*Macromol. Symp.* **2004**, *205,* 163—170

# Spectroscopic Characterization of Micro-Phase Separated Blends of Polystyrene/Polymethyl Methacrylate (PS/PMMA)

*Athina Korakianiti,*[1] *Siobhan Walsh,*[2] *Vasilis G. Gregoriou**[1]

[1]Foundation for Research and Technology-Hellas, Institute of Chemical Engineering and High Temperature Processes, (FORTH-ICE/HT), Patras 26500, Greece
[2]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02131 USA
E-mail: gregoriou@iceht.forth.gr

**Summary:** An investigation of the miscibility behaviour in polystyrene/ polymethyl methacrylate (PS/PMMA) blends of various compositions under different evaporations protocols using Fourier transform infrared (FT-IR) and Raman Spectroscopic techniques took place in the study. Solvent selection and evaporation rates, coupled with variations in the blend composition resulted in completely different miscibility behaviour for these systems. In particular, it was found that blends with low PMMA content result in systems that exhibit PMMA domains of less than 7 microns on average. Finally, depth profiling studies of the PMMA moiety in the PS matrix show that the distribution of the low content phase is highly affected by the solvent selection as well as the blend composition.

**Keywords:** infrared spectroscopy; miscibility; phase separation; polymer blends; polymethyl methacrylate; polystyrene; solvent selection; tacticity effect

## Introduction

The structure and morphology of various compositions of polystyrene (PS)/ polymethyl methacrylate (PMMA) blends using different solvent and evaporation procedures were studied in an attempt to produce cost efficient materials that have better thermal and mechanical properties. The final morphology of any polymer blend is largely affected by the rate of evaporation as compared to the rate of phase separation through nucleation and growth. It has already been demonstrated that it is essentially the surface morphology of a polymer blend that determines its functionality. [1] When evaporation takes place over an extended period, phase separation occurs rapidly at the surface and very slowly in the bulk. Previous work has indicated that slow evaporation can give rise to ordered domains of the minor phase in the surface layer. [2] In this study, both the effects of solvent alteration and blend composition were investigated in trying to

DOI: 10.1002/masy.200450115

create miscible polymer blends of industrial interest. Miscibility was considered to be achieved if domains of less than five microns were observed in the majority of areas on the sample. It is important to note that a binary polymer blend will consist of a matrix rich in the substance of lower surface energy. Despite the similar surface energies of polystyrene and polymethyl methacrylate, it has been shown that the PS/PMMA blend is characterized by domains of PMMA amidst a matrix of PS.[3] A variety of techniques including FT-IR spectroscopy, (both transmission and Attenuated Total Reflectance (ATR) modes), micro-Raman Spectroscopy, optical microscopy, atomic force microscopy (AFM), differential scanning calorimetry (DSC) were employed in this study in an attempt to examine the surface and bulk morphologies of these casts.

## Experimental Section

### Blend Preparation

Different polymer blends of PS/PMMA were obtained by solvent casting 5% to 9% tetrahydrofuran (THF) or toluene solutions on a "boat" of aluminum foil. A "boat" was constructed by folding the edges of approximately a 5cm by 5cm square piece of foil so as to create a topless box into which solution could be pipetted. The compositions of blends are 10/90, 20/80, 30/70, 66/33, 50/50, 70/30, 80/20, and 90/10 cast from toluene and THF, respectively. Also, the molecular weight of polystyrene is 212,400 and the molecular weight of PMMA varies from 34,600 to 133,500, respectively. It is noted that the molecular weight of the poly(methyl methacrylate) utilized in this study was determined by size exclusion chromatography.

### Blend Characterization

A Renishaw Raman Imaging Microscope was employed to record Laser Raman Spectroscopic data. The incident beam of a HeNe laser (632.8nm) was focused on the samples through an Olympus BH2 microscope with a 50x objective and a numerical aperture value of 0.8. Samples were illuminated for approximately 40 minutes and Raman spectra were collected. The spectrograph is designed as an on-axis system which is stigmatic and as a consequence provides an undistorted image on the detector. Optical Microscopy was performed with an additional Olympus BH2 Microscope. Micrographs were obtained in reflectance mode with both a

50x(NA=0.8) and a 20x(NA=0.3) objective. Finally, Attenuated Total Reflectance (ATR) FT-IR Spectroscopy was performed using a Nicolet 20DXB spectrometer. A zinc selenide (ZnSe) crystal was used as the internal reflection element. The spectrometer is equipped with a Mercury Cadmium Telluride (MCT) detector.

## Results and Discussion

Atactic PS (aPS) has been shown to possess a significant amount of syndiotactic sPS trans isomers. [4] In addition, $^1$H NMR analysis showed that our particular polystyrene sample contains a small residual amount of isotactic polystyrene. In 1999, Lee et al. [5] reported that they generally observed that a dispersed morphology is formed when the blend composition is highly asymmetric whereas a co-continuous morphology is formed when the blend composition is symmetric. For this reason, a dispersed blend morphology is formed where the minor component with the higher melt viscosity forms the discrete phase (i.e droplets), and the major component with the lower melt viscosity forms the continuous phase (i.e matrix). Atomic force microscopy (AFM) has the ability to characterize the surface and interface morphologies in solvent cast PS/PMMA films, as this technique is considered to be a very sensitive method for revealing the phase morphology of polymer blends. The AFM image in Figure 1 indicates again that the domains and the matrix regions are composed of the PMMA and the PS rich phases, respectively.[1]

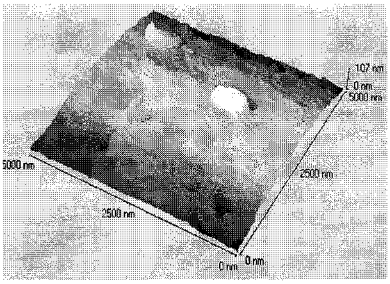


Figure 1. AFM image of a 66/33 PS/PMMA blend cast from THF

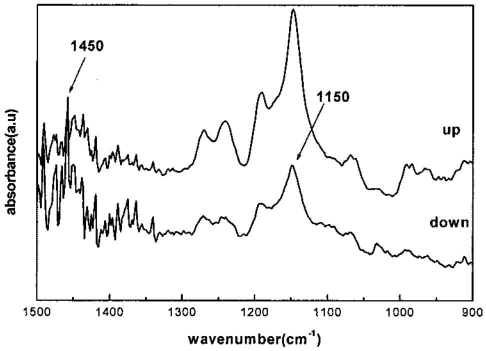


Figure 2. ATR-FTIR spectra of 66/33 PS/PMMA blend cast from THF

The above spectra in Figure 2 indicate that PMMA is selectively located on the surface of the blend. The ratio of the 1500 cm$^{-1}$/ 1150 cm$^{-1}$ band is a criterion which reveals the difference in chemical composition between the top and bottom of the polymer films. These ATR-FTIR spectra support the idea of a difference between bulk and surface morphologies. It should be also noted that what is referred to as the top is the portion of the blend allowed interaction with the air, whereas bottom refers to the portion allowed interaction with the aluminum foil. Moreover, optical microscopy helps us further to examine the miscibility behavior of the blends. The PMMA domains are prominent against the dark PS background. Our analysis showed that low PMMA content (90/10) results in blends that exhibit domains of less than 7 microns on average.

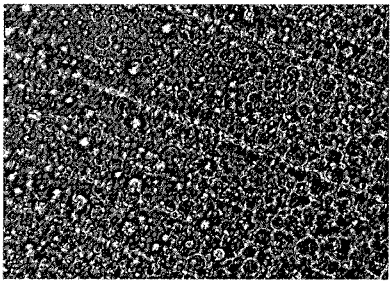
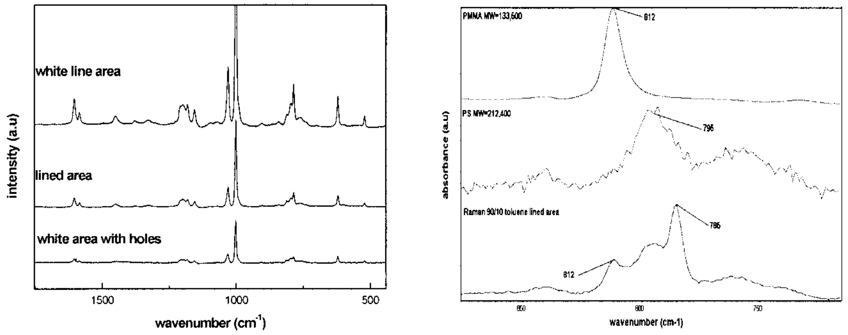


Figure 3. A 50x micrograph of the 90/10 PS/PMMA blend cast from toluene exhibits a sheet-like appearance

The spherical shape which is observed in Fig.3 is a consequence of surface energy minimization within each droplet. In addition, the presence of small droplet size reflects not only the small tension between PS and PMMA but also the much smaller surface tension between PS and PMMA in the presence of toluene.



(a) (b)

Figure 4. Raman spectra of the 90/10 in toluene. The individual spectra of PS and PMMA are shown only for comparison

According to the data in Figure 4, the appearance of new bands at 785 cm$^{-1}$ and 513 cm$^{-1}$ is attributed to the crystalline portion of syndiotactic PS. The upper line in Figure 4a represents the spectrum of the 90/10 PS/PMMA blend cast from toluene in the white line area of the Figure 3, the middle one the lined area and the lower one the white area with holes of the same blend. The spectra in Figure 4b represent the specific Raman spectroscopic region where the new bands are observed. Even though the possibility that residual toluene solvent contributes to the Raman spectra of 90/10 PS/PMMA blend, strong evidence exists that support the idea of the crystallization of the sPS portion of the PS matrix based on the comparison of the location of these new bands to bands of crystalline sPS from the literature.[6] It is well known, that diluents are known to affect the use and processing properties of polymers, partly because of their influence on both the crystallization kinetics and the resulting morphology of diluted polymer systems. The phenomenon of solvent-induced crystallization (SINC) in polymers has been discussed by several authors and theoretical interpretations of the events related to crystallization have been put forth. [7] The selection of the suitable solvent results in blends that are characterized by different degrees of crystallinity. The solvent induces the molecular motion of the amorphous polymer chains, indicating that the solvent dissolves the polymer chains even partly in the glassy state and has the role as a kind of plasticizer.[8] The relative composition of the blends has also an effect on their behavior towards miscibility and crystallinity. The increase in the PMMA content in the blend results in shifting of bands associated with isotactic and syndiotactic polystyrene to new location. In particular, the presence of higher portion of PMMA in the blend results in a shift of the 906 cm$^{-1}$ band to 908 cm$^{-1}$. As more and more PMMA is added into the sPS matrix, a certain fraction of TTGG chain conformation is retained, while the TTTT chain conformation begins to appear.

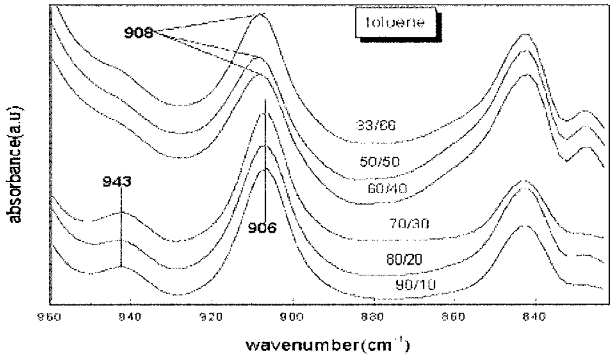


Figure. 5 Blends with low level of PMMA and high of PS show bands at 943 cm$^{-1}$, indicative of the helical conformation of sPS.

Figure 5 shows that crystallinity only occurs at high ratio of PS in the blend, based on the appearance of the 943 cm$^{-1}$ band. The possibility that the shift of the 906 cm$^{-1}$ band is due to the absorption of PMMA can not be excluded.

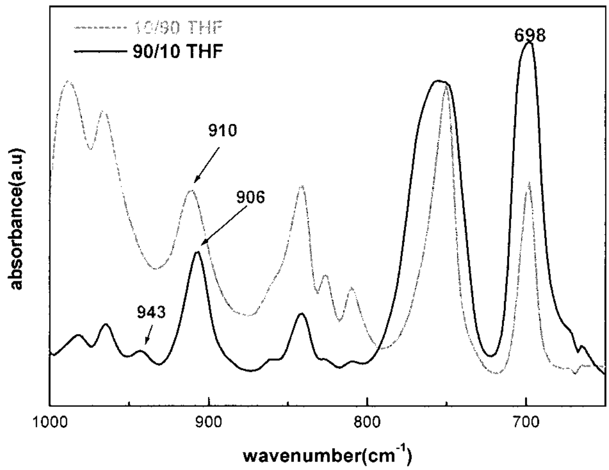


Figure 6. The effect of the solvent and the composition in the blend

Also, it can be seen from Figure 6 that the band at 943 cm$^{-1}$ that is attributed to the syndiotactic polystyrene is directly associated to the relative composition of PMMA in the blend. This picture also shows an increase in the absorption of 698 cm$^{-1}$ band. The 698 cm$^{-1}$ band is attributed to the out-of-plane bending mode of the phenyl C-H. It can be noticed that the height of the band at 698 cm$^{-1}$ is twice than the height of the band with solvent THF. This can be an indication of solvent induced crystallinity in iPS. The fact that crystallinity is observed in the blend cast in toluene can be explained by the fact that toluene has a small evaporation rate; therefore it is present for a longer period of time in the sample allowing crystallization both on the surface and in the bulk. [8]

## Conclusions

It has been shown in this work that the use of toluene and THF as solvents induces crystallization of both syndiotactic and isotactic PS in the polymeric blend of PS/PMMA. According to our results, blends with low amount of PMMA also show indications of enhanced PS crystallinity in the polymeric matrix of PS. It was also found that the evaporation rate of the solvent is a key parameter in influencing the final morphology of these blends. Moreover, the difference between the two other surfaces of the cast is an important indication of inhomogeneity based on depth profiling studies from ATR-FTIR. Finally, it was observed that PMMA has a tendency to concentrate on the surface of the blend whereas PS is more prominent in the bulk.

[1] Keiji Tanaka, Atsushi Takahara, and Tisato Kajiyama, *Macromolecules* **1998**, *31*, 863.

[2] Eugenia Kumacheva, Lin Li, Mitchell A. Winnik, Doug M. Shinozaki, and P. C. Cheng, *Langmuir* **1997**, *13*, 2483.

[3] Lin Li, Stanislaw Sosnowskli, Charles E. Chaffey, Stephen T. Balke, and Mitchell A. Winnik, *Langmuir* **1994**, *10*, 2495-2497.

[4] C.G Zimba, J.F. Rabolt and A.D. English, *Macromolecules* **1989**, *22*, 2867.

[5] Je Kyun Lee, Chang Dae Han, *Polymer* **1999**, *40*, 2521.

[6] R.A Nyquist, C. L. Putzig, M. A. Leugers, R. D. McLachlan, and B. Thill, *Applied Spectroscopy*, **1992**, *46*, Number 6.

[7] Nancy J. Tyrer, Terry L. Bluhm, and Pudupadi R. Sundararajan, *Macromolecules* **1984**, *17*, 2296-2303.

[8] Fangning Gu, Lirong Bao, Min Chen and Haishan Bu, *Makromol. Rapid Commun.* **1998**, *19*, 367-369.