Abstract

Polymers can crystallize in different crystalline forms; polymorphism is the term to indicate this ability. It is known that processing and physical properties of polymer-based materials are strongly affected by the occurrence of ‘‘polymorphism’’[1] and ‘‘metamorphism’’ (i.e., the occurrence of ‘‘disordered’’ crystalline phases, characterized by a degree of structural organization that is intermediate between those identifying crystalline and amorphous phases)[2a]

My PhD thesis is focused on the study and on the characterization of polymer films with co-crystalline and nanoporous crystalline phases. Many polymers are able to form co-crystals i.e. molecules of low molecular weight (guest) trapped in the crystalline polymer lattice (host). Over the past two decades it has been observed that some polymers, with co-crystalline phases, such as syndiotactic polystyrene (sPS) and poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) after guest removal can form nanoporous crystalline phases, able to absorb suitable guest molecules also at low activity. During this work, I have studied the possible molecular orientations that may be induced by solvents during cocrystallization process in polymeric films, (chapter 2); the development of chiro optical response, after co-crystallization with temporary chiral guest (chapter 3) and the possibility to realize photonic crystals by using polymers able to form nanoporous crystalline forms (chapter 4).

In detail, in chapter 1 the procedure to obtain disordered nanoporous crystalline phases in sPS films and their possible application is reported. This disordered nanoporous crystalline phase rapidly absorb low molecular mass molecules, also from very dilute aqueous solutions.

It is known in literature that nanoporous δ form of sPS is also able to absorb ethylene[2b] and carbon dioxide [2c-d], that have negatively effects for vegetable. Active packaging by nanoporous-crystalline films, based on the removal of molecules generated by the vegetables being detrimental for their preservation [2e], could be complemented by the slow release of antimicrobial molecules, which could be included as guest of the film crystalline cavities. Therefore the preparation of s-PS co-crystalline films that include guests with antimicrobial activity, in particular the carvacrol guest has been studied and reported in chapter 1. The kinetics of release, in variable concentrations of carvacrol in films with different thickness, has been analyzed. It was observed that the location of antimicrobial molecules mainly in the crystalline phase assure a decrease of desorption diffusivity and hence a long-term antimicrobial release.

In chapter 2, the study of the possible molecular orientations that can be developed in polymer films able to form cocrystalline phases, are reported. This phenomenon has been observed only for sPS films until now. In particular, in my thesis has been shown that also other polymers, such as poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) and poly (L-lactide) (PLLA), able to form co-crystalline phases, can develop orientations during the co-crystallization process with solvents. These orientations can be useful to the structural studies on PPO and PLLA co-crystalline forms.

We have also investigated on the shrinkage behaviour developed in syndiotactic polystyrene (sPS) films after cocrystallization procedures leading to co-crystalline phases.

High shrinkage values have been measured on sPS δ cocrystalline phase showing a crystalline phase orientation. In order to minimize this effect, novel procedures have been developed.

Another aspect of my work is focused on the study of chiro optical response of a racemic polymer crystallized with a temporary chiral guest, as reported in chapter 3. In particular, I evaluated the degree of circular polarization of different thickness sPS films, and of the achiral guests, such as azulene and 4-nitroaniline, included in the polymer crystalline phase after guest exchange procedure. These studies have been useful to investigate on the nature of this phenomenon.

Finally, in chapter 4, a method to realize a photonic crystal (PhC) with polymeric materials is reported. A PhC is an object composed by two or more materials with different refractive index and an alternated periodicity. The main advantage to use polymers rather than inorganic materials is the ease and the speed to obtain thin films by spin coating and the low cost of materials.

In order to realize a photonic crystal, by using thin layers of PPO presenting nanoporous crystalline phase, it has been necessary to characterize amorphous as well as crystalline phases for this purpose. Techniques such as IRRAS and ellipsometry have been used (as reported in section 4.3 of chapter 4).

1. a) Tashiro, K.; Tadokoro, H. In Encyclopedia of PolymerScience and Engineering. Supplement **1989**; p 187 b) Corradini, P; Guerra, G. *Adv. Polym. Sci*. **1992**, 100, 183
2. a)Auriemma, F.; De Rosa, C.; Corradini, P. *Adv. Polym Sci*. **2005**, *181*, 1–74. b) A. R. Albunia, T. Minucci, G. Guerra, J. *Mater. Chem*. **2008**, *18*, 1046. c) Larobina D., Sanguigno L., Venditto V., Guerra G., Mensitieri G., *Polymer* **2004**, 45, 429. d) Annunziata L., Albunia A. R., Venditto V., Guerra G., *Macromolecules* ,**2006**, 39, 9166 e) P. Rizzo;C. Daniel; A. De Girolamo Del Mauro; G. Guerra **2006** SA2006A22 Università di Salerno ID:1517898 Brevetto