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Properties and Applications of Nanoporous-Crystalline Polymers

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ABSTRACT

Nanoporous-crystalline (NC) forms, i.e. crystalline structure presenting nanocavities or nanochannels inside the crystalline lattice, are possible only for two polymers, both commercially available: syndiotactic polystyrene (sPS) and poly(2,6-dimethyl-1,4-phenylene) oxide (PPO). In particular, the two NC phases of sPS, named delta (δ) and epsilon (ε), showing pores as cavities or channels, are well described and characterized in literature since 1994 and 2007, respectively; whereas, as for PPO, evidences of the formation of NC phases have been established only in 2011.

NC phases present several features which make them interesting for many industrial fields, for instance they can absorb suitable guest molecules, even at low activity from water and air, making them useful for applications such as air and water purification and/or molecular sensors. Moreover, the capability to absorb suitable guest molecules inside the NC lattice, leading to the formation of co-crystaline (CC) phases, can open the possibility of applications of these CC polymeric materials, in many different fields depending on the chemical nature of the guest molecule, as for instance fluorescence, photoreactivity, magnetism, ferroelectricity and antimicrobial.

The present Ph.D. thesis aimed to investigate on new properties as well as on possible applications of these peculiar thermoplastic polymers, and the goals achieved are reported as follows.

Firstly, WAXD and FTIR measurements have shown the formation of two well-separated NC (and CC) forms of PPO, named alpha (α) and beta (β). The NC α and β forms not only exhibit different chain packing but also slightly different chain conformations ($\boldsymbol{c}$ = 5.28 and 5.47 Å, respectively). Additionally, the α-form is favored by hydrophobic (with solubility lower than 0.11 mmol per 100 ml of water) and bulky guest molecules (with molecular volumes higher than 230 $Å^3$) while the β-form (being characterized by a higher chain periodicity) is favored by hydrophilic (with solubility higher than 2 mmol per 100 ml of water) and small guest molecules (with molecular volumes lower than 149 $Å^3$).

Another important aspect which has been point out is the strong influence of the crystalline phase orientation of NC PPO α phase with respect to the film plane on guest molecules diffusivity. In particular, NC PPO films exhibit higher diffusivity of the pollutant perchloroethylene (PCE) from vapors (5.6×10^{-10} cm^2 s^{-1}) as well as from aqueous solutions (2.1×10^{-10} cm^2 s^{-1}) when the orientation of the NC α phase is preferentially perpendicular to the film plane ($c_\perp$ orientation). Specifically, diffusivity values are higher than for films with $c_{//}$ orientation (1.5×10^{-11} cm^2 s^{-1}) and much higher than NC sPS films (6.7×10^{-12} cm^2 s^{-1}). Moreover, guest uptakes for NC $c_\perp$ PPO films, when expressed as mass of guest per polymer volume, are also much higher than for NC

PPO powders and aerogels. This advantage becomes very important considering that for most purification processes the limiting factor is the volume of the absorbent material.

Furthermore, it has been also found that guest diffusivity values of PCE on NC PPO films presenting high surface area (up to 620 $m^2 g^{-1}$) are even much higher than for $c_\perp$ oriented NC PPO films, both for sorption from vapor phase (3.3×10^{-9} $cm^2 s^{-1}$) and from diluted aqueous solutions (3.8×10^{-10} $cm^2 s^{-1}$). These features make NC PPO films (especially with high surface area) particularly suitable for air and water purification.

In addition, preliminary results about potential gas sensors made with PPO films/coatings have been reported. Two approaches have been proposed based on the transduction methods: electrical and optical. About electrical approach, a potential gas sensor based on a metal insulator semiconductor has been proposed. This sensor presents a PPO coating (≈1μm) as dielectric material between two metal contacts (Au, gold). When the sensor is exposed to different gases (i.e., methyl ethyl ketone and carbon tetrachloride), a diverse response pattern has been achieved, therefore a discrimination among volatile chemicals seems to be possible. As concern optical approach, PPO films containing 1–2 wt% of the fluorophore umbelliferone has been tested in saturated chloroform vapours. Once exposed to these vapours, fluorescence rapidly turned on within the first minutes thanks to the solvation effect provided by the polar vapours. Such vapochromic response has appeared also to be reversible after many cycles. The whole set of data has suggested that PPO films/coatings could be very suitable for developing new advanced materials for detection of harmful volatile organic compound vapours.

Furthermore, sorption of carboxylic acids in NC phases of axially oriented sPS phases has been explored. The main results which have been observed are that ε sPS phases can host hydrogen-bonded molecules to form a “polymer” into the crystalline channels (i.e., with the dicarboxylic adipic acid). This could be particularly interesting for films exhibiting the $c_\perp$ orientation, in which the crystalline channels and hence the hydrogen-bonded “linear polymers” are preferentially perpendicular to the film plane. This procedure could possibly lead to formation of isolated semiconductive linear polymers perpendicular to the plane of insulating sPS films for new membranes with electrical properties.

Finally, the phenomenon of crystallization associated to the unusual induction of axial orientation in sPS unstretched fibers has been also observed. Different guests (as pure solvent or in aqueous diluted solutions) have been tested finding that they are able to induce crystallization in CC phases associated to high degree of axial orientation (in the range $0.7 < f_c < 0.8$). The high degree of axial orientation can be also completely retained after guest removal leading to NC phases. The

occurring of axial orientation improves mechanical property of sPS fibers and hence could be notably relevant from an industrial point of view.

Moreover, axially oriented CC sPS fibers including natural antimicrobial guest molecules (i.e., eugenol, carvacrol and thymol), have been also studied during time. They present a slow and controlled release in air at room temperature; this long-term antimicrobial release makes them usable for months in many biomedical applications where the inhibition of microorganisms' growth is crucial.