrochemical and partly chemical. The results imply that isomerization occurs continuously during the doping step.

Acknowledgement

This work was supported jointly by the Office of Naval Research and Defence Advanced Research Projects Agency (through a grant monitored by the Office of Naval Research), and the National Science Foundation.

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Figure 1: Visible-near ir absorption spectral changes during the cis-trans isomerization of $(CH)_x$ film by electrochemical n-type $(Bu_4N)^+$ doping.

(1) ○——○——○ V_{oc}=2.7 V; (cis-$(CH)_x$)

(2) ●——●——● $V_{applied}$=1.5V

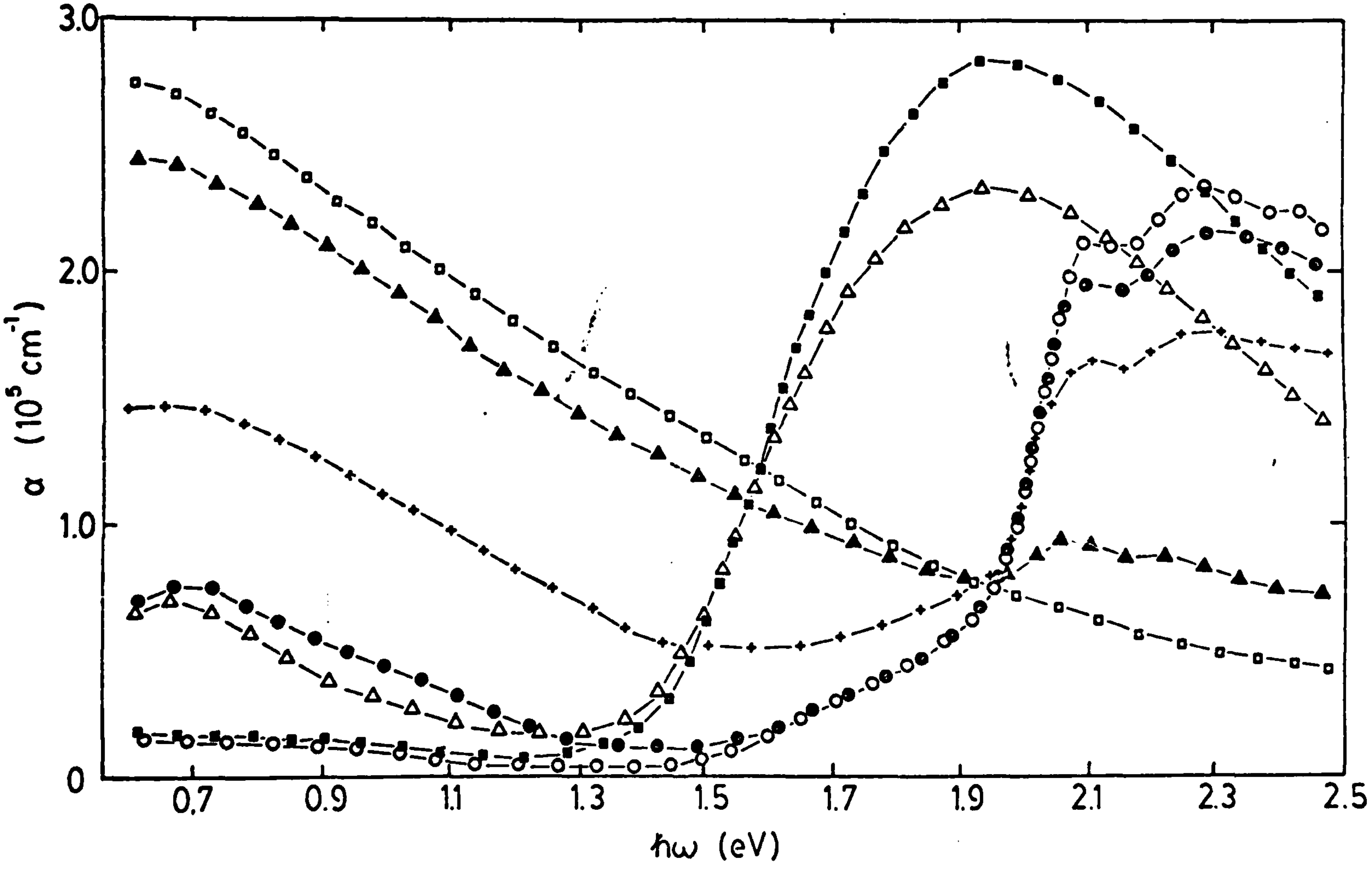
(3) ×——×——× $V_{applied}$=1.35V

(4) ▲——▲——▲ $V_{applied}$=1.3V

(5) □——□——□ $V_{applied}$=1.25V

(6) △——△——△ $V_{applied}$=2.0V

(7) ■——■——■ $V_{applied}$=2.8V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1.0
0
α (10^5 cm^{-1})
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0.9
1.1
1.3
1.5
1.7
1.9
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