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Ab initio Hartree–Fock Raman spectra of polyacrylonitrile

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Because of the recent progress in near-infrared Fourier transform (n.i.r.–*FT*) Raman spectroscopy, it has become possible to circumvent the fluorescence problem which precludes recording Raman spectra of many important systems, such as some polymers widely used in industry. Being especially concerned with polyacrylonitrile (PAN), we have carried out preliminary ab initio SCF calculations in order to assess how the Raman intensities depend on the molecular structure of this material. The results reported are expected to be useful for future n.i.r.–*FT* Raman studies of PAN in order to interpret the differences that should be observed between various samples. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In principle, Raman spectroscopy has a number of advantages over its complement infrared (i.r.) spectroscopy for studies of the molecular structure of polymer materials. Thus, whenever possible, it is usually easier to study the molecular structure of a polymer material using Raman rather than i.r. spectroscopy[1,2]. Unlike mid-i.r. absorption, Raman scattering is basically sensitive to single or multiple carbon–carbon bonds in non-polar environments[3]. As a consequence, it is especially well fitted for studies of polymer backbones, which determine the conformation of the chains, whereas information from i.r. absorption spectroscopy concerns polar substituent groups[4].

Unfortunately, many technical problems have prevented the former from become a standard method like i.r. absorption spectroscopy, because of, for instance, lack of sensitivity, difficulty of applying Fourier transform (*FT*) methods to Raman scattering, etc.[5]. For many materials, however, the main problem stems from fluorescence, caused either by impurities or by the sample studied itself, which hamper Raman spectroscopic studies of many important polymers. Nonetheless, *FT*–Raman spectroscopy is expanding at an incredible rate[6–8] and recent advances in the field show how to circumvent the fluorescence problem, namely to trigger Raman scattering using near-i.r. photons, whose energy is too low to start a significant amount of electronic transitions, thereby eliminating fluorescence photons. In practice, a 1064.1 nm excitation is used in n.i.r.–*FT* Raman spectroscopy, instead of the conventional 514.5 nm excitation[5,9–11].

This paper deals with the contribution of Raman spectroscopy to the elucidation of the molecular structure of polyacrylonitrile (PAN), one of the most widespread polymers for which structural studies using other techniques provide no clear-cut results[12–15], excepted maybe n.m.r. spectroscopy. In view of the cost and lack of convenience of the latter, a handier technique is needed, in order to characterize PAN samples in an industrial context[16,17], or whenever n.m.r. studies are impossible[18]. In previous work, we focused on the information that may be drawn from i.r. spectra of PAN, by comparing them with theoretical spectra calculated for model oligomers of various tacticities and conformations[19]. Despite their interest, the usefulness of the results obtained was hampered by the fact that while i.r. intensities are known to be very sensitive to environmental effects, the latter were not directly considered. Instead, they were estimated independently by performing calculations on acetonitrile clusters[20,21]. On the other hand, Raman intensities are often less sensitive to intermolecular effects than their i.r. counterparts. As a result, they should be easier to interpret on the basis of the isolated molecule model. Although Raman frequencies of PAN have been available for years[22], Raman studies of this polymer were hampered by fluorescence (P. Viel, personal communication). However, this problem can now be overcome by using n.i.r.–*FT* Raman spectroscopy. For instance, the Raman spectrum, including intensities, of acrylic fibres based on an acrylonitrile (94%) methacrylate (6%) copolymer has been recently reported[23]. Therefore, further experimental investigations of the molecular structure of PAN samples using this technique are expected in the near future. However, getting the most from these spectroscopic studies requires establishing relationships between Raman spectra of PAN and its structural features: first steps towards this goal are presented in the present paper, relying on the calculation of zero-frequency Raman characteristics at the self-consistent field (SCF) ab initio level for several model oligomers.

After a first section devoted to the computational procedure, preliminary calculations on simple alkanenitriles are presented. The aim is to assess the validity of this approach. The influences of the basis set, of molecular environment and of end-effects associated with the oligomer approach are successively addressed. Then,

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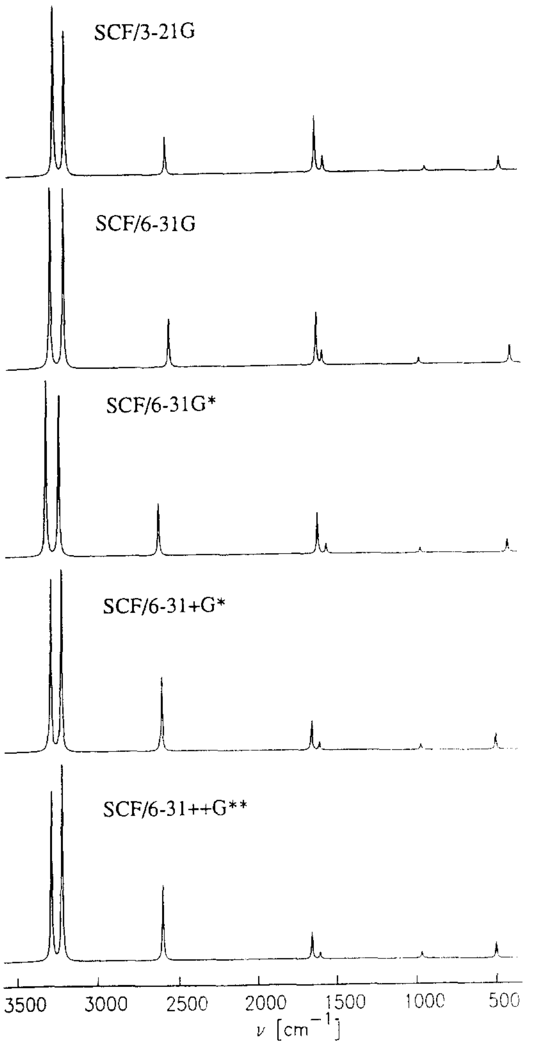

Figure 1 Raman spectra of acetonitrile calculated at the SCF level using different basis sets

some aspects of the dependence of PAN Raman patterns *versus* the tacticity and conformation of the chain are pointed out.

COMPUTATIONAL DETAILS

To date, a number of ab initio Raman intensity calculations have been reported in the literature for many different compounds, mainly at the SCF or MP2 levels[24-32]. In addition to confirm the validity of the usual harmonic approximation[33,34], previous experience indicates that zero-frequency polarizabilities should provide a good approximation to the finite frequency results[24]. At the SCF level, scaled quantum mechanical (SQM) force fields have sometimes been used; nevertheless, the scaling procedure, whose primary goal concerns frequencies, is not expected to improve intensities as well[26]. From this extensive experience, it can be concluded that the SCF level usually provides useful qualitative intensities which are not necessarily improved on going to MP2. In fact, SCF Raman intensities often agree with experiment as well as with their i.r. counterparts. Furthermore, they turn out to be less sensitive than i.r. intensities to basis set effects[24], in line with the suggestion that normal mode composition might be as sensitive to basis set effects as polarizability and its derivatives[25]. However, this is somewhat unexpected since Raman intensities are determined by polarizability derivatives, when in fact large bases are generally required for polarizability calculations.

In the present study, the SCF level for which Raman intensities can be calculated efficiently using analytical derivative techniques[35] was retained. The MP2 level is not suitable here because of its poor description of such moieties as the nitrile group[36]. Various basis sets, ranging from 3-21G to 6-31 + + G**, were used. The calculations were carried out with the GAUSSIAN90 program running on a Cray II computer, using standard convergence parameters[37]. All geometries were fully optimized, the only constraint being that imposed by symmetry. Energy derivatives were calculated analytically to obtain force constants and polarizability derivatives.

INFLUENCE OF THE BASIS SET

Preliminary calculations were performed with various bases (3-21G, 6-31G, 6-31G*, 6-31 + G* and 6-31 + + G**) on the simplest of all alkanenitriles, namely acetonitrile, in order to assess the influence of the basis set employed. The Raman spectra obtained are shown on *Figure 1*. As expected, frequencies remain overestimated by ~10–13%. With regard to Raman intensities, they turn out much less sensitive to the basis set used than corresponding i.r. intensities[21], at least with the bases considered in this paper. The main evolution on improving the basis set concerns the relative intensities of the two C–H stretching bands. This small basis set dependence is in line with previous results on pyridine[24]. Therefore, only the most affordable bases, 3-21G and 6-31G, are retained for calculations on more extended systems reported in the following sections.

The spectra presented on *Figure 1* may be compared with experimental results reported in the literature, for instance with the Raman spectra of acetonitrile trapped in solid argon[38], keeping in mind that the Raman intensities thus measured may be affected by the argon matrix. The relative intensities of the C–H stretching band differ from experiment, and the relative intensity of the $C\equiv N$ stretching band is underestimate. However, in view of the simplifications involved, namely the SCF approximation, basis set limitation, lack of environmental influence and anharmonicity, better agreement could hardly be expected.

MAGNITUDE OF ENVIRONMENTAL EFFECTS

In order to estimate the magnitude of environmental effects, the Raman spectra are calculated at the SCF/6-31G level on model acetonitrile clusters, dimers to tetramers, spanning three kinds of arrangements: linear, antiparallel and cyclic, whose geometries, relative energies, frequencies and i.r. intensities are discussed in previous work[39]. Strictly speaking, this supermolecule approach yields the Raman spectra of the model clusters. To compare these spectra to that of the isolated molecule, we simply scale the intensities according to the number of molecules in the cluster (*Figure 2*). At that point, maybe it should be emphasized that for clusters whose molecules are not all equivalent by symmetry, the spectra thus obtained are in a sense averaged over the various environments felt by non-equivalent molecules.

According to *Figure 2*, intermolecular effects are found to be most important concerning the two C–H stretching bands, especially for linear and, to a lesser extent, cyclic arrangements. While the lower frequency band is significantly stronger than the other in most cases, the two intensities become almost equal for the linear clusters.

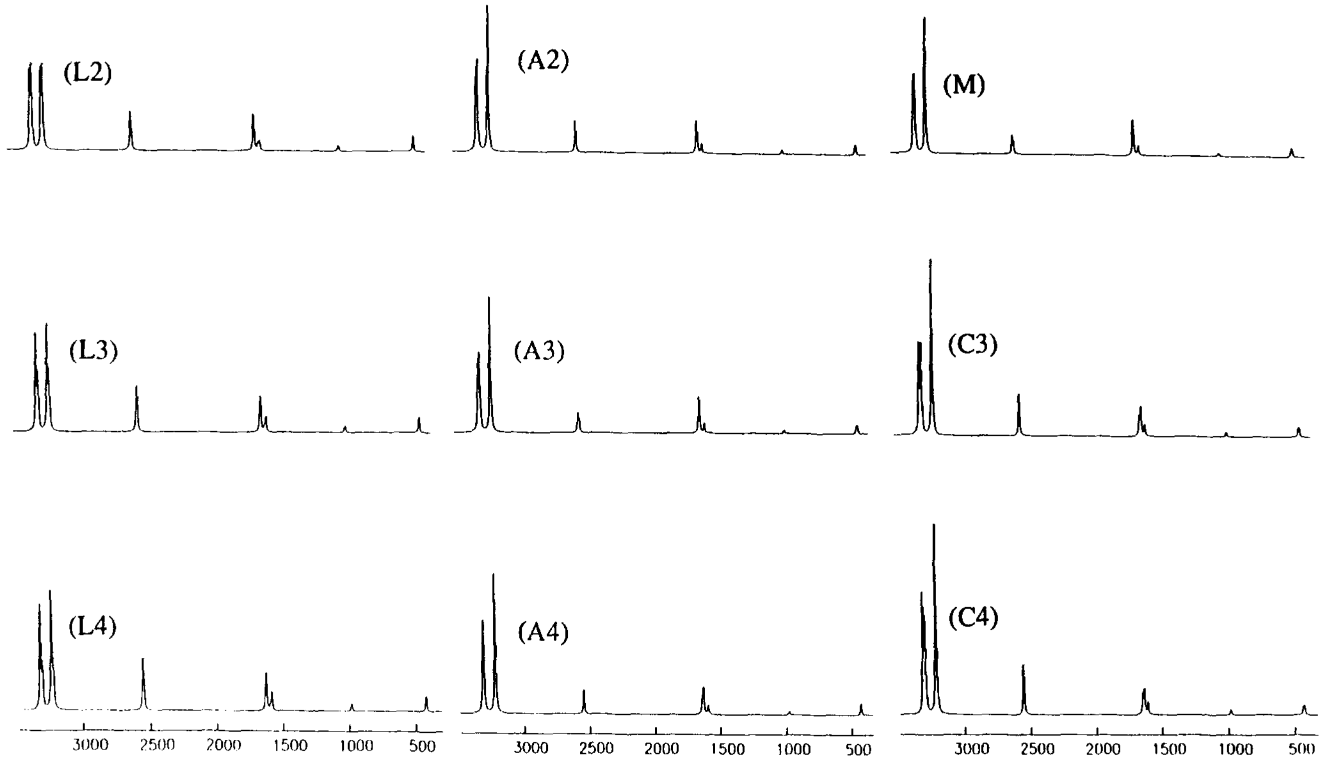

Figure 2 Raman spectra for acetonitrile clusters (x-mers) of different sizes and packing: linear (L_x), antiparallel (A_x) and cyclic (C_x), obtained at the SCF/6-31G level of theory and normalized to one molecule. Frequencies in cm^{-1}

Except for these two bands, the relative Raman intensities of acetonitrile are virtually unaffected by the environment. However, another effect worth pointing out is the fact that the $C\equiv N$ stretching band is enhanced for linear and cyclic arrangements, in contrast to antiparallel arrangements. As for the fingerprint region, *Figure 2* shows that it is not much affected by intermolecular effects. In contrast, as will be seen in the following, variations in chain tacticity or conformation result in dramatic changes in this frequency region. Therefore, intermolecular effects do not preclude studying the influence of molecular structure on Raman intensities on isolated model compounds, provided that the latter is more significant, as is the case in this study.

ASSESSMENT OF THE OLIGOMER APPROACH

As thoroughly discussed previously, considering model oligomers to study the vibrational characteristics of such a disordered polymer as PAN is a more suitable approach than using periodic conditions[36]. It was found that the i.r. features of acrylonitrile x-mers were essentially stabilized for $x = 5$, allowing one to study the influence of molecular structure on the i.r. spectra by considering pentamers[19,36]. In this section, the convergence of Raman spectra (per monomer unit) of the same acrylonitrile oligomers[19] is monitored. The oligomer approach has already been used to predict Raman characteristics of polyacetylene, providing

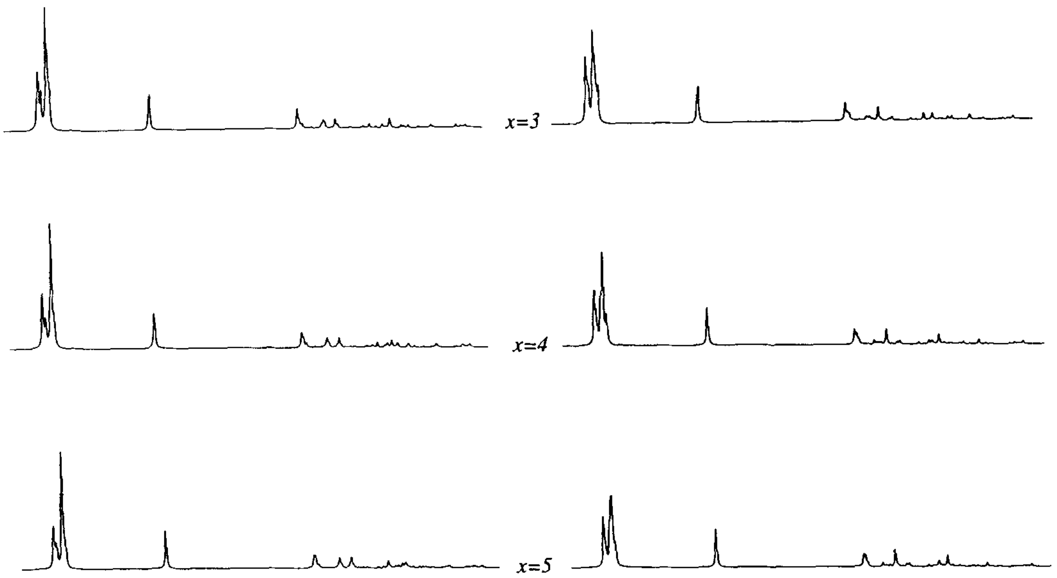

Figure 3 Raman spectra of isotactic (left) and syndiotactic (right) acrylonitrile oligomers (x-mers) in all-trans conformations, calculated at the SCF/3-21G level of theory. Frequencies in cm^{-1}

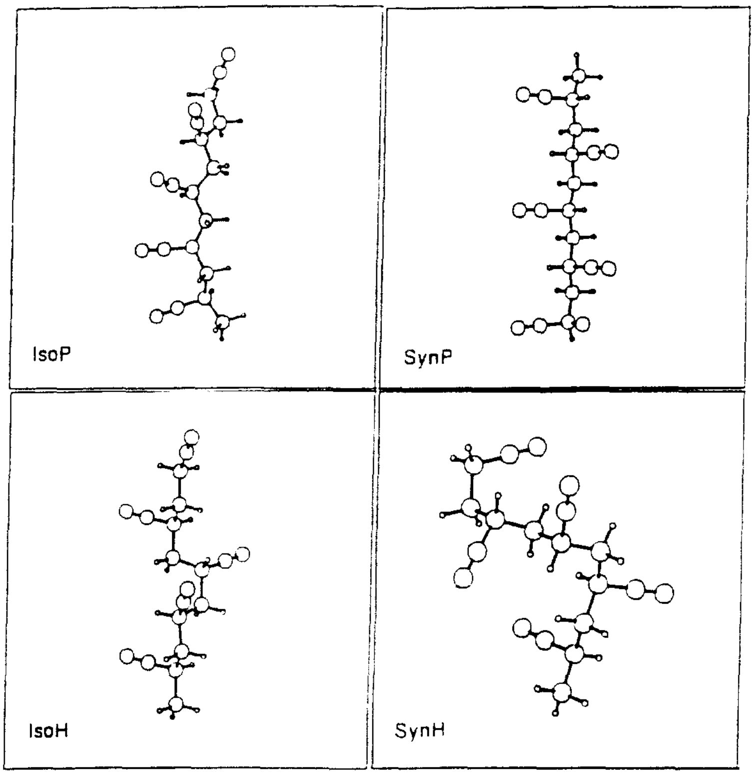

Figure 4 Acrylonitrile pentamers: all-trans isotactic (IsoP), helical isotactic (IsoH), all-trans syndiotactic (SynP) and all-trans syndiotactic (SynH)

Raman intensities in good agreement with the experimental relative intensities[32].

Isotactic and syndiotactic model oligomers of acrylonitrile are considered, both in a trans conformation. In contrast to isotactic structures, syndiotactic chains remain approximately planar zigzag after full geometry optimization. Total energies, geometries, dipole moments and i.r. characteristics of these oligomers have been discussed previously[19]. The

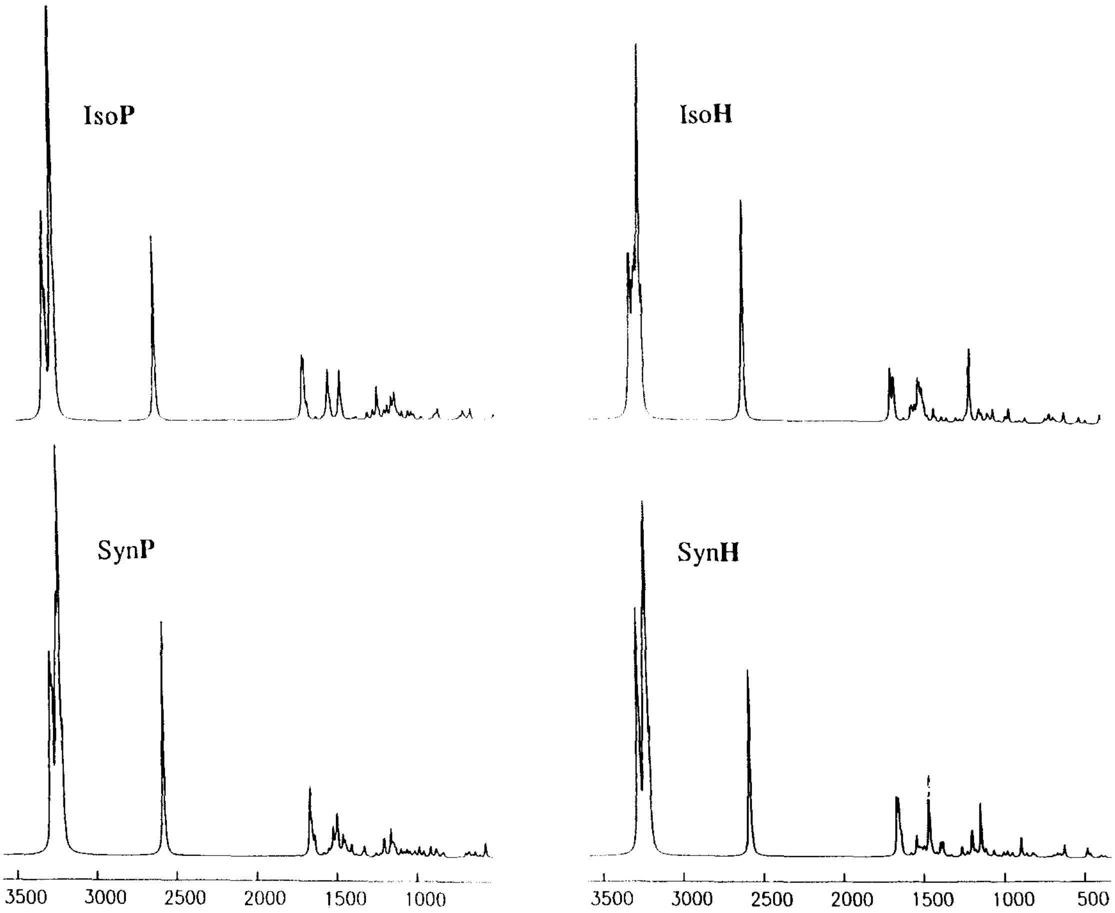

Figure 5 Raman spectra of acrylonitrile pentamers IsoP, IsoH, SynP and SynH. Frequencies in cm^{-1}

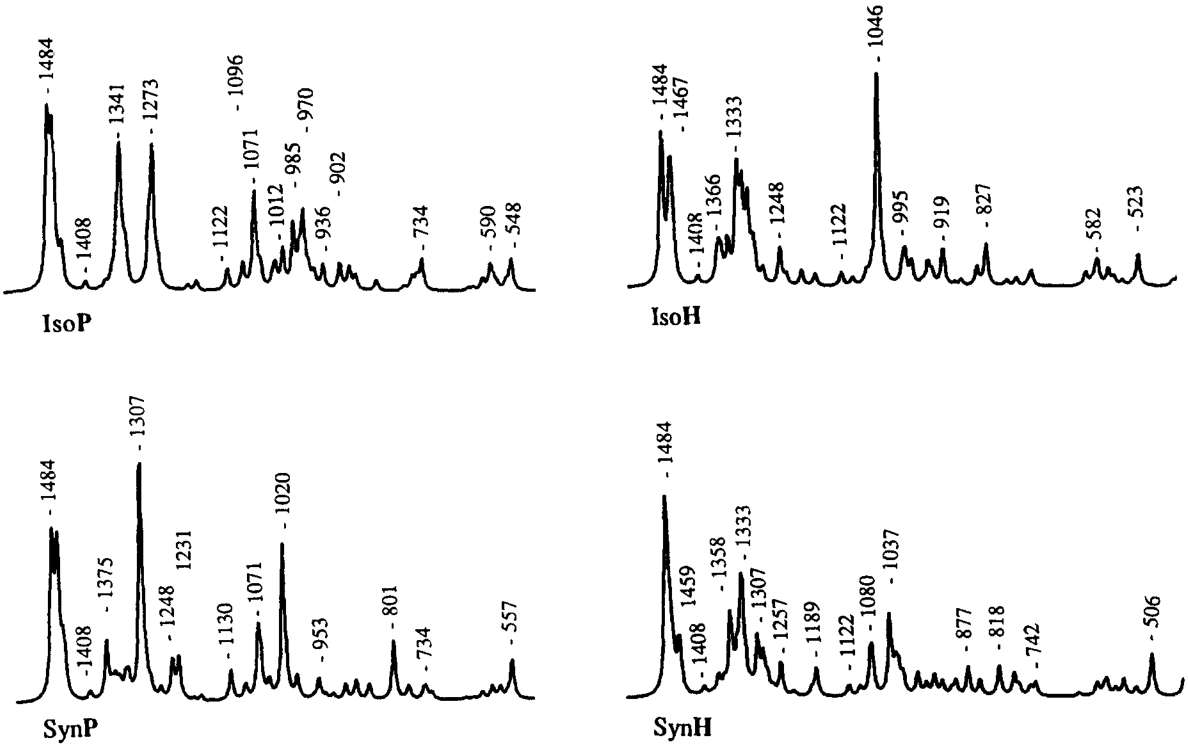

Figure 6 Extended view of the Raman spectra of the acrylonitrile pentamers IsoP, IsoH, synP and SynH in the 1500–500 cm^{-1} frequency range. Reported peaks (in cm^{-1}) have been scaled with the usual 0.89 factor[28].

Raman spectra obtained on these model structures are shown on *Figure 3*, with intensities scaled according to the number x of monomer units considered. Chain conformations are shown in *Figure 4* for the pentamers. For a given tacticity, the spectra are hardly different, whatever the value of x. This indicates that the differences between left and right spectra in *Figure 3* are true configurational effects and do not stem from edge effects. Thus, the latter do not preclude studying the dependence of Raman spectra of PAN *versus* the molecular structure of the chains by considering rather small model oligomers, such as pentamers.

A similar situation was found to prevail concerning i.r. spectra[19]. However, Raman intensities appear to converge even faster than their i.r. counterparts, at least in the systems considered here. This could be explained by the fact that the contribution of each monomer unit to Raman scattering may be rather insensitive to long-range intrachain interactions and therefore to end effects. Moreover, end units differ from others by the replacement of skeleton C–C bonds by terminal C–H bonds: despite the large difference in the polarities of these bonds, responsible for the much stronger i.r. absorption in the case of C–H bonds, the corresponding contributions to polarizability should be low in both cases. In fact, end effects would be more significant should they involve removing highly polarizable bonds, for instance in the case of conjugated polymers.

On the basis of this fast convergence, acrylonitrile pentamers are considered in the following section as models for studying the influence of chain conformation and tacticity on the Raman activities of PAN.

DEPENDENCE OF RAMAN INTENSITIES ON MOLECULAR STRUCTURE

With the aim of examining the influence of molecular structure on the Raman features of PAN, the Raman spectra of four model pentamers were calculated at the SCF/3-21G level. These pentamers shown on *Figure 4* were first considered in a previous paper where their total energies, geometries and i.r. characteristics were studied[40]. The corresponding Raman spectra are presented on *Figure 5*.

As regards the Raman features in the fingerprint region, it is obvious from *Figures 5, and 2* that the influence of molecular structure is much more important than the role of environment. Therefore, the approach used in this paper, namely considering isolated model oligomers to study structural effects, is valid.

The spectra thus obtained show very strong C–H and C≡N stretching bands, while the bands in the fingerprint region are much less intense. On comparison of these spectra with the spectrum of an acrylonitrile (94%) methacrylate (6%) copolymer[23], the intensity of the C–H stretching bands seem much overestimated with respect to the intensity of the C≡N stretching band, though this apparent discrepancy could result from the fact that the bands in the C–H stretching region are broader. The calculated C–H and C≡N stretching bands also seem too intense when compared with the lower-frequency bands. This may result because the SCF approximation may induce a spurious decrease—hence a significant change—of the molecular polarizability as bond lengths are elongated, because of the ionic contribution to the electronic wavefunction being overweighted. Nonetheless, whereas this ionic contribution tends to increase the change in dipole moment on vibration, thus accounting for too large i.r. intensities at the Hartree–Fock level; whether an explanation along the same line is also valid concerning Raman scattering intensities remains to be investigated.

Since the main differences between the Raman spectra of IsoP (all-trans isotactic), IsoH (helical isotactic), SynP (all-trans syndiotactic) and SynH (all-trans syndiotactic) obviously arise in the fingerprint region, extended views of this area are shown on *Figure 6*. The frequencies reported there are scaled using the empirical factor 0.89[41] for comparison with experiment. The various parts of the spectra will be discussed on the basis of these scaled frequencies.

Between 1500 and 1400 cm^{-1}, two bands insensitive to molecular structure are observed, at 1484 and 1408 cm^{-1}, the latter being virtually inactive. The constancy of these lines is expected as they involve to a greater extent vibrations of the terminal methyl group, in addition to deformations of the $-CH_2-$ groups. Nevertheless, the 1484 cm^{-1} band shows a twin band at a lower frequency, more or less intense and which depends significantly on the molecular structure.

In the 1400–1200 cm^{-1} frequency range, two main bands of similar intensities are observed for IsoP at 1341 and 1273 cm^{-1}. In contrast, only one band dominates this region for IsoH, SynP and SynH, being surrounded by weaker bands or shoulders. The frequency of this dominant band is 1307 cm^{-1} for planar zigzag SynP and 1333 cm^{-1} for the helical conformations IsoH and SynH.

In the 1200–1000 cm^{-1} region, the spectra of isotactic oligomers are dominated by a single strong band located at 1071 cm^{-1} for IsoP and 1046 cm^{-1} for IsoH, the latter being particularly intense. On the contrary, two bands of significant intensities are observed for the syndiotactic structures, located at 1071 and 1020 cm^{-1} for SynP, and at 1080 and 1037 cm^{-1} for SynH.

Below 1000 cm^{-1}, only moderate intensity bands are obtained, except perhaps for IsoP which presents significant scattering at 985–970 cm^{-1}. These bands may be hard to observe experimentally.

Overall, the four structures considered show striking differences which may be used as a probe into the PAN molecular structure. Moreover, they do not stem essentially from tacticity. Indeed, maximum similarities are noted between IsoH and SynH despite their tacticities being different. On the other hand, tremendous changes are noted on going from IsoP to IsoH, or from SynP to SynH, because of conformational effects.

CONCLUSION

Since it can provide excellent *FT* Raman spectra of acrylic fibres quickly and easily, n.i.r.–*FT* Raman spectroscopy may turn out to be a convenient and reliable tool to check the quality of PAN samples and to get a further insight into their molecular structure. This technique is expected to be particularly useful, in addition to i.r. spectroscopy, whenever n.m.r. studies cannot be carried out.

After a preliminary study of basis set effects on the Raman intensities of acetonitrile, which indicated that 3-21G spectra agree qualitatively with those obtained with larger bases, an oligomer-approach used previously for i.r. spectra was applied with a view to estimating the role of the molecular structure of PAN in its Raman characteristics. It turns out that acrylonitrile pentamers provide a good approximation to the Raman spectra of PAN as calculated at the same theoretical level. In addition, it is suggested that Raman intensities of alkanenitriles do not depend much on surrounding effects. As is the case concerning i.r. absorption, conformation is found as significant as tacticity. Considerable differences are predicted between the Raman spectra of samples differing by the structure of their chains. Thus, strong bands are expected towards 1341 and 1273 cm^{-1} for trans isotactic segments, 1307 and 1020 cm^{-1} for trans zigzag planar syndiotactic segments, while IsoH structures, in other words $(TG)_3$ isotactic helixes, should give rise to a strong absorption towards 1046 cm^{-1}.

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