Macromol. Symp. ***141****, 283–292 (1999)*

Advantages of Near Infrared Spectroscopy for the Analysis of Polymers and Composites

Gilbert Lachenal *(1) and Yukihiro Ozaki *(2)

(1) Université Claude Bernard Lyon 1 Laboratoire des matériaux plastiques
43 Bd du 11 Novembre 1918 69622 Villeurbanne Cedex, France
(2) School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501, Japan

Abstract

There is an ever increasing need for better quality control of polymers and polymeric composites in order to improve product quality and reduce production costs. Measurements need to be performed rapidly and give precise chemical and physical information to enable a good understanding to be made of the parameters leading to higher quality products. NIR spectroscopy is ideally suited for studies of a large variety of composites and requires minimal sample conditioning. The composition, degree of conversion, crystallinity, water content and interaction, and filler content can be monitored in real-time using NIR spectroscopy. Moreover, the water content and the water interactions can be analyzed simultaneously. Water can be used therefore as a probe molecule to study polymers and composites.

Key words: NIR, near infrared spectroscopy, in-situ analysis, polymer, water, hydrogen bonding, composite.

Introduction

Although near infrared (NIR) absorbances of polymeric materials are often broad and overlapped, spectroscopic studies of polymers and polymeric composites can often be carried out in the similar manner to those by which the investigations are made for the mid IR region, using peak absorbance changes of functional groups, intensities or peak locations. NIR spectroscopy, as a rapid and non-destructive method, has been successfully used in various ways for the polymer characterization. Unfortunately, too often for many researchers, NIR is mainly applied as an empiric technique using statistical packages because of the difficulties associated with the bands assignments.

Nevertheless, studies of spectra and intramolecular dynamics of coupled vibrational high energy states of small polyatomic molecules have progressed markedly, due to some sophisticated experimental techniques, (1-4). For large molecules, the potential of generalized two dimentional (2D) FT NIR correlation spectroscopy (5) has begun to be applied to investigate structural changes of

CCC 1022-1360/99/$ 17.50+.50/0

polymers, leading to a better fundamental understanding of the inter- and intramolecular interactions and of conformational changes. Based on this approach, the assignment of the bands is facilitated.

Some examples of the use of NIR transmission spectroscopy for water analysis in the field of polymers and composites are presented and reviewed in this paper.

Experimental

Commercial and laboratory made samples of epoxy /glass fiber, (polyamide 6 (PA 6)/glass fiber and polyethylene terephthalate (PET) / glass fiber composites (sample A, long fibers ; samples B and C, short fibers), 0.8 to 2mm thick, between 20 and 50 per cent of fiber by weight and with different coatings were investigated. Before soaking, the PET samples were dried in a desicator at 40°C until at constant weight, the other samples were dried in an oven at 110°C.

NIR spectra were recorded with a Perkin Elmer FTIR 2000 (Beaconsfield, UK) fitted with a ceramic light source, a KBr beamsplitter and DTGS (deuterated triglycine sulfate pyroelectric crystal) detector, fitted with a KBr window. Spectra were recorded at 4 cm^{-1} resolution in transmission, between 50 and 200 scans being recorded per spectrum.

Results and Discussion

Transmission spectroscopy in the mid-IR region is restricted by the strength of absorption bands, limiting the study of polymers mostly to very thin samples. Many composites may only be examined using reflection spectroscopy, due to the high absorbance of the reinforcing materials in the fingerprint region.

Diffuse Reflectance (DRIFT) in the mid-IR region has been used successfully to investigate sizing and glass fiber/polymer composites (6). However this technique requires sample preparation, e.g, cutting or grinding and blending with a non-absorbant matrix. Also the radiative properties of fibrous samples depend on the relative orientation of the incident beam radiation with respect to the fiber axis (7). Furthemore, the particle size strongly affects the spectra and the high level of mid-IR absorbance necessitates dilution of the sample in powdered alkali halides (8).

Internal Reflection Spectroscopy (IRS or ATR) can be used to characterize the surface of polymer (9). It can be used also to study the interface between the fiber and the polymer by modeling of the fiber surface by the surface of the ATR crystal (10). The main advantage of this technique is its ability to study the interphase in-situ, for example, reactions between amino silanes (sizing agents of fibers) onto the ATR crystal and epoxy resins. The main disadvantage of this technique is that the chemical composition of the model flat surface, the IRS element, is different from the real fiber surface so that the surface effects upon the kinetics of a reaction may be modified.

In contrast, due to the lower coefficient of extinction of the absorption bands in the NIR region thicker sample (ca 1-10 mm thick) can be studied by transmission. In addition, the transparency of glass (and some mineral fillers) in the NIR region allows examination of glass-reinforced composites. The overall NIR signal level of composite (unidirectional or glass cloth) is generally reduced from 10% to 30% of the value obtained with the polymer alone mainly because of scattering of the light. Nevertheless the quality of NIR spectra are good enough for composites studies and the control. Scattering losses generally increase with a poor wetting of fibers by the polymer. Even if small spectral modifications are observed due to the effects of refractive index of dispersion on reflection at interfaces, these effects are limited by the weak refractive index of dispersion of NIR bands.

CRYSTALLINITY

The near-IR spectra of glass / PET composites up to 2 mm thick can be recorded using an FT-IR spectrometer configured for mid-IR use. The noise level is generally adequate (for 50 scans and up) in the 4000-5500 cm^{-1}. However the absorbance level may be too high for precise quantitative measurements for thicker samples. The use of higher overtones with a dedicated NIR spectrometer allows thicker pathlenghs to be used. Valuable qualitative information are still available and the 4000 - 4500 cm^{-1} region seems very informative (11), particulary with developments of new light fibers allowing remote sensing applications in this region (12). The comparison between spectra of the matrix alone and spectra of the composite, following the same thermal treatments, may be used to study wether fibers (and the sizing treatment) act as a nucleating agent for the matrix. Raman spectroscopy and FTIR coupled with photoaccoustic detection have been shown to be useful tools for the studies of quantitative structural changes taking place in PET and PET-glass composite during the annealing process (13,14). These lastest techniques give information essentially only on the surface of the composite.They can therefore be a very useful complement to NIR transmission spectroscopy in comparison of the surface and the bulk of a polymeric material.

DEGREE OF CONVERSION

The cure of epoxy composites may be monitored in the same way as for epoxy formulation(15-18). Differential Scanning Calorimetry (DSC) can be used to check the curing state of the resins, although the kinetic mechanisms obtained by DSC values are questionable (19). The advantage of NIR spectroscopy, in comparaison with DSC, is its ability in real-time monitoring of each functional group simultaneously.

The influence of the fibers and of the coating upon the curing and the kinetics of the reaction between the epoxy resin and the hardener can be studied in-situ. On-line measurement of the degree of cure of printed circuit card (glass/ epoxy) substrates have been installed in many production sites (20). The NIR transmission sensor allows control of degree of cure by closed loop control of the drying tunnel. Cellulosic fiber or aramide fiber-polymer composites can be also studied by NIR even tough some matrix and fibers bands are overlapped; however the opacity of carbon fibers generaly hinders the examination of carbon composites (21) .

WATER CONTENT and WATER INTERACTIONS

The combination and overtone bands of water have been widely used, for instance, for satellite determination of crop yields, to study aqueous electrolyte solutions (22) or determine the moisture content of food or chemical products. In addition, with this technique it is possible to distinguish water from the hydroxyl groups belonging to the polymer.

Near infrared spectra of pure water have been studied by Buijs and Choppin (23,24) and by Vand and Senior (25). These authors proposed that the water was composed of three molecular species differing in their level of hydrogen bonding. Tables of absorption band positions and molecular extinction coefficients of water and heavy water have been presented by Baly et al. (26). More recently, Abe et al. (27) applied a curve fitting technique to analyse the fine structure of the NIR spectra of water, while Maeda et al. (28) studied the temperature-dependent spectral variations in NIR region of the spectrum of water, and relationships between spectral changes and hydrogen bonds.

The ability to monitor water uptake is a particularly noteworthy feature of the infrared spectroscopy techniques. Methods based on FTIR ATR spectroscopy have been developed for measuring the diffusion of water in the polymer coated onto an internal reflection crystal (29,30). However the water migration through a free sample and an applied film may not be the same (31). Also the cleaning of an expensive ZnSe or Se crystal is sometimes difficult or impossible. Molar absorptivity of water bands depends on the environment and requires calibration for each material (32). In the NIR range two main bands at about 5200 and 7000 cm^{-1} are sensitive to the water content of sample under investigation. The 5200 cm^{-1} band is assigned to a combination band of stretching and bending ($\nu_{asOH} + \delta_{OH}$). The diffusion of the water and the nature of the water sorbed within polymeric materials can be investigated using these bands (32-35). Recently, NIR spectroscopy has been applied to determine the water permeability of coating on plastics lenses (36); the area of the peak of the water combination (between 5010 -5370 cm^{-1}) changed linearly with the water content, the peak located at 5820 cm^{-1} is not influenced by the moisture uptake and has been used as an internal standard. Measurements at different points of coated surfaces may be made in order to detect heterogeneities.

This combination band shifts according to the strength of hydrogen bonding. However, the stretching band shifts to lower wavenumber while the bending band shifts to higher wavenumber (37), so that this band is not very suitable for quantitative studies of the strength of hydrogen bond formation (34). Using principal component analysis, Dreassi et al. (38) have investigated interactions between the skin and water or lipids. In this study, an interesting displacement of the peaks was observed in the region attributable to the first overtone bands of water, whereas no shift was observed for the combination band. Nevertheless, useful information can be obtained about the nature of adsorbed water and the process for diffusion of water (35). Also, the 5200 cm^{-1} band is often less overlapped than the 7000 cm^{-1} band.

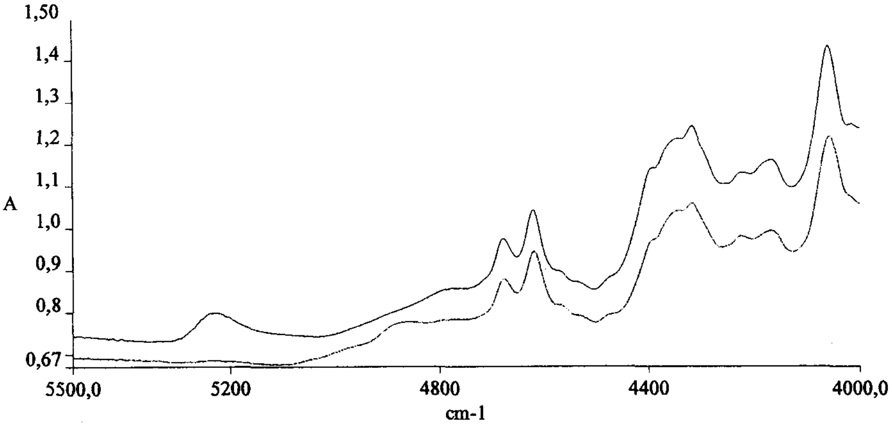

Fig. 1: Epoxy glass-cloth composite (commercial printing board substrate) Dried sample (bottom), immersed in water for one week (top)

For an epoxy (with amine hardener) glass composite, the water band is located near 5240-5220 cm^{-1} (figure 1). The peak position for a given formulation is not affected by the water level (within 2 cm^{-1}), although this peak may shift to near 5200-5180 cm^{-1} for a partialy cured matrix or a non-stoichiometric formulation, probably due to water-amine interactions. With increasing water content, a shoulder seems to appear near the 5000 -5100 region. The shape of the water overtone bands seems also to be modified, probably due to the interaction changes of hydroxyl groups of the epoxy resin formed as a consequence of the opening of oxirane rings. However neither the position nor the intensity of C-H combination or overtone absorption bands are modified by the water uptakes for fully DGEBA cured resins. Although, very strong modifications have been observed throughout the NIR spectrum for an cyclo-aliphatic epoxy resin cured with an aromatic diamine (35). Not only, was the peak position of water combination band shifted but a doublet appeared as the time of soaking increased. The intensity of the first CH overtone is also affected strongly.

Theoretical and practical studies of the influence of hydrogen bonding on the near infrared spectra, and information concerning the intensity and the position of overtone and combination bands have been presented by Sandorfy (39 and ref therein).

For hydrated PET-glass composites, the water band absorbs near 5240 cm^{-1}, suggesting weakly bonded water molecules (figure 2), in good agreement with mid IR measurement of PET films (40). The peak position of this combination band is not affected by the amount of water.

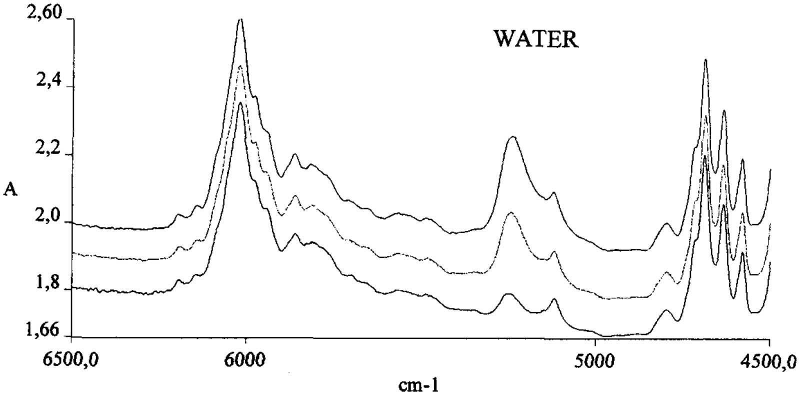

Fig. 2: PET glass fiber (2mm thick): upper curve, composite water soaked (1 week), middle curve, composite water soaked (1 month); lower curve, composite stoked in the laboratory

In contrast, the band of water is shifted to near 5150 cm^{-1} for a glass fiber-nylon 6 composite, indicating strong hydrogen bonding (figure 3), and is in good agreement with NIR studies of the nylon matrix (33). The amide I + $(\nu)_{NH}$ and amide II + $(\nu)_{NH}$ combination bands near 5000 cm^{-1} are also affected by the water content confirming the high sensivitivity of tNIR spectroscopy for hydrogen bonding studies. To a first order for the composite, the glass fibers donot shift the water peak for this sample.

In some composites the water band shapes differ somewhat from the water bands of the polymeric matrix (figure 4). Broading or shifting of the water band can be observed for the samples B and C (composites with the short fibers coated with different aminosilane sizing) suggesting that new sites are accessible (due to matrix modifications or fiber interactions). Severe deterioration of mechanical properties of the samples B and C are observed after evaporation of water, in contrast with the good behaviour of sample A. For this study, NIR can be more informative than gravimetric methods (31-32).

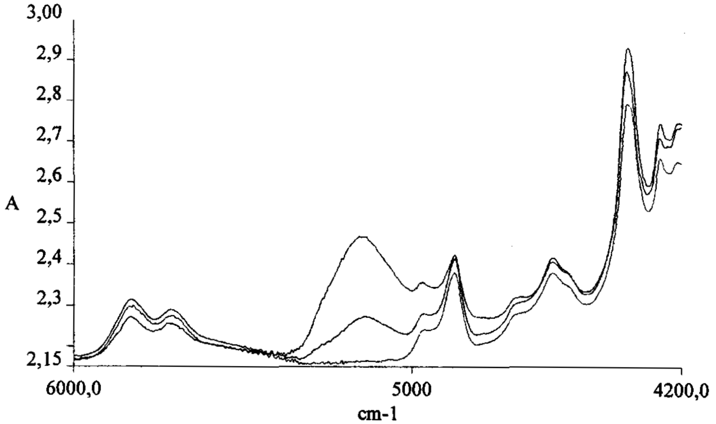

Fig. 3: NIR spectra of Polyamide 6 Glass fiber, dried composite (botton), stoked in the laboratory (middle), immersed in the water (top)

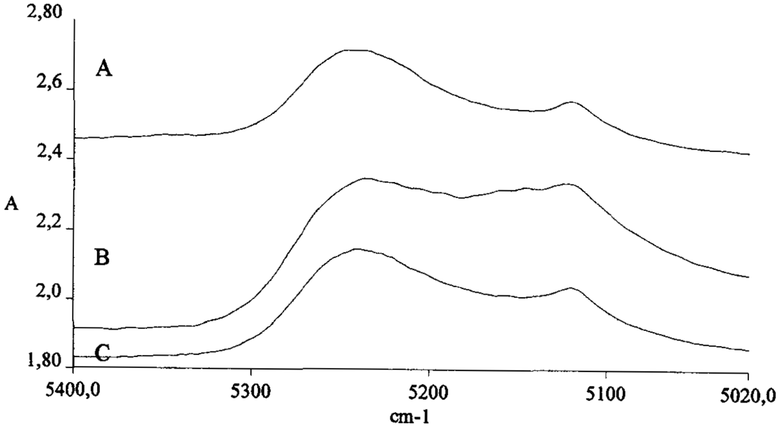

Fig. 4: NIR spectra of PET glass fiber composites: upper curve, composite A same as fig 2; middle curve, composite B short fibers, coating 2; lower curve, composite C, short fibers, coating 3 (new absorption bands appear near 5200-5150 for B and C)

Hydrothermal aging at elevated temperature tends to induce degradation in epoxy resins (41). The gravimetric results show a weight increase during the initial aging process period followed by a decrease at a later time. This degradation process is complex and NIR spectroscopy can aid the understanding of the mechanisms involved in this aging process of resins, and also of composites. The water molecules maybe used as a probe to study composites and sizing, however the contribution between the different types of bounded water species is difficult to assess, and needs careful studies of band shapes and positions.

The combination peak positions of the water sorbed in some polymers and composites are sumarized (Tab. 1).

	wavenumber, cm^{-1}
Water vapor	5320
EPOXY glass fiber EPOXY glass fiber, printed circuit substrate	5220 5240
PET long glass fiber coating 1	5245-5240
PET short fiber glass coating 2 or 3	5240-5150 (bands overlapped)
PA 6 glass fiber	5150
PES/ EPOXYblends	5220-5530

Table 1. Positions of water combination band ($\nu_{as}OH + \delta_{OH}$)

Surface treatments of reinforcing fibers are very effective in making a useful interface between the matrix and the fiber. Therfore it is important to analyse ***in-situ*** the surface of reinforcements after the sizing treatments. NIR spectroscopy is very useful for examining textile materials (42), where a rapid and reliable determination of finishing oil content on fibres is necessary to improve productivity and product quality. Recently, the potential of NIR light fiber optics spectroscopy has been demonstrated for direct analysis (without any sample pretreatments) of sizing agents on glass fiber or aramid knitted fabrics, used as reinforcement for the composites (42), and for the rapid determination of finishing oil in acrylic fibers (43). These studies are promising for the direct studies of prepregs quality and aging.

Conclusion

Studies in the NIR region often allow more realistic polymeric samples to be examined than the classic transmission technique in the mid-IR region, where very thin samples must often be used. Some problems associated with mid-IR sampling are alleviated through the use of NIR spectroscopy. Information on water uptakes in the polymeric materials and the degree of hydrogen bonding must be observed by NIR spectroscopy, but the type of hydrogen bonding have to be taken into account for quantitative analysis. Water can be used as a probe molecule to study polymers and composites. The capabilities of NIR spectroscopy make this technique very suitable for rapid and non-destructive analyse of polymeric composites, providing ease of sampling, low cost and high reliability even tough band assignments are generally complexe and for these are conflicts of opinion. Good quantitative results of NIR are achieved in conjunction with multivariate procedures, better interpretation of NIR spectra can open up the opportunity for gaining useful information for studying interaction and hydrogen bonding.

References

1 M. Quack, *Annu. Rev. Phys. Chem.*, **41**, 839 (1990).
2 H.G. Kjaergaard, R.J. Proos, D.M. Turnbull and B.R. Henry, *J. Phys. Chem.*, **100**, 19273 (1996).
3 D. Lucklaus, J.M. Coffey, M.D. Fritz and F.F. Crim, *J. Chem. Phys.*, **104/10**, 3472 (1996).
4 G. Lachenal, *In : "Méthodes d'analyse rapide par spectroscopie dans l'infrarouge proche et moyen"* (D. Bertrand, Ed.), Lavoisier, Paris, in press.
5 Y. Ozaki, Y. Liu and I. Noda, *Macromol. Symp.*, **119**, 49 (1997).
6 M.K. Antoon, R.E. Sacher and J.L. Koenig, *Polym. Comp.*, **2/2**, 81 (1981).
7 C.R. Bull, *Analyst*, **116**, 781 (1991).
8 M. Papini, *Vibrational Spectrosc.* , **11**, 61 (1996).
9 M. Urban, in *Attenuated Total Reflectance Spectroscopy of Polymers*, ACS, Washington DC (1996).
10 A. Garton, in *Fourier Transform Infrared Characterization of Polymers*, ed. H. Ishida, Plenum Press, New York, p 363 (1987).
11 G. Lachenal, *Int. J. Polym. Anal. Charact.*, **3**, 145 (1997).
12 H. Maeda, Y. Ozaki, I. Noda, Y. Mimura, T. Nakai and T. Tani, *J. Near Infrared Spectrosc.* , **3**, 43 (1995).
13 J.C. Rodriguez-Carbello, J.C. Merino, M.R. Fernandez and J.M. Pastor, *J. Raman Spectrosc.*, **27**, 23 (1996).

14 L. Quintanilla, M. Alonso, J.C. Rodriguez-Carbello and J.M. Pastor, *J. of Appl. Polym. Sc.*, **59**, 769 (1996).
15 G. Lachenal, A. Pierre and N. Poisson, *Micron* , **27/5**, 329 (1996).
16 B. Chabert, G. Lachenal and C. Vinh Tung, *Macromol. Symp.*, **94,** 145 (1995).
17 N. Poisson, G. Lachenal and H. Sautereau, *Vibr. Spectrosc.*, **12**, 237 (1996).
18 G. Lachenal, N. Poisson and H. Sautereau, *Macromol. Symp.*, **119**, 129 (1997).
19 G. Lachenal and I. Stevenson, *NIR news*, **6/2**, 10 (1995).
20 I. B. Benson, in: *Near Infrared Spectroscopy: The Future Waves*, A.M.C. Davies and P. Williams eds, NIR Publication, Chichester U.K., p 239 (1996).
21 A. Garton,*"Infrared Spectroscopy of Polymers Blends, Composites and Surfaces"* Hanser, Munich (1992).
22 W.A.P. Luck, in: *Water in Polymer* , S.P. Rowland ed., ACS, Washington, p 43 (1980).
23 K. Buijs and J.R. Choppin, *J. Chem. Phys.* , **39**, 2035 (1963).
25 V. Vand and W.A. Senior, *J. Chem. Phys.*, **43,** 1878 (1965).
26 J.G. Baly, V.B. Kartha and W.H. Stevens, *Infrared Physics*, Vol 3, Pergamon Press UK, p 211 (1963).
27 T. Kusama, S. Kawano and M. Iwamoto, *Bunkou-kenkyu (J. Spectrosc. Soc. Japon)*, **44**, 247 (1995).
28 H. Maeda, Y. Ozaki, M. Tanaka, N. Hayashi and T. Kojima, *J. Near Infrared Spectrosc.*, **3**, 191 (1995).
29 C. Sammon, N. Everall, J. Yarwood, *Macromol. Symp.*, **119**, 189 (1997).
30 T. Nguyen, E. Byrd, D. Bentz and C. Lin, *Int Conf. Coatings Sc. and Tech.*, Athens, Greece, pp 401-420 (1994).
31 H.N. Rosen and J.M. Martin, *J. Coat. Tech.*, **63/792**, 85 (1991).
32 G. Lachenal, *Vibr. Spectrosc.*, **9/1**, 93 (1995).
33 M. Fukuda, M. Miyagawa, H. Kawai, N. Yagi, O. Kimura and T. Otha, *J. Polym.*, **19**, 785 (1987).
34 M. Fukuda, H. Kaway, N. Yagi, O. Kimura and T. Otha, *J. Polym.*, **31**, 295 (1990).
35 J. Derouault, in *Advances in practical spectroscopy, proceeding of ESIS*, G. Lachenal, H.W. Siesler Eds, UCB, Lyon, Fr, p 41 (1994).
36 U. Schulz and N. Kaiser, *Appl. Optics*, **36/4**, 862 (1997).
37 G.C. Pimentel, A.L. Mc Clellan, in *The Hydrogen Bond*, W.H. Freeman and Co, San Fransisco, pp 108-112 (1960).
38 E. Dreassi, G. Ceramelli, L. Fabbri, F. Vocioni, P. Bartalini, P. Corti, *Analyst*, **122/8**, 767 (1997).
39 C. Sandorfy, *Bull. Polish Acad. Sci., (Chemistry)*, **43**, 7 (1995).
40 D.R. Rueda, A.Viksne, J. Kajaks, F.J. Balta-Calleja and H.G. Zachmann, *Macromol. Symp.*, **94**, 259 (1995).
41 M.E.R. Shanahan, G.Z. Xiao, *J. Polym., Sc.*, Part B, **35**, 2659 (1997).
42 K. Kitagawa, S. Hayasaki, Y. Ozaki, *Vibr. Spectrosc.*, **15**, 43 (1997).
43 J. Coello, J.M.G. Fraga, H. Iturriaga, S. Maspoch and J. Pages, *Analyst*, **122/8**, 777 (1997).