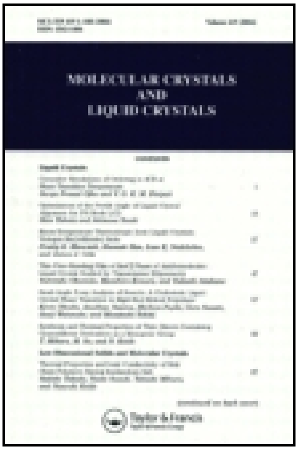

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Vibrational Spectra of Soluble and Highly Oriented Polyacetylenes

Riccardo Tubino [a]
[a] Istituto di Chimica delle Macromolecole, CNR, 20133, Milano, Italy

Version of record first published: 17 Oct 2011.

To cite this article: Riccardo Tubino (1985): Vibrational Spectra of Soluble and Highly Oriented Polyacetylenes, Molecular Crystals and Liquid Crystals, 117:1, 319-326

To link to this article: http://dx.doi.org/10.1080/00268948508074645

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 319-326
0026-8941/85/1174-0319/$15.00/0

Printed in the United States of America

VIBRATIONAL SPECTRA OF SOLUBLE AND HIGHLY ORIENTED POLYACETYLENES[+]

RICCARDO TUBINO
Istituto di Chimica delle Macromolecole,CNR, 20133 Milano,
Italy

Abstract Resonant Raman excitation profiles of a novel form of soluble polyacetylene, obtained using the solvent lines as internal standards, are reported. The experimental data are interpreted within the framework of a displaced oscillator model which provides information on the strength of the electron-phonon coupling, on the lifetime of the optical excitation and on the inhomogeneous distribution of the electronic energies in solution.

Vibrational spectra of highly oriented (extension ratio ca. 7) polyacetylenes are also presented. The polarization properties of the IR and Raman active phonons, as well as those of the dopant-induced infrared absorptions, have been determined and a vibrational assignment is proposed for both the isomers.

INTRODUCTION

It is well known that the conventional Shirakawa's procedure of polymerization of the acetylene yields spongy films consisting of a fleece of loosely nested fibrils, randomly oriented [1]. The poor stretchability of the film, combined with its complete insolubility and infusibility, have considerably complicated the interpretation of the structural and spectroscopical data. In this note I shall briefly review the most relevant results obtained in our group from an IR and Raman study carried out on two non conventional forms of polyacetylene (PA) which are more suitable for spectroscopical studies, namely a grafted PA, which is soluble in the common organic solvents and an highly stretchable form of PA, which yields almost perfectly aligned films.

[+] Supported by "Progetto finalizzato Chimica Fine e Secondaria" CNR

SOLUBLE POLYACETYLENE

It has been recently reported [2] that a novel form of polyacetylene, soluble in the common organic solvents, can be obtained by polymerization of acetylene onto catalytic sites of Titanium bonded to a polybutadiene chain, which acts as the soluble carrier. By the proper choice of the reaction temperature, solvent and concentrations it is possible to produce samples with a controlled ratio of the cis/trans configuration of the polyenic chain [3] . Optical absorption, fluorescence and time-resolved emission have been already reported on this material [4,5] . The observation of the infrared photoinduced absorptions seems to indicate that trans PA is capable of supporting solitons even in solution [5].

In fig. 1 is shown the Raman spectrum of a predominantly cis sample of soluble PA in cyclohexane solution. The spectrum has been obtained with a Rhodamine dye laser equipped with an Ar^+ pump.

The spectrum contains the three strong Raman active bands (905,1250 and 1545 cm^{-1}) which are peculiar of the polyenic chain in its cis configuration. The relative intensities of the peaks, their position and shape are quite similar to those observed in the film at comparable exciting wavelength [6] , thus indicating that the vibrational properties of the isolated polyenic chain are only slightly affected

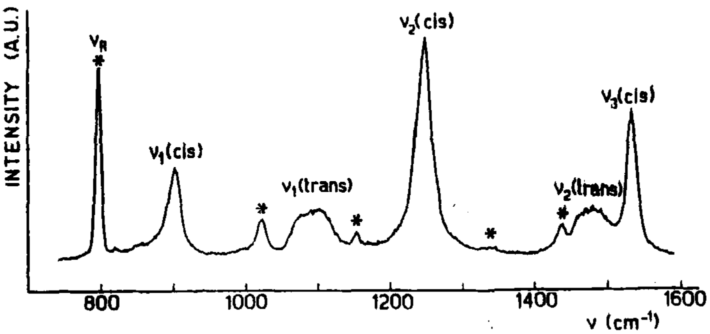

FIGURE 1 Resonant Raman spectrum of soluble cis-rich PA. λ = 6005 A. Solvent lines are marked with * .

by its environment. Two weak bands at ≃ 1100 and 1490 cm^{-1} due to the residual trans content are also observed. Their shapes clearly indicate that only short conjugated trans segments are formed during the early stages of the isomerization in solution.
In fig. 2 are reported the Raman spectra of a predominantly trans sample of soluble PA (toluene solution) at various exciting wavelengths in the visible region . An analysis of the observed changes in the bandshapes with the laser frequency indicates that, probably because of bond rotations, a reduction in conjugation length with respect to that observed in "high quality" films [6] takes place in solution. We have found that the predominantly trans sample which we have examined exhibits a bimodal distribution of chain lengths, with maxima corresponding to 40 and 20 conjugated double bonds (hereafter called "long" and "short" chains respectively) .

The lines of the solvent (which is in off-resonance conditions) can be used as an internal standard to construct the Raman Excitation Profiles (REP) . Fig. 3 shows both the integrated and the sliced REP's. A detailed analysis of these curves is reported elsewhere [7]. We give here only a brief summary of the most relevant results and conclusions. Unlike what is observed in the solid samples [6,8] , the REP's of the trans PA in solution exhibit a relatively narrow principal maximum (zero-phonon line), followed by sidebands of vibronic origin. The analysis of the integrated profiles, which are complicated by the dependence of the electron-vibrational couplings and of the oscillator strength on the conjugation length and by the uncertainties on a quantitative distribution function of the conjugation lengths, will not be attempted here.
On the other hand an interpretation of the sliced REP's can be attempted in terms of the conventional Franck-Condon picture [9] (displaced harmonic oscillator approximation) commonly used for molecular systems with localized electronic states. Following Penner and Siebrand [10] we have included in our theoretical analysis of the profiles also the effects of the inhomogeneous line broadening (Δ),co-

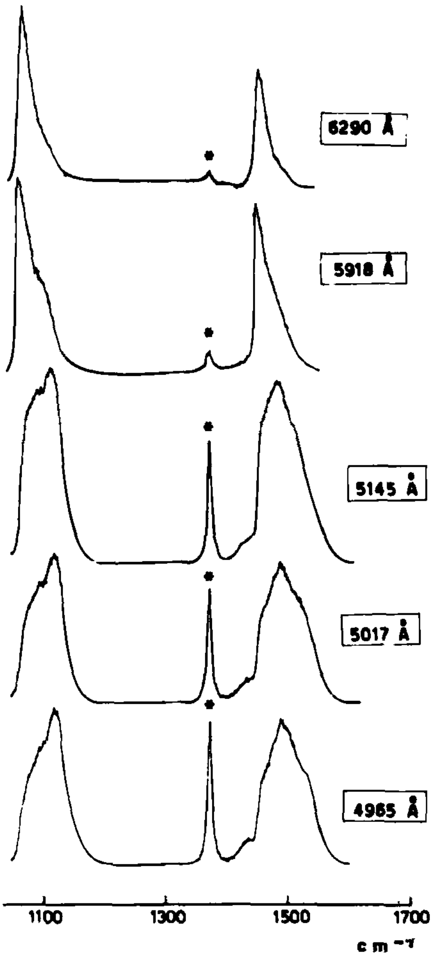

FIGURE 2 Resonant Raman spectrum of soluble, trans-rich PA. Solvent bands are marked with * .

ming from a distribution of electronic energies of inequivalent absorbing sites. This allows to interpret the experimental data without the use of unphysically large values of the inverse lifetime Γ and provides some information on the interaction of the polyenic chain with the environment. Solid lines in fig. 3b represent the results of the calculations using the following parameters: S_1=0.40

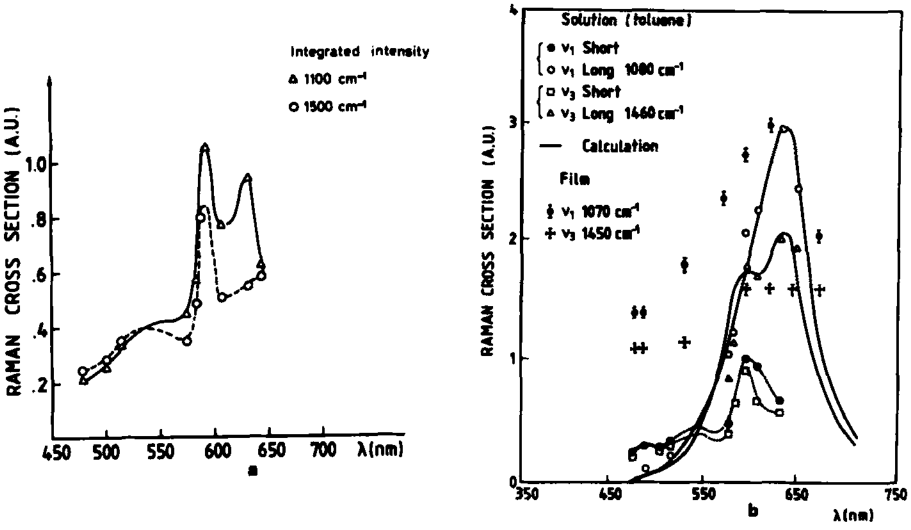

FIGURE 3 Raman Excitation Profiles of soluble trans-rich PA (a) Integrated profiles, (b) sliced profiles. Results of the calculations are shown by solid lines in fig. 3b. Data for the film are taken from ref. 8

S_2=0.28, Γ =50 cm^{-1}, Δ =650 cm^{-1}, S_i being the individual Huang-Rhys factors [11]. Our calculations are therefore consistent with a moderately strong electron-phonon coupling in the excited state ($S= \Sigma_i S_i$= 0.68), with a lifetime of the optical excitation ($\tau=1/2\pi c\Gamma$ $=10^{-13}$ sec) in perfectagreement with the decay time of the electron hole pair into a soliton/antisoliton pair evaluated by Su and Shrieffer [12] and with a moderately inhomogeneous distribution of the electronic energies in solution, possibly indicative of the formation of micellar aggregates.

HIGHLY ORIENTED POLYACETYLENES

Stretched films (extension ratio of ca. 7) with contents of trans configuration ranging from 15 to 100 % have been prepared at the Assoreni Labs. Detailed X-ray investigations have revealed an almost perfect aligmment of the fibrils along the stretching direction[13]. The 1-d anisotropy of the vibrational properties peculiar to the chain structure can be therefore detected in this material. In figs. 4 and 5 polarized IR and Raman spectra of the aligned samples are reported. Further details can be found in a recent paper[14]. Table I summarizes the polarization properties of the fundamental IR and Raman active phonons for both the isomers. A vibrational assignment to the proper simmetry species is also proposed on the basis of the present polarization data. Fig. 6 shows the polarization properties of the three dopant induced IR absorptions at 830, 1390 and 5000 cm^{-1}. All these bands have a transition moment strictly directed along the chain axis. This result is in agreement with the theoretical model proposed by Mele and Rice[15] who have predicted that the vibrational excitations of charged solitons in a polyenic chain should give rise to two IR active modes of massive oscillator strength. These authors have also pointed out that the computed eigenvectors for these defect modes describe an overall contraction at one side of the defect and an overall expansion on the other, thus giving rise to a charge oscillation along the chain as indeed observed.

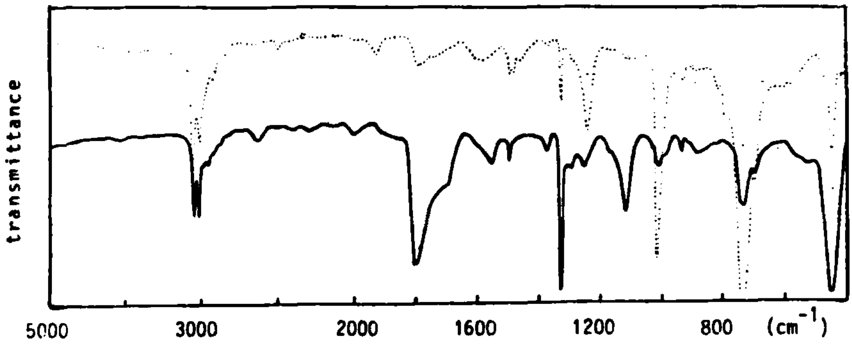

FIGURE 4 Polarized IR spectra of highly oriented PA containing a mixture of cis and trans configurations.
(———) parallel and (••••••) perpendicular components

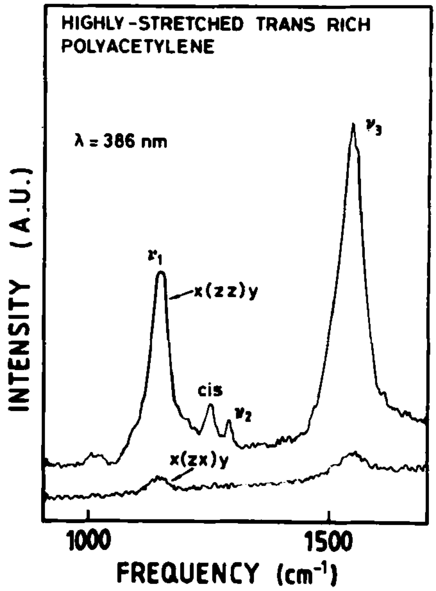

FIGURE 5
Polarized Raman spectrum of highly oriented PA. Extension direction:z axis

FIGURE 6
Polarized, dopant induced IR spectrum of trans PA. (———) parallel and (-----) perpendicular component

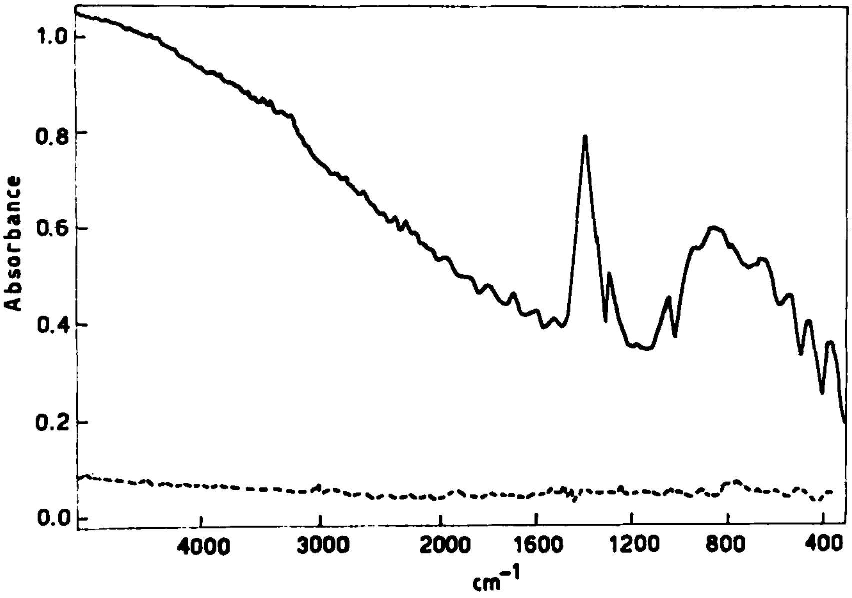

TABLE I Polarization properties and assignment of the zone center phonons for polyacetylene cis (C) and trans (T)

ν (cm^{-1})	pol.	Assignment (T)	ν (cm^{-1})	pol.	Assignment (C)
3011	μ_z	B_u CH str.	3057	$\mu_\perp$	B_{3u} CH str.
3010	$\mu_\perp$		3044	μ_z	B_{1u} CH str.
1293	μ_z	B_u CH in pl.def.	1328	μ_z	B_{1u} CH in pl.def.
1292	$\mu_\perp$	A_u out plane	1246	$\mu_\perp$	B_{3u} CH in pl.def.
1014	$\mu_\perp$		740	$\mu_\perp$	B_{2u} CH out of pl.
1470	α_{zz}	A_g C=C str.	448	μ_z	B_{1u} CCC def.
1070	α_{zz}	A_g C-C str.	1545	α_{zz}	A_g CC str.
			1250	α_{zz}	A_g CC str.
			905	α_{zz}	A_g CC str.

ACKNOWLEDGMENTS

I wish to aknowledge the very fruitful cooperation with my colleagues and friends in the field, in particular L. Piseri, G. Dellepiane and P. Piaggio.

REFERENCES

1. J.C.W. Chien, Y. Yamashita, J.A. Hirsch, J.L. Fan, M.A. Shen, F.E. Karasz, *Nature*, *299*, 608 (1982)
2. S. Destri, M. Catellani and A. Bolognesi, *Makromol. Chem., Rapid Commun.*, *5*,353 (1984)
3. S. Destri, M. Catellani and A. Bolognesi, This Conference
4. R. Dorsinville, *Solid State Commun.*, submitted
5. R. Tubino, R. Dorsinville, W. Lam, R.R. Alfano, J.L. Birman,A. Bolognesi, S. Destri, M. Catellani and W.Porzio, *Phys. Rev.B* in press
6. D.B. Fitchen, *Mol. Cryst. Liq. Cryst*, *83*,1127 (1982)
7. R.S, Cataliotti, G. Paliani, G. Dellepiane, S. Fuso, S. Destri L. Piseri and R. Tubino, J. Chem. Phys., submitted
8. L. Lauchlan, S.P. Chen, S. Etemad, M. Kletter, A.J. Heeger and A.G. MacDiarmid, *Phys. Rev. B27*,2301 (1983)
9. A.C. Albrecht, *J. Chem. Phys.*, 34,1476 (1961)
10. A.P. Penner and W. Siebrand, *Chem. Phys. Lett.*, *39*,11 (1976)
11. Yu.E. Perlin, *Sov. Phys. Usp.*, *6*,542 (1964)
12. W.P. Su and J.R. Schrieffer, *Proc.Nat.Acad.Sci*.NY,77,5626(1980)
13. G. Lugli, U. Pedretti and G. Perego, J. Polym. Sci.,Polym. Lett. Ed., submitted and also This Conference
14. P. Piaggio, G. Dellepiane, L. Piseri, R. Tubino and C. Taliani, *Solid State Commun.*,*50*,947 (1984)
15. E.J. Mele and M.J. Rice, *Phys. Rev. Lett.*, 45,926 (1980)