CHEMISTRY LETTERS, pp. 1637 - 1640, 1984.

ROLE OF LONG CONJUGATED SEGMENTS IN THE ELECTRICAL PROPERTY OF *TRANS*-POLYACETYLENE

Tsutomu ARAKAWA, Yukio FURUKAWA, Hideo TAKEUCHI, Issei HARADA,*
and Hideki SHIRAKAWA†
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
†Institute of Materials Science, University of Tsukuba, Ibaraki 305

Raman spectra and electric conductivity of *trans*-polyacetylene and doped polyacetylene have been studied. A linear relationship holds between contents of long conjugated segments in pristine films and values of conductivity at their maximally iodine-doped states. At the early and intermediate doping stages an apparent correlation exists between contents of doped long segments and conductivity. Enrichment of long conjugated segments is essential to the improvement of the electrical property of *trans*-polyacetylene.

It may be taken as a matter of course that close packing of long conjugated segments in pristine *trans*-polyacetylene is important for realization of high electric conductivity at the doped state. Since a break in conjugation of any kind (twisting of the polymer chain, saturation of a double bond by cross linking or branching etc.) in a pristine polymer necessarily disturbs the traveling of electrons within that polymer when doped, fewer breaks of conjugation are considered to be desirable. For an efficient intermolecular electron transfer, close contact of at least parts (conductive parts) of neighboring polymers throughout the film seems to be indispensable. However, relationships between composition (especially the content of long conjugated segments) and electrical property have not been fully investigated yet.$^{1-3)}$ In the present paper we have studied the Raman spectra of *trans*-polyacetylene isomerized under various temperature-time conditions and their conductivities at maximally iodine-doped state (σ_{max}). Resonance Raman spectra of these films with 457.9 nm excitation exhibit the ν_1 and ν_3 bands each of which is composed of two peaks due to segments of long and short conjugations at lower and higher frequencies, respectively (Fig. 1).$^{4-10)}$ Hence, by taking ratio (to be called R_1 and R_3 for ν_1 and ν_3, respectively) of the intensity of lower frequency peak (I_L for ν_1 in Fig. 1) vs. the sum of the intensities of two peaks ($I_L + I_S$) a value closely related to the proportion of long conjugated segments is obtained and it becomes possible to compare the composition of a polymer film with its σ_{max}. At the early stage of doping, uneven decreases in intensities of the Raman bands are noticed (Fig. 2). This is because the doping does not take place uniformly and only the undoped segments contribute to the resonance Raman bands at the frequencies. It is expected that the doped segments give Raman bands at different frequencies (owing to a drastic structural change on doping) with significantly decreased

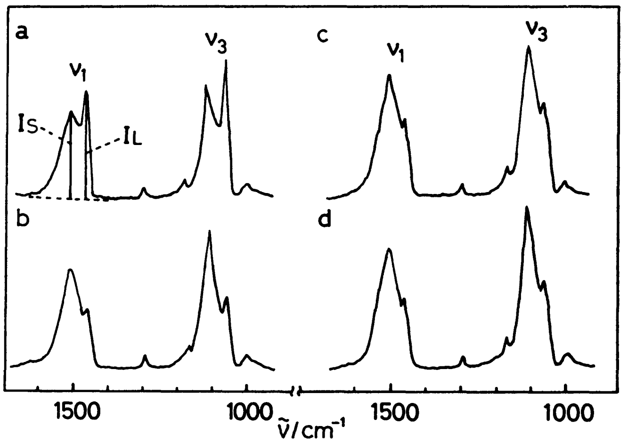

Fig. 1. Raman spectra of two extreme *trans*-$(CH)_x$ films obtained by different isomerization conditions from the same *cis*-$(CH)_x$ film (457.9 nm excitation, 80 K).
a, shiny side and b, dull side of a film (isomerization condition; 190 °C, 15 min). c, shiny side and d, dull side of another film (230 °C, 180 min).

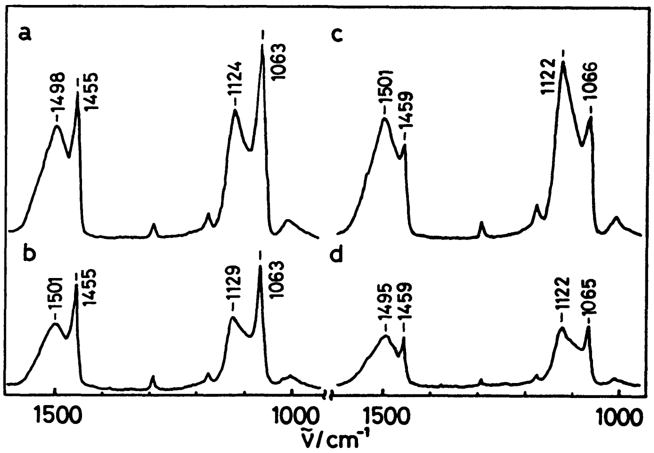

Fig. 2. Raman spectra of pristine and iodine-doped *trans*-$(CH)_x$ (457.9 nm excitation, 80 K).
a, as-isomerized film (190 °C, 15 min) and b, after iodine doping [σ = 0.5 Scm^{-1}, $(CHI_{0.011})_x$] of the film. c, as-isomerized film (230 °C, 180 min) and d, after iodine doping [σ = 1 Scm^{-1}, $(CHI_{0.042})_x$]. The spectra are normalized to the intensity of the 987 cm^{-1} band of $BaSO_4$.

intensities due to the absence of strong absorption in the wavelength region of the exciting laser light (off resonant condition). Accordingly, decreases in intensities (normalized to that of a standard band) of the Raman bands due to doping gives information on correlations between the contents of doped long and short segments and conductivity. The results are also reported.

Cis-rich polyacetylene films [92% *cis*, called *cis*-$(CH)_x$ hereafter] were synthesized following the procedure described earlier at -78 °C using $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$ as catalyst.[11)] *Trans*-$(CH)_x$ films were obtained by thermal isomerization from *cis*-$(CH)_x$ under vacuum or in nitrogen (99.9995%) atmosphere at several temperatures in the range of 120-230 °C. These *trans*-$(CH)_x$ films were doped with iodine by exposing them to the iodine vapor. Electric conductivities and the Raman spectra with 457.9 nm and 632.8 nm excitation were measured at several iodine concentrations. In the Raman study a transparent single crystal plate (150 μm thick) of $BaSO_4$ was pressed against the sample film and the spectra of $BaSO_4$ and the sample were recorded simultaneously in the back scattering geometry. The Raman intensities of the samples were corrected to that of the SO_4^{2-} symmetric stretching band at 987 cm^{-1} of $BaSO_4$.

Compositions of long and short conjugated segments depend significantly on the conditions of isomerization as is reflected in the intensity patterns of the ν_1 and ν_3 Raman bands. Figure 1 illustrates two extremes of the Raman spectra of *trans*-$(CH)_x$ films obtained by different isomerization conditions from the same original *cis* film. Since the low and high frequency peaks of the two bands arise from the long and short segments as described above, it is apparent that the content of long segment is rich and poor in the polyacetylenes which give Figs. 1a and b, respectively. We call the former 'good film' and the latter 'bad film', hereafter. It is noticed that even in the good film the content of long segments is poor on the dull back surface (Fig. 1c). (The surface of the side which has been in contact with the wall of a polymerization flask is shiny while that of the other side is dull.) It has turned out that the electrical property is closely related to the spectral pattern of the shiny side. Accordingly, the Raman spectra of shiny side are taken account of in the following discussion.

The R_1 and R_3 values of thick *trans*-$(CH)_x$ films (ca. 135 μm) isomerized under various temperature-time conditions are in the ranges of 0.38-0.56 and 0.39-0.58, respectively. The best film (the film with the maximum R values) is obtained under a condition, 190 °C-15 min. The amount of long segments in the worst film is about 60% of that in the best film. This can be estimated from the difference between the two films in intensity of the 1455 cm^{-1} peak with the 632.8 nm excitation. The values of σ_{max} are plotted against R_1 and R_3 in Fig 3. Approximately linear relationships between σ_{max} and R_i's are apparent. It is interesting to note that the iodine contents of the films at maximum doping are not much different from one another (e.g., 22.4% for the best film and 24.5% for the worst one) while the values of σ_{max} vary from 190 (for the best film) to 11 Scm^{-1} (for the worst one). Accordingly, a considerable amount of dopant is not contributing efficiently to the electric conductivity in the bad films.

Figure 2 shows the Raman spectra of a good and a bad films at their pristine states (Figs. 2a and c) and slightly doped states (Figs. 2b and d). The reason for the intensity decreases on doping is described above. Figures 2a and b look similar to each other except the overall intensity. This implies that the good films are doped uniformly, which may seem anomalous since ionization potential is expected to be lower for the longer polyene than for the shorter one and the longer polyene to be doped more easily. However, the present observation reflects rather the nature of the segments on the surface than the intrinsic property of pure

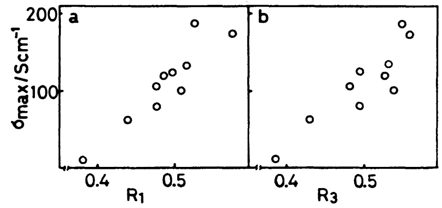

Fig. 3. Relation between σ_{max} and R_i's.
a, relation between σ_{max} and R_1. b, relation between σ_{max} and R_3.

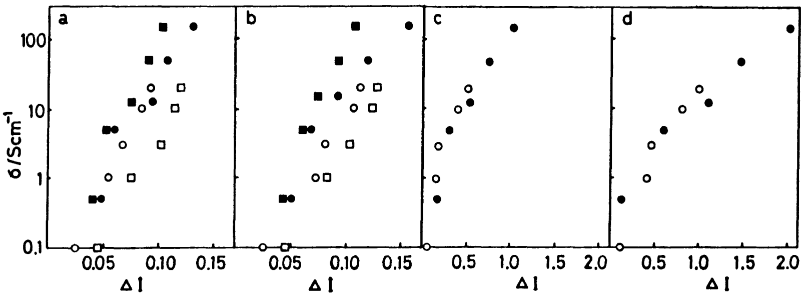

Fig. 4. Relations between σ and ΔI's. Abscissas in a, b, c, and d are ΔI's of ν_1 (457.9 nm), ν_3 (457.9 nm), ν_1 (632.8 nm), and ν_3 (632.8 nm), respectively. ●; ν_1 (1455 cm^{-1}) and ν_3 (1063 cm^{-1}) due to long segments in good films and ○; the corresponding ones in bad films. ■; ν_1 (1498 cm^{-1}) and ν_3 (1124 cm^{-1}) due to short segments in good films and □; the corresponding ones in bad films.

isolated polyenes. Presumably, the short segments of polyacetylene are less stable than the corresponding isolated polyenes due to possible strain on both ends of the segments. Figures 2c and d are different in the intensity patterns in addition to the overall intensity. A straightforward interpretation is that the short segments on the surface of the bad film are less stable and can be doped more easily than the long segments.

Figure 4 shows the relations between conductivity (σ) and the difference in corrected intensity of each Raman peak at the pristine and doped states [ΔI = I(pristine) - I(doped)]. The latter is directly related to the amount of doped segments at the relevant region of the film. As shown in Figs. 4a-d, good correlations exist between conductivity and the 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 σ and the ΔI's of short segments (Figs. 4a and b). If we assume that the doped short segments play the dominant role in electric 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. Rather, the present observations seem to indicate that the doped long segments play the major role in electric conduction. Existence of short segments itself leads to possible disruption of regular close packing of polymers which is important in inter-polymer conduction. For this reason the conductivity of the worst film is extremely low although the content of long segments is still about 60% of that in the best film. Presumably, shortage in the amount of long segments and the deficiency of their regular close 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 electric conductivity of the bad films. Coversely, enrichment of long conjugated segments and their appropriate packing are essential to the improvement of the electrical property of *trans*-polyacetylene.

References

1) B. Francois, M. Bernard, and J. J. Andre, *J. Chem. Phys.*, 75, 4142 (1981).
2) S. Lefrant and M. Aldissi, *J. Phys.*, 44, 235 (1983).
3) P. Bernier, S. Lefrant, M. Rolland, M. Aldissi, M. Galtier, A. Montaner, C. Linaya, and F. Schue, *J. Electron. Mater.*, 12, 289 (1983).
4) I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, *Chem. Lett.*, 1978, 1411.
5) S. Lefrant, L. S. Lichtmann, H. Temkin, D. B. Fitchen, D. C. Miller, G. E. Whitwell II, and J. M. Burlitch, *Solid State Commun.*, 29, 191 (1979).
6) H. Kuzmany, *Phys. Status Solidi*, B, 97, 521 (1980).
7) L. S. Lichtmann, A. Sarhangi, and D. B. Fitchen, *Chemica Scripta*, 17, 149 (1981).
8) S. Lefrant, E. Faulques, L. Lauchlan, M. J. Kletter, and S. Etemad, *Mol. Cryst. Liq. Cryst.*, 83, 117 (1982).
9) D. B. Fitchen, *Mol. Cryst. Liq. Cryst.*, 83, 95 (1982).
10) P. Knoll, H. Kuzmany, P. Surjan, and M. Kertesz, *J. Phys. Colloq.*, 44, C3-155 (1983).
11) H. Shirakawa and S. Ikeda, *Polym. J.*, 2, 231 (1971).

(Received June 13, 1984)