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H-bonded Carboxylic Acids in Crystalline Nanoporous of Syndiotactic Polystyrene

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ABSTRACT: Co-crystalline (CC) forms between a polymeric host and low-molecular-mass guest molecules are known for many polymers [1]. For most host polymers, CC phases are formed only with a very limited number of guest molecules due to specific host–guest interactions.

Completely different behavior is for syndiotactic polystyrene (s-PS), it is a relevant commercially polymer able to form not only CC forms with a large number of guest molecules [2] but also nanoporous-crystalline (NC) forms whose density is lower than the corresponding amorphous phases.

In this communication we present CC forms of s-PS with a carboxylic acid (hexanoic acid, HA) [3], which has an antimicrobial activity against *E. coli* and *S. aureus*, as well as an antifungal activity on *Botrytis cinerea*.

The analysis is mainly based on axially stretched s-PS films, both NC δ and ε phases, which have been characterized by Polarized FTIR spectra. The most relevant feature of these FTIR spectra is that two additional guest peaks clearly appear after HA sorption in axially s-PS δ film: a carbonyl stretching at 1751 cm^{-1} and a OH stretching peak at 3443 cm^{-1}. These two peaks are dichroic, so they can be related to HA molecules isolated into δ cavities of the crystalline phase. On the other hand, after HA sorption in axially s-PS ε film, the dichroism is observed only for the carbonyl peak at 1709 cm^{-1}, corresponding to hydrogen-bonded guest molecules. This suggests that HA dimers are included in the crystalline ε nanochannels of the crystalline phase.

This is the first reported case of a polymeric CC phase including a hydrogen-bonded dimeric species. Moreover, since this phenomenon occurs in the NC s-PS ε form, exhibiting continuous crystalline channels parallel to the polymer chain axis, our results suggest the possibility of inclusion in crystalline nanochannels of continuous molecular chains formed by hydrogen bonded dicarboxylic acids opening new perspectives in the use of CC polymer films as functional materials.

KEY WORDS: nanoporous-crystalline forms; crystalline polymer hosts; low-molecular-mass guests; carbonyl stretching peaks; hydrogen bonding; polarized FTIR; WAXD.

References

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