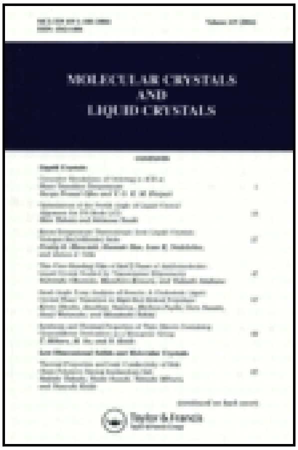

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Characterization and Vibrational Properties of Undoped and AsF_5-Doped $(C_6H_4)_x$

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CHARACTERIZATION AND VIBRATIONAL PROPERTIES OF UNDOPED AND AsF_5-DOPED $(C_6H_4)_x$

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Abstract A vibrational study of poly-p-phenylene (PPP) prepared by the Kovacic method is presented. A comparison is made between the vibrational features (in both IR and Raman) of undoped PPP, PPP chemically doped using AsF_5 or electrochemically doped with AsF_6^-, and finally dedoped by a thermal treatment. In the last case, using the exciting wavelength λ_L = 647.1 nm, additional modes are observed in the Raman spectra (460 cm^{-1}, 920 cm^{-1} and 1700 cm^{-1}). In AsF_5 doped PPP, the IR absorption spectrum reveals also new modes (1552 cm^{-1}, 1273 cm^{-1} and 1184 cm^{-1}). These features are discussed in the basis of a vibrational model.

I UNDOPED PPP (Kovacic)

Raman spectra of undoped PPP are always perturbed by a very strong fluorescence with a maximum peaked around 600 nm, and which depends upon the synthetis of the material as well as upon the washing procedure. Catalyst residues, for example, lead to a slight doping of the PPP powder, and quinoïd structures or other defects are expected to be created. The catalyst residues contents can, according to ref. (1), give rise to polymer powders of different colors (dark brown or clear brown), whose infrared spectra are similar except a band at 1600 cm^{-1}. It is reported that the dark brown powder may contain more quinoïd structure in the chain, leading to a shift to 385 nm of the optical absorption band (2) while the maximum absorption of a p-polyphenyl sample is predicted at 339 nm when n is infinite (3).

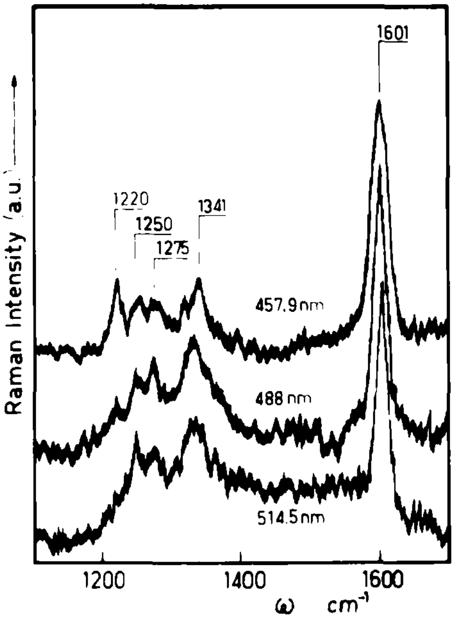

FIGURE 1 Raman spectra of PPP (Kovacic) at T = 10 K for λ_L = 457.9 nm, 488 nm and 514.5 nm.

In figure 1 are whown the Raman spectra of a PPP prepared by the Kovacic procedure (dark brown powder) for different excitation wavelengths, in which the fluorescence background has been substracted. They are composed of a strong band at 1600 cm^{-1} and many weaker bands at 1220, 1250, 1275 and 1341 cm^{-1}.

II AsF$_5$-DOPED PPP

Raman spectra of AsF$_5$-doped PPP have been reported previously (4). Upon doping, the fluorescence disappears completely and three Raman bands are mainly observed : 1598 cm^{-1}, 1320 cm^{-1} and 1236 cm^{-1} for λ_L = 647.1 nm. The mode at 1598 cm^{-1} does not depend on λ_L. On the contrary, going to λ_L = 647.1 nm to λ_L = 406.7 nm, it must be noticed that the 1236 and 1320 cm^{-1} decrease in intensity while two other modes at 1216 and 1275 cm^{-1} appear, resulting in an apparent shift. By electrochemical doping, similar results are roughly observed, the Raman spectra of PPP doped electrochemically being composed of modes at 1224, 1280 and 1595 cm^{-1} respectively.

III THERMAL STABILITY OF AsF_5-DOPED PPP

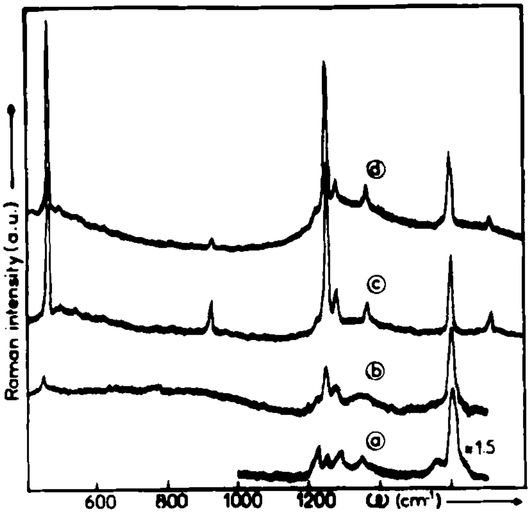

FIGURE 2 Raman spectra at 78 K of PPP Kovacic - doped chemically with AsF_5 and dedoped by heating at 250° C during 15 mn.
a) λ_L = 457.9 nm ; b) λ_L = 514.5 nm
c) λ_L = 647.1 nm ; d) λ_L = 676.4 nm

An AsF_5 doped PPP sample has been heated at several temperatures from 100° C to 250° C. Until 200° C, the sample does not show any apparent modification but its color goes from green to blue at 250° C. During this treatment, new modes appear at 920 and 1700 cm^{-1} as shown on Figure 2. In addition, a mode at 460 cm^{-1}, which was very weak in the doped sample, is now very strong in intensity. Also, the mode at 1240 cm^{-1} becomes very strong. All these new features are observed for λ_L = 647.1 nm or 676.4 nm. When we use a higher energy excitation (λ_L = 457.9 ou 514.5 nm), the Raman spectrum is very much like that of the undoped PPP (Figure 2).

IV CONCLUSION

The problem whether a quinoïd structure exists or not in the PPP chain will certainly be resolved from the vibrational studies. Concerning the Raman spectroscopy, a very strong resonant behavior is detected with new strong modes appearing in the red range excitation. This resonance is connected with the absorption in this region and the differences existing in samples with and without contact with air and moisture (5). Moreover, we showed previouly (4) that, in the Raman spectra of oligomers and PPP prepared by the Yamamoto method, the Raman modes at 1220 and 1275 cm^{-1} do not depend on λ_L, while the 1246 and 1350 cm^{-1} modes are not seen. Therefore, the latter Raman modes could be connected to a quinoïd structure in PPP chains prepared by the Kovacic method. It must be noticed that the assignment of the differents modes is under way with a vibrational model, as well as with that predicted recently by Zannoni and Zerbi (6).

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