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Thermal *cis-trans* Isomerization of $(CH)_x$ and $(CD)_x$

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Synopsis. Thermal *cis-trans* isomerization of poly(acetylene), $(CH)_x$, and poly(acetylene-d_2), $(CD)_x$, is investigated by visible spectroscopy over the temperature range 90—150 °C. The reaction does not obey simple kinetics. The initial time activation energy for the *cis-trans* isomerization is 11 kcal/mol for $(CH)_x$ and 16 kcal/mol for $(CD)_x$.

In recent years, various properties have been reported for poly(acetylene) since the discovery that it can increase the conductivity by many orders of magnitude up to metallic levels when doped with electron donors or acceptors.[1] For example, the electrical conductivity after strong doping is always smaller for *trans*-$(CH)_x$ than for *cis*-$(CH)_x$ and the doping may induce the *cis-trans* isomerization of $(CH)_x$ films. Furthermore, many studies have focused on the magnetic properties of the neutral soliton defects which appear in *trans*-$(CH)_x$ upon isomerization.[2] Accordingly, detailed studies about the isomerization are necessary to determine the physics and chemistry of poly(acetylene). In the present paper, we show the optical study on the thermal *cis-trans* isomerization mechanism of pure $(CH)_x$ and $(CD)_x$.

The thin $(CH)_x$ and $(CD)_x$ films polymerized at −78 °C show the reddish cupuric color and the film becomes blue on heating it in vacuo. This color change was explained by the analysis of IR vibrational spectra to be due to the *cis-trans* isomerization of $(CH)_x$ and $(CD)_x$.[3,4] Figure 1 describes the visible absorption spectral change of the thin $(CD)_x$ film during the course of heat treatment in vacuo. *cis*-Rich $(CD)_x$ has two vibronic peaks at 17300 and 18500 cm^{-1} and the second peak (18500 cm^{-1}) is the most intense. On heating, the broad band in the region of 15000 cm^{-1} becomes more intense and the 18500 cm^{-1} peak of *cis*-$(CD)_x$ becomes weaker. Finally, the 15000 cm^{-1} band of *trans*-$(CD)_x$ has the same absorption intensity as that of the 18000 cm^{-1} band of *cis*-$(CD)_x$ before heating. Furthermore, it should be noted that an isosbestic point is observed at 17000 cm^{-1}. The same phenomenon can be observed for the $(CH)_x$ film, too.[5]

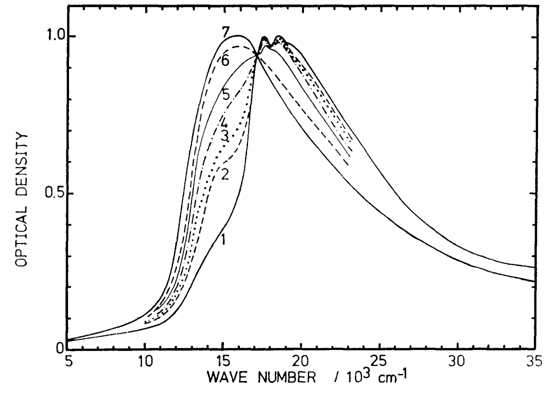

Fig. 1. The visible absorption spectral change due to the *cis-trans* isomerization of the thin $(CD)_x$ film at 140 °C after heating for 1) 0 min, 2) 0.5 min, 3) 1 min, 4) 2 min, 5) 3 min, 6) 5 min, and 7) 20 min.

Then, the rate equation of the *cis-trans* isomerization is given as follows,

$$C_{cis}(t) + C_{trans}(t) = C \tag{1}$$

and

$$-\frac{dC_{cis}(t)}{dt} = k\,C_{cis}(t). \tag{2}$$

Here, $C_{cis}(t)$ and $C_{trans}(t)$ are the concentration of *cis*- and *trans*-forms at time t and C is the total concentration.

The integration gives

$$C_{cis}(t) = C - C_{trans}(t) = C_{cis}(0)\exp(-kt). \tag{3}$$

On the other hand, the observed optical density at time t, $OD(t)$, can be expressed by using the molar extinction coefficients ε_{cis} and ε_{trans} of *cis*- and *trans*-polymers and the thickness, d, of the film,

$$OD(t) = d\,\varepsilon_{cis}C_{cis}(t) + d\,\varepsilon_{trans}C_{trans}(t). \tag{4}$$

Then, Eqs. 3 and 4 lead to

$$OD(\infty) - OD(t) = d\,C_{cis}(0)\{\varepsilon_{trans} - \varepsilon_{cis}\}\exp(-kt)\,, \tag{5}$$

where $OD(\infty) = d\,\varepsilon_{trans}\,C$ is the observed optical density at infinite time. The ratio of Eq. 5 for time t and initial time and the logarithm of the result give

$$\ln\left|\frac{OD(\infty) - OD(t)}{OD(\infty) - OD(0)}\right| = -kt, \tag{6}$$

where $OD(0)$ is the observed optical density at initial time.

Figure 2 shows kinetic plots for the thermal *cis-trans* isomerization at 16000 cm^{-1} by using Eq. 6. The plot does not give the straight line as is pointed out by Ito, *et al.*[4] That is, the rate of isomerization becomes slow and the slope of the plot becomes small as the reaction proceeds. This means that the activation energy increases with increasing *trans*-

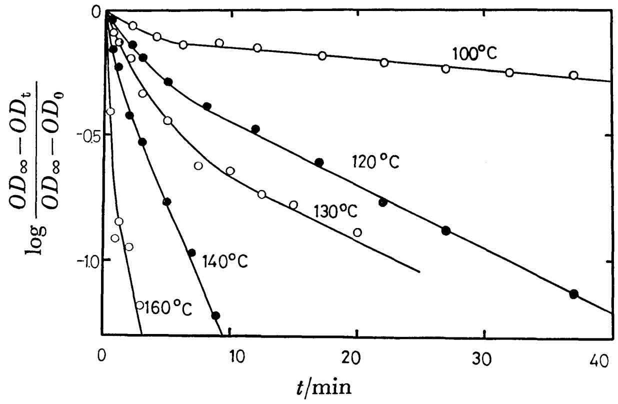

Fig. 2. Kinetic plots for the thermal *cis-trans* isomerization of $(CD)_x$ at 16000 cm^{-1}.

contents.

Arrhenius plots are shown in Fig. 3 and the activation energies at initial time are estimated to be 11 kcal/mol for $(CH)_x$ and 16 kcal/mol for $(CD)_x$. In contrast to Ito, Shirakawa and Ikeda's data (17 kcal/mol for 88% *cis*-rich $(CH)_x$),[4] our value of 11 kcal/mol for $(CH)_x$ corresponds to that of more than 90% *cis*-rich polymer. Furthermore, the larger activation energies for $(CD)_x$ than for $(CH)_x$ may be due to the mass difference between the hydrogen and deuterium atoms. That is, the out of plane C–H or C–D vibration plays an important part of the isomerization process and the difference between the zero point energies of C–H and C–D vibration may be considered to contribute to the difference between the activation energies for $(CH)_x$ and $(CD)_x$. This conclusion supports Ikeda's explanation for the difference between the *cis* and *trans* content ratio for the $(CH)_x$ and $(CD)_x$ polymers.[6]

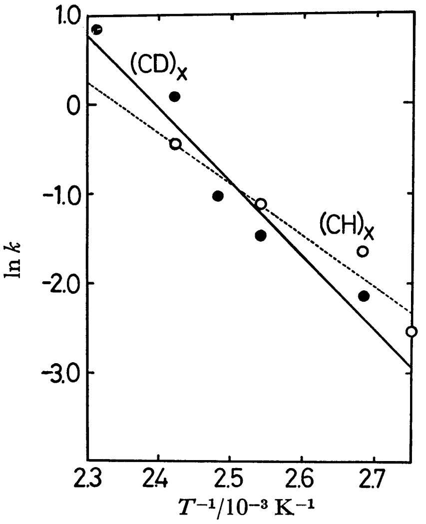

Fig. 3. Arrhenius plot for the thermal *cis-trans* isomerization of $(CH)_x$ and $(CD)_x$.

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