

phys. stat. sol. (b) 165, K105 (1991)

Subject classification: 78.30; S12.1

Changchun Institute of Physics, Academia Sinica¹) (a)
and Department of Environmental Science, Jilin University,
Changchun¹) (b)

Study on Resonance Raman Spectra in a Soluble Polyaniline

By

CHANG QING JIN (a), WEI NA LIU (a), XIANG GUI KONG (a),
and XING JUAN LIU (b)

Study and preparation of soluble polyaniline (PAn) are important for both science and technology. PAn can be synthesized chemically or electrochemically in acidic media and can be oxidized and reduced in both aqueous and non-aqueous electrolytes. The structure of the various states of PAn is conceived as being a mixture of leucoemeraldine, emeraldine, and their protonated forms /1/. Recently, the fractal structure of the PAn film surface has been evidenced /2/.

In this note, we present an extended study of the resonance Raman scattering together with an investigation of the X-ray diffraction for various forms of PAn. The observed behaviours of the spectra can be well understood in terms of the quinoid-benzoid transition /3/, disorder and fractal structure, respectively. Soluble PAn samples were synthesized chemically in acidic media of PH = 1 to 2 /4/. For Raman spectral measurements PAn pellets using soluble PAn powder were used. The Raman spectra were measured at room temperature by using a Jobin-Yvon T-800 laser Raman spectrometer with photon counting system and a 90° scattering configuration was adopted. Excitation was by an argon ion laser with 488.0 nm.

The X-ray diffraction trace is taken with CuK α radiation and the result is shown in Fig. 1 for the soluble PAn sample. The 3.174(d-value) peak appears only as a shoulder at the dominant 3.587(d-value) peak. The X-ray diffraction trace indicates that the crystallite size is smaller than the amorphous region. The soluble PAn pellet clearly showed the amorphous character of more local structure. The experimental results also indicate that the crystallinity of non-soluble PAn is much larger than that of soluble PAn.

In Fig. 2 two strong Raman lines at 1609.5 and 1192.9 cm⁻¹ (or at 1612.2 and 1187.7 cm⁻¹) are observed and are assigned to modes of benzene rings. The Raman peaks of curve B are sharper than curve A and the Raman peak in the 1100 cm⁻¹ region shifts towards lower energy, but that in the 1600 cm⁻¹ region shifts

¹) Changchun 130021, People's Republic of China.

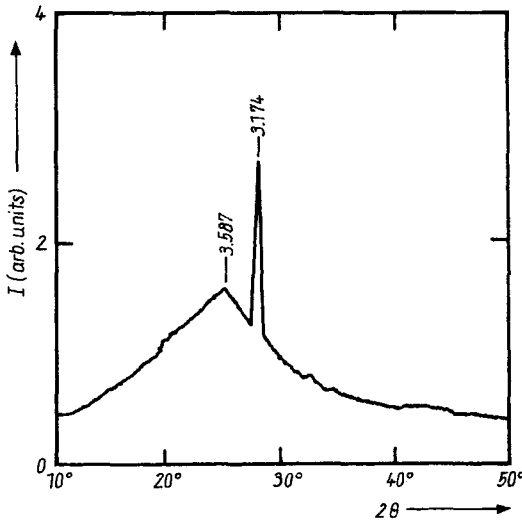


Fig.1

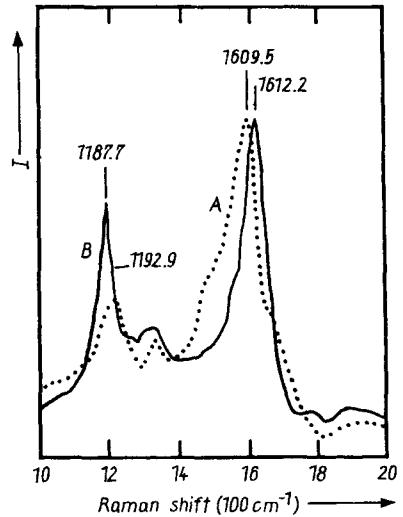


Fig.2

Fig. 1. X-ray diffraction pattern of the soluble PAN sample

Fig. 2. Raman spectra of PAN as excited with 488.0 nm: (A) soluble, (B) non-soluble

towards higher energy. These results are in agreement with Fig. 1. The broad peaks are due to disordering of soluble PAN (see Fig. 2 and 4). The shapes of the Raman spectra were observed to depend strongly on the disorder of the sample. In the high frequency region, the Raman lines are slightly shifted because of the increase of the concentration of benzenoid rings and the resonance enhancement /3, 5/.

The low frequency Raman spectrum of soluble PAN with 488.0 nm laser excitation is shown in Fig. 3. The spectrum shows only the broad intense band around 57.5 cm^{-1} . Based on the fractal theory /6/ Shuker and Gammon /7/ and Alexander et al. /8/ set up a theoretical basis for solving this kind of problems, predicting that the experimental intensity $I(\omega)$ of light scattering is given by

$$I(\omega) \propto \omega^{\nu'} [n(\omega) + 1] . \quad (1)$$

Here $\nu' = (\bar{d}/D)(2d\phi + D) - 2$, ω is the frequency shift, $n(\omega) + 1$ is the Bose factor for Stokes scattering, D is the Hausdorff dimension of the fractal, \bar{d} is the spectral or fracton dimension, and $d\phi$ is a geometrical exponent describing the localization in real space. In Fig. 4 the normalized intensity, i.e. $I(\omega)\omega / [n(\omega) + 1]$ is represented in double-logarithmic coordinates from 30 to 100 cm^{-1} . In this

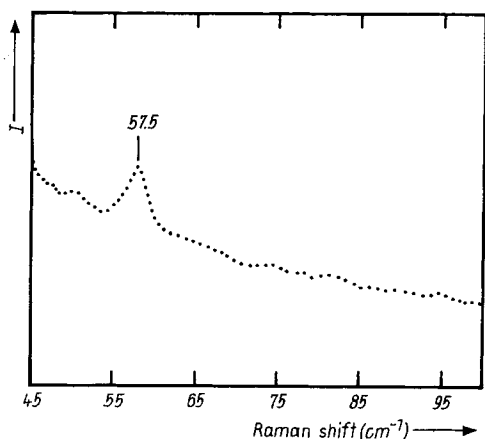


Fig.3

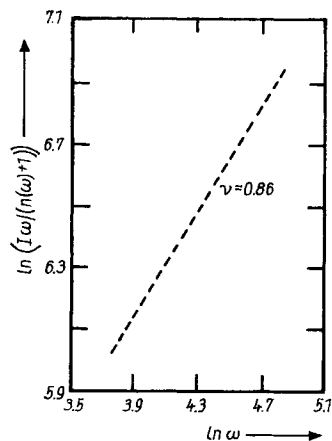


Fig.4

Fig. 3. Low frequency Raman spectrum of soluble PAN as excited with 488.0 nm

Fig. 4. Plot of $\ln \left[\frac{I(\omega)\omega}{n(\omega) + 1} \right]$ versus $\ln \omega^\nu$ for ω varying between 30 and 100 cm^{-1} for soluble PAN; $\nu = 0.86 \pm 0.05$

region the normalized Raman scattering intensity obeyed the equation

$$I(\omega)\omega / [n(\omega) + 1] \propto \omega^\nu, \quad (2)$$

where $\nu = (\bar{d}/D)/(2d\phi + D) - 1$ is the slope of the straight line and it was experimentally found that $\nu = 0.86 \pm 0.05$. If the values of $d\phi$ and D are chosen, \bar{d} is obtained from the experimental value of ν . We point out that the intensity of the Raman light scattering from localized vibrational modes in PAN molecule chains is expressed as a function of frequency shift, fractal and spectral dimensions. This work shows for the first time that the low frequency Raman scattering reveals clearly the fractal structure of disordered soluble PAN materials which is well explained in terms of a fracton description of localized vibrations.

We acknowledge Prof. Yong Nian Zhao for his valuable discussion and measurements. This work was supported by the National Science Fund Committee of China and the Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Science.

References

- /1/ A.G. MAC DIARMID, J.C. CHIANG, W.S. HUANG, B.D. HUMPHREY, and N.L.D. SOMASIRI, *Mol. Cryst. liquid Cryst.* **125**, 309 (1985).
- /2/ B. VILLERET and M. NECHTSCHHEIN, *Solid State Commun.* **64**, 435 (1987).

- /3/ M. OHIRA, T. SAKAI, M. TAKEUCHI, and Y. KOBAYASHI,
Synth. Metals 18, 347 (1987).
- /4/ F.S. WANG, J.S. TANG, X.B. JING, S.R. NI, and B.C. WANG,
Acta Polymerica Sinica 5, 384 (1987).
- /5/ H. KUZMANY and N.S. SARICIFTCI, Synth. Metals 18, 353 (1987).
- /6/ B.B. MANDELBROT, The Fractal Geometry of Nature,
Freeman, San Francisco 1982 (p. 14).
- /7/ R. SHUKER and R.W. GAMMON, Phys. Rev. Letters 25, 222 (1970).
- /8/ S. ALEXANDER, ORA ENTIN-WOHLMAN, and R. ORBACH,
Phys. Rev. B 32, 6447 (1985).

(Received March 19, 1991)