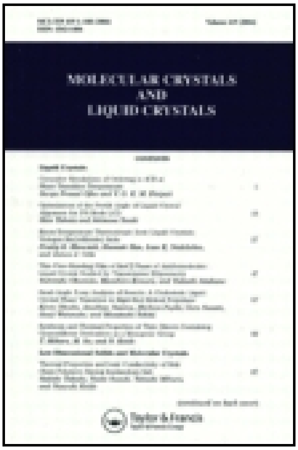

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Dependence of Vibrational Spectra and Conductivities of Poly-Acetylenes on Isomerization Processes and Hydrogenation

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To cite this article: Issei Harada , Yukio Furukawa , Tsutomu Arakawa , Hideo Takeuchi & Hideki Shirakawa (1985): Dependence of Vibrational Spectra and Conductivities of Poly-Acetylenes on Isomerization Processes and Hydrogenation, Molecular Crystals and Liquid Crystals, 117:1, 335-342

To link to this article: http://dx.doi.org/10.1080/00268948508074648

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 335-342
0026-8941/85/1174-0335/$15.00/0

DEPENDENCE OF VIBRATIONAL SPECTRA AND CONDUCTIVITIES OF POLYACETYLENES ON ISOMERIZATION PROCESSES AND HYDROGENATION

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Abstract Effects of hydrogenation and thermal processes on vibrational spectra and electrical conductivity of *trans*-polyacetylenes have been examined on the basis of new assignments of IR and Raman bands. Enrichment of long conjugated segments and their proper packing are indispensable for high electrical quality.

INTRODUCTION

In the structural studies on *trans*-polyacetylenes, Raman spectroscopy has been useful as a probe for composition of various conjugated segments.[1-7] The composition is most clearly reflected in the intensities of the doublet peaks of ν_1 and ν_3 bands (with blue-violet excitation at low temperature), peaks arising from vibrations of long and short segments at lower and higher frequencies, respectively.[3-6] It has turned out that the Raman spectrum (composition) depends critically on the condition of thermal and chemical perturbations applied on the sample.[3-7] The effect of perturbations is also noticed in the infrared spectrum. In the present paper, we first describe briefly the assignment of infrared and Raman bands based on a normal coordinate analysis (for in-plane modes) on isotopically substituted *trans*-polyacetylenes [t-$(CH)_x$, t-$(^{13}CH)_x$, and t-$(CD)_x$] and oligoenes (butadiene, hexatriene, and octatetraene).[8] Relations between number of conjugated double bonds ($N_{C=C}$) and the Raman ν_1 and ν_3 frequencies will also be shown. Secondly, effects of partial hydrogenation on the vibrational spectra and electrical conductivity are examined. Finally, the relations between conductivity and composition of *trans*-polyacetylenes obtained through different temperature-time conditions from the same *cis* film are discussed.

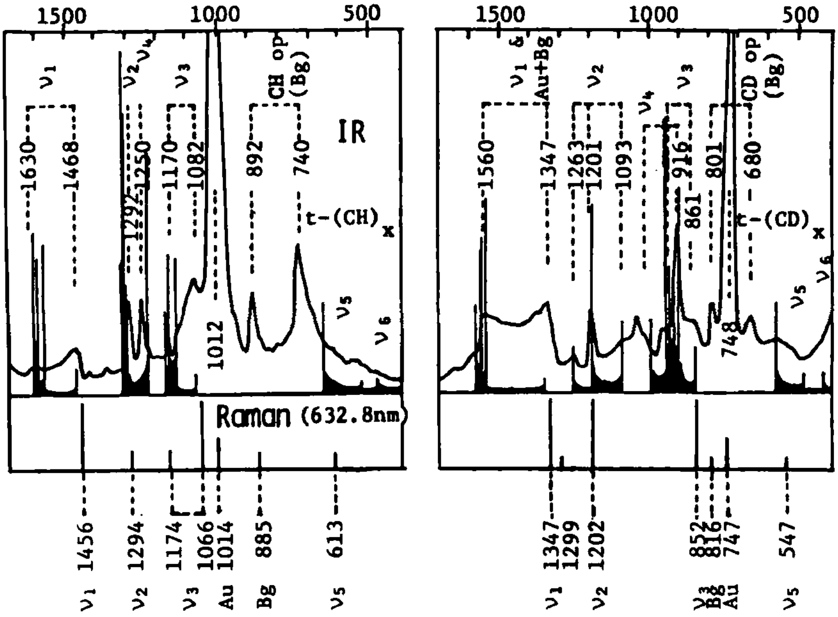

FIGURE 1. IR (upper) and Raman (lower) spectra, densities of states (in plane), and assignments of t-$(CH)_x$ (left) and t-$(CD)_x$ (right). Notations are given in text.

ASSIGNMENT OF IR AND RAMAN BANDS OF *TRANS*-POLYACETYLENES[8]

Figure 1 shows the IR and Raman spectra (with 632.8 nm excitation) of 'good films', densities of states of in-plane vibrations,[8] and assignments, for t-$(CH)_x$ and t-$(CD)_x$. (A film rich or poor in long conjugated segments, judged from the above-mentioned peak intensities of 457.9 nm excited Raman bands, is called a 'good' or 'bad' film, respectively.) Notations, ν_1– ν_6 in the figure are those of vibrational branches of an infinite polyene chain: viz., ν_1 (A_g, the C=C stretching), ν_2 (A_g, a mixed mode of the CC stretching and CH in-plane bending), ν_3 (A_g, a mixed mode of the CH in-plane bending and CC stretching), ν_4 (B_u, the CH in-plane bending), ν_5 (B_u, longitudinal acoustic mode), and ν_6 (B_u, a transverse acoustic mode). A single mode in A_u and that in B_g, both of which are the CH out-of-plane bendings, are simply denoted as A_u and B_g, respectively. Apparently, the selection rule of infinite chain does not hold, since most of the above-mentioned branches are observed in both the IR and Raman spectra. This is reasonably understood considering that the conjugation is interrupted for some reason and an ordinary film is composed of segments of various conjugation lengths (from four to more than 100 conjugations).[1,2] A break in conjugation of any kind would lower the symmetry of the polymer chain and the vibrations of various finite segments appear in the spectra. Hence, ungerade ν_1 modes of the segments are observed in the infrared as a broad band ranging from 1630 (due to short segments) to 1468 cm^{-1} (long segments) and the band shape reflects the composition. In accordance with this assignment the intensity of 1468 cm^{-1} peak relative to that of 1630 cm^{-1} one is stronger in the spectrum of a good film than in that of a bad film. Such trends are less significant in the ν_2, ν_3, and ν_4 regions partly because of band overlaps.

The infrared band at 740 cm^{-1} is not due to remnant *cis* segments because other *cis* bands, especially the strong 447 cm^{-1} band, do not remain in the spectrum and no such bands are observed in that of t-$(CD)_x$. Rather, the 892-740 cm^{-1} series [801-680 cm^{-1} in t-$(CD)_x$] is assigned to the CH (CD) out-of-plane bending mode (B_g), arising from long-short segments, correspondingly. (The relative intensities of high vs. low frequency peaks are stronger in good films than those in bad films.) A series of combination bands of these and the A_u band (1012 cm^{-1}) is observed at 1907-1720 cm^{-1} region of t-$(CH)_x$ and the series overlaps with the ν_1 band in the case of t-$(CD)_x$ (1560-1347 cm^{-1}).

RELATIONS BETWEEN $N_{C=C}$ AND ν_1 AND ν_3[7]

The relation between $N_{C=C}$ and ν_1 is well known.[1,9,10] Adopting 1454 cm^{-1} as the $\nu_{1\infty}$, we propose a modified relation in the form,

$$\nu_1\ (cm^{-1}) = 1454 + 727(N_{C=C} + 1)^{-1} \quad \text{for } N_{C=C} \geq 4.$$

Since ν_3 is a mixed mode of CH bending and CC stretching vibrations with a large contribution from the former, its frequency is sensitive to the types of side chains and end groups. For instance, the frequencies of isoprenoid compounds are different from those of polyenes without side chains. A simple relation holds between $N_{C=C}$ and ν_3 frequency of polyene without side chains:

$$\nu_3\ (cm^{-1}) = 1060 + 1020(N_{C=C} + 1)^{-1} - 2910(N_{C=C} + 1)^{-2}$$

for $N_{C=C} \geq 6$.

PARTLY HYDROGENATED *TRANS*-POLYACETYLENES[7]

It is known that partial hydrogenation takes place when an alkali-metal doped polyacetylene is treated with alcohol.[11] In this process, conjugation system is inevitably shortened by the intervening methylene groups. In Figure 2 are compared the IR spectra

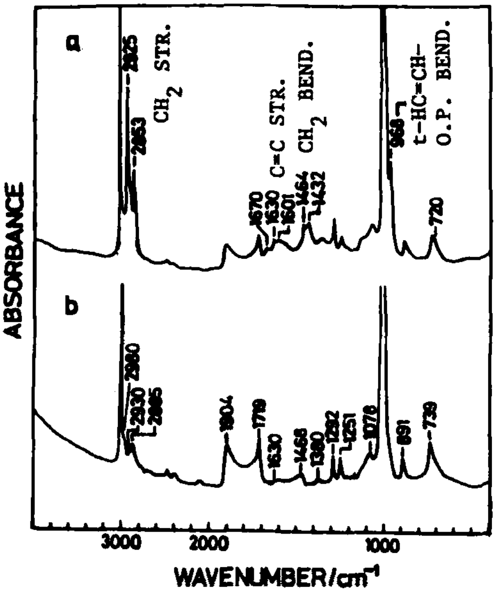

FIGURE 2. IR spectra.
a, t-$(CH_{1.17})_x$; b, t-$(CH)_x$.

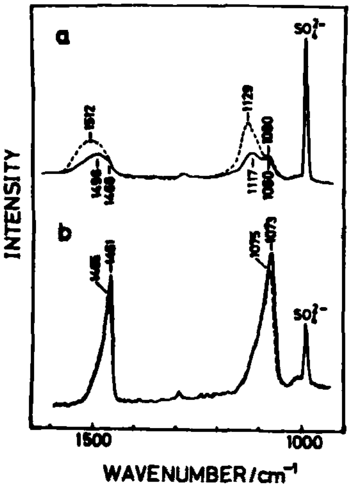

FIGURE 3. Raman spectra of t-$(CH_{1.16})_x$ (dotted line) and t-$(CH)_x$ (solid line).
a, 457.9 nm, and b, 632.8 nm excitation.

of t-$(CH_{1.17})_x$ and pristine t-$(CH)_x$. A spectral analysis indicates the followings.[7] (1) Numbers of consecutive methylene groups are mostly less than five. (2) Isolated C=C double bonds exist in the film. (3) The amount of very short conjugated double bonds is much larger than that in pristine film. Raman spectra of t-$(CH_{1.16})_x$ shown partly in Figure 3 reflect an increase in amount of short conjugated segments ($N_{C=C} = 8 \sim 55$) and a decrease in that of long conjugated segments.[7]

It is interesting to see what happens when these films are doped again. As may be expected, the conductivities are low even at maximum doping: σ_{max} values are 74, 0.81, and $<10^{-4}$ Scm^{-1} for t-$(CH_{1.06})_x$, t-$(CH_{1.17})_x$, and t-$(CH_{1.34})_x$, correspondingly. Nevertheless, lightly iodine doped t-$(CH_{1.17})_x$ gives an IR spectrum very much similar to that of doped polyacetylene (Figure 4). Accordingly, it is clear that the appearance of three infrared bands does not simply correlate with the overall conductivity. In the case of a heavily hydrogenated sample [t-$(CH_{1.34})_x$], changes in band shapes are observed as the doping proceeds (Figure 4c). These observations indicate that the shortened conjugated segments with the methylene groups at both ends are actually doped and the

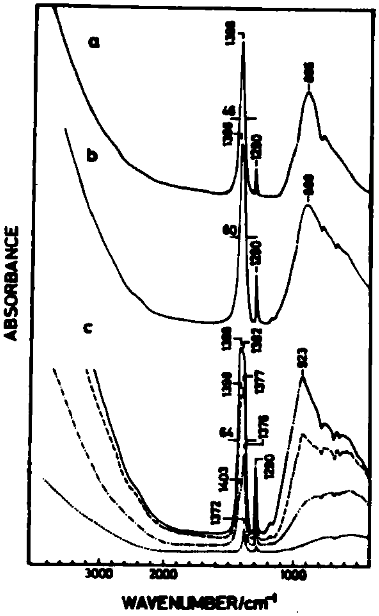

FIGURE 4. IR difference spectra of iodine doped samples. a, doped t-$(CH)_x$ (iodine content, less than 0.1 %); b, doped t-$(CH_{1.17})_x$ (1 %); doped t-$(CH_{1.34})_x$ (1 % for the solid-line spectrum).

structure of the doped parts is similar to that of doped polyacetylene. Also, the structure in very short segments is slightly different from that in longer segments.

EFFECTS OF THERMAL TREATMENT ON RAMAN SPECTRA AND CONDUCTIVITY

Several *trans* films were prepared through different isomerization conditions from the same *cis* film, the Raman spectra were recorded, and then the films were doped with iodine to maximum, which is followed by measurement of conductivity. Figures 5a and c are 457.9 nm excited Raman spectra of the best and the worst films, respectively. As mentioned above, the peaks at higher frequencies [e.g., 1498 (ν_1) and 1124 cm^{-1} (ν_3) in Figure 5a] are due to short segments and those at lower frequencies (1455 and 1063 cm^{-1}) arise from long segments. If we take the ratio of Raman intensity of the low frequency peak vs. the sum of those of the doublets [e.g., I(1455) over the sum of I(1455) and I(1498) in the case of ν_1 of the best film], the value (R_1 for ν_1 and R_3 for ν_3) is closely related to the proportion of long conjugated segments in the film.

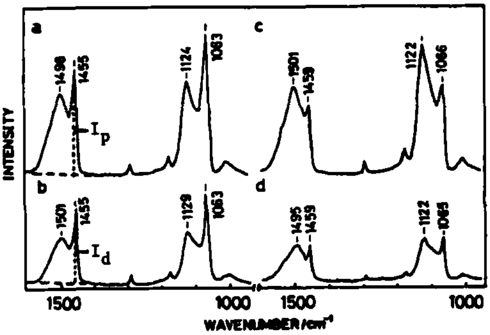

FIGURE 5. Raman spectra (457.9 nm excitation, 80 K) normalized to the intensity of 987 cm^{-1} band of $BaSO_4$. a, the best film (190 °C, 15 min.) and b, after iodine doping [σ= 0.5 Scm^{-1}, $(CHI_{0.011})_x$]. c, the worst film (230 °C, 180 min.) and d, after iodine doping [σ= 1, $(CHI_{0.042})_x$].

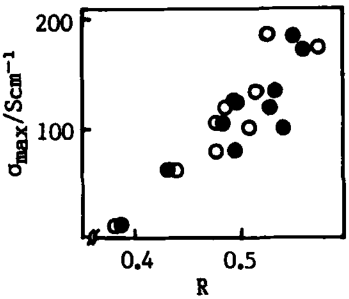

FIGURE 6. Relation between σ_{max} and R_1 (○) and R_3 (●).

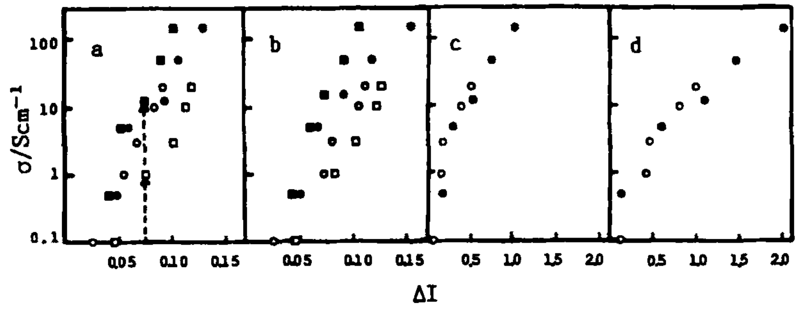

FIGURE 7. Relations between σ and ΔI's. Abscissas in a, b, c, and d are ΔI's of the ν_1 (457.9 nm excitation), ν_3 (457.9 nm), ν_1 (632.8 nm), and ν_3 (632.8 nm), respectively. ●; ν_1 (1455 cm^{-1}) and ν_3 (1063 cm^{-1}) due to long segments in good films and ○; the corresponding ones in bad films. ■; ν_1 (1498 cm^{-1}) and ν_3 (1124 cm^{-1}) due to short segments in good films and □; the corresponding ones in bad films.

As is clear in Figure 6, an approximately linear relation exists between σ_{max} and R_i's. If we compare the best film and the worst film, iodine contents at maximum doping are nearly the same (0.45 and 0.49 iodine per C=C bond, respectively) and content of long segments in the worst film is about 60 % of that in the best film, while the conductivities are different significantly (190 and 10 Scm^{-1}, respectively). This means that the amounts of doped parts are almost the same in two samples but the doped parts are inefficiently arranged in the worst film intra- and inter-chain-wise.

Figures 5c and d are the Raman spectra of the best and the worst films at lightly doped states. On doping, intensities decrease because only the undoped segments contribute to the resonance Raman bands. Doped segments are expected to give bands at different frequencies owing to drastic change in structure on doping and the bands to be very weak due to absence of strong absorption of doped parts in the wavelength region (off-resonant condition). The intensities decrease evenly in good films and unevenly in the bad films because the doping does not necessarily take place uniformly. In Figure 7, value of conductivity (σ) of doped film measured beforehand is plotted against the corresponding decrease in intensity, ΔI, (I_p - I_d), a quantity directly related to the amount of doped segments.

As shown in Figures 7a-d, good correlations exist between conductivity and ΔI's of long segments irrespective of the quality of the films, viz., the data points of long segments in good and bad films lie on the same line. On the other hand, no such correlations are noticed between conductivity and the ΔI's of short segments (Figures 7a and b). If we assume that the doped short segments play the dominant role in electrical conduction, we immediately become confronted with difficulties in explaining the reason why the doped short segments in good films conduct much more efficiently than those in bad films in spite of less content of short segments in the good films than in the bad films (see the arrows in Figure 7a). Rather, the present results including those on hydrogenated samples seem to indicate that the doped long segments play the major role in electrical conduction. Existence of excessive amount of short segments itself leads to possible disruption of properly close packing of polymers which is important for inter-polymer conduction. For this reason, the conductivity of the worst film is extremely low although the content of long segments is still 60 % of that in the best film. Shortage in the amount of long conjugated segments and deficiency of their proper packing at the pristine state and inefficient contribution to the conductivity from the short segments at the doped state are all responsible for the low electrical conductivity of the bad films. Conversely, enrichment of long conjugated segments and their appropriate packing are essential to the improvement of electrical property of *trans*-polyacetylene.

It is emphasized that 'appropriate packing' or 'properly close packing' does not mean 'homogeneous and crystalline throughout the film'. It means that there is room in the film adequate for dopant to be uptaken without destroying inter-chain contact of long conjugated segments, or moreover, such sites are so located that uptake of dopant increases the inter-chain contact.

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in-Aid for Special Project Research No. 59212001 from the Ministry of Education, Science, and Culture.

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