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RESONANT RAMAN SCATTERING OF Er^{3+} DOPED AND PARTIALLY ISOMERIZED POLYACETYLENE

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ABSTRACT

The results of experimental studies of resonant Raman scattering (RRS) spectra from Er^{3+} implantation doped and partially isomerized polyacetylene are presented. Thin cis-$(CH)_x$ films were synthesized by the method of rare earth complex catalysis polymerization. Doping technique is ion implantation. The surface density of implanted Erbium ion is about $5x10^{13}/cm^2$. In the case of cis-$(CH)_x$, RRS bands at 1160, 1270 and 1540 cm^{-1} have been observed λ_L = 488 nm (10K) and it was shown clearly that a shift in frequency of the peaks assigned to the remaining trans segments occurs during the isomerization process. In the case of Er^{3+} doped cis-$(CH)_x$, Er^{3+} induced Raman bands at 1145, 1320 and 1510 cm^{-1} have been measured (λ_L = 488 nm, RT) for the first time and it is observed that the Raman bands from Er^{3+} doped trans/cis-$(CH)_x$ are shifted to lower frequencies. We point out that the effect of Er^{3+} dopant is associated with the defects.

The experimental results are discussed by using the model based on the hypothesis that the sample properties can be interpreted in terms of a bimodal distribution of long and short conjugation length segments (for trans-$(CH)_x$) and the bipolaron microscopic model on the basis of multi-phonon lattice relaxation theory (for cis-$(CH)_x$). Our studied results support further the bimodal distribution model and the bipolaron microscopic model.

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INTRODUCTION

In recent years, the conducting polymer $(CH)_x$ has been extensively investigated by using a variety of spectroscopic techniques and among them, Raman scattering has proved to be extremely helpful at least in the case of undoped $(CH)_x$.

Several papers have been devoted to the behavior of Raman spectra as a function of the excitation wavelength and different models have been developed (1).

As usual, $(CH)_x$, investigated by Raman spectroscopy, has been chemically or electrochemically doped with appropriate alkali-metal, halogen or AsF_5, etc..., but relatively few studies have appeared on the characteristics of Raman spectra of rare earth ion implanted $(CH)_x$. Davenas et al. (2) studied the stability of ion implanted $(CH)_x$ films. Recently, Kuczkowski et al. (3) discussed the change in electrical conductivity of H_2^+ ion implanted trans-$(CH)_x$. It is noticed that the ion implantation technique is well known to modify the morphology of polymers and was recently successfully applied for doping of conducting polymer (4). Therefore, in this paper we present the main Raman results obtained in partially isomerized $(CH)_x$ and in $(CH)_x$ doped with Er^{3+} by ion implantation doping technique to provide further information on the behavior of Raman spectra.

EXPERIMENTAL

For Raman spectral studies, the thin (10 ∿ 100 µm) film of $(CH)_x$ was synthesized by the method of directional polymerization with rare-earth complex catalytic system (5). The trans-$(CH)_x$ was obtained by the heat treatment of cis-$(CH)_x$ at 180°C for about 20 min. Doping technique is the ion implantation. With $(CH)_x$ films at 300K, implantation fluences of $5x10^{13}$ ∿ $5x10^{14}$ erbium ions/cm^2 with an ion flux of 0.2 micro A/cm^2 and a beam energy of 80 KeV were used.

Raman spectra were measured at room and low temperature using standard equipment and a 90° scattering geometry configuration was adopted. Additional background scattering was minimized by setting $(CH)_x$ film in an appropriate position. The laser lines were provided by an argon cw laser.

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RESULTS AND DISCUSSION

RRS spectra from partially isomerized samples

In Figure 1, we show the RRS spectra recorded in cis-trans isomerization $(CH)_x$ for three different contents of cis after a heat treatment of a undoped cis-$(CH)_x$ sample. For the fully trans-$(CH)_x$ (see curve c in Fig. 1), the Raman bands are recorded at 1110 cm^{-1}, 1490 cm^{-1}. The peaks of RRS spectra due to the vibrational modes of the trans segments shift lightly to high frequency side with the increase of cis isomer content (see curve a,b in Fig. 1). For a cis-rich $(CH)_x$, the RRS bands are recorded at 1120 cm^{-1}, 1510 cm^{-1}.

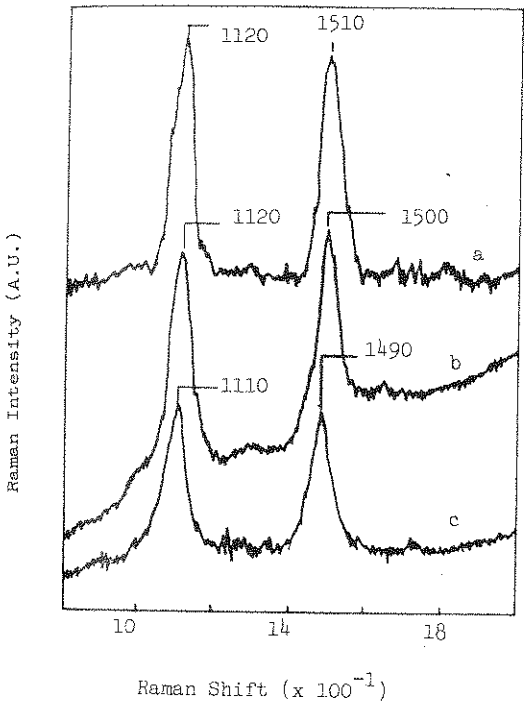

Fig. 1. RRS spectra at room temperature of undoped polyacetylene for λ_L = 488 nm. a) rich cis-$(CH)_x$; b) 50 % cis-$(CH)_x$; c) trans-$(CH)_x$.

At 10K, we have measured RRS spectra from cis-trans isomerization $(CH)_x$ as illustrated in Figure 2. In this figure, RRS spectra recorded in $(CH)_x$ are also shown as a function of the cis isomer content of the polyacetylene. With trans-$(CH)_x$ (see curve c in Fig. 2), the peaks of RRS are 1115 cm^{-1}, 1495 cm^{-1} and the spectra exhibit the new peaks at 1270 cm^{-1}, 1250 cm^{-1} (see curve a,b in Fig. 2). The peaks also shift to high frequency side with the increase of cis isomer content, but the shift tendency of the peak at 10K is more obvious than that measured at room temperature.

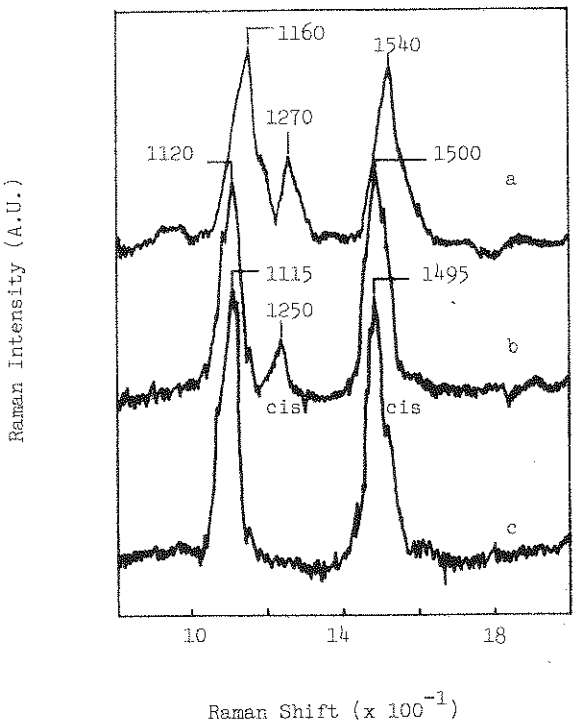

Fig. 2. RRS spectra at 10K of undoped polyacetylene for λ_L = 488 nm. a) rich cis-$(CH)_x$; b) 50 % cis-$(CH)_x$; c) trans-$(CH)_x$.

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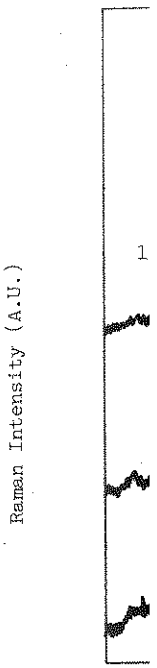

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RRS spectra of Er^{3+} doped sample

In Figure 3, we show the Raman spectra recorded at room temperature in polyacetylene for different contents of cis isomer after an Er^{3+} implanted $(CH)_x$ sample. For a fully trans-$(CH)_x$ and 50 % cis-$(CH)_x$, the peaks of the Raman spectrum recorded with λ_L = 488 nm are at 1110 cm^{-1} and 1480 cm^{-1} on one hand and 1120 cm^{-1} and 1490 cm^{-1} on the other hand. At the same time, no Raman peak is detected between 1110 cm^{-1} and 1480 cm^{-1} is absent (see curve b,c in Fig. 3). With the rich cis-$(CH)_x$, the peaks of the Raman spectrum are at 1145 cm^{-1}, 1510 cm^{-1} and there is the indistinct Raman peak at 1320 cm^{-1} (see curve a in Fig. 3). The change tendency of position of the Raman peak with cis isomer content is similar to that observed that in Fig. 1 and Fig. 2.

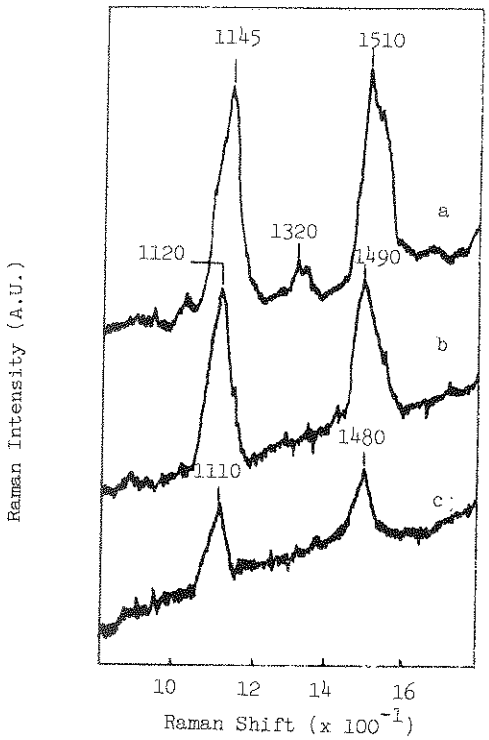

Fig. 3. RRS spectra at room temperature of Er^{3+} implanted polyacetylene for λ_L = 488 nm : a) rich cis-$(CH)_x$; b) 50 % cis-$(CH)_x$; c) trans-$(CH)_x$.

It is well known that the experimental data of RRS spectra of trans-$(CH)_x$ have been explained by using the model based on the hypothesis that the sample properties can be interpreted in terms of a bimodal distribution of long and short conjugation length segments (6-9). In particular, this model can be applied successfully to partially isomerized $(CH)_x$ samples as well as to samples implanted with Erbium in a medium range of concentration level (7).

In the case of partially isomerized samples, according to the bimodal distribution model developed by Mulazzi and Lefrant (8), the positions and shifts of Raman peak (see Fig. 1-3) in RRS spectra obtained at different degrees of isomerization can be interpreted by the bimodal distribution which weights the different contributions as a function of the conjugation length segments of trans-$(CH)_x$.

Guo Youjang, Yu Lu (10) have proposed a bipolaron microscopic model and interpreted reasonably the Raman scattering data in cis-$(CH)_x$ on the basic of lattice relaxation theory. Since the ground state of cis-$(CH)_x$ is not degenerate, so the polarons can be only excited. The polarons might serve as intermediate states for Raman processes. At rich cis-$(CH)_x$, we can consider only the polaron state. The polaron state which is quasi-resonant with the incoming laser light gives the Raman scattering for cis-$(CH)_x$. This resonanting state presents obviously the effect of lattice relaxation. According to this model, the theoretical results obtained for RRS spectra in cis-$(CH)_x$ are also in well agreement with our experimental results.

Therefore our studied results support further the bimodal distribution model and the bipolaron microscopic model. Details will be published elsewhere.

We note that the shifts of peaks and broadening of spectra in RRS spectra from Er^{3+} implanted $(CH)_x$ (compare Fig. 3 with Fig. 2 and Fig. 1) are due to the contribution to the RRS spectra coming from of the perturbed conjugation length segments because of the dopant Er^{3+} presence and of the breaking of the symmetry. But the origin of the small Raman peak at 1320 cm^{-1} (see curve a Fig. 3) is not clear yet.

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