New Molecular-Scale Information of Polystyrene Dynamics in PS and PS-BaTiO$_3$ composites from FTIR spectroscopy

D.Olmos,$^{a}$ E.V. Martín$^{a}$ and J. González-Benito$^{a,*}$

A new idea to understand the macromolecular motion occurring along the thermal relaxations of polystyrene (PS) and PS-barium titanate composites is proposed. Detailed analysis of PS infrared bands provides a better knowledge of the factors affecting polymer dynamics. Average spectral positions and integrated absorbance of bands in the region of C-H out-of-plane vibrations showed a continuous decrease with temperature, whereas those in the region of aliphatic and aromatic C-H stretching vibrations showed the sharpest changes with temperature. Relaxation temperatures were determined from the changes observed in the bands wavenumber or area with temperature. These results were attributed to changes in the distribution of the phenyl π-electron cloud, causing important dipole moment variations in the different vibration modes when the thermal transitions are taking place. Finally, although the presence of BaTiO$_3$ particles does not seem to exert any specific effect on the PS dynamics in the glassy state, the Curie transition of these particles might induce a kind of confinement effect observable by FTIR.

**Fig. S1.** Evolution of $\langle \nu \rangle$ (cm$^{-1}$) vs temperature (°C) for the bands centered at 540, 757, 840 and 907 cm$^{-1}$. The insets in each graph show a schematic representation of the phenyl ring deformations associated with each vibration mode. The plus and minus signs indicate the two opposite directions of the out of plane vibrations. The color code shows the content in BaTiO$_3$ particles.
Fig. S2. Evolution of $\nu$ (cm$^{-1}$) vs temperature (°C) for the bands centered at 1028, 1069 and 1154 cm$^{-1}$. The insets in each graph show a schematic representation of the phenyl ring deformations associated with each vibration mode. The arrows indicate the relative motions of the atoms in space. The color code shows the content in BaTiO$_3$ particles.
Fig. S3. Evolution of band area vs temperature (°C) for the bands centered at: (a) 540; (b) 757; (c) 840 and (d) 907 cm$^{-1}$. The insets in each graph show a schematic representation of the phenyl ring deformations associated with each vibration mode. The plus and minus signs indicate the two opposite directions of the out of plane vibrations. The color code shows the content in BaTiO$_3$ particles. Although the band area at 540 cm$^{-1}$ is influenced by the Ti-O vibration at 560 cm$^{-1}$, it was also included in this figure for comparison.
Figure S4. Temperature dependence of band areas for bands centered at 1028 (top), 1069 (middle) and 1154 (bottom) cm$^{-1}$ in PS. The insets in each graph show a schematic representation of the phenyl ring deformations associated with each vibration mode.