Photoacoustic FT-IR and FT-Raman Spectroscopic Study of Cross-Linked Copolymers

Ottó Berkesi
Institute of Physical Chemistry, University of Szeged, H-6720 Szeged, Rerrich B. tér 1, Hungary, **oberkesi@chem.u-szeged.hu**

János Mink
Department of Molecular Structure, Institute of Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri út 59-67. **jmink@chemres.hu**

István Somogyi and Imre Bacza
Iontech Kft. H-8196 Litér, Árpád u. 38., **iontech@invitel.hu**

The quality evaluation of cross-linked polymer products is one of the most challenging tasks, since sample preparation is impossible from these polymers for most of the spectroscopic methods without altering the sample itself. Photoacoustic spectroscopy is one of the simplest solutions for this problem. There is no need for sample preparation, and the detected signal originates from the bulk of the spherical particles, carrying the potential of dept-profiling. The volume of the measured sample also makes possible a kind of averaging. FT-Raman spectroscopy provides similar possibilities as well, thus, employing these two methods in combination, gives a good chance to gain information on these difficult samples. Our pilot study has proved that monitoring the quality of the cross-linked polymers can be established concerning the monomer ratio, the nature and concentration of the initiator. It is also possible to characterize or compare the polymer samples produced.

1 Introduction

Sample preparation is an essential question in infrared spectroscopy (IR). Most sample handling methods do alter the physical state or even the chemical composition of the sample. Thus, it is very difficult to get convinced that the spectrum gained, gives an account on the same sample, which were also studied by other methods. Since Raman spectroscopy has become more easily available, the identical state of the sample studied is even more important. In spite of this obvious demand, photoacoustic spectroscopy (PAS) and other methods based on the photothermal effect (PE) are nearly unknown for chemists. Few books on IR spectroscopy mention it as a final tool, when all other sophisticated methods, e.g. diffuse reflectance (DR), attenuated total reflectance (ATR) etc. fail to produce proper spectrum. Unfortunately, most of the chemists give up at that stage.

Cross-linked polymers are very difficult samples, since they are usually produced by suspension polymerzation in the form of pearl-like spheres with size between some tenths of millimetre and few millimetres. They do not dissolve in any solvent, cannot be ground and mixed with KBr or pressed into thin foil. Horizontal ATR devices can provide spectra with proper quality, if the size of the spheres is small enough, but the information included in the spectra originates only from a tiny portion of the surface layer of the spheres.

Since the application of these types of resins is rather wide in separation techniques, environmental and biochemistry, it is very important to characterize the final product.

This article gives an account on the results of a pilot project, which demonstrates the kind of information gained by the combination of Fourier transform photoacoustic infrared and Raman spectroscopies on polystyrene-based cross-linked polymers.

2 Experimental

2.1 Materials

Cross-linked polymer samples were taken from the normal industrial production line of polystyrene cross-linked with divinyl-benzene. The samples were selected in groups to cover the factors varied in the industrial production process, the types of initiator, the ratio of styrene to divinyl-benzene, etc., and were unknown for the academic staff performing the studies.

2.2 Equipment

IR spectra were recorded on a Bio-Rad Digilab Division FTS 65A/896 Fourier transform (FT) infrared spectrometer equipped with an MTEC 200 photoacoustic detector, between 4000-400 cm^{-1}, at 4 cm^{-1} optical resolution. A carbon black sample, provided by the producer of the detector, were used to record the background spectrum. Raman spectra were recorded with the same optical resolution between 3600-100 cm^{-1} Raman shift region, on a Bio-Rad Digilab Division dedicated Fourier transform Raman spectrometer equipped with a liquid nitrogen cooled Ge detector. A continuous-wave Spectra Physics Nd:YAG-laser provided the excitation line at 1064 nm (9395 cm^{-1}) with 500 mW laser power. A 5 mm NMR tube was used as sample holder to avoid fluorescence.

2.3 Software

Spectra recorded using Digilab's Win-IR Pro 3.3 were converted into GRAMS format and all spectral manipulations were performed using GRAMS/AI Version 7 program of Thermo Galactic running on a PC under MS Windows98.

Basic assignment of the peaks were done by using the IR Mentor Version 1.05 program of Bio-Rad Sadtler Division and data found in G. Socrates' book [1].

Figures were transferred to MS PowerPoint 2000 for further refinement and annotation.

3 Results and Discussion

3.1 Spectral features indicating the changes in the ratio of the cross-linking monomers

Polystyrene can be considered as a phenyl-substituted polyethylene chain, so their spectra contain the bands characteristic of the polyethylene chain and the mono-substituted phenyl group. The cross-linking di-substituted phenyl groups also put their fingerprints into the spectra according to their ratio in the monomer mixture thus the spectral differences should contain their signs.

All normal modes of these polymers are active in IR and Raman, since the symmetry is low enough, but the intensities of the bands vary strongly due to the different selection rules of infrared and Raman spectroscopies. Infrared spectra are mainly dominated by the modes of the polar functional groups, while strong Raman bands are arising from the skeletal modes, i.e., they can supply complementary information.

A group of the recorded photoacoustic spectra showed only minor differences and spectral subtraction produced difference spectra, very similar to those of the original, but the intensities of certain bands were magnified, like in Fig. 1. The signal-to-noise ratio of the difference spectra were good enough for attempting interpretation, due to the extended linearity of the photoacoustic signal with concentration.

The first region to be interpreted was the C-H stretching range. The similarity of the spectra was extremely high. The difference spectra contained all bands of the original spectra. The only really new band was merely a shoulder around 2960 cm^{-1} (Fig 2.).

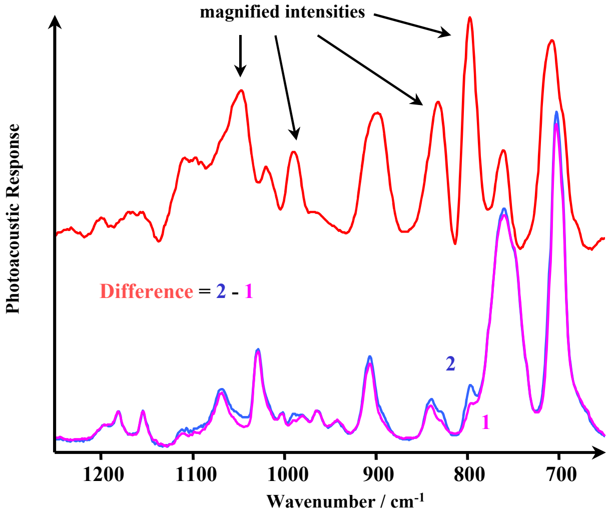

Figure 1: Typical photoacoustic spectra of cross-linked polystyrene samples and their difference spectrum with enhanced intensities

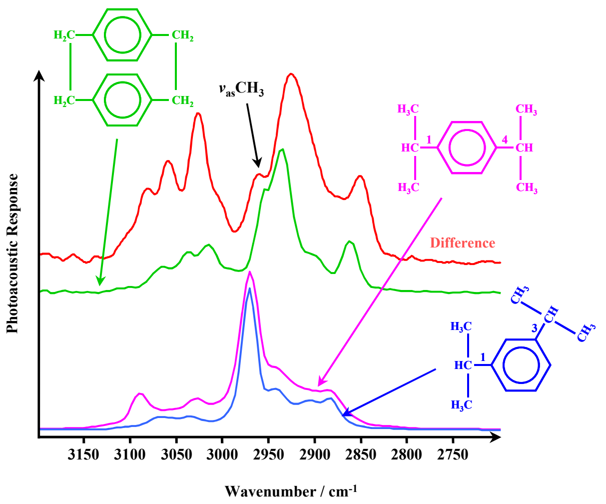

Figure 2: The intensities in the difference spectrum suggested that they carry information on the cross-linking groups of the polymer. The only new band around 2960 cm^{-1} was assigned to the asymmetric stretching mode of a methyl group

Reference spectra of diisopropyl-substituted benzene derivatives were downloaded from NIST Chemistry WebBook [2]. Their spectra suggested that the main information carried by the difference spectrum is attributed to the cross-linking groups in the polymer. The new band was assigned to the asymmetric stretching mode of a methyl group. Its symmetric counterpart cannot be distinguished from the neighbouring strong CH_2 stretching bands.

Since the samples originated from the industrial production line, it was obvious to assume that the monomer mixtures were made from technical grade ingredients, containing various other disubstituted monomers, due to the previous steps in their production.

The region of the skeletal bands of the substituted benzene ring showed a complex band at around 1490 cm^{-1}, which cannot be assigned to the linking disubstituted benzene rings (Fig.3.). The reference spectra of the methyl-substituted styrene derivatives confirmed that this band could be attributed to the presence of *ortho*- and *meta*-substituted methylstyrenes in the mixture.

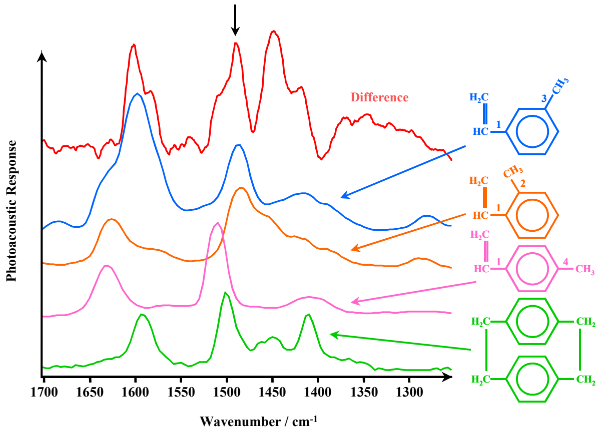

Figure 3: The compound band around 1490 cm^{-1}, marked with an arrow, in the difference spectrum, indicated the presence of methyl-substituted benzene rings beside the cross-linking disubstituted rings

Further support was found in the lower wavenumber region of the difference spectrum, including the out-of-plane deformation modes – characteristic on the mode of substitution – of the benzene ring (see Fig.4.). The band marked with (a) around 990 cm^{-1}, cannot be found in the spectra of the above-mentioned diisopropyl-substituted reference materials, but in the *para*-disubstituted ones.

The band, marked with (b), around 760 cm^{-1} was a clear indication of *ortho* substitution, while the third (c) marked band at ca. 900 cm^{-1} was a common feature of all reference spectra of the disubstituted compounds.

The relative intensity changes in the difference spectra of the studied samples qualitatively followed the monomer compositions used for the production of the samples. A more detailed study might lead to a more accurate characterization method.

Difference Raman spectra of the same pairs of samples were also studied. Since few reference Raman spectra were available, the Raman peak tables for the possible monomers and the disubstituted isopropylbenzene molecules, collected by Zhizhin *et al.*, were also used in the assignment [3].

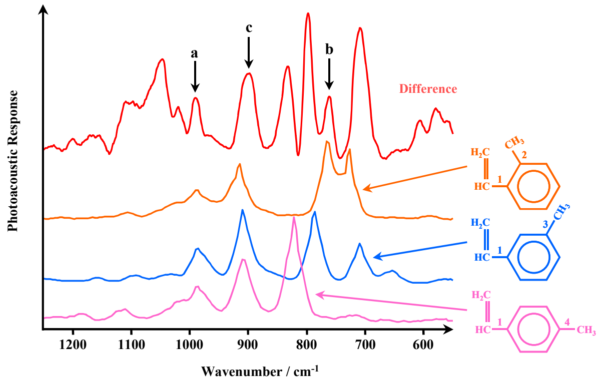

Figure 4: Bands (a) and (b) at ca. 990 cm^{-1} and 760 cm^{-1} cannot be assigned to the *para*- and *meta*-substituted cross-linking groups, but (a) can be found in the methyl-substituted monomers, while (b) is the sign of the *ortho*-substitution. Band (c) is a common feature in all reference spectra

The C-H stretching region confirmed the presence of the methyl group in the products containing higher ratios of cross-linking polymers. The characteristic asymmetric methyl stretching band was found at 2930 cm^{-1} (Fig.5.), which is closer to the expected value for a methyl group bonded to a benzene ring, than the band found in the PAS difference spectrum.

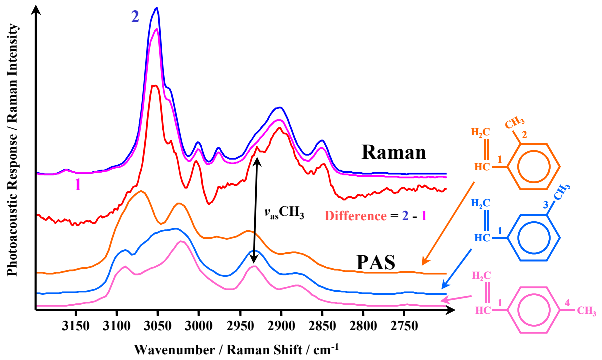

Figure 5: Raman difference spectra confirmed the presence of a methyl group bonded to a benzene ring

The most intense band was always found at 1629 cm^{-1} in the difference Raman spectrum of samples with different monomer compositions (Fig.6. band (a)).

This peak was missing from the reference spectrum of polystyrene given in Ref.4. It might be the sign of cross-linking between the main chains. The weak, broad, compound band (see Fig. 6. band (b)) at 1410 cm^{-1} is characteristic of the *para*-substituted cross-linking benzene ring [3].

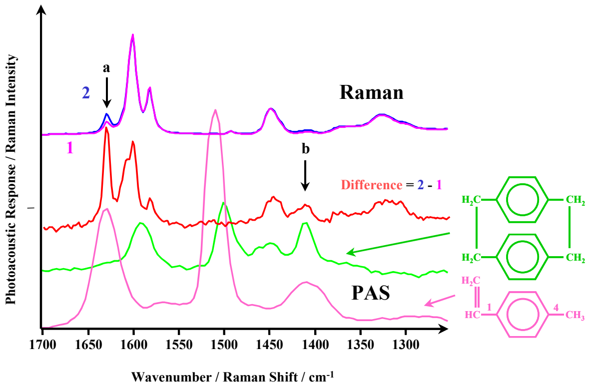

Figure 6: Band (a) could serve as a sign of the cross-linking in polystyrene copolymers [4]. Band (b) indicated the presence of *para*-substituted phenyl group [3]

The *ortho-* and *meta-*substitution was indicated by two bands in the in-plane C-C-H bending range at 1228 cm^{-1} and at 1168 cm^{-1} [3] (Fig. 7.).

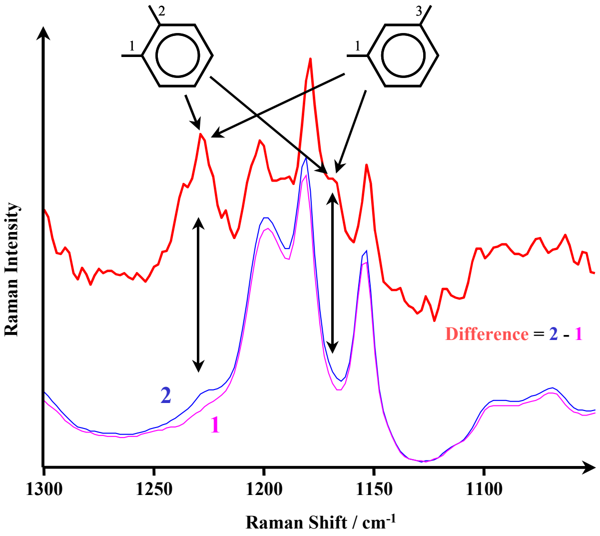

Figure 7: The presence of *ortho-* and *meta-*substituted cross-linkage can be monitored in the C-C-H in-plane bending region [3]

3.2 Monitoring the nature of initiator of the polymerzation process

The initiator produces free radicals, which start the polymerzation chain-reaction. Its amount strongly influences the average length of the polymer chain, thus, it is an important factor in the production process. Usually, some kind of peroxide is used in the practice of suspension polymerzation. The initiator might be soluble in water – inorganic peroxides – or in the mixture of monomers, the oily phase of the system – organic peroxides.

Pairs of samples were found where the bands of the polymer cancelled out, nearly perfectly, by subtraction in the photoacoustic difference spectrum, but certain weak bands out of these ranges remained intact. It was possible to classify these spectra into two groups.

The first group produced a band at approximately 1740 cm^{-1} and somewhere around 1250 cm^{-1} (see Fig.8.). These bands are characteristic of the stretching modes of aromatic carboxylic acids in monomeric form [1]. The higher wavenumber one is the mode dominated by the C=O bond, while the other at the lower wavenumbers is a more complex but dominated by the bonds of the C-C-O(H) part in the carboxylic group.

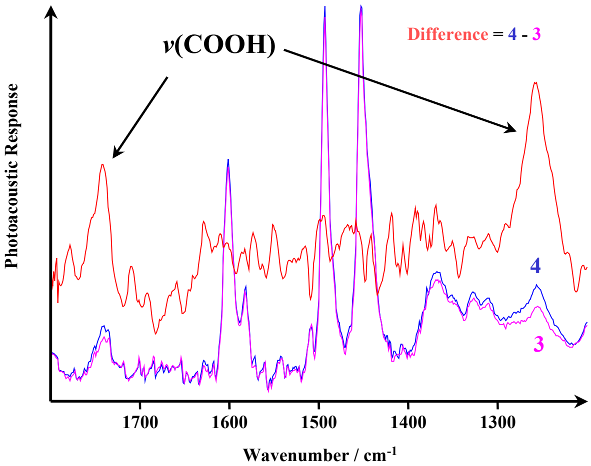

Figure 8: Characteristic bands for the decomposition product of the most common type of organic initiator, a carboxylic acid, were also found in the difference spectra

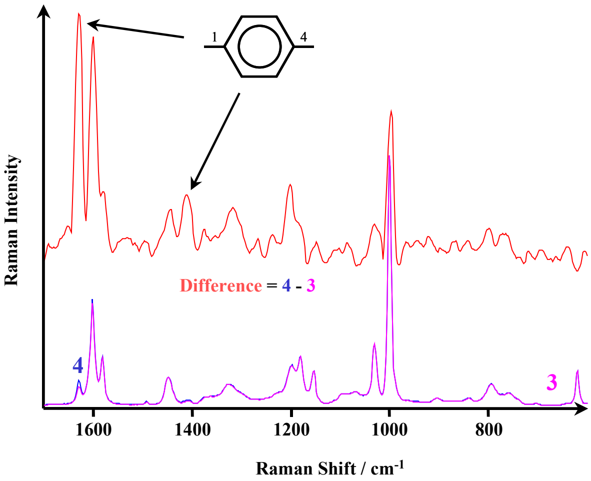

Figure 9: Substraction of Raman spectra suggested that the initiator was one of the *para*-substituted benzoil-peroxides

The subtraction of the corresponding Raman spectra produced difference spectra containing the bands characteristic of the *para*-substituted compound (see Fig.9.), while the bands for *ortho*- and *meta*-substitution cancelled out. Since carboxylic acids are the decomposition products of the most widely used organic initiators, it could be concluded that one of the *para*-substituted benzoic peroxides was used.

The other group of difference PAS spectra did not show well-defined bands but wide, diffuse ones around 1000 cm^{-1} (Fig. 10.). An additional band was found at 670 cm^{-1}. Infrared spectra of oxygen-containing inorganic anions show similar features [5], thus, it was suspected that an inorganic initiator was used to produce these samples. Always two bands were found so the anion must be one of the tetrahedral oxo anions, since in case of the trigonal planar ones there are three infrared active bands in the region [6]. The position of the bands [6] confirmed that it must be the sulphate ion, which is the decomposition product of the most widely used inorganic initiator: potassium peroxodisulphate.

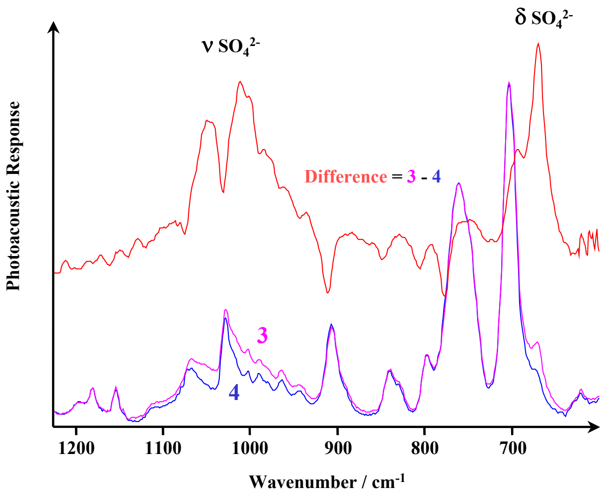

Figure 10: Characteristic bands of sulphate ion, the decomposition product of the most commonly used inorganic initiator.

3.3 Spectral features in the sulphonated derivatives of cross-linked polystyrene.

All above studied polymers were intermediates in the industrial production of polymer pearls with high ion-exchange capacity. The spectra of the final products were also recorded. Unfortunately, the air-dry samples released water vapour at the temperature of measurement, in the photoacoustic chamber, so extended purging was necessary before proper spectra were gained. The recorded spectra were essentially different from the spectra of the corresponding cross-linked polymers, thus, no spectral subtraction was used prior to interpretation.

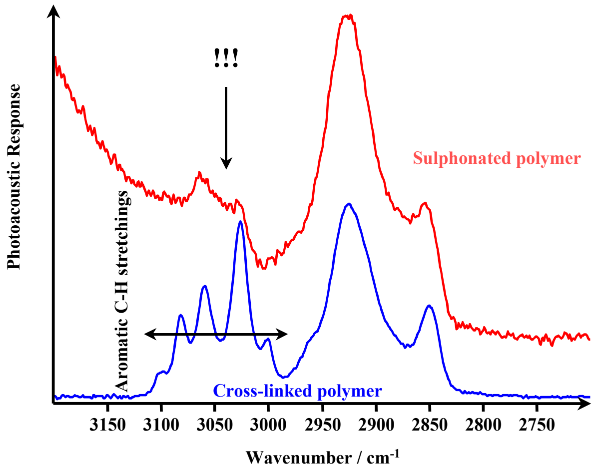

Figure 11: The final step of production essentially altered the aromatic part of the cross-linked polymer.

The most obvious conclusion from the changes of spectra that the final step of production altered the aromatic portion of the cross-linked polymer (see Fig. 11.). Since the normal modes dominated by the OH groups are very weak in the Raman spectra, the broad band at 1638 cm^{-1} was attributed to the bending mode of water strongly associated with the polar groups in the samples (Fig. 12.). The broad feature below 800 cm^{-1} was also caused by associated water molecules.

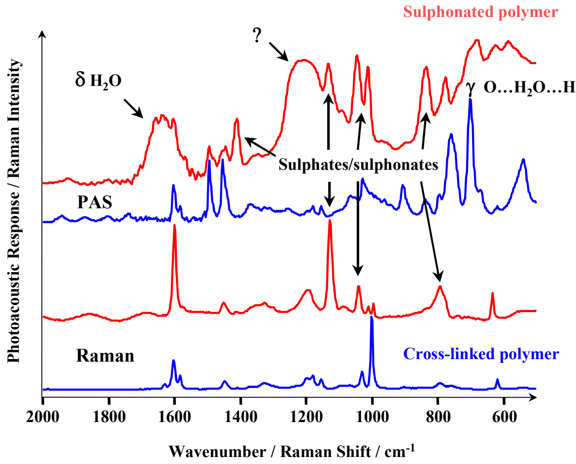

Figure 12: The band at 1201 cm^{-1}, marked with a question mark, was assigned to the $–SO_3H$ group according to Ref. 7.

The origin of the other broad band at 1201 cm^{-1} might be a bit suspicious, because the in-plane C-O-H bending bands are very similar in shape and position. Beside, the description of the bands assigned to the organic sulphonato or sulphato groups did not allow an accurate assignment [1]. Fortunately, an example for a polymer-containing sulphonic acid group attached to an aromatic ring was found in another collection of vibrational spectra by Zhizhin *et al.* [7]. The presence of a similar band, exactly at the same position convinced us that the band in question must be assigned to sulphonic acid group. All other new bands between 1410 and 1000 cm^{-1} could be assigned to either sulphonate or sulphate groups attached to various positions on the polymeric chain [1].

3 Summary

Photoacoustic FT-IR spectroscopy combined with FT-Raman spectroscopy proved to be a powerful tool to monitor the most important factors varied in the industrial production of cross-linked polystyrene based copolymers, the intermediate products for gaining polymer pearls with high ion-exchange capacity. Set of bands were proposed to monitor the composition of the monomer mixture. The substitution modes of the cross-linking groups were also revealed. Characteristic bands for the decomposition products of both inorganic and organic initiators were also successfully identified. The final step of the industrial process, the sulphonisation, essentially alters the aromatic part of the cross-linked copolymer. Mainly organic sulphonic acid and sulphate groups were responsible for the ion-exchange capacity of the final product.

References

[1] G. Socrates, '*Infrared Characteristic Group Frequencies*', J. Wiley & Sons, New York, 1980.

[2] NIST Chemistry WebBook, in April and May of 2005. http://webbook.nist.org/chemistry/

[3] H.E Sterin, V.T.Aleksanyan and G.N. Zhizhin: '*Catalog for Raman Spectra of Hydrocarbons*', (ed. by G.N. Zhizhin), Izd. Nauka, Moscow 1976. (in Russian).

[4] B. Schrader: '*Raman/Infrared Atlas of Organic Compounds (Second edition)*' VCH Publishers, New York, 1989.

[5] R.A. Nyquist and R.O. Kagel: '*Infrared Spectra of Inorganic Compounds*' Academic Press, New York, 1971.

[6] K. Nakamoto: '*Infrared and Raman Spectra of Inorganic and Coordination Compounds (5th Edition), Part A and Part B*' J. Wiley & Sons, New York, 1997.

[7] A.H Kuptsov, and G.N. Zhizhin: '*Handbook of Fourier Transform Raman and Infrared Spectra of Polymers*', Fizmatlit, Moscow 2001 p: 121. (in Russian) (Also published by Elsevier in Physical Sciences Data, V.45 (1998) under the same title.).