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Crystal Structure of Poly(ethylene-oxide) Supramolecular Assemblies

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SUMMARY: The formation of poly(ethylene oxide) (PEO) supramolecular complexes is discussed in terms of intermolecular interactions and molecular packing. On the basis of the different known crystal structures, several mechanisms are proposed. First, the PEO complexes can be formed by an Intercalation or Inclusion process, guest molecules diffusing into the PEO unit cell. On the other hand, molecular complexes based on hydrogen bonding cannot be obtained by such a way, their formation requires the complete removal of the initial PEO structure either by melting or dissolution. Finally the relations between the crystal lamellar morphology, the host-guest interactions and the PEO chain mobility are discussed.

Introduction

Last few years, the number of papers devoted to the study of solid state supramolecular assemblies of organic molecules or composite organic-inorganic systems has amazingly increased. So the growth of mixed crystals rapidly appears to be a first class method to prepare "tailor-made" materials exhibiting specific optical or electronical properties.
The control of the molecular arrangement in the crystal obviously depends on the intermolecular interactions and the molecular packing. A crystalline material can therefore be considered as a very large supramolecular assembly, its structure being dictated by the molecular recognition and the self-organization of the different molecular species1). This self-organization process involve interactions such as electrostatic forces, hydrogen bonds, van der Waals and donor-acceptor effects. For instance, Masse and co-workers have crystallized in a non-centrosymmetric way *p*-nitroaniline molecules via the formation of electrostatic interactions with inorganic salts, such crystals being used in NLO applications for second harmonic generation2).

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Poly(ethylene oxide) host-guest complexes

Several years after the report on the complexation of crown ether by alkali salts(3), the first poly(ethylene oxide) (PEO) complexes, prepared with urea(4) or mercuric chloride(5), were described by Tadokoro and co-workers in 1960's. Later, the formation of mixed crystals with a large number of substituted aromatic molecules *p*-dihalogenobenzenes(6), resorcinol(7), *p*-nitrophenol(8), hydroquinone(9) or 2-methyl-resorcinol(10) was reported. As schematically illustrated in Figure 1, the growth of mixed crystals with a polymer involves several energetic contributions, i.e. the polymer-guest molecules, guest molecules-guest molecules and polymer-polymer intermolecular interactions AND an intramolecular energetic contribution related to the chain conformation. For PEO, several studies have demonstrated that the most stable chain conformation corresponds to the trans-trans-gauche conformation very close to the 7_2 helical conformation (Figure 2) observed for the monoclinic form reported by Tadokoro et al.(11). As we will show throughout this paper, the final crystal structure and morphology of the molecular complexes reflect the balance between the following tendency, sometimes opposed, i) to form intermolecular interactions with guest molecules, ii) to maintain a chain conformation close to the canonical (ttg) conformation.

Formation of the PEO molecular complexes

On the basis of their mode of preparation, the different known PEO complexes (see Table 1) can be divided in two classes. Some of them are prepared simply by immersing a solid semi-crystalline PEO film in vapor (p-dichlorobenzene) or solutions (mercuric chloride, alkali salts, 2-methyl-resorcinol α). Some other PEO complexes usually involving hydrogen bonds, are only formed when the polymer is either melted or dissolved (resorcinol, p-nitrophenol, hydroquinone, 2-methyl-resorcinol β). In the latter, the crystal structure of the PEO has to be destroyed to ensure the formation of the complex. We will discuss later the relation between the intermolecular interactions and the mode of preparation of the complexes.

One of the major problems concerning the study of these co-crystallized system is to determine if there is formation of a molecular complex or not. To achieve this, the binary phase diagram of the system suspected to form a compound can be determined and analysed. Some examples of such phase diagrams are given in Figures 3, 4 and 5. They are constructed by plotting the different transition temperatures observed during the heating of both

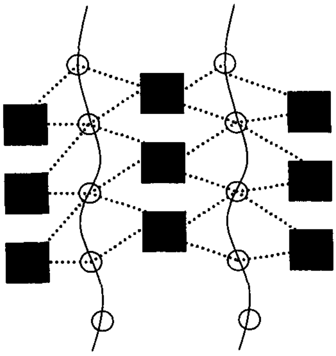

Figure 1. Schematic drawing of a polymer host-guest molecules assembly. The lines and black square represent the polymer chains and the small molecules, respectively.The dotted lines mimic the formation of intermolecular interactions.

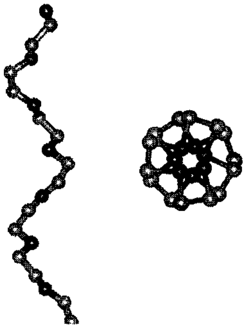

Figure 2. Views of the PEO chain in the 7_2 helical conformation, showing the position of the ether oxygen able to interact with the guest molecules.

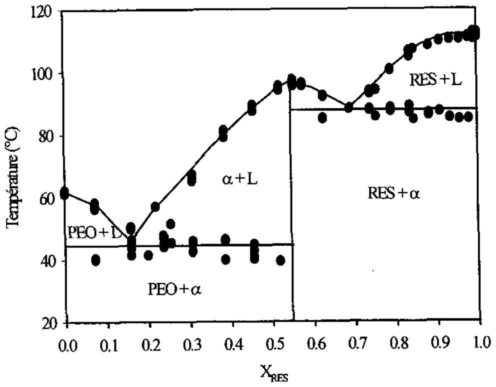

Figure 3. Phase diagram of the PEO-resorcinol system. The formation of a molecular complex with a 0.55 weight fraction is observed (stoichiometry : 2 EO monomers / 1 resorcinol molecule).

components mixtures which were previously melted several times to ensure homogeneity of the sample. The melting transitions are used instead of crystallization transitions in order to minimize the kinetic effects and, therefore, to be as close as possible to the thermodynamic phase diagram. According to the nature of the guest molecules, different phase diagrams can be observed. In some cases, a simple eutectic without any evidence of a molecular complex is found (e.g. PEO-trioxane12) or PEO-p-nitroaniline systems). On the contrary, the PEO-resorcinol (meta-dihydroxybenzene) phase diagram given in Figure 3 clearly demonstrates the formation of a stable molecular compound, corresponding to a new crystalline form. This diagram actually corresponds to the juxtaposition of two, PEO-complex and complex-resorcinol, eutectic diagrams. Due to the small difference between the melting temperatures of the complex (100°C) and pure resorcinol crystals (111°C), the compound melts via a congruent melting transition giving a liquid phase having the same stoichiometry of the complex. By comparison, the phase diagram obtained for the para isomer of dihydroxybenzene (hydroquinone) reveals some differences (Figure 4). The occurrence of two constant transitions, related to an eutectic and a peritectic, also indicates the formation of a compound with a 2 EO monomers / 1 molecule stoichiometry. However, the molecular complex melts via a peritectic reaction as expected by considering the large difference between the melting temperatures of pure crystalline hydroquinone (179°C) and molecular complex (about 100°C). At the transition, the complex decomposes in two phases, pure crystalline hydroquinone and a liquid phase. The phase diagram of the PEO-2-methyl-resorcinol system, given in Figure 5, illustrates the flexibility of these polymer host-guest structures where only weak intermolecular interactions are involved. Two complexes, corresponding to 7/2 and 2/1 stoichiometry, are observed (see the 3 constant transitions). The X-ray diffraction curves recorded for PEO-2-methyl-resorcinol mixtures (Figure 6) show that these complexes actually correspond to different crystal forms (α and β). More complicated phase diagrams can also be obtained, see for instance the phase diagram of PEO-lithium triflate system which involves 3 molecular complexes, a liquid-liquid phase separation and a solid-solid transition of the pure salt13).

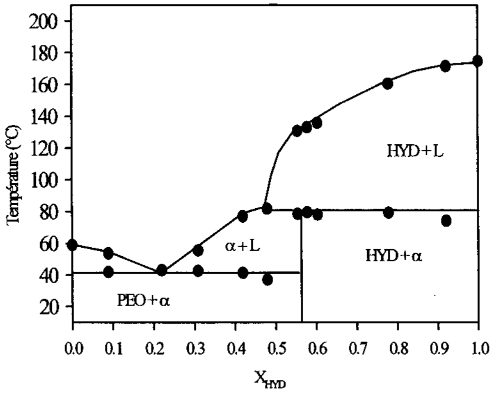

Figure 4. Phase diagram of the PEO-hydroquinone system. The molecular complex is observed at 0.55 weight fraction (stoichiometry : 2 EO monomers / 1 hydroquinone molecule). The phase diagram also reveals the incongruent melting of the complex (peritectic) which yields a liquid phase and a solid phase of pure hydroquinone.

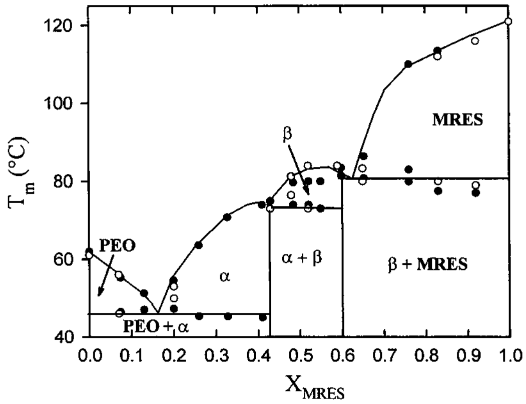

Figure 5. Phase diagram of the PEO-2-methyl resorcinol system. Polymorphism is directly observed. The two complexes have a stoichiometry of 3.5 EO/ 1 MR and 2 EO/ 1 MR, respectively.

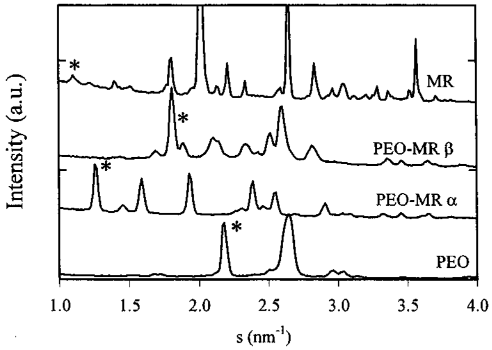

Figure 6. X-ray diffraction curves of pure 2 methyl-resorcinol (MR), pure PEO and of both supramolecular complexes PEO-Mr α and β. The reflections used for the construction of the phase diagram are marked with an asterisk.

Table 1. Summary of the characteristics of the crystal structures of the different PEO-molecular complexes.

Guest molecule	Stoichiometry (EO/mol.)	Space group	Chain conformation	Interaction
---	---	Mono – $P2_1/a$	7_2 helix	---
Mercuric chloride I	4/1	Ortho – Ccmm	(ttt ttg ttt tt-g)	Elect.
Mercuric chloride II	1/1	Ortho – Pnc2	(tgg t-g-g)	Elect.
p-dichlorobenzene	10/3	Ortho – $Cmc2_1$	10_3 helix	V.d.W
Alkali salt I	3/1	Mono – $P2_1/a$	$(ttg\ ttg\ tt\text{-}g)_2$ "helix"	Elect.
Alkali salt II	1/1	Mono – $P2_1/c$	(tgg t-g-g)	Elect.
Resorcinol	2/1	Ortho – $Pna2_1$	4_1 helix	H-bonds
p-nitrophenol	3/2	Tric – P_{-1}	(ttg ttg ttt tt-g tt-g ttt)	H-bonds
Hydroquinone	2/1	Tric – P_{-1}	4_1 helix	H-bonds
2-methyl-resorcinol α	7/2	Mono – $P2_1/a$	7_2 helix	V.d.W
2-methyl-resorcinol β	2/1	Ortho – Pbca	4_1 helix	H-bonds

Determination of the crystal structures

The determination of the crystal structure of a polymer host-guest molecular complexe usually requires the combination of several experimental techniques including X-ray diffraction and spectroscopic techniques (mainly, FTIR and Raman). In some cases, when the structure includes heavy atoms, a complete analysis can be achieved with X-ray diffraction, e.g. the determination of the PEO-$HgCl_2$ structure[5)]. As an example, the procedure used to determinate the PEO-resorcinol crystal structure will be described[7)]. Figure 7 shows the X-ray diffraction pattern obtained for a film stretched from the glassy state. First, the unit cell parameters (a=1.05 nm, b=1.01nm , c= 0.98nm) and the space group (orthorhombic, $Pna2_1$) are deduced from the analysis of the reflections observed in this pattern. From density measurement, the following unit cell content is derived, 4 resorcinol molecules and 8 EO monomers. Afterwards, polarized FTIR spectroscopy investigations on oriented samples were used to determine the average orientation of resorcinol molecules in the unit cell and that PEO chains adopt a 4_1 nearly (ttg) helical conformation. By considering the symmetry of the crystal and the packing of the different molecules, we obtain a first trial model of the crystal

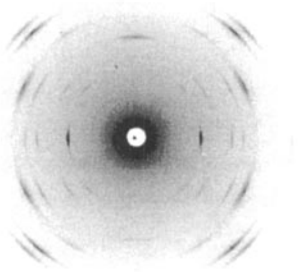

Figure 7. 2D X-ray diffraction pattern of oriented PEO-RES film. The sample was prepared by stretching a melted film of complex from the glassy state.

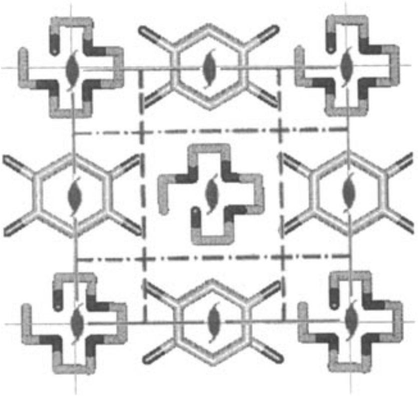

Figure 8. View of the ab plane of the 2/1 PEO-resorcinol supramolecular complex trial structure, the symmetry elements of the Pna2_1 space group being superimposed. The PEO chains have a ttg conformation (4_1 helix) and appears as cross. Two RES molecules are stacked along the c parameter. As an effect of the screw symmetry, RES molecule appear as four times substituted aromatic molecule.

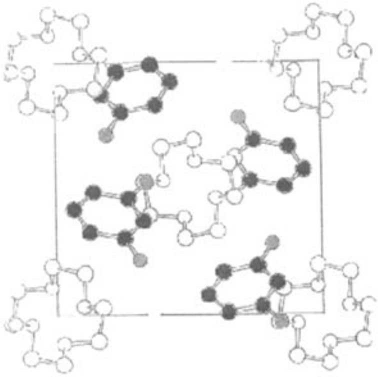

Figure 9. View of the PEO-RES crystal structure obtained from a Rietveld refinement. The refinement were achieved with the Rietveld FWR program from two-dimensional X-ray diffraction pattern recorded for a stretched film. We note the difference in molecular packing with respect to the trial structure (Figure 8).

structure given in Figure 8. The final step consists in the refinement of the starting model on the basis of the X-ray diffraction intensities. In collaboration with Prof. P.Iannelli (Universita di Salerno, Italy), a two-dimensional Rietveld refinement[14)] was performed to give the final crystal structure (Figure 9) in agreement with the X-ray data. Note the differences between the trial and final structures.

Crystal structures

As described before, the PEO molecular complexes can be divided in two classes depending on their mode of formation. The crystal structures of these complexes at the molecular level reflect this difference. The molecular complexes directly formed by immersing a solid PEO film in vapor or solutions are formed by either an intercalation or an inclusion of the guest molecules inside the PEO unit cell with only slight modifications of the chain packing. This is clearly illustrated by the structure of the PEO-*p*-dihalogenobenzene complex (Figure 10). This structure can be easily obtained from the pure PEO monoclinic structure (Figure 11) by increasing the distance between polymer layers to accomodate the aromatic molecules. This structure, called Intercalate, only involves weak van der Waals interactions which are not strong enough to disturb the packing of PEO macromolecules. The PEO chains still maintain a 10_3 helical conformation very close to the canonical 7_2 helix of pure PEO. The mercuric chloride complexes prepared from ether solutions are formed by an intercalation mechanism. This structures is however astonishing since its formation requires the diffusion of atoms as large as mercuric atoms in the PEO crystal. The structure determined for alkali salts complexes form I[15)], also prepared by an immersion of PEO film in solutions, significantly differs from the intercalates. In these systems, the PEO chains adopt a very large helical conformation with 6 monomers per turn (instead of 3.5 per turn for pure PEO), the pitch of the helices averaging 0.8 nm. In fact, the PEO chain wrapped alkali ions by forming a structure close to that reported for the crown ether – alkali salts complexes. However, despite the large distortion of the PEO conformation, the chain packing remains essentially the same as for monoclinic PEO. The formation of these complexes are made by the inclusion of alkali ions in the unit cell to form electrostatic interactions with the oxygen atoms of the polymer. Contrary to the intercalates, the PEO complexes made of resorcinol, hydroquinone or *p*-nitrophenol can only be prepared from melted or dissolved polymer. As shown by NMR investigations[16)], the chain mobility in these molecular complexes is considerably reduced by the formation of hydrogen bonds with the guest molecules. The monoclinic structure of pure

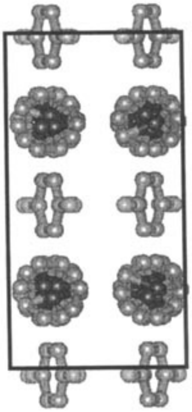

Figure 10. Crystal structure of the PEO-p-dichlorobenzene complex prepared by intercalation of aromatic molecules in between polymer layers. The chains adopt a 10_3 helical conformation.

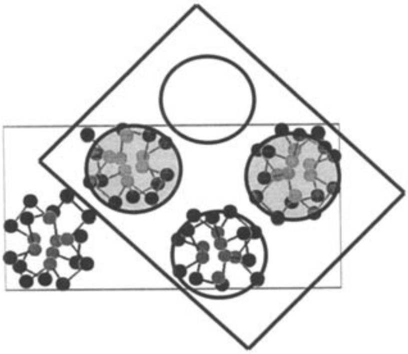

Figure 11. View of the chain packing as observed in PEO-*p*-dichlorobenzene complex, the crystal structure of monoclinic pure PEO is superimposed. Filled and hollow circles refer to left and right handed helices.

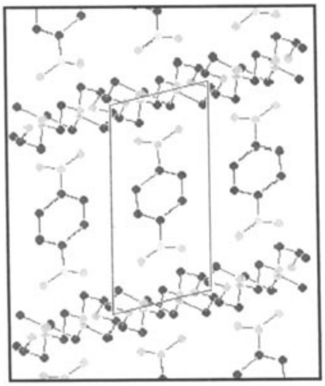

Figure 12. View along the chain axis of the PEO-*p*-nitrophenol (PNP) structure deduced from FTIR and X-ray diffraction study. The formation of molecular stacks is observed along the c parameter. The period correspond to 4 antiparallel PNP molecules. The unit cell contains 1 PEO chain with a unusual glide conformation.

PEO then looses its flexibility and cannot accommodate these aromatic molecules. Therefore, these complexes cannot be obtained by an intercalation or inclusion mechanism. A typical example of these complexes is given by the PEO-*p*-nitrophenol, the structure being shown in Figure 12. The unit cell contains 1 PEO chain of 6 monomers and 4 *p*-nitrophenol molecules which form stacks of antiparallel molecules along c parameter. This arrangement is very likely due to the strong dipole-dipole interactions between aromatic molecules. To interact with the hydroxy groups, the PEO chains surround these stacks and adopt an unusual glide (ttg ttg ttt tt-g tt-g ttt) conformation in order that 4 oxygen atoms of PEO interact with the *p*-nitrophenol molecules. For these complexes, the crystal structure is fully determined by the formation of hydrogen bonds between host and guest molecules, by the intermolecular interactions, the distortion of the PEO chain and by packing considerations. In this case, the chain packing can be very different from that of pure PEO (compare Figures 11 and 12).

Crystal morphology

The morphology of semi-crystalline polymers is usually described in term of a two phases model. The polymers usually crystallize as spherulites, these superstructures being made of a very large number of lamellar crystals assembled in stacks. PEO oligomers is well known to crystallize with a very high degree of crystallinity and characterized by a well defined lamellar thickness. As previously shown by several authors, the macromolecules in the PEO oligomer crystals either adopt an extended chain (EC) configuration or are folded an integral number of times (IF)17). However, the occurrence of a transient state with non integral folded chains (NIF) was observed at the beginning of the crystallization18). These NIF crystals transform rapidly into the more stable states (EC, IF) by a thickening or thinning process. The Figure 13 gives a schematic description of EC, IF and NIF crystals. In this paragraph, we will discuss *How the presence of guest molecules affect the crystallization of the PEO oligomers from the melt.* First of all, optical microscopy and small angle X-ray scattering (SAXS) investigations showed that, despite the presence of several tens of percent of aromatic molecules (e.g. 68% by weight for PEO-*p*-nitrophenol), the molecular complexes still adopt a lamellar morphology typical of semi-crystalline polymers. However depending on the nature of the small guest molecules different morphologies are observed. Figures 14 and 15 show the SAXS data recorded for PEO-resorcinol and PEO-*p*-nitrophenol molecular complexes, respectively. On one hand, for PEO-resorcinol, correlation function analysis of the SAXS curves reveals the growth of EC or IF 1 crystals as pure PEO, the relative proportions of both

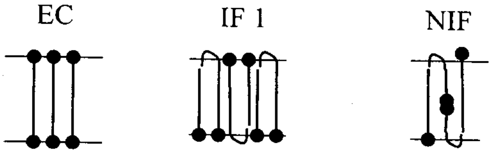

Figure 13. Schematic view of the chain arrangement in PEO oligomers crystals. EC, IF 1 and NIF refer to extended chain, one folded chain and non integral folded chain crystals, respectively.

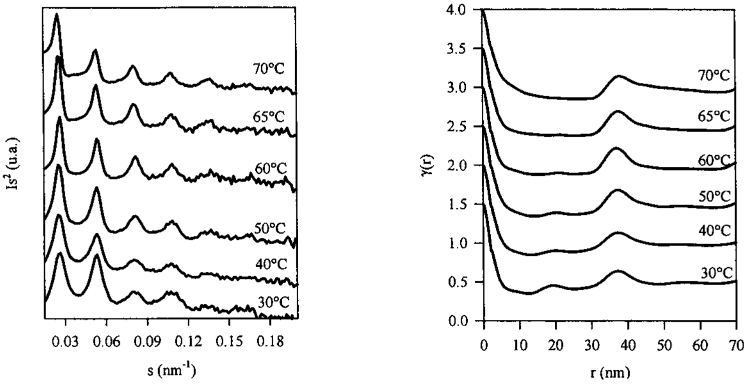

Figure 14. SAXS intensity curves (left) and correlation functions (right) of PEO(Mw=6000)-RES complex crystallized from the melt at various temperatures, as indicated. PEO-RES lamellar thickness is constant indicating the growth of IF or EC crystal .

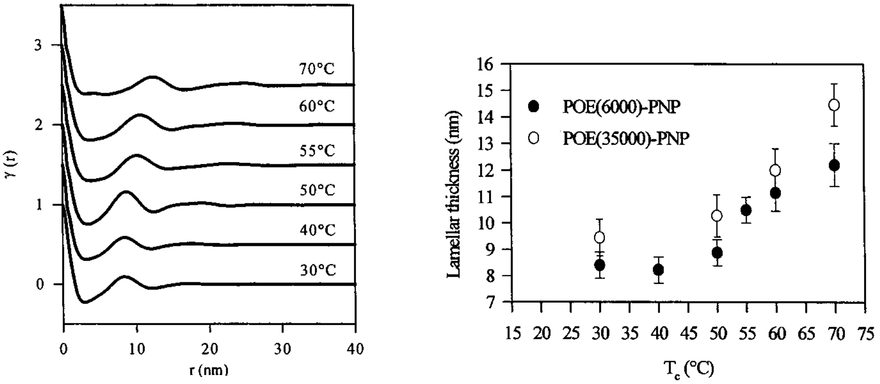

Figure 15. SAXS correlation functions (left) and lamellar thickness (right) observed for PEO-p-nitrophenol molecular complex crystallized from the melt at various temperatures, as indicated. We note the increase of the crystal thickness with the temperature.

species depend on the crystallization temperature. On the other hand, contrary to the pure PEO, the crystals of PEO-*p*-nitrophenol complex adopt a NIF morphology whatever the growth conditions. The occurrence of NIF crystals is deduced by the significant evolution of the lamellar thickness with the crystallization temperature (Figure 15), a constant crystal thickness being expected for EC or IF crystals. This unusual observation can be related to the chain mobility in the crystals. From X-ray time resolved experiments, it appears that PEO chains adopt a NIF configuration in the first stages of crystallization. Afterwards, due to the high flexibility of PEO chains in the solid state, the NIF crystals reorganize to form thermodynamically more stable EC or IF crystals. As revealed by FTIR measurements, hydrogen bonding are more efficient with *p*-nitrophenol molecules than resorcinol. Thus, the intermolecular interactions in the PEO-*p*-nitrophenol complex allow less chain mobility and therefore hinder the reorganization of the NIF crystals into EC or IF configurations. This interpretation was further confirmed by NMR investigations. The relaxation times of the chain in the PEO-*p*-nitrophenol crystal are one order of magnitude higher than that measured for PEO-resorcinol16). In addition, the crystallization of PEO-2-methyl-resorcinol β molecular complex appears to be atypical. As shown in Figures 16 and 17, two crystallization domains can be defined from the evolution of the lamellar thickness. At low crystallization temperatures, the growth of NIF crystals, similar to that of PEO-*p*-nitrophenol, is observed. Although, a crystallization behaviour identical to the PEO-resorcinol (IF crystals) is found at high crystallization temperatures. These observations also support the influence of the chain mobility on the crystal morphology. In fact, the reorganization of the lamellar crystals can only take place at high temperatures when the chain mobility becomes large enough.

Conclusions

Depending on the type of guest molecules and the strength of the intermolecular interactions (van der Waals, hydrogen bonds or electrostatic), several modes of formation of the molecular complexes can be proposed from the simple intercalation or inclusion mechanisms to the formation of hydrogen bonds network. The molecular assembly in the structure of the PEO complexes reflects the competition between different contributions, the formation of intermolecular interactions, the distortion of the polymer chains from the stable helical conformation and the molecular packing. As deduced by direct observation of the lamellar thickness by SAXS, the guest molecules were found to affect the morphology of the crystals. In fact, the stronger are the host-guest interactions the lower are the chain mobility in the

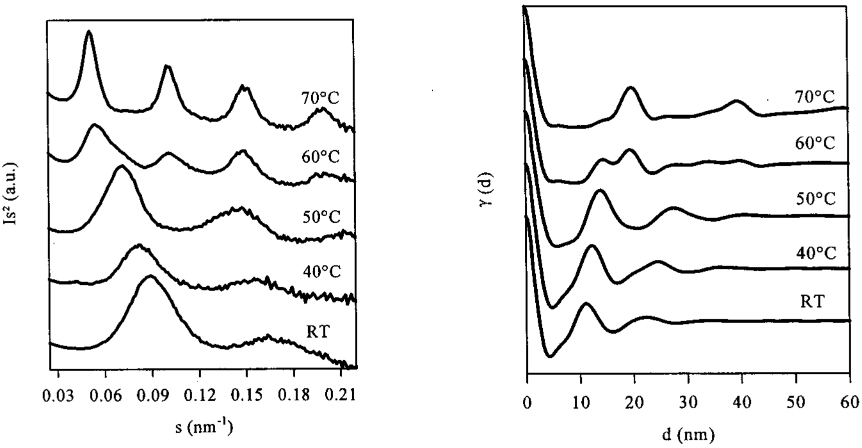

Figure 16. SAXS intensity curves (left) and correlation functions (right) of PEO(Mw=6000)-2-methyl-resorcinol complex β form crystallized from the melt at various temperatures, as indicated. The stoichiometry of the α form corresponds to 2 EO monomers / 1 MR molecule.

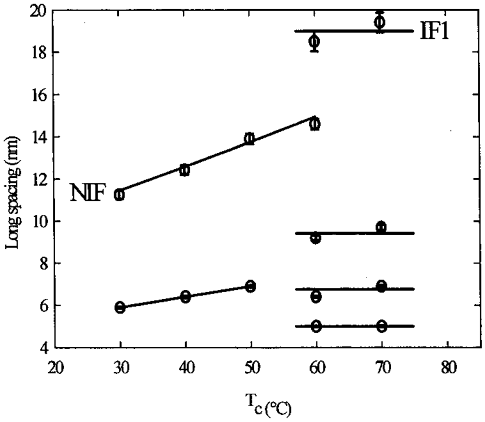

Figure 17. Plot of the lamellar thickness versus the crystallization temperatures. Two crystallization domains are observed, i.e. the growth of NIF and IF lamellar crystals is observed at low and high crystallization temperatures, respectively.

crystals. For strongly interactive systems (e.g. PEO-*p*-nitrophenol), the chain mobility becomes so low that the solid state reorganization of the crystals usually observed for PEO are completely hindered.

Acknowledgments

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