Polymer-Solvent Molecular Compounds: A Brief Presentation

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Summary: Molecular compounds formed through the co-crystallization of polymer chains and solvent molecules are briefly presented with special emphasis on isotactic and syndiotactic polystyrenes. The temperature-concentration phase diagrams, the molecular structure and the various morphologies of these systems are discussed.

Keywords: molecular compounds; phase diagrams; properties; structure

Introduction

A *compound* is a "*chemical substance consisting of two or more elements chemically-bonded with a well-defined ratio, the stoichiometry*". The compounds of interest here are those that are formed between polymer and solvent molecules, or small molecules, through "weak" bonds, such as van der Waals or hydrogen bonds.[1] These systems are therefore not chemical compounds, which are formed through strong covalent bonds, and are usually designated as *molecular compounds*.

Molecular compounds of this type are also often designated as *crystallosolvates*, *complexes*, *clathrates*, *intercalates, inclusion compounds* whose name depends upon the systems, and/or the field of research.

The most straightforward way of describing the three possible types of compounds is by means of temperature-concentration phase diagrams (Figure 1). A ***congruently-melting compound*** behaves as a pure substance as they melt at a well defined temperature at the stoichiometric composition. An ***incongruently-melting compound*** transforms into another phase (solid phase or another compound of different stoichiometry) before melting through a *solid-solid phase transition*. The intermediate case between the congruently-melting and the incongruently-melting compound, the ***singular-melting compound***, behaves like a congruently-melting compound, in that no transformation of the type *compound* → *solid phase* + *liquid* occurs but direct melting.[2]

Molecular compounds possess a molecular arrangement in the solid state where each position of the crystalline lattice is occupied by a given atom or molecule. The crystal unit cell of a molecular compound is not that of any of its constituent but one of its own. As a result, the diffraction pattern of a molecular compound differs from that of any of its components

Molecular compounds were already known at the turn of the 20th century for biopolymers such as cellulose and amylose. The first molecular compounds with synthetic polymers that were thoroughly studied were certainly those formed between polyoxyethylene (PEO) and *para*-dihalogenobenzene molecules.[3,4] Since then, other molecular compounds have been found, particularly with the recently-synthesized syndiotactic polystyrene,[5,6] but also with poly(vinylidene fluoride),[7] poly(vinyl chloride),[8] and many others.[1] Here a few examples will be detailed with a main focus on syndiotactic polystyrene molecular compounds.

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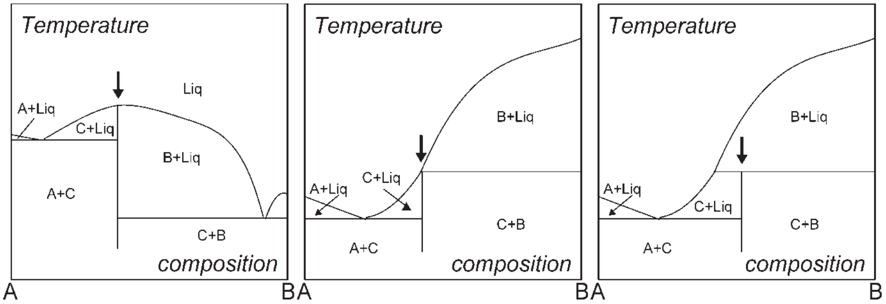

Figure 1.

Typical temperature-composition phase diagrams for binary systems. **left**: congruent-melting compound; **right**: incongruently-melting compound; **middle**: singular-melting compound. C stands for the compound, A and B for the two components of the binary system. The arrows indicate the compound stoichiometry.

Thermodynamics: Temperature-concentration Phase Diagrams

The mapping out of the temperature-concentration phase diagram is certainly what should be carried out in the first place when studying polymer-solvent molecular compounds. This type of diagram provides one with invaluable information about the compound formation, the different phases and domains, and in many cases about the stoichiometry(ies). Once the various phases and domains have been identified, then the molecular structure and the morphology can be investigated.

It is often considered that Gibbs phase rules can be only applied to systems that have been obtained from the homogeneous

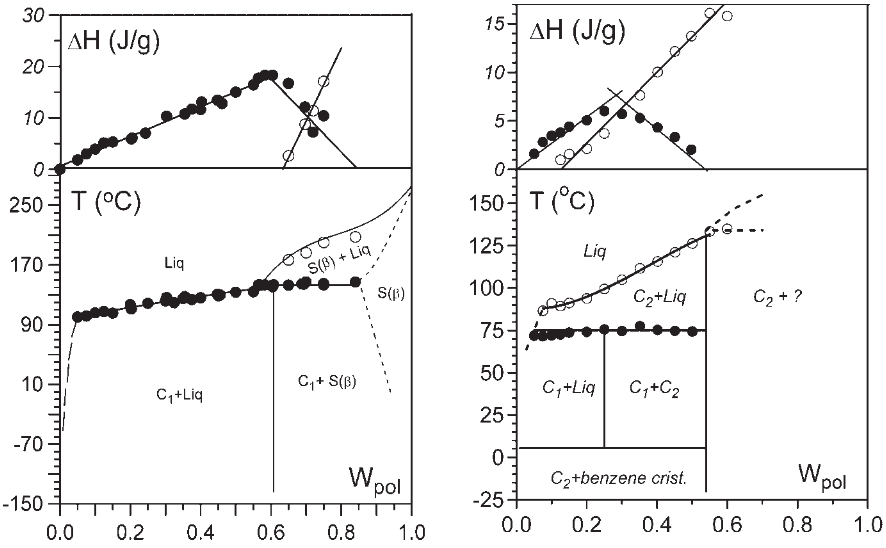

Figure 2.

Temperature-concentration phase diagrams (lower part) together with the Tamman's diagrams (upper part).[11] *left*: sPS/toluene systems. Only one compound is observed with a stoichiometric composition of $W_{pol} = 0.6$ which corresponds to a "thermodynamic" stoichiometry of about 1/1. The morphology of these systems is fiber-like so that for $W_{pol} \ll 0.6$ the system is therefore a thermoreversible gel. $S(\beta)$ is a non-solvated phase; *right*: sPS/benzene systems. Here two compounds of stoichiometric compositions $W_{pol} = 0.26$ and $W_{pol} = 0.54$ are seen, which gives "thermodynamic" stoichiometries of 4/1 and 1/1. Here, too the systems are fiber-like so that for $W_{pol} \ll 0.26$ the systems are thermoreversible gels.

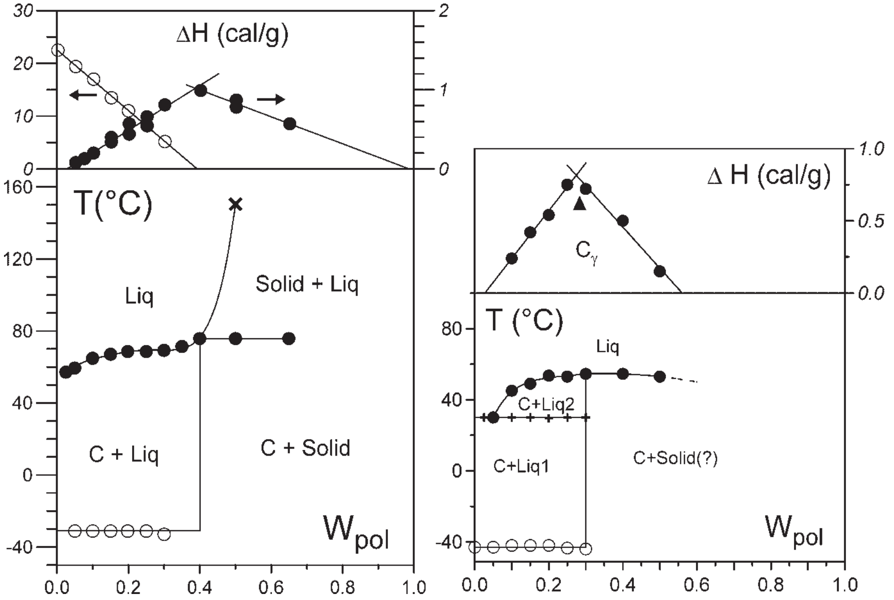

Figure 3.

Temperature-concentration phase diagrams (lower part) together with the Tamman's diagrams (upper part).[15] *left*: iPS/*trans*-decalin systems. The stoichiometric composition is $W_{pol} = 0.4$ which corresponds to a stoichiometry of about 1/1. *right*: iPS/*cis*-decalin systems. The stoichiometric composition is $W_{pol} = 0.3$ which corresponds to a stoichiometry of about 2/1. In both cases the morphology is fiber-like so that these systems form thermoreversible gels for composition lower than W_{pol}.

liquid state through a very slow cooling. This is so because *thermodynamic* equilibrium and *thermal* equilibrium are intermingled. Systems at equilibrium are *stable systems*, namely there is no detectable time-evolution. Such systems can therefore be obtained by cooling rapidly provided the temperature remains the same or nearly the same throughout the sample. That stable phases can be produced through rapid cooling might be questioned as metastable phases could grow instead simply because their formation kinetics could be faster at low temperature (*kinetically-controlled* as opposed to *thermodynamically-controlled* phenomenon). Although these metastable phases should gradually transform into a stable phase, their lifetime could be very long, and so give the deceptive impression that stable phases are dealt with (a glass for instance for a crystallizable polymer). Evidently, Gibbs phase rules would not hold any longer under these conditions. Discriminating metastable phases from stable phases can be easily achieved by calorimetry experiments (such as DSC).: transformation of a *stable phase into another stable phase* always gives an *endothermic latent heat*. Conversely, transformation of a *metastable phase into a stable phase* always produces an *exothermic latent heat*. DSC is therefore an essential tool both for establishing the temperature-concentration phase diagrams and for allowing to find out whether Gibbs' phase rule are applicable for a given system, particularly the use of the Tamman's diagram (plot of the different latent heats vs composition) based on the lever rule.

It is worth emphasizing that the Tamman's diagram provides one with a "thermodynamic" stoichiometry that may differ significantly from the structural stoichiometry as derived from the crystalline lattice.[1,9]

The phase diagrams highlight the effect of the solvent shape on the formation of molecular compounds. For instance

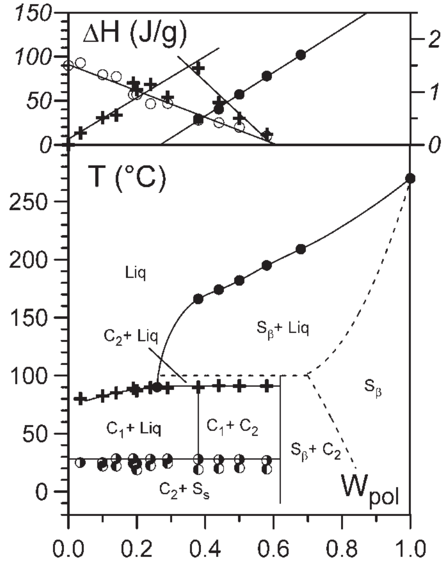

Figure 4.
Temperature-concentration phase diagrams together with the Tamman's diagrams for sPS/diphenyl methane.[9] Two compounds of "thermodynamic" stoichiometries 1/1 and 1/3 are observed. In the temperature range 91–100 °C another domain has to be considered (labeled $C_2 + Liq$) in order to avoid having the coexistence of 4 phases. Note that, as with benzene, the highly solvated compound transforms into the less solvated one. In the Tamman's diagram open circles are related to the left ordinate scale.

compounds formed from sPS/benzene or sPS/toluene systems are clearly differentiated thanks to their phase diagrams (see Figure 2). While sPS/benzene systems can produce 2 compounds (C_1 and C_2) of differing stoichiometries, only one compound is obtained with sPS/toluene systems.[10]

Another example is iPS/*cis*-decalin and iPS/*trans*-decalin systems[11] (Figure 3). Here the mere change of solvent conformation produces compounds with differing thermal behaviour and, more importantly, different stoichiometries (about 2 solvent molecules/monomer unit in iPS/*cis*-decalin, and about 1 solvent molecules/monomer units in iPS/*trans*-decalin).

In the case of sPS/benzene a non-variant thermodynamic event at $T = 75$ °C is seen as expected from Gibbs phase rules, and corresponds to the C_1 to C_2 transformation. Also, in all the Tamman's diagram the latent heats associated with 1st order events vary linearly with composition. This again ascertains that the Gibbs rules are obeyed, of which the lever rule.

Another interest of the phase diagram is its predictive aspect. For instance in the case of sPS/diphenyl methane systems, these rules imply that not more than three phases can coexist for binary systems (variance = 0). As a result, in the temperature range 91–100 °C one has to introduce an additional domain so as to fulfill this rule, although the resolution of the DSC thermograms does not permit to detect it with certainty.[9] As seen in the section devoted to structure, this phase is actually spotted by time-resolved X-ray diffraction experiments.

Morphologies

Various morphologies can be observed for compounds: spherulitic, fibrillars, lamellar... (see examples in Figure 5). The fibrillar structure, which gives rise to thermoreversible gels is obtained through the helix stabilization of the polymer chain as shown by neutron scattering both for isotactic polystyrene (iPS) and syndiotactic polystyrene (sPS).[10,12–13] Other surface morphologies are observed, especially with samples prepared by exposing solid sPS to vapours or liquid.[14,15] These are not well-defined, in the sense that no fibrils nor spherulites can be identified beyond doubt. Guenet and coworkers[16] have described the underlying phenomenon giving rise to these morphologies as "*physical corrosion*". This term conveys the idea that the alteration of the polymer surface, while resembling a chemical corrosion, actually arises from a physical origin, namely the formation of molecular compounds.

The morphology is related to the chain conformation in these compounds. It has been shown by small-angle neutron scattering that the fibrillar morphology is due to

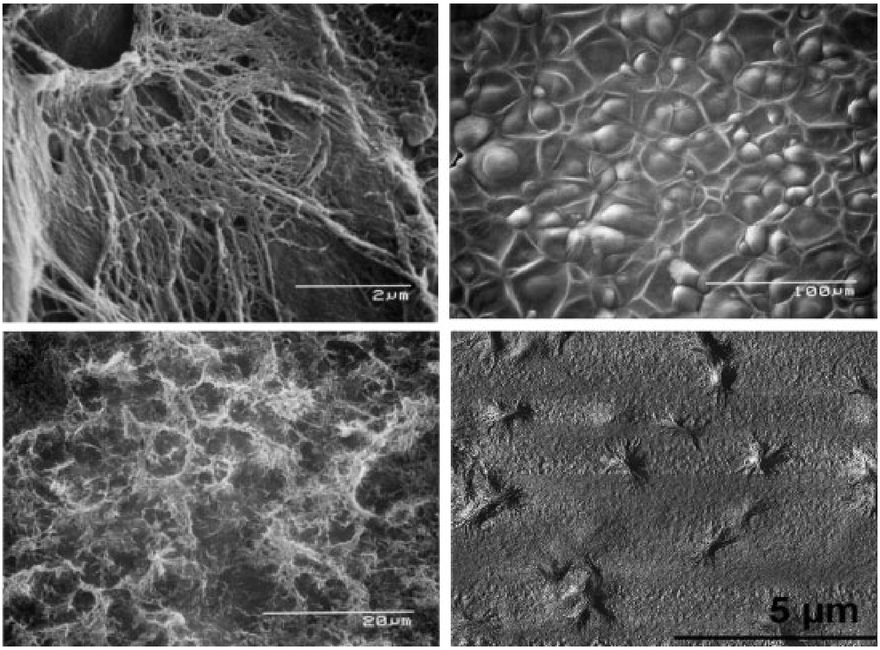

Figure 5.
Various morphologies of polystyrenes compounds:[1] *top left* SEM picture of sPS/biphenyl systems after sublimation of biphenyl showing fibrillar structures; *top right* SEM picture of sPS/Dimethyl phenyl showing spherulitic structures; *bottom left* SEM picture of sPS/benzophenone systems, here a wrinkled surface is rather observed; *bottom right* AFM picture of the surface of amorphous iPS after exposure to liquid *cis*-decalin exhibiting nascent spherolites.

the chain persistence length enhancement, which in turns results from the formation of the compound.[10,12,13] Indeed, the helical structure of the polymer is stabilized thanks to the solvation process which prevents the chain from folding. As a result, chain-folded crystals cannot be formed, and correspondingly no spherulitic structure can be obtained. Instead, fibrils are produced as this is the only remaining possibility for the chains to organize. While the formation of a polymer-solvent compound is required to produce fibrils with otherwise flexible polymers, the formation of a complex does not necessarily implies that a fibrillar morphology will be obtained. As has been shown with isotactic polystyrene (iPS) above a given temperature chain folding reappears, first to a limited extent (1 to 2 folds per chain), and then to a much larger extent when increasing the temperature.[17]

Crystal Structure

In the case of sPS or of polyoxyethylene the crystal structure have been derived from X-ray diffraction studies on oriented samples.[3,18–20] In the case of sPS three forms have been proposed, whose occurrence depends on the solvent molecules: the chathrate form (δ_c form),[5,6,20] the intercalate form (δ_i form)[9,19,20] and a liquid crystalline-like form (δ_N form).[9]

The δ_c form is usually characterized by two reflections at 5.5 nm^{-1}, and 7.4 nm^{-1} (010 and $2\bar{1}0$ planes) with slight variation depending upon the solvent type.[18] In the case of the intercalates, the δ_i form, the first reflection is shifted from 5.5 nm^{-1} to 3.9 nm^{-1}, again with variations depending on the solvent type.[10,19,20]

Compound C_1 in toluene and compound C_2 in benzene correspond to the δ_c form, while compound C_1 in benzene and

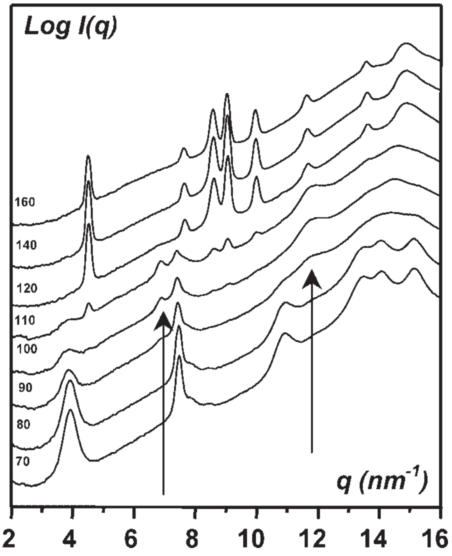

Figure 6.
Time-resolved X-ray diffraction experiments on sPS/diphenyl methane system for $W_{pol} = 0.5$. Heating rate 2 °C/min. The three different phases are observed, and particularly the δ_N form (arrows, and C_2 in Figure 4) between $T = 90$ °C to 110 °C. Actually, this form should also be seen with the δ_i form for $T < 90$ °C (C_1 in Figure 4), yet the diffraction power for the latter is so large that it obliterates that of the δ_N form. Only above the incongruent melting of the δ_N form can we observe the diffraction pattern of the δ_N form.

compound C_1 in diphenyl methane correspond to the δ_i form. The δ_N form corresponds to compound C_2 in diphenyl methane.

Thanks to the availability of X-ray sources of ultra-high brilliance (Synchrotron radiation facilities), time-resolved X-ray experiments can be carried out and examined against DSC results. These experiments are particularly useful for confirming the outcomes derived from the temperature-concentration phase diagrams as highlighted in Figure 6.

Neutron diffraction experiments can also be of use as is shown in Figure 7 where the transformation from the δ_i form to the δ_c form is observed. Neutron diffraction are also of further interest thanks to the possibility of deuterium-labelling of either the polymer and/or the solvent. This provides one with four different structures factor instead of just one when X-ray diffraction is used.[1] The general equation for neutron diffraction can be written:

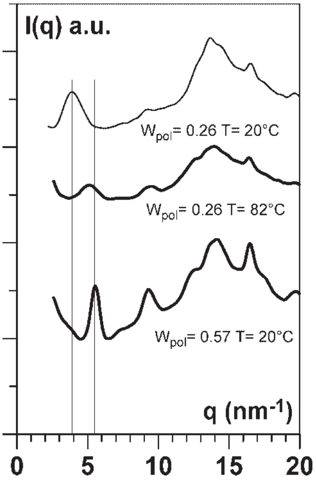

Figure 7.
Neutron diffraction patterns for sPS/benzene systems. Compositions and temperatures as indicated. The transformation from C_1 into C_2 at 75 °C is seen through the shift of the first reflection from $q = 3.9$ nm^{-1} to $q = 5.5$ nm^{-1}. The pattern obtained at $W_{pol} = 0.57$ (stoichiometric composition of C_2 corresponds to that obtained at $W_{pol} = 0.26$ after the transformation has taken place.[10]

$$I(q) = A_p^2(q)S_p(q) + A_s^2(q)S_s(q) + 2A_p(q)A_s(q)S_{ps}(q)$$

where $A_i(q)$ and $S_i(q)$ are the scattering amplitude of the polymer or the solvent, respectively and the structure factor of the polymer and of the solvent. $S_{ps}(q)$ is a cross term which can be dropped in the case of non-solvated systems, but is important in the case of polymer-solvent molecular compounds. As a result, in the latter case, the labelling of the solvent can change drastically the diffraction pattern as is shown in the case of sPS/toluene systems for the δ_c form.

Concluding Remarks

A partial flavour of polymer-solvent molecular compounds has been given in this paper. Emphasis has been put on the characterization of these compounds both

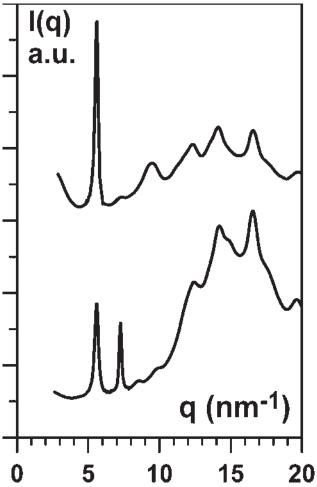

Figure 8.
Neutron diffraction pattern highlighting the effect of solvent labelling. *upper pattern* = sPS_D/$Toluene_H$, *lower pattern* = sPS_D/$Toluene_D$. $W_{pol} = 0.6$.

from the thermodynamic viewpoint and the structural aspect. The industrial future of these compounds is clearly in the field of materials, and particularly nanomaterials. The best example so far is certainly the making of nanoporous materials that are obtained after removal of the solvent from the crystalline lattice, as the latter remains unaltered which creates nanopores.[21–23] This nanoporous syndiotactic polystyrene is capable of absorbing a large variety of solvents molecules in the range of molar volumes 50–150 cm^3 dispersed in very small amount in water.

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