On the structure of poly(2,4-dichlorophenylacetylene) from the data of resonance Raman spectra

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The resonance Raman spectra of poly(2,4-dichlorophenylacetylene) in the range of wavelengths of the exciting radiation between 457.9 and 647.1 nm were studied. It was shown that the frequencies, intensities, and shapes of the bands related to the backbone stretching vibrations changed as the frequency of the exciting light varied. This was explained by a rather broad distribution of the conjugated segments of the polymer over the number of conjugated C=C bonds. A possible structural model involving a *trans-cis* conformation of the chain of the polymer studied was proposed.

Key words: polyphenylacetylene, resonance Raman effect.

The resonance Raman method is the most efficient technique for investigating the structure of the chain in conjugated polymers that exhibit intense absorption bands (AB) in the visible region.[1]

The resonance Raman spectra of the simplest polyconjugated polymer, polyacetylene (PA), have been studied most extensively.[2–4] Data on *cis-trans* isomerization, on doping PA, which results in a dramatic increase in the electric conductivity of the material,[5,6] and on the statistics of defects in the specimens synthesized[7,8] have been gained.

Polyphenylacetylene, $(-CH=C(C_6H_5)-)_x$, which ranks below PA in its quality and, therefore, has been poorly investigated, is another example of polymer with the polyene structure. In particular, little is known about the conformations of the polyene chains in polyphenylacetylenes that have been prepared using various catalysts. X-ray structural studies of these materials are very difficult, and in their IR spectra, bands corresponding to the vibrations of side-chain phenyl groups predominate.

In contrast to the IR spectra, the resonance Raman spectra of polyphenylacetylenes mostly contain bands associated with the vibrations of the main chain,[9] and the positions of these bands, as in the case of PA, depend on the wavelength of the exciting light (λ_{excit}), which reflects the degree of disorder of the specimen and, most of all, a rather broad distribution of defectless sections over the lengths of conjugation.

In the present work we studied the resonance Raman spectra of three specimens of poly(2,4-dichlorophenyl)acetylene (PFA) synthesized in the presence of the $WCl_6/SnPh_4$ catalyst. The spectra were recorded on a Ramanor U-1000 spectrometer using an Ar^+/Kr^+ laser. The "reflection" scheme was applied; the specimens were used as films positioned on the walls of evacuated flasks. The spectra of all of these materials are almost identical. The stretching frequencies of the PFA backbone (1120, 1187, 1459, and 1495 cm^{-1}, λ_{excit} = 647.1 nm) are close to the frequencies calculated for polyphenylacetylene in the *trans-cis* conformation (1172, 1187, 1447, and 1533 cm^{-1}),[10] but considerably differ from those for other planar conformations, *viz.*, *trans-trans* and *cis-trans*.

The helical *cis-cis* structure of the main chain of PFA is also theoretically possible. In this case, the AB in the electronic spectrum should shift to shorter wavelengths due to the decrease in the π-electron conjugation, as is typical of polyphenylpropyne,[11] which has a helical structure and is, therefore, colorless. However, the samples of PFA studied by us are dark red, which indicates planar polyconjugated structures of their main chains.

In addition, the results obtained in the present work are in good agreement with the data on the frequencies of the most intense resonance Raman bands exhibited by PFA II, whose backbone has the *trans-cis* conformation. Therefore, the planar *trans-cis* conformation is the most likely for the PFA under study.

The decrease in λ_{excit} from 647.1 to 457.9 nm results in changes in the frequencies (1126, 1212, 1470, 1520 cm^{-1}), intensities, and contours of the bands corresponding to the stretching vibrations of the backbone of PFA (Fig. 1). A similar result was obtained previously[7,8] for various specimens of PA. These variations in the resonance Raman spectra of PA were interpreted by

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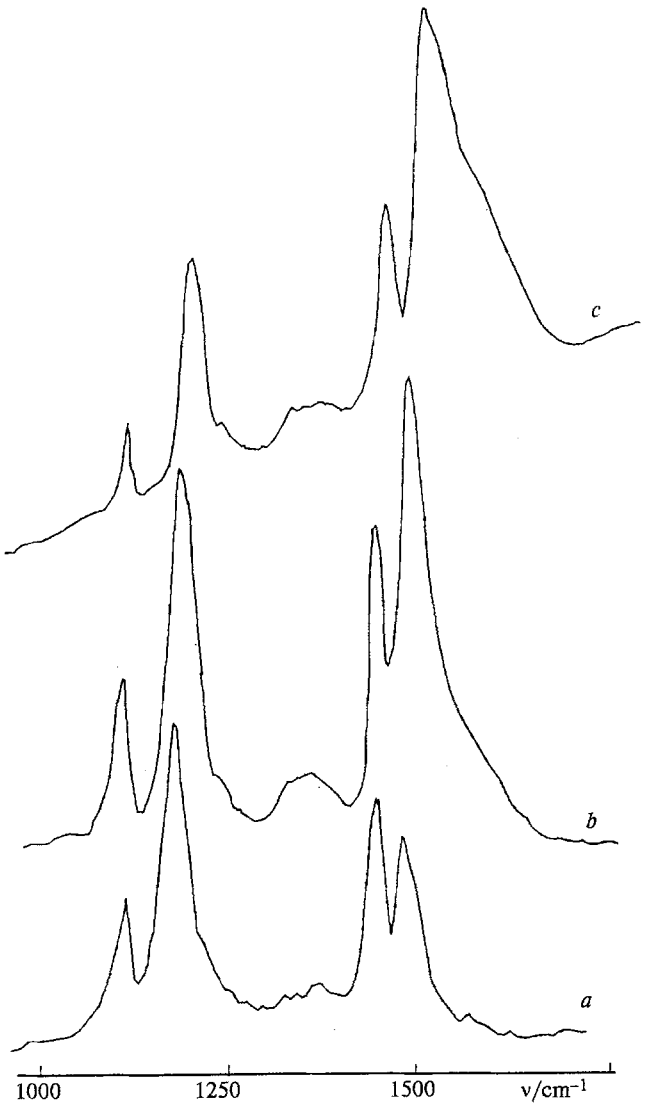

Fig. 1. Resonance Raman spectra of poly(2,4-dichlorophenylacetylene)): λ_{excit} = 647.1 (*a*), 514.5 (*b*), and 457.9 nm (*c*).

introducing a model of the distribution of defectless sections of the backbone over the numbers of conjugated π-bonds: these sections are restricted by breaking of the chain of conjugation by structural defects. By using this model one can calculate all of the changes in the spectra of PA that occur as λ_{excit} varies (see Ref. 8). The analogous variations in the resonance Raman spectra of PFA found in this work can probably be explained by the fact that the distribution of the conjugated defectless sections of the chain of this polymer over the lengths of conjugation is rather broad. The tentative estimates based on an analysis of both the literature data and the results of the present study suggest that the average length of these conjugated defectless sections is 10—30 C=C double bonds.

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