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TESI DI DOTTORATO DI RICERCA IN CHIMICA

English abstract

Polymorphism and co-crystalline phases of polymers

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Crystalline phases are extremely relevant for properties and applications of many polymeric materials. In fact, their amount, structure and morphology constitute the main factors controlling physical properties of fibers, films and thermoplastics and can be also relevant for properties of rubbers and gels.

It is also well known that processing and physical properties of polymer-based materials are strongly affected by the occurrence of *polymorphism* (i.e. the possibility for a given polymer to crystallize in different crystalline forms) and *mesomorphism* (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).

Different has been the destiny of polymeric *co-crystalline forms*, i.e. structures where a polymeric host and a low-molecular-mass guest are co-crystallized.

Systems composed of solid polymers and of low molecular mass molecules find several practical applications, including advanced applications. In several cases, additives (often improperly referred as guest molecules) are simply dispersed at molecular level in polymeric amorphous phases, although frequently, to reduce their diffusivity, the active molecules are covalently attached to the polymer backbone, either by polymerization of suitable monomeric units or by grafting the active species onto preformed polymers.

A more simple alternative method to reduce diffusivity of active molecules in solid polymers and to prevent their self-aggregation consists in the formation of co-crystals with suitable polymer hosts.

Polymeric co-crystalline forms are quite common for several regular and stereoregular polymers, like e.g. isotactic and syndiotactic polystyrene (s-PS), syndiotactic poly-*p*-methyl-styrene, syndiotactic poly-*m*-methyl-styrene, syndiotactic poly-*p*-chloro-styrene, syndiotactic poly-*p*-fluoro-styrene, polyethyleneoxide, poly(muconic acid), polyoxacyclobutane, poly(vinylidene fluoride), syndiotactic polymethylmethacrylate.

The removal of the low-molecular-mass guest molecules from co-crystals can generate nanoporous-crystalline phases. In this respect, it is worth noting that nanoporous crystalline structures can be achieved for a large variety of chemical compounds: inorganic (e.g., zeolites), metal-organic as well as organic. These materials, often referred as inorganic, metal-organic and organic “frameworks” are relevant for molecular storage, recognition and separation techniques.

The removal of the low-molecular-mass guest molecules from polymer co-crystalline forms generates host chain rearrangements, generally leading to crystalline forms that, as usual for polymers, exhibit a density higher than that one of the corresponding amorphous phase. However, in few cases (to our knowledge, up to now only for s-PS), by using suitable guest removal

conditions, nanoporous crystalline forms, exhibiting a density definitely lower than that of the corresponding amorphous phases are obtained.

Poly-4-methyl-1-pentene isotactic (i-P4MP1) is a polymer characterized by a complex polymorphism and 4 different crystalline forms, some of which are obtainable only by crystallization with solvent, have been described in the literature.

Monolithic and highly crystalline aerogels of isotactic poly(4-methyl-pentene-1) (i-P4MP1) have been prepared by sudden solvent extraction with supercritical carbon dioxide from thermoreversible gels. The cross-link junctions of i-P4MP1 gels, depending on the solvent, can be constituted by pure polymer crystalline phases (I or III or IV) or by polymer-solvent co-crystalline phases (for cyclohexane and carbon tetrachloride gels). Gels with co-crystalline phases lead to aerogels exhibiting the denser crystalline form II while all the other considered gels lead to aerogels exhibiting the thermodynamically stable form I. The effect of solvent on the aerogels pore structure and morphology has been also investigated by scanning electron microscopy and N₂ sorption measurements. In all cases the aerogels present highly porous interconnected structures with macropores and a large heterogeneity of mesopore size but without micro-sized pores.

Poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) is a linear regular polymer, which as s-PS has the advantage to be a commercial thermoplastic polymer. PPO exhibits a high free volume or ultrapermeable amorphous phase and has been recognized as a membrane material with high permeation parameters. Although few papers have recognized that PPO crystalline phases can play a role in gas sorption and transport processes, no correlation between the amount or nature of the crystalline phase and guest sorption properties has been reported. This is mainly due to the scarce information available in the literature relative to the crystalline phases of PPO.

Crystalline modifications, exhibiting largely different X-ray diffraction patterns, have been obtained for poly(2,6-dimethyl-1,4-phenylene)oxide (PPO), by gel desiccation procedures as well as by solvent-induced crystallization of amorphous films. The choice of the solvent allows controlling the nature of the crystalline phase. Both amorphous and semicrystalline samples of this commercial thermoplastic polymer exhibit a high uptake of large guest molecules (like, e.g., benzene or carbon tetrachloride), both from vapor phases and from diluted aqueous solutions. Surprisingly, the semicrystalline PPO samples present guest solubility much higher than fully amorphous PPO samples. These sorption experiments, as well as density measurements and classical BET experiments, clearly indicate that the obtained PPO crystalline phases are nanoporous. For these thermally stable PPO-based materials exhibiting nanoporous crystalline and amorphous phases, many applications are predictable.

Finally, the preparation procedures and the thermal stability of the co-crystalline phase and FTIR and VCD analysis are presented. In particular co-crystalline phases with racemic and non-racemic guest molecules have been prepared and characterized. The experimental data indicates that the PPO/ α -pinene co-crystalline form is chiral, i.e. the unit cell includes all right or left handed polymer helices and (1S-(-) or (1R-(+) α -pinene guest molecules, respectively.