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On the Use of Vibrational Spectroscopy to Characterize the Structure and Aroma Barrier of Food Packaging Polymers

J. M. Lagarón,[*1] *D. Cava,*[1] *E. Giménez,*[2] *P. Hernandez-Muñoz,*[1] *R. Catala,*[1]
R. Gavara[1]

[1]Packaging Lab., Institute of Agrochemistry and Food Technology, CSIC, Apdo. Correos 73, E-46100 Burjassot, Spain
E-mail: lagaron@iata.csic.es.
[2]Dpt. Of Technology, Area Materials, University Jaume I, Castellón 12071, Spain

Summary: High barrier polymers are of increasing interest and use in nowadays food packaging applications. The reason for that is packaging being more often regarded as a very efficient and convenient means of preserving foodstuffs from deterioration during products handling, transport and shelf-life. This study reports on some novel morphological characterization aspects by means of vibrational spectroscopy of one of the most widely used families of high gas and aroma barrier materials in commercial food packaging, i.e. the ethylene-vinyl alcohol copolymers (EVOH). Nevertheless, and as a result of the highly hydrophobic character of the EVOH resins, it is usually low density polyethylene (LDPE) the high water barrier material that is put in direct contact with foods. A description of a simple methodology, yet effective, based on FT-IR to determine diffusion coefficients of aroma components in LDPE is also presented.

Keywords: barrier properties; EVOH copolymers; Raman and Infrared spectroscopy

Introduction

The introduction of polymer based structures as packaging materials for foodstuffs has been increasing over the last decades. The main commercial appealing of these materials lays on their ability to offer a broad variety of tailor-made properties and yet be cheap, and easily processed and conformed into a myriad of shapes and sizes. Given the diversity of food products and the various packaging requirements of those, a large number of packaging technologies have also been put into place, i.e. multilayer structures, modified and equilibrium modified atmosphere packaging, active packaging, etc.[1]

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Nevertheless, one of the limiting properties of polymeric materials in the food packaging field is their inherent permeability to low molecular weight substances, including permanent gases, water and organic vapours. This has boosted the interest for developing new resins with higher barrier properties and to carry out research aimed at the understanding of the structure/barrier properties relationship. The most efficient and widely used high barrier polymeric materials are the ethylene-vinyl alcohol copolymers (EVOH), although there are also other new high barrier material developments and specific improvements like perfectly alternating aliphatic polyketones [2] and thermoformable EVOH-based blends [3], respectively.

According to the above, barrier properties in polymers are necessarily associated to their inherent ability to permit the exchange, to a higher or lower extent, of low molecular weight substances through mass transport processes like permeation. The permeation of low-molecular weight chemical species most usually takes place through the polymer amorphous phase and is generally envisaged as a combination of two processes, i.e. sorption and diffusion. A permeate gas is first sorbed into the upstream face of the polymer film, and then, undergoes a molecular diffusion to the downstream face of the film where it desorbs into the external phase again. A sorption-diffusion mechanism is thus applied, which can be formally expressed in terms of permeability (P), being this the product of solubility (S) and diffusion (D) coefficients, as defined by Henry's and Fick's laws, respectively.

The excellent properties of EVOH resins in terms of high gas, hydrocarbon and aroma barrier, and transparency have allowed them to become widely implemented in many commercial applications where high barrier is needed to minimized product losses or deterioration. Despite the excellent performance of these materials in high barrier food packaging applications, the materials are easily plasticized by moisture and, consequently, in most packaging applications are commonly encapsulated in multilayer structures between hydrophobic polymers like polypropylene or polyethylene.

Polyethylene is in terms of volume the most widely used polymer in food packaging applications. This polymer is most often used as inner layer in direct contact with foodstuffs due to its excellent water barrier, inertness and thermosoldability characteristics at a very low price.

As a result, finding appropriate and advantageous characterization methodologies for these materials in terms of morphology and barrier properties is of significant relevance. In this context, vibrational spectroscopy can potentially offer many advantages of which we report in this paper some examples.

Experimental

The high barrier EVOH resins used (Soarnol^{TM}) corresponded to 10 and 75 µm thickness films of ethylene-vinyl alcohol copolymers supplied by The Nippon Synthetic Chemical Industry Co., Ltd. (NIPPON GOHSEI) (Japan) with ethylene mol% contents of 29 and 32, named throughout the manuscript as EVOH29 and EVOH32. A general purpose extruded low density polyethylene, LDPE, grade (80 µm thickness) for use in contact with foods was also supplied by NIPPON GOHSEI, and an ex-reactor perfectly alternating ethylene-carbon monoxide copolymer, PK, in powder form was kindly supplied by BP Chemicals (UK).

Samples were measured by FT-Raman using a FT-IR, NIR-FT-Raman Perkin-Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU with a spectral resolution of 2 cm^{-1}. Transmission IR experiments were carried out with the Tensor 37 from Bruker with 1 and 4 cm^{-1} (in the case of evaluating diffusion coefficient) resolution.

Morphological aspects

Vibrational spectroscopy has proven to be an excellent tool for the characterization of physical parameters in polymeric materials, including chain conformational order, which is generally within the polymer crystals. Nevertheless, this technique has not been extensively used, from this morphological point of view, to characterize EVOH materials, and it is therefore of interest to asses the possibilities of this technique to tackle this particular topic.

It is common knowledge that by changing the thermal history of a polymer, one can often produce a number of significant morphological changes. Thus, by modification of the kinetics of crystallization, it is, for instance, possible to increase or decrease the degree of metastability, and as a result, alter the way in which polymer chains are allowed to pack within crystals. Consequently, it is very desirable to have means of rapid identification of the particular morphologies arising from different thermal histories. Figure 1 (left) shows two Raman spectra in the range of -CH_2- bending of an EVOH29 copolymer (comprising 29 mol% of ethylene) exhibiting clear differences. These spectra were recorded on specimens obtained by slow cooling from the melt (15°C/min) and by direct quenching in water. In the crash cooled sample, there is a band present at 1424 cm^{-1}, which is assigned, by analogy with polyethylene, to one of the components of the factor group splitting of the orthorhombic symmetry. This band, is absent or appears shifted, at ca. 1429 cm^{-1} (and largely overlapped with the other splitting component at 1440 cm^{-1}), in the slow cooled sample. From supporting wide angle X-ray scattering (WAXS) results (Figure 1, right), it becomes apparent that a thermodynamically more stable monoclinic crystalline morphology is established on the slow cooled specimen, whereas a less stable and lower crystalline density orthorhombic morphology is formed by quenching from the melt [4,5]. The reason for the differences in the -CH_2- bending range are attributed to the fact that this vibrational mode is very sensitive to unit cell intermolecular interactions resulting in factor group splitting. The high sensitivity, in terms of splitting, of this particular mode arises from (i) the fact that it involves a motion perpendicular to the chain direction and, possibly, from (ii) interaction enhancement due to Fermi resonance. This spectroscopic phenomenon has now been known for many years and affects, to a different extent, the vibrational spectrum of a number of polymers [6 and therein]. Nevertheless, this is the first time that this phenomenon is reported in the Raman spectrum of EVOH copolymers. Curiously enough, the factor group splitting phenomenon appears stronger, i.e. higher interaction and therefore separation of the splitting components, in the lower crystalline density structure of the crash cooled sample (with orthorhombic morphology analogous to the one of orthorhombic polyethylene) than in the higher crystalline density packing of the monoclinic symmetry (more similar to the one corresponding to the parent polymer polyvinyl alcohol). The reason for that is attributed to a very different arrangement of the chains in the monoclinic cell symmetry [5], where the hydroxyl groups are more efficiently facing each other to enhance intermolecular interactions through hydrogen bonding, and this probably results in weakening of the -CH_2- groups intermolecular interaction.

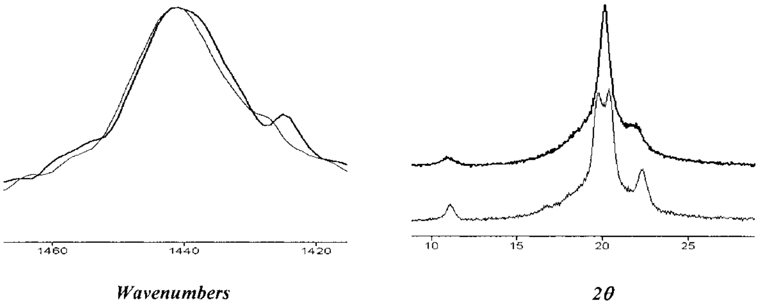

Figure 1. Raman spectra in the CH_2 bending range (left) and WAXS patterns (right) of crash cooled (thicker line) and slow cooled EVOH29

Vibrational spectroscopy can also be of help to determine the degree of crystallinity of EVOH copolymers due to the presence in the IR spectrum of these materials of bands at 1140 cm^{-1} and at 1093 cm^{-1}, which have been assigned to all-trans, mostly within a crystalline environment, and gauche, mostly within amorphous regions, conformers, respectively (see Figure 2). In Figure 2, while the 1140 cm^{-1} band increases intensity with increasing crystallinity, the 1093 cm^{-1} band decreases intensity. A reliable determination of the degree of crystallinity, even from a relative view point, by means of more conventional techniques like DSC and WAXS has proven to be a very difficult task to do for these copolymers, due to a number of reasons that have been outlined elsewhere [7]. However, by considering these two bands and a methodology previously described and successfully applied to other polymers [8], an estimation of the degree of crystallinity can be obtained for these materials [9].

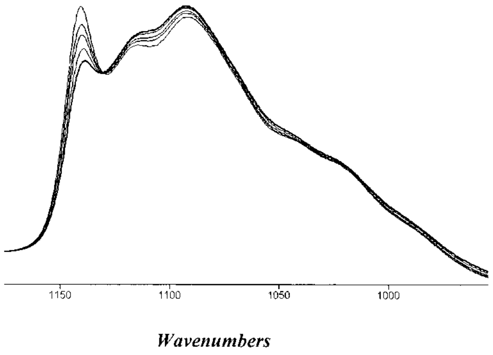

Figure 2. FT-IR spectra of EVOH32 samples with different crystallinity levels obtained by annealing

The use of these very sensitive bands to provide information about alterations in the degree of order present in the polymer can be very helpful to quickly ascertain particular effects occurring in the polymer as a result of different treatments. For instance, it is found for these polymers that annealing leads to an expected increase in crystallinity due to thermally-activated molecular rearrangements. On the other hand, Figure 3 shows that annealing in the presence of water vapour in an autoclave, treatment simulating an industrial food retorting process, leads to a decrease in the intensity of the 1140 cm^{-1} band, and therefore, to some crystallinity disruption. Crystallinity losses or alterations are usually detrimental in high barrier packaging applications because they lead to increased permeability of potentially damaging low molecular weight gases and vapours. The morphological alterations subjected by these polymers in the presence of temperature and water vapour have, to the best of our knowledge, never been shown or expected before, but clearly support the need, during industrial implementation of these materials in retortable food packages, for multilayer structures comprising as outer layers highly hydrophobic materials to protect EVOH from the damaging humidity effect [9].

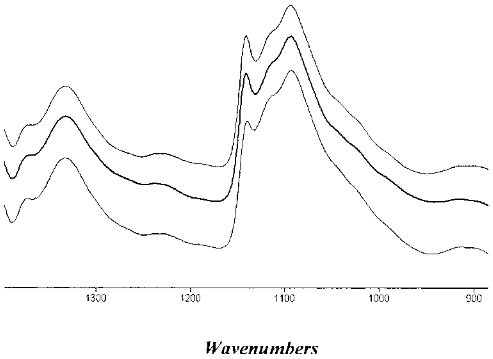

Figure 3. FT-IR spectra of an EVOH29 sample untreated (middle) annealed at 100°C in an oven (top) and retorted at 100°C (bottom) in an autoclave

Temperature-induced chemical modifications are also a concern during processing of most polymers, because inappropriate drying or processing temperatures, processing machinery and screw designs, and residence times can affect the properties and performance of these materials in real applications. Vibrational spectroscopy is most adequate in terms of sensitivity to identify chemical alterations for the analysis of polymeric materials and, therefore, to help design optimum processing protocols and conditions. Figure 4 shows two examples, where vibrational spectroscopy has made it possible to follow structural and chemical changes occurring in high barrier polymers, EVOH32 and PK, as a result of thermally-induced chemical alterations.

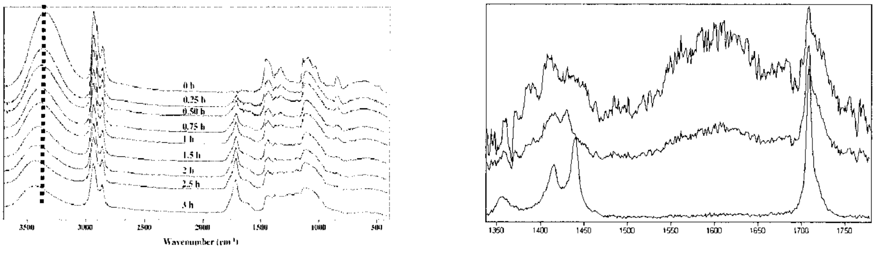

Figure 4. FT-IR spectra (left) of EVOH32 taken after thermal treatment at 200°C during several time intervals; and FT-Raman spectra (right) of a PK sample recorded, from bottom to top, on the untreated sample and after thermal treatments at 270°C during 5 and 30 minutes

Figure 4 shows for the case of a solvent cast EVOH32 specimen (maximum of melting by DSC at 183°C) that during isothermal treatments at various time intervals in an oven the polymer begins to develop some chemistry, which is clearly reflected in the 1700 cm^{-1} range. Simultaneously, a decrease in intensity and a shift towards higher wavenumbers of the O-H stretching band can be seen. From previous results [10], the cited features appear clearly in the spectrum between 15 and 30 minutes after exposure at 190°C, and, as can be seen in Figure 4, before 15 minutes at 200°C. In particular, a band emerges at ca. 1712 cm^{-1} with a low and a high wavenumber contribution. This band at 1712 cm^{-1} and perhaps the higher wavenumber contribution are assigned to C=O stretching modes. The low wavenumber component could arise from the creation of some double bonds in the polymer chain. Accordingly, the experiments suggest that the transformation of the polymer goes, at least in the first instance and in a first approximation, through the formation of (i) carbonyl groups at expenses of the OH groups and of (ii) some double bonds in the polymer chain. Some other minor changes also occur in the IR spectrum of the samples, which would in principle support the transformation of the OH groups. Thus, the bands at ca. 1331 cm^{-1} and 1455 cm^{-1} assigned to O-H deformation, show a tendency to vanish in the treated samples.

Property-wise, it is worth noting the significant reduction in intensity and shift towards higher wavenumber (cm^{-1}) of the OH stretching band as temperature exposure progresses. This band is confidently assigned to hydrogen-bonded O-H stretching vibrations. This vibration is not a conformationally sensitive mode; therefore, its broadness is thought to arise from a distribution of hydrogen bonded O-H groups of varying strengths and geometries; these coming from intra- and inter-molecular hydrogen-bonded OH dimer and multimers. As the excellent barrier properties of this material arise from intense hydrogen bonding provided by the hydroxyl groups, and as the band decreases intensity and shifts towards higher wavenumbers hence indicating that the number of high barrier elements and the overall strength of the hydrogen bonding diminish over time, it is clear that barrier properties are being reduced as a result of excess high temperature exposure.

Figure 4 shows Raman results clearly indicating that the PK copolymer (with maximum of melting by DSC at 255°C) also undergoes chemical modifications at temperatures immediately above its melting point. This is one of the reasons why industrial developers pursue PK commercial grades comprising a second α-olefin substituting randomly for ethylene to produce tailor made terpolymers with adequate melting points and properties and, therefore, more viable from a commercial point of view [2]. In Figure 4, one can easily observe that upon heating the polymer for over a certain period of time, the Raman spectra exhibit some chemistry developments in the 1600 cm^{-1} range, which have been ascribed to the formation of conjugated double bonds chemistry. These are likely to be created at expenses of the carbonyl groups (spectroscopically seen in the 1700 cm^{-1} range) present in a 50 mol% proportion across the polymer chains. The carbonyl groups are essential to the polymer because they form strong dipolar inter- and intra-molecular interactions that render the material high barrier. As a result, barrier properties can be detrimentally affected by excess thermal exposure of the PK copolymer. Additionally, Figure 4 also indicates crystallinity decrease (band broadening) and solid-solid phase transformation from the alpha crystalline phase (denser) to the beta (more defective) form as indicated by the clear changes in the CH_2 bending range between 1400-1450 cm^{-1}. This vibrational mode exhibits a very clear and intense factor groups splitting phenomenon in these polymers, which has been well characterized in previous works [11].

Vibrational spectroscopy applied to the characterization of transport properties

As mentioned earlier, polymers are permeable materials to the transport of low molecular weight molecules including gases, water and organic vapours, oligomers, additives and inks. However, by appropriate molecular design of the chemistry comprising the polymer macromolecules, material developers have been able to vary polymer oxygen permeability by over five orders of magnitude. Moreover, and for a given chemistry, changing morphology and molecular architecture, including additives or fillers, blending and coating, or by using different processing technologies, it is possible to alter the barrier properties of a material to a significant extent. As a result of that, evaluating barrier properties has become a very heavily researched field for product manufacturers, applied and fundamental researchers. Consequently, finding appropriate and reliable means to measure transport properties of penetrants is of key importance.

Most of conventional techniques existing today, for measuring barrier properties, are gravimetry and permeation coupled with various kinds of detection methods. Some of these testers make use of FT-IR as detection for quantitative purposes, particularly for carbon dioxide and water. Nevertheless, vibrational spectroscopy has a tremendous potential in this field not only to evaluate solubility (penetrant uptake) but also for direct measurements of diffusion coefficients, and therefore, permeability ($P = S \times D$) of various penetrants in polymers. Some studies can already be found in the literature were FT-IR (through mostly the use of an ATR accessory) has been used to determine diffusion coefficients of, mostly, water vapour in various polymers [12,13,14,15]. The use of an ATR accessory has the drawback of measuring the properties of the very near surface of a polymer, in some cases obtained by casting from solution to achieve and ensure a good adhesion between the ATR crystal and the film, and of having a complex relationship between absorbance and concentration [15]. Most films used in food packaging are, however, obtained by extrusion processes, which yield a thin heterogeneous sample in terms of morphology along the thickness; therefore, it is more preferable to measure averaged properties across the whole film thickness.

Generally, the FT-IR technique offers the advantages, when measuring transport properties, of being capable of measuring the simultaneous permeability of various penetrants and of assessing penetrants/polymer interactions, by way of analyzing band shifts and band shape changes. Furthermore, FT-IR is also advantageous as compared to, for instance conventional gravimetry, for evaluating transport properties through very thin films, because these films are usually difficult to handle and depending on penetrant uptake may even be below the limit of detection of conventional gravimetry.

In this paper, we will show some pioneering results about the use of transmission FT-IR to determine the diffusion coefficient of standard citric fruit juices essence oil aroma components through an 80 μm extruded film of low density polyethylene (LDPE). Figure 5 shows typical substraction FT-IR spectra of a chosen band characteristic of limonene as a function of time during desorption from LDPE.

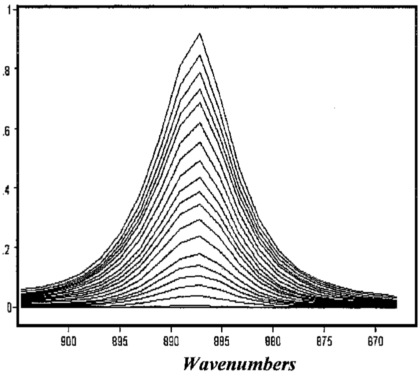

Figure 5. Substraction spectra from a completely desorbed LDPE sample of a CH deformation mode of limonene as a function of time

By fitting the relative area of the chosen band (A_t/A_e) as a function of time to the modified solution form of the second law of Fick [16] for a desorption case in an FT-IR experiment (equation 1) it is easy to derive the corresponding diffusion coefficient (see equation below).

$$\frac{A_t}{A_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{L^2} \right\} \qquad (1)$$

In the above equation (only strictly valid if we assume Fickian behavior, no changes in films thickness and constant absorption coefficient), A_t is the absorbance of the chosen band at a given time and A_e is the absorbance at saturation or equilibrium sorption, L is the thickness of the film and D the diffusion coefficient. We carried out measurements for a number of aroma components of which only data for limonene, α-pinene and citral are gathered in Table 1.

Table 1. Diffusion coefficients (m^2/seg) of limonene, α-pinene and citral

Aroma component	D (gravimetry)	D (FT-IR)
Limonene	$(20.0\pm0.3)*10^{-13}$	$(18.5\pm0.6)*10^{-13}$
α-Pinene	$(9.7\pm0.2)*10^{-13}$	$(9.6\pm0.6)*10^{-13}$
Citral	$(3.5\pm0.2)*10^{-13}$	$(5.5\pm0.1)*10^{-13}$

In order to assess the goodness of the determination of diffusion coefficients with FT-IR we also measured desorption of these penetrants with gravimetry, i.e by weight loss measurements. Figure 6 shows the corresponding fits of the desorption experiments of α-pinene by FT-IR and gravimetry showing an excellent correspondence.

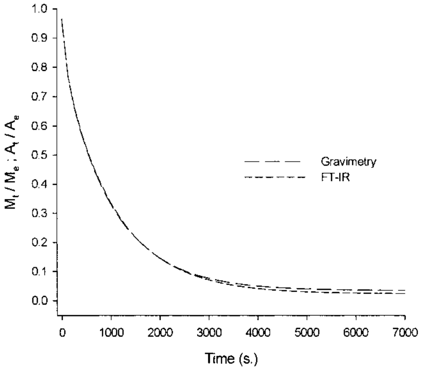

Figure 6. Fickian-like desorption experiments of α-pinene in LDPE by FT-IR and gravimetry

A good correspondence is the general case for all aroma compounds measured, although in some cases some differences can be found (see Table 1) due to the different nature and characteristics of the two types of experiments. The general criteria for selecting a good IR band in terms of evaluating transport properties is that it should not undergo significant changes in shape and position during desorption, because this is indicative of vibrational modes highly sensitive to the different levels of interactions that can be established, depending on the sorption level, between the penetrant and the polymer matrix. The reason why strong frequency shifts and changes in band shape, often the case for N-H or O-H stretching bands and C=O stretching bands, may not give good correlations with for instance gravimetry, lies on the fact that absorption coefficients are changing during the desorption process, and therefore, the relation between absorbance and concentration may be significantly different during the experiment.

Conclusions

This paper gathers a number of examples where vibrational spectroscopy has been successfully applied to characterize the morphology and barrier properties of a number of polymers widely used in food packaging applications. More specifically, Raman and infrared proved to be adequate tools to determine crystallinity, morphological and chemical alterations occurring in high barrier ethylene vinyl alcohol (EVOH) copolymers as a result of changing thermal history, annealing and thermal degradation of the sample. Moreover, the results proved the suitability of the FT-IR technique to determine the diffusion coefficients of a number of citric fruit aroma components in polyethylene.

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[1] J.M. Lagaron, R. Catala, R. Gavara, *Mat. Sci. and Tech.*, **2004**, 20, Issue 1.
[2] J.G. Bonner, A.K. Powell, *"New Plastics'98"*, London, **1998**.
[3] R. Gavara, R. Catala, E. Gimenez, J.M. Lagaron, C. Sanz, *"WorldPack2002: Improving The Quality of Life Through Packaging Innovation"*, CRC Press LLC. Boca Raton (USA), 2002, V. 1, 400.
[4] M.L. Cerrada, E. Perez, J.M. Pereña, R. Benavente, *Macromolecules,* **1998**, 31, 2559.
[5] M. Takahashi, K. Tashiro, S. Amiya, *Macromolecules*, **1999**, 32, 5860.
[6] J.M. Lagaron, *Macrom. Symp.*, **2002**, 184, 19.
[7] J.M. Lagaron, E. Gimenez, R. Gavara, J. J. Saura, *Polymer*, **2001**, 42, 9531.
[8] J.C. Rodriguez-Cabello, J. Monje, J.M. Lagaron, J.M. Pastor, *Macrom.Chem. Phys.*, 1998, 199, 2767.
[9] A. Lopez-Rubio, D. Cava, J.M. Lagaron, R. Catala, R. Gavara, *21st IAPRI Symposium*, 2003, 92.
[10] J. M. Lagaron, E. Gimenez, J. J. Saura, *Polym. Int.*, **2001**, 50, 635.
[11] J.M. Lagarón, A.K. Powell, N.S. Davidson, *Macromolecules*, **2000**, 33, 1030.
[12] G.T. Fieldson, A.T. Barbari, *Polymer*, **1993**, 34(6), 1146
[13] C. Sammon. N. Everall, J. Yarwood, *Macromol. Symp.,* **1997**, 119, 189.
[14] CM Balik, WH Simendinger III, *Polymer*, **1998**, 39, 4723,
[15] S. Cotugno, D. Larobina, G. Mensitiere, P. Musto, G. Ragosta, *Polymer*, **2001**, 42, 6431,
[16] J. Crank, *"The Mathematics of Diffusion"*, Oxford University Press, London, 1975.