

Dodecylbenzenesulfonic acid doping of Polyaniline and Poly-3-methylaniline Studied by Resonance Raman Spectroscopy

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Abstract:

In this work resonance Raman spectroscopy is used for the characterization dodecyl benzenesulfonic acid doping polyaniline and poly-3-methylpolyaniline. Raman spectra were recorded with the excitation lines from the blue range to the red region. As expected results are clearly affected during both processes to all polyanilines substituted. These modifications can be interpreted in terms of electronic and conformational changes of the chains, consistent with an increase of the conjugation length and of the delocalization of polarons. These results lead to a clear understanding of photo-induced IR spectra recorded on the same samples.

Keywords : Polyaniline,Poly-3-methylaniline,Dodecylbenzenesulfonic acid, Raman pectroscopy

1. Introduction:

In recent years, several research reports devoted to various aspects of the chemistry and physics of polyaniline have been published. This scientific interest was stimulated mainly by the fact that polyanilines exhibits extremely interesting properties which make these polymers suitable for a variety of technological applications. Polyaniline and substituted polyanilines relate to a large class of polymers since several forms of these compounds can be obtained [1]. These different forms are described by two parameters: the average oxidation state and the degree of protonation. The form emeraldine base of polyaniline and polyaniline derivatives can be converted to the conducting emeraldine salt from either the charge transfer doping or protonation [2-4],but, recently it was found that by using an association of a functionalized protonic acid (Dodecylbenzenesulfonic acid) and we suggest that the increase in conductivity due to the conformation change of the polymeric chain from a coil structure to a more extended one [5,6]. The aim of the present work is to characterize, from the vibrational point of view, doped polyaniline. This characterization means the identification of charged segments (radical cation or dication), produced through the doping process by dodecylbenzenesulfonic acid. Resonance Raman results are complemented by a good fit between experimental and calculated frequencies that could be obtained for all compounds.

2. Experimental:

The chemical synthesis of all the different forms of polyanilines have already been described in details elsewhere [7-9].

Resonance Raman Scattering requires a good knowledge of the optical transition of the compounds. The optical absorption spectrum of emeraldine base (EB) of polyanilines

presents two large bands, the first at 330 nm corresponding to the π --- π^* transition and the second centered at 640 nm attributed to the exaction band [10]. Resonance Raman Scattering (RRS) spectra were recorded with standard equipment in a 90° scattering geometry and either argon or krypton laser lines were used. A multichannel Jobin-Yvon T64000 spectrometer connected to a CCD detector was used in all experiments. In order to avoid any local degradation of the compounds, the laser beam power was limited to (20 mW) and the incident beam was defocused ($\sim 3 \text{ mm}^2$). All experiments were performed at room temperature. The leaser beam power was limited (100 m W) for chemical prepared polyanilines.

RESULTS and DISCUSSION

Polyanilines have been for many years the subject of both experimental and theoretical, structural and electronic studies [11,12]. In spite of these different reports, no complete analysis and no definitive assignment have been reported for all fundamental vibrations of these different forms of polyanilines.

Raman spectra of models compounds and of the all polyaniline and polyaniline derivatives have been published in previous papers [5,13]. The redox / conductivity state affects the degree of protonation, aratio of benzoamine to quinoimine units, acounter ion content, and hydrogen bond interactions (including salvation) in the polymers phase. All these factors contribute to the structure and dynamics of the polymer phase. For emeraldine base of polyanilines doping with dodecylbenzensulphonic acid (DBSA) from CHCl_3 solution the spectrum is characteristic of polyemeraldine salt as experimental. The exposition of these polymer results in a drastic change of the UV – Vis – nir spectrum. Two absorptions can now be seen : one at 457.9 nm peak and one starting from 647.1 nm to the IR region (" free – carrier tail "). These features are characteristic of polyaniline in its" expanded coil " conducting form. Raman spectra of half oxidized from of polyanilines i.e. emeraldine base (200 – 2000 cm^{-1}). Two different excitation wavelengths are presented according to the particular resonance conditions of these polymers. In the spectrum of emerldine base of doping polyaniline obtained with 457.9 nm as excitation wavelength, two intense bands are observed at 1620 and 1186 cm^{-1} , the characteristic of C – C stretching and C – H bending modes respectively (similar to those observed at 1618 and 1181 cm^{-1} in previous work [13]. Other bands are present compared to the spectrum of the previous work at 1162 , 1420 , 1486 and 1590 cm^{-1} . these bands are interpreted as signs of the oxidised units, that is supported by their resonance enhancement using the red laser line. The band at 1162 cm^{-1} is related to the C – H bending mode centered on the quinoid ring and the intense peak at 1480 cm^{-1} corresponds to the $>\text{C} = \text{N}$ vibration. The weak peak at 1332 cm^{-1} is a well-known Raman band in emeraldine base of doping polyanilines i.e. conductive from of polyanilines, characteristic of the protonation [14]. Thus , it is probably due to the protonated structure. The C = C stretching of the quinoid ring is related to the band at 1595 cm^{-1} which seems slightly enhanced using the red excitation wavelength. One can notice that the band at 1186 cm^{-1} in polyanilines (with 457 nm) has disappeared in poly(3-methylaniline) and that could be due to the –CH₃ substituant on the ring. The resonance Raman results lead to the conclusion that the doping process of polyaniline induces not only conformational and structural changes of polymeric chains but also a transformation of quinoid units into semiquinone ones. We have also presented a study of a substituted polymer derivative from polyanilines. Experimental data are consistent with the changes occurring in this compound by the substituant. This result may be useful to study the novel class of polyaniline called self – doped polyanilines.

Referances:

- 1- J. G. Masters, Y. Sun, A. G. MacDiarmid and A. J. Epstein, Synth. Met., 41, 715, 1991.
- 2- M. Cochet, B. Corraze, S. Quillard, J. P. Buisson, S. Lefrant and G. Louarn, Synth. Met., 84, 757, 1997.
- 3- Y. Cao and P. Smith, Synth. Met., 69, 191, 1995.
- 4- A. G. MacDiarmid and A. J. Epstein, Synth. Mat., 69, 85, 1995.
- 5- J. E. Pereira da Silva, M. L. A. Temperini and S. I. Cordoba de Torresi, Electrochimica Acta, 44, 1887, 1999.
- 6- H. G. M. Edwards, A. F. Johnson and I. R. Lewis, J. Raman Spect., 24, 475, 1993.
- 7- A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri and A. J. Epstein in Conducting polymers, edited by L. Alcacer CD. Reidel Publishing Company, 105, 1987.
- 8- A. G. Green and A. E. Woodhead, J. Chem. Soc. Trans., 101, 1117, 1912.
- 9- Y. Sun, A. G. MacDiarmid and A. J. Epstein, J. Chem. Soc., Chem. Commun., 529, 1990.
- 10- J. L. Bredas, in " Proceedings of the 1991 Noble symposium On conjugated polymers and Related Materials ". edited by W. R. Salaneck, Oxford Univ. Press., 1993.
- 11- M. Grzeszczuk and R. Szostak, Solid State Ionics, 157, 257, 2003.
- 12- T. Lindfors, S. Ervela and A. Ivaska, J. Electroanal. Chem., 560, 69, 2003.
- 13- K. Berrada, S. Quillard, G. Louarn and S. Lefrant, Synth. Met., 69, 201, 1995.
- 14- T. Lindfors and A. Ivaska, J. Electroanalytical. Chem., 580, 320, 2005.

Table (1) : Experimental frequencies (in cm^{-1}) of Emeraldine base of polyaniline

Polyaniline		Polyaniline-DBSA		Poly-3-methylaniline-DBSA		Description of vibrations
457.9 nm	647.1nm	457.9 nm	647.1nm	457.9 nm	647.1nm	
1620	1618	1622	1620	1621	1644	C-C stretching (Benz 8a)
1551	1553	1586		1559		C-C stretching (Benz 8b)
1590	1586		1580			C=C stretching Q
1486	1480		1515			C=N stretching (X- sens.)
1420	1420		1486			C-C stretching Q
		(1330)		(1330)		Protonated structure
1220	1217	1249	1251	1254	1253	C-N stretching
1186		1190		1189		C-H Bending
1162	1160		1164		1169,1144	C-H Bending Q
880	870	877	868	877	846	Ring deformation B
828	826	824		720		Amine deformation
	788			677		Ring deformation
720	750					Imine deformation
668						Amine deformation
	640					Ring deformation B

حامض عشاري كبريتات البنزين المشوب للبولي أنيلين والبولي -3- مثيل أنيلين دراسة بواسطة مطيافية رامان

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المخلص :

في هذا العمل استخدمت مطيافية رامان لدراسة خواص بوليمرات البولي أنيلين والبولي -3-مثيل أنيلين المشوب بواسطة عشاري كبريتات البنزين. المطيافية أظهرت انزياح من المنطقة الزرقاء الى المنطقة الحمراء , وهذا كان متوقعا وظهر في جميع انواع البوليمرات المدروسة. هذا التشويب يؤثر على خواص البوليمرات اعتمادا على طول السلسلة والتعاقب للبولرونات الموجود فيها . هذه النتائج مهمة جدا في فهم الخواص الضوئية للبوليمرات المدروسة بواسطة هذه المطيافية