Macromol. Symp. **2003**, *202*, 269—279

Analysis of Multicomponent Polymer Systems by Raman Microscopy

*A. Szép, B. Marosfői, Gy. Bertalan, P. Anna, Gy. Marosi**

Budapest University of Technology and Economics, H-1111 Budapest, Műegyetem rkp. 3, Hungary
E-mail: gmarosi@mail.bme.hu

Summary: The Raman microscope is one of the most convenient instruments for analyzing the structural characteristics and changes in the interfacial region of multicomponent systems. This is confirmed by the results obtained in the field of packaging materials, nanocomposites, and basalt fibre reinforced composites. In the course of this study, the chemical character of the surface and interfacial regions were investigated and, in addition, the local characteristics of the crystallization process of the polymer matrix could be determined.
Keywords: crystallization; interfaces; Raman microscopy; surfaces

Introduction

The scope of an analytical process applicable for characterizing polymer systems is basically determined by the sensitivity of the method to the physical and chemical differences between the samples and by the modifying or destructive effects caused during sample preparation or analysis.

In order to answer the current questions emerging in materials science, especially in the area of multi-component polymer systems, the applied analytical methods have to meet more and more complex requirements. These are, for example, high sensitivity to the chemical and physical differences, good localizability, possibility for depth profiling, high lateral and depth resolution. In most cases, macroscopic samples are available for the examinations and it is a basic requirement to avoid structural changes of the sample during the measurement. The development of multicomponent polymer systems requires a comprehensive knowledge about the interfaces.

The importance of vibrational spectroscopic methods has been increasing during the recent decades. The conventional macroscopic spectroscopic methods are usually suitable for

DOI: 10.1002/masy.200351223

description of the chemical and physical state of the sample providing overall information on the content of the sample but they do not provide local information at microscopic level. Furthermore, the examined sample may be damaged due to the operations during sample preparation and measurement of the studied material. The follow-up of the transformation and transport processes is often excluded from the scope because of the presence of a component disturbing or even impeding the analysis. For instance the biomedical application of IR spectroscopy is significantly restricted by the strong absorption by water. Raman spectroscopy, however, being much less sensitive to water, enables the examination of morphological differences and requires considerably simpler sample preparation compared to other vibrational spectroscopic methods. In the Raman spectrum there are fewer overlapped, compound band and furthermore, with certain limitation, the intensity of the bands is directly proportional to the concentration of material. Due to differences in selection rules, Raman and IR spectroscopy are complementary analytical methods; the examined wavenumber ranges largely overlap, thus both of them provide information on the vibrational or vibrational-rotational states of the molecules.[1]

A Raman microprobe, combining a spectroscope with an optical microscope, enables one to make local measurements at microscale as well.[2,3] Regarding the optical resolution, the Raman microprobe allows analysis of a sample area of 500 nm in diameter and the examination of the layers under the surface can be carried out without damaging the surface.[4]

Raman microscopy can be applied in various fields of material science, pharmaceutical industry, biology, and chemistry to local qualitative and quantitative analyses, process control,[5] determination of thermodynamic quantities and equilibriums and to studies of isomeric transformations. In biology and medicine Raman spectra can be recorded even under in vivo circumstances.[6,7] Further important examples of application are the assessment of the age and origin of paintings based on the pigment type used and forensic examinations (e.g. authentication of signatures or detection of drugs).[8] Raman micro-spectroscopy is an excellent method for detecting local morphological differences.[9,10] Owing to the recently used low power laser beam, the examination can be repeated on the same sample any number of times, because the sample does not undergo a structural change even during prolonged measurements.[11] By means of the visual image projected with the mediation of the microscope on the computer screen, the exact fixation of the examined detail of the sample is simple. Local characteristics like contamination, defect of crystallization, etc. can be characterized easily this way.[12] For industry, this method offers the possibility of quality control during the manufacturing process without any waste product.[13]

As we have shown above, the application range of Raman microscopy increases rapidly and is becoming a very important method for material analysis especially in polymer laminates, surface-treated and multicomponent systems. In multicomponent polymer systems, the method may give valuable information about the individual layers, their surfaces and interfaces, i.e. of polymer-polymer or polymer-substrate interfaces,[14] inter-diffusion and inter-reaction effects,[15] etc.

The aim of this paper is to demonstrate the versatility of the application of Raman microscopy in polymeric material investigation. The main examples are: multilayered materials, surface-modified polymer, effects of flame and heat treatment on chemical structure and transport processes, the structure of nanocomposites and fibre reinforced polypropylene.

2 Experimental

2.1 Sample Preparation

2.1.1 Preparation of Multi-layered Packaging Material Sample

A multilayer packaging material including an aluminum layer of 40 μm thickness and a polyamide layer of 25 μm thickness, with an adhesive promoter between them was investigated "as received". The quality and thickness of the adhesive layer was examined using depth profiling and on the cross-section of the multi-layered package.

2.1.2 Preparation of Surface Coated and Nanocomposite Containing Samples

Compounds were prepared in a Brabender mixing chamber at 200°C using the following components: polypropylene (PP, Tipplen H 535, TVK Co, Hungary, density: 0,9 g/cm^3, melt index: 4g/10min at 21.6 N, 230°C); polyboroxosiloxane (BSil), prepared by reacting silicon oligomer (Tegomer 2111, Th. Goldschmidt AG) with boric acid[16] and montmorillonite of Benton SD-1 type (MMT, nanoclay organophillized with cationic surfactant, Reox Inc., particle size <1μm). Coating of the particles was performed in-line during compounding.

2.1.3 Preparation of a Sample for Crystallization

PP with basalt fibre (Toplan Ltd, Hungary) was prepared in a Brabender mixing chamber at 200°C.

2.1.4 Raman Spectroscopic Analysis

A LabRam confocal Raman microscope (Jobin Yvon) was used for the examinations. The optical resolution of the instrument, that is the size of the examined area was adjustable by means of changeable objectives according to the features of the sample. The instrument was operated with three changeable excitation light sources: a He-Ne laser (632 nm), a frequency doubled Nd-YAG laser (532 nm), and a diode laser (785 nm). A good spatial resolution was ensured by means of a confocal aperture at a back-focal image plane and by using a charge-coupled device (CCD) detector as an "electronic" aperture. The location of the accumulation of a spectrum was chosen on the optical image enlarged by the microscope and projected on the monitor, and in the selected spots or places the accumulations were performed automatically according to a predetermined program.

For examination of a multilayered packaging material, a section of the sample was made and on it a line-mapping spectral image was accumulated along a 50-micrometer long line with 1-micrometer resolution. The He-Ne laser and a 50× objective were used in this type of examination. Recording of the spectra composing the Raman mapping image required an acquisition time of 45 seconds per spot with double accumulation for elimination of noises.

For determination of the heat-induced structural changes in the coating layer of polypropylene, the spectra were accumulated using He-Ne laser excitation, but with a shorter, 20-second acquisition times and double accumulation. In favour of the improvement of the precision of the focus in depth, the 100x objective was chosen with a confocal hole diameter of 200 μm, in accordance with the results described by Everall.[17,18]

The Raman signals of nanocomposites were detectable only with the 532 nm laser-excitation (owing to the fluorescence at other frequencies) during a short acquisition time of 20 seconds and double accumulation. The heat treatment of the samples was carried out by a heating-cooling stage that could be directly connected to the Raman microscope.

The study of crystallization of polymer composites was also carried out on the heatingcontrolling stage. Raman signals were detected in 60 seconds using the He-Ne laser and a 50× objective.

3 Results and Discussion

In this paper we discuss examples of the application of the Raman microscope for investigation of multicomponent polymer systems. Further details of the research work carried out on the studied materials are given in the cited papers of the authors.

3.1 Examination of Multilayered Packaging Materials

In case of multilayered packaging material developed for ensuring improved gas barrier properties, the purpose of the analysis was to explore the internal structure of the combined material. Earlier it was stated for multilayer materials (in which the refractive index of the layers are similar) that a cross-sectional profile obtained after sample sectioning shows very good agreement with a confocal depth profile determined using immersion lens.[19] In the studied case, however, the Al layer acts as a mirror decreasing the accuracy of the depth profile measurement therefore the films were investigated by cutting the sample in cross section direction to obtain spectra of the individual layers. The Raman spectra were collected using a step size of 1 μm along a line perpendicular to the layers on the section. The optical image of the cross-section taken by an optical microscope can be seen in Figure 1a. The thickness of the composite film layers can be easily determined by visual examination, but in fact the adhesive layer is not visible in the optical image; it can be detected accurately only in the Raman spectra. The resulting spectral map is shown in Figure 1b. After the „peak-free" black spectra of the aluminium layer, from 70 μm, the spectra of the approximately 10 μm thick adhesive layer with a strong band of substituted benzene at 1006 cm^{-1} (aromatic ring breathing) and 1616 cm^{-1} (ring stretches) as well as a weak band characteristic of a carbonyl group at 1720 cm^{-1} (C=O stretch) can be observed. This result made it clear that the layer consisted of a resorcinol-formaldehyde resin with a relatively small degree of crosslinking. From 80 μm to 105 μm, the Raman spectrum of the 25 μm thick polyamide layer can be seen. The characteristic bands of the spectra of the layers are highlighted in grey boxes in Figure 1c. The intensity change of characteristic bands of the neighbouring layers can be seen in Figure 1d. The penetration of the adhesive into the polyamide phase is clear from the slower gradual decrease of its characteristic band on the polyamide side. The thickness of this inter-diffusion layer is 5-10 μm.

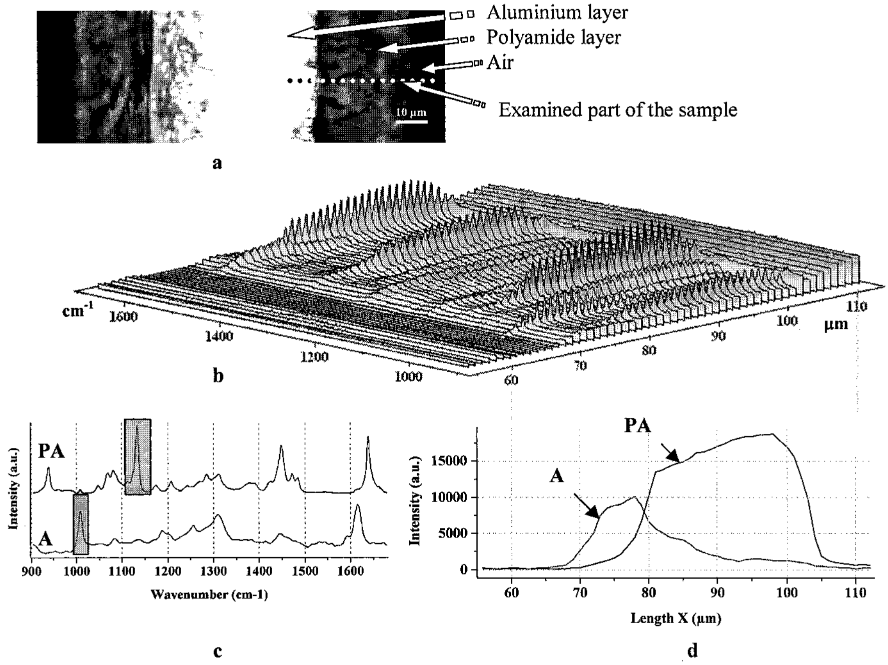


Fig. 1. a, Visual cut-section image of the multilayered packaging; b, Collected Raman spectra map at the examined part of the sample; c, Raman spectra of polyamide (PA) and adhesive (A); characteristic bands used for *d* diagram highlighted in gray boxes; d, Change in the intensity of the characteristic peaks of the adhesive (A) and polyamide (PA) layer

3.2 The Effect of the Exposure to Flame on the Chemical Structure and Properties of a Surface Coating

Surface modification of polymers offers an opportunity for changing the physical and chemical characteristics such as barrier properties, adhesion, mechanical and electrical characteristics. The gas permeability has been decreased by both micrometer and nanometer thick layers inside or outside of the materials. Forming compact SiO_x layer on surface of polypropylene for decreasing the rate of gas permeability can be used not only in packaging technology, but also in other important application fields. However, it is not easy to examine these structures and detect the eventual changes. We have found that not only the identification of coatings but also their chemical reactions can be followed by Raman microscopy. In a recent work we have investigated, how the chemical structure and properties of a coating can be affected by means of flame treatment. Favourable results were obtained in fire retardancy by means of SiO_X layer generated from boroxosiloxane precursor.[16] Flame or plasma treatment on the surface forms a flexible, glassy-like structure decreasing the gas transport, i.e. oxygen from air to the burning material, consequently the combustion of the polymer material can be extinguished.[20]

In Figure 2 the Raman spectra of polypropylene covered by boroxosiloxane (BSil) is shown before and after exposure to flame.

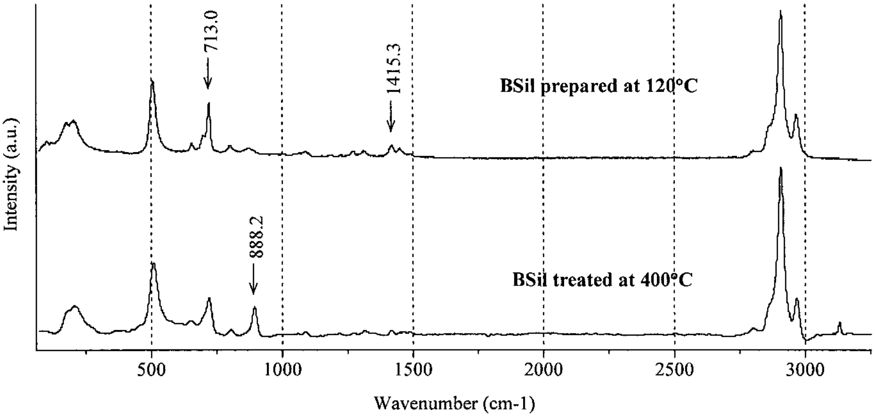
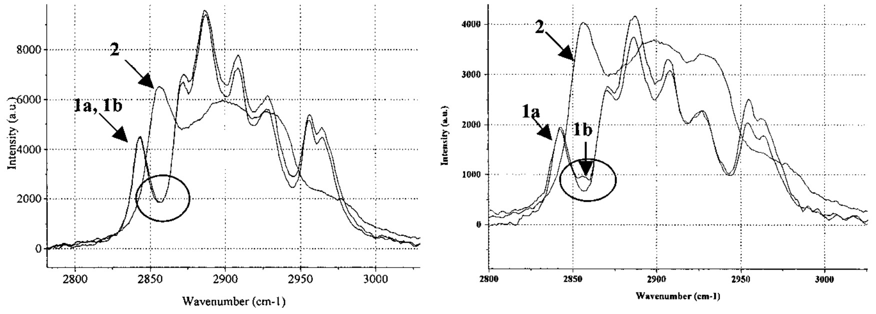


Fig. 2. Raman spectra of boroxosiloxane layer before and after flame treatment.

In the spectra collected after exposure to flame, the intensity of the characteristic bands of the symmetrical stretching of C-Si-C bonds at 713 cm^{-1} and the symmetrical deformation of CH_2 groups at 1415 cm^{-1} decrease. (The intensity in Raman spectra is directly proportional to the occurrence of the structural moieties responsible for the band). A new band appears at 888 cm^{-1} that is characteristic of Si-OH bonds. After flame treatment the carbon content decreases on the surface suggesting the increase of the inorganic character. Furthermore, at the burning temperature of the polymer, the transformation of the precursor is not complete: even after a sustained, intensive flame treatment an organic silicon containing component remains on the surface, with flexible, high performance fire barrier properties.

3.3 Examination of Polymer Nanocomposites

Polymer nanocomposites exhibit novel property combinations in which the filler shape, particle size distribution, dispersion and interfacial adhesion play very important roles. With nanofillers a new set of properties can be achieved, e.g. improved mechanical, thermal, electrical properties, reduced permeation of gases, etc.[21] Consequently, it is very important to investigate how the nanofillers are distributed in nanocomposites.



A B

Fig. 3. A) 1. Raman spectrum of polypropylene containing MMT after heat treatment at 250°C (a) and 300°C (b) 2. Raman spectrum of MMT; B) 1. Raman spectrum of polypropylene containing MMT + BSil after heat treatment at 250°C (a) and 300°C (b); 2. Raman spectrum of MMT.

It was proven earlier that not only the gas barrier properties but also the flame retardancy could be improved by nanocomposites. The relationship between these effects and the migration of nanoplatelets in nanocomposite was also suggested.[22] We have investigated, whether the Raman microscope is suitable to follow the migration processes towards the surface induced by heat treatment. Figure 3 shows the Raman spectra of two nanocomposites (1) heat treated at 250°C (a) and 300°C (b) respectively and the organophillic montmorillonite (MMT) (2) as reference. The composition of nano-composites: I), polypropylene containing 1% organophillic montmorillonite (MMT), and II.) polypropylene containing 2% BSil and 1% organophillic

MMT. In Figure 3 the marked part of the spectrum, (measured at an ~0.5 μm thick surface layer) verifies that the Raman microscope is able to detect the slight changes (accumulation of 1% additive on the surface) caused by heat treatment.

The spectra of composites filled with organophillized montmorillonite without boroxo-siloxane show no significant differences when heat treated at 250°C or 300°C (Figure 3 (A)). A characteristic change can be observed, however, at 2860 cm^{-1} in presence of BSil after heat treatment at 300°C (Figure 3 (B)). This change appears at the same wavenumber, at 2858 cm^{-1}, where the strong band of organophillized MMT was observed. This change can be explained by decreasing the compatibility of the polymer and clay platelets. On the other hand, the heat resistant BSil surface treatment promotes migration of layered silicates from the bulk towards the surface. Consequently, their quantity near to the surface will be increased. Due to this enrichment, the characteristic band of organophillized MMT becomes detectable.

3.4 Examination of Semi-crystalline Structure in Polymer Composites

A great benefit of Raman microscopy is that, in principle, it requires no sample preparation. It means that the Raman microscope makes possible the exact spectroscopic monitoring of the thermoanalytical process, for example crystallization. The temperature of the sample stage can be controlled, which allows one to continuously follow the spectral changes occurring with changes in temperature.

In a Raman spectrum, the phase transformation is reflected in the shape and the shift of bands. In Figure 4 the change of the characteristic bands in the spectral range between 800-850 cm^{-1} is presented, where a strong band of CH_2 rocking and CC stretching is changing its shape from a broad diffuse band to a narrow one.[23] The photo in Figure 4 shows the polarizing optical microscopic image of the basalt fibres in polypropylene matrix during the crystallization process. Spectra were accumulated during the crystallization of polypropylene phase in a basalt fibre reinforced composite at the interfacial region and in the bulk. Focusing the exciting laser beam on the surface of the fibre, Raman spectra were detected in every minute whilst the temperature of the sample was decreased continuously with a rate of 1°C/min in the range of the melting point. In case of nucleating effect of basalt fibre, the characteristic band in this region becomes sharp much faster than in the bulk.[24] In this case, however, the examinations performed in other places of the polymer melt did not show any detectable change in the rate of the crystallization, no difference was found in the temperature dependent spectra of interface and bulk. Thus it can be stated that the basalt fibre does not have any nucleating effect, does not act as heterogeneous nucleant and, differently from several other fibres and fillers, does not produce an interfacial, transcrystalline layer in polypropylene.

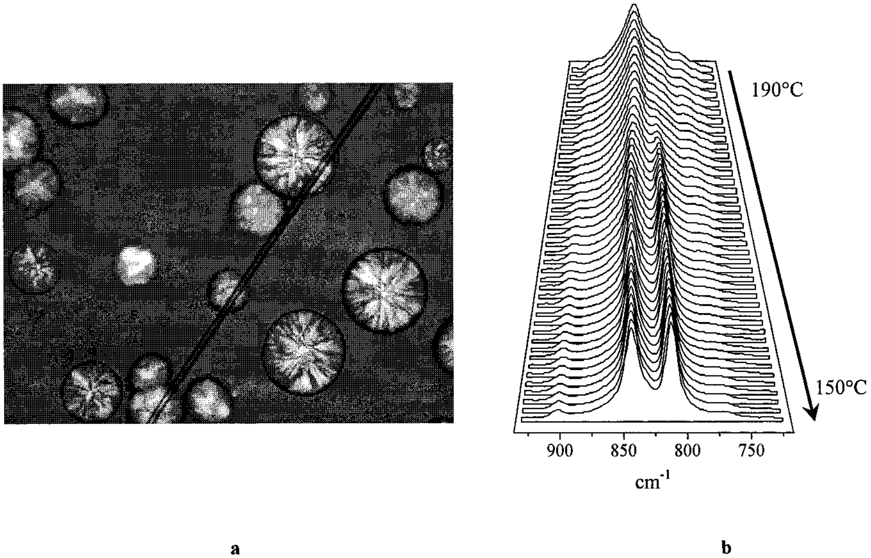


Fig. 4. Crystallization of basalt-reinforced polypropylene examined by Raman microscope.
a) Spherulites observed by a 50x objective at 120°C.
b) Changes in intensity and shape of the characteristic band during crystallization (the arrow shows the temperature decrease in the range of 190-150°C).

4 Conclusions

As it has been discussed above, Raman microscopy offers several alternative possibilities in the field of materials science, especially in the polymer area. The examinations require minimum sample preparation and owing to this, the structure of the sample changes during measurements only slightly or not at all.

This method allows determination of the layer-structure of multilayered packaging materials, the quality and width of the adhesive layer and even the depth of its penetration into the neighbouring polymer layer.

Raman microscopy of boroxosiloxane, a precursor of the surface barrier layer, has verified that the organic character and the flexibility of the surface layer is preserved even after a permanent exposure to intensive flame.

Based on the investigation of the polypropylene samples containing montmorillonite nanoparticles it could be stated that in case of heat or flame treatment the nanoparticles appeared at the surface in abundance if a layer of low compatibility to the polymer matrix covered their surface.

The combination of the heating-cooling sample stage with the Raman microscope made it possible to gain novel information on the crystallization features of the polypropylene composites reinforced by basalt fibre.

Acknowledgment

This work has been financially supported by the Hungarian Research Fund through projects OTKA T32941, NKFP 00169/2001 and NKFP 3A/0036/2002.

[1] J. Corset, P. Dhamelincourt, J. Barbillat, *Chem. Britain,* **1989**, 25(6), 612.
[2] B. Schrader, *Fresenius J. Anal. Chem.* **1990**, 337(7), 824.
[3] W. Schrof, J. Klingler, W. Heckmann, D. Horn, *Colloid Polym. Sci.* **1998**, 276, 577.
[4] R. Tabaksblat, R. J. Meier, B. J. Kip, *Appl. Spectrosc.* **1992**, 46(1), 60.
[5] J. Breitenbach, W. Schrof, J. Neumann, *Pharm. Res.* **1999**, 16(7), 1109.
[6] F. F. M. Demul, A. G. M. Vanwelie, C. Otto, J. Mud, J. Greve, *J. Raman Spectrosc.* **1984**, 15(4), 268.
[7] J. Maruani,"*Molecules in Physics, Chemistry and Biology*" IV. Kluwer, Dordrecht, 1988, p. 87.
[8] P. V. Huong, *Vibrational Spectroscopy* **1996**, 11, 17.
[9] M. Tsuboi, T. Ikeda, T. Ueda, *J. Raman Spectr.* **1991**, 22(11), 619.
[10] C. M. Deeley, R. A. Spragg, T. L. Threlfall, *Spectochimica Acta* **1991**, 47A, 1217.
[11] R. L. McCreery, A. J. Horn, J. Spencer, E. Jefferson, *J. Pharm. Sci.* **1998**, 87(1), 1.
[12] E. D. Williams, L. D. Marks, *Crit Rev. Surf. Chem.* **1995**, 5(4), 275.
[13] P. V. Huong, *J. Pharm. Biom. Anal.* **1986**, 4, 811.
[14] C. Sammon, C. Mura, P. Eaton, J. Yarwood, *Analysis* **2000**, 28(1), 30.
[15] C. Sammon, S. Hajatdoost, P. Eaton, C. Mura, J. Yarwood, *Macromol. Symp.* **1999**, 141, 247.
[16] Gy. Marosi, A. Márton, P. Anna, Gy. Bertalan, B. Marosfői, A. Szép, *Polym. Degrad. Stab.* **2002**, 77, 259.
[17] N. J. Everall, *Appl. Spectrosc.* **2000**, 54(6), 773.
[18] N. J. Everall, *Appl. Spectrosc.* **2000**, 54(10), 1515.
[19] H. Reinecke, S. J. Spells, J. Sacristan, J. Yardwood, C. Mijangos, *Appl. Spectrosc.* **2001**, 55(12), 1660.
[20] I. Ravadits, A. Tóth, Gy. Marosi, A. Márton, A. Szép, *Polym. Degrad. Stab.* **2001**, 74(3), 414.
[21] C. Z ilg, F. Dietsche, B. Hoffman, C. Dietrich, R. Mulhaupt, *Macromol. Symp.* **2001**, 169, 65.
[22] Gy. M arosi, R. Lágner, Gy. Bertalan, P. Anna, A. Tohl, *J. Therm. Anal.* **1996**, 47(4), 1163.
[23] A. S. Nielsen, D. N. Batchelder, R. Pyrz, *Polymer* **2002**, 43, 2671.
[24] C. Shen, A. J. Peacock, R. G. Alamo, T. J. Vickers, L. Mandelkern, C. K. Mann, *Appl. Spectrosc.* **1992**, 46(8), 1226.