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Polymer-Solvent Complexes and Intercalates Prepared under Various Conditions

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Summary: The relevancy of temperature-composition phase diagrams for the study of polymer-solvent complexes and intercalates is discussed. In particular the use of Tamman's diagrams for determining the stoichiometric composition is evaluated. Examples of the validity of this approach are taken from isotactic or syndiotactic polystyrene compounds. Also, the effect of the path followed for reaching a T,C coordinate is examined. It is shown that cooling hot, homogeneous solutions at composition C or allowing solvent to diffuse in a solid polymer matrix at temperature T yields basically the same thermal behaviour.

Keywords: crystallization; gelation; intercalates; phase diagrams; polystyrene

Introduction

Temperature-concentration phase diagrams have been seldom used in the domain of polymer crystallization until the discovery of the occurrence of polymer-solvent compounds (also termed complexes or intercalates).[1,2] It has been realized that these diagrams can be useful and efficient tools for characterizing these materials.[3-7] Yet, as in most cases these compounds are not obtained under strict "thermodynamic" equilibrium the use of GIBBS phase rules has continuously been questioned. The purpose of this paper is to show that in many cases these rules apply provided some precautions are taken.

On the Use of Gibbs Phase Rules and the Relevancy of Phase diagrams to Thermodynamics of Complexes and Intercalates

Phase rules for systems exhibiting 1st order transitions have been established by Gibbs on the basis that the chemical potential of one constituent is the same in all the phases at equilibrium. Under these conditions, one can define the variance v of the system, which stands for the number of parameters that can be varied without modifying the equilibrium. It correspondingly gives the maximum number of phases φ in equilibrium as a function of the number of constituents N. At constant pressure it simply reads:

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$$v = N - \varphi + 1 \tag{1}$$

For 2 constituents the maximum number of phases in equilibrium is 3 as $v = 0$ under these conditions. As a result, equilibrium between the 3 phases can only occur at one temperature, hence the occurrence of temperature-non-variant transformations. Note that v can also be defined as the locus where φ phases coexist. For $N = 2$ and $\varphi = 3$ the locus reduces to a point ($v = 0$). This allows one to draw a temperature-composition phase diagram (T-C phase diagram), which shows the different domains where phases coexist.

Another important outcome from Gibbs phase rule is the lever rule. This is the same rule as that used for calculating the resulting forces acting on a lever, hence the name. For instance for a system at composition C giving two phases of composition C_1 and C_2 (with say $C_1 > C_2$) the proportion of each phase, X_i, will be given through:

$$X_1 = \frac{C - C_1}{C_2 - C_1} \qquad X_2 = \frac{C_2 - C}{C_2 - C_1} \tag{2}$$

As the latent heat associated with the thermal event, ΔH, is either proportional to the fraction of *phase 1* or *phase 2*, namely to X_1 or X_2, it follows that ΔH must varie linearly with composition C. In the case of polymer-solvent compounds the stoichiometry can be obtained by a so-called Tamman's plot, ΔH_c vs C, where ΔH_c is the enthalpy associated with compound melting (congruent or incongruent). Since for $C < C\gamma$ ΔH_c increases linearly while for $C > C\gamma$ ΔH_c decreases linearly, a maximum will occur that directly yields the stoichiometric composition $C\gamma$. From this composition the number of solvent molecules by monomer can be derived.

It is often unduly considered that these rules can be only applied to systems that have been obtained from the homogeneous liquid state through a very slow cooling. Here, the confusion between ***thermodynamic*** equilibrium and ***thermal*** equilibrium is made. Systems at equilibrium are ***stable systems***, namely there is no detectable time-evolution. Such systems can still be obtained by cooling rapidly provided the temperature remains the same or nearly the same throughout the sample. This can hold for systems where growth rates of the phases is slow enough, and for samples of size small enough for achieving homogeneous temperature. Under these conditions the occurrence of a high-temperature phase can be by-passed so as to give birth to a low-temperature phase that would never have existed under slow-cooling conditions. For instance, in binary polymer-solvent systems, where polymer crystallization rate is slow enough, the miscibility gap can be reached,[8] which creates two phases wherein crystallization will proceed next. Another example is the gelation of isotactic polystyrene in cis-decalin:[9,10] slow-cooling gives chain folded crystals that melt at about 120°C while rapid cooling to below the gelation threshold produces a polymer-solvent compound (fibrillar thermoreversible gel) that melts at 50°C.

One way of describing this effect would be to consider ***"phantom" formation phase diagrams*** (see Figure 1). Reaching the domains of these "phantom" phase diagrams, which would give birth to new stable phases, will obviously depend upon the cooling rate and the quenching temperature.[11] To be sure, the resulting melting phase diagram will be a direct imprint of the "phantom" formation phase diagram.

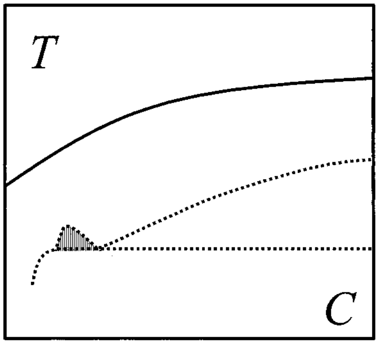

Fig. 1. A schematic representation of the temperature-composition formation phase diagram for a binary system displaying crystallization. The full line stands for an infinitely-slow cooling rate while the dotted lines stand for a rapid cooling rate. In the second case, which is termed ***"phantom"*** formation phase diagram, the system may be quenched within the miscibility gap (hatched area). The resulting melting phase diagrams will have the same shape (monotectic transition). For further reading see ref. 11.

That stable phases can be produced through rapid cooling might be questioned on the ground that 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 disappear and transform into a stable phase, a possible slowing-down of molecular motion could considerably increase their lifetime, and give the deceptive impression that stable phases are dealt with (a glass for instance for a crystallizable polymer[12]). Evidently, Gibbs phase rules would not hold any longer under these conditions. Differentiation between metastable phases and stable phases can be easily achieved by calorimetry experiments (DSC). A transformation from a ***stable phase into another stable phase*** always gives an ***endothermic latent heat***. Conversely, the transformation from a ***metastable phase into a stable phase*** always produces an ***exothermic latent heat***. A well-known example is the crystallization on heating of the metastable frozen liquid state of PET which gives off an exothermic peak.[12]

It is worth stressing that deviations from Gibbs phase rules established for macroscopic phases, namely phases of infinite size, may arise from finite size effects. For systems of finite size, surface free-energy comes into play so that the transformation temperatures may be significantly lowered. If size varies with composition, this has to be taken into account for interpreting the shape of the T-C phase diagram. Similarly, in the case of crystallizable polymers, one may argue that the degree of crystallinity can vary with composition. Such an effect can be easily spotted since no linear variations should be observed in Tamman's plots.

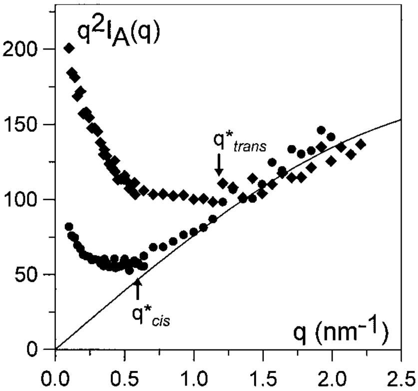

Fig. 2. Scattering curve plotted as $q^2I_A(q)$ vs q for the binary systems (gels) in *trans*-decalin (◆) and in *cis*-decalin (●). In both cases C_{pol}=0.04 g/cm^3. The solid line stands for the "single" chain scattering calculated from relation 3. For further reading see reference 13.

Some Experimental Cases

Isotactic Polystyrene Gels

The temperature-concentration phase diagrams established by Guenet and McKenna[5] have led them to conclude that the stoichiometry of thermoreversible gels produced from isotactic polystyrene differs whether *cis*-decalin (≈ 2 solvent molecules/monomer) or *trans*-decalin (≈ 1 solvent molecules/monomer) are used as a solvent. The differing stoichiometry as well as their values are confirmed by totally different experiments. Neutron scattering experiments carried out on gels systems[13] where all the chains are labelled are shown in Figure 2. At large q-values the "single" chain behaviour, as expressed through the following relation, is seen:

$$q^2 I_A(q) = C_{pol}\pi\mu_L q \frac{J_1^2(qr_H)}{q^2 r_H^2} \tag{3}$$

in which μ_L is the mass per unit length and r_H the helical structure radius, and J_1 the Bessel function of first kind and first order. Incidentally, these two parameters are consistent with a near-3_1 helical structure.

At smaller q-values a strong upturn is seen which corresponds to the cross-sectional effect of the gel fibrils. Interestingly, the single chain behaviour is observed at larger q-values (q*) in *trans*-decalin than in *cis*-decalin. This simply means that chains are more spaced in the gel fibrils prepared from iPS/*cis*-decalin than from iPS/*trans*-decalin gels. This is certainly consistent with the stoichiometry found by Guenet and McKenna.

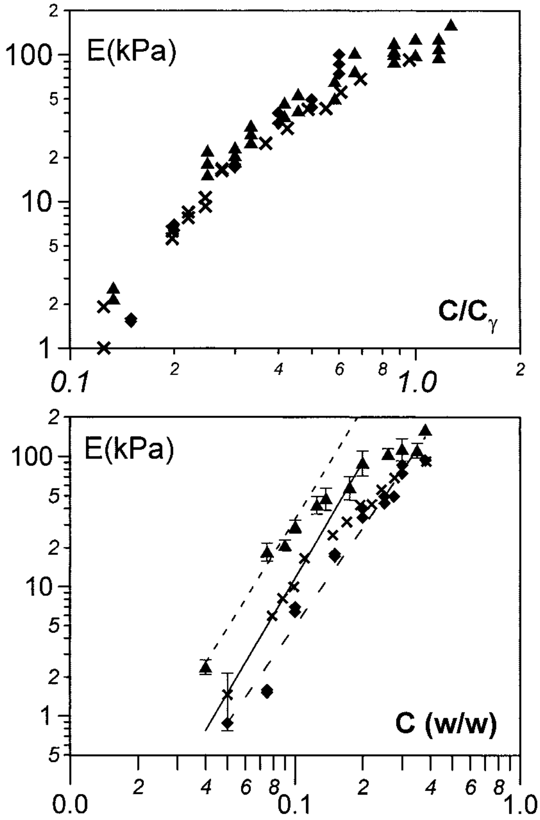

Fig. 3. *lower figure*: isochronal elastic modulus vs polymer concentration for gels prepared with iPS in *cis*-decalin (▲), in *trans*-decalin (✖), and 1-chlorodecane (♦). *upper figure*: the same data plotted as a function of C/C$_\gamma$ (the polymer-rich fraction). From references 14, 15.

Another example for which the value of the stoichiometry derived from the Tamman's plot can be directly used deals with the mechanical properties in three different solvents: *trans*-decalin, *cis*-decalin and 1-chlorodecane.[14,15] As far as Flory's interaction parameters are concerned, these three solvents are nearly identical although the stoiciometries determined from T-C phase diagrams differ significantly (*cis*-decalin≈ 2 solvent molecules/monomer, *trans*-decalin≈ 1 solvent molecules/monomer, 1-chlorodecane≈ 0.5 solvent molecules/monomer[5,16]). As can be seen in Figure 3 (lower), the variation of the isochronal ***elastic modulus vs polymer concentration*** shows significant discrepancies with respect to the solvent type. To be sure, one should plot the ***elastic modulus vs the fraction of elastic material.*** While in the case of chemical gels, this fraction is virtually the same as the polymer concentration, and more importantly does not depend upon the solvent type, this is no longer valid here. Due to the existence of polymer-solvent compounds a large part of the solvent is included in the fibrils. Consequently, the fraction of elastic material φ_{el} is obtained, to a first approximation, by rescaling the polymer concentration by the stoichiometric concentration:

$$\varphi_{el} = C / C_\gamma \tag{4}$$

As can be seen in Figure 3 (upper), by using the values of C_γ derived from T-C phase diagrams, an universal behaviour independent of the solvent is found. This again gives strong support to the values of the stoichiometries derived from the T-C phase diagrams.

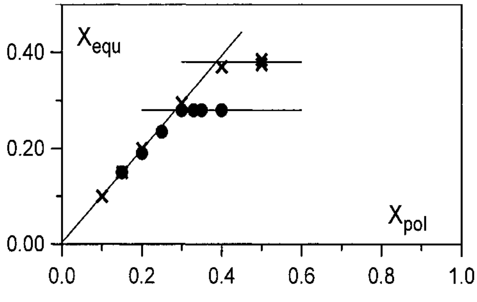

Fig. 4. Plot of the the terminal concentration (X_{equ} in w/w) vs the starting concentration (X_{pol}, w/w) in gels from iPS/*cis*-decalin (•) and of iPS/*trans*-decalin (✖).

Finally, a third example deals with the swelling properties of these gels that are shown in Figure 4 where the terminal concentration (X_{equ} in w/w) is plotted as a function starting concentration (X_{pol}, w/w).

The swelling behaviour differs totally from those in chemical gels. Below a given concentration, which turns out to be the stoichiometric concentration, no swelling occurs while above the gels swell always to the same concentration independent of the starting concentration.[17] Such a behaviour makes sense in view of the existence of polymer-solvent compound: below C_γ the stoichiometry is fulifilled so that there is no need for solvent uptake, while, above C_γ there is a solvent deficit which triggers solvent uptake to such an extent as to reach the stoichiometric concentration. Here again, simple swelling experiments yield values of the stoichiometric concentration in agreement with those derived from the T-C phase diagrams.

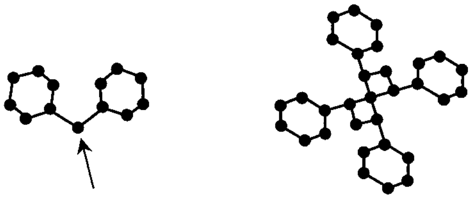

Fig. 5. Sketch of the two possible helical forms for sPS chains as seen parallel to the helix axis. The arrow (left) indicates the "polyethylene-like" side of sPS when taking on the zig-zag form.

Syndiotactic Polystyrene Intercalates

The chain ***helical structure in polymer-solvent compounds*** from syndiotactic polystyrene (sPS) is ***always a 2_1 helix*** independent of the solvent used.[18,19] To be sure, there are two stable form for sPS: the *planar zig-zag* and the *2_1 helix*, the former being energetically-stabler than the latter. The presence of solvent most probably enhances the stability of the 2_1 helix to the detriment of the zig-zag form. This can be understood by simply noticing that the zig-zag form displays on one side a "polyethylene-like" character whereas on the other side benzene rings protude. Clearly, this form is assymetric as far as solvation is concerned. Conversely, the 2_1 helix is totally symmetric in the sense that benzene rings protube in all directions. As a result, solvent interaction is enhanced.

That sPS in solution tends to adopt a conformation close to the 2_1 helix is borne out by neutron scattering experiments. Daniel et al. have shown in the case of benzene and toluene[6,7] that the local conformation of sPS chains in the solution state is very close to the 2_1 form. Under these conditions cooling sPS solutions will directly produce compound with the 2_1 form.

Interestingly, sPS produces compound with a large number of solvents of differing molecular structure (benzene, toluene, chloroform, decalin...). As somehow expected, in spite of the formation of compounds in all these cases, the thermal behaviour is dependent upon the solvent type (see Figure 6). In particular, in the range of concentration 0.40-0.70 the incongruent-melting of the compound (release of solvent) is followed by an exothermic event in *trans*-decalin and chloroform, but not in toluene or benzene (not shown here). The corresponding Temperature-Concentration phase diagrams are drawn in Figures 7 (sPS/*trans*-decalin) 9 (sPS/benzene) and 10 (sPS/toluene).

As can be seen the shape of these phase diagrams differs with solvent type. In the case of sPS/*trans*-decalin there is the formation of only one compound of stoichiometry ~ *1 solvent molecule/monomer*. At 150°C the transformation of this compound into the β-phase occurs as is ascertained by the diffraction experiments shown in Figure 8. Here, it is worth stressing that the occurrence of an exotherm is probably due to the transformation of a non-solvated 2_1 helix into the planar zig-zag form. The first endotherm is the incongruent-melting of the compound, namely the desolvation process. As the non-solvated 2_1 helix is a metastable state (it cannot be obtained from pure molten sPS) it must transform into the planar zig-zag form through an exothermic event as explained in the previous section.

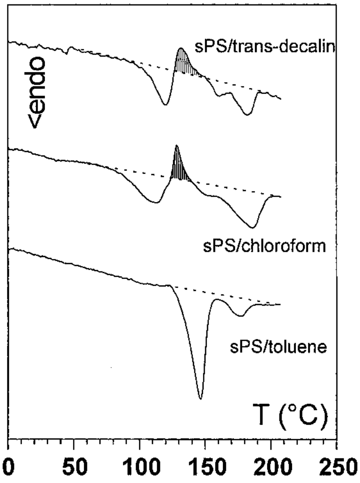

Fig. 6. DSC thermogrammes for sPS compounds in different solvents. Hatched areas highlight the exothermic events. The first endotherm is the incongruent-melting of the first compound formed at low temperature and low concentration.

According to the phase diagram and diffraction experiments in the case of sPS/benzene and sPS/toluene systems the first compound transforms into another compound of lesser degree of solvation but of same helicity (2_1). This does suggest that the ***exotherm event*** seen after the incongruent-melting of the compound in sPS/*trans*-decalin does ***originate in the conformational transition*** $\boldsymbol{2_1}$***-planar zig-zag***. Consequently, the ***absence of exotherm*** also means that the incongruent-melting is ***but a partial desolvation of the compound***, and that compound(s) of lower degree of solvation still exist at higher temperature.

Also, we note that in the Tamman's plot the enthalpy associated with the incongruent-melting at 150°C in sPS/*trans*-decalin systems displays a maximum at virtually the same concentration as the enthalpy associated with the exotherm. This again is consistent with the above statement that necessarily implies that the fraction of chains which transforms from the 2_1 form into the planar zig-zag form is directly proportional to the fraction of compound.

It ought to be stressed that the crystalline lattice propose by Chatani[20] seems unappropriate for accomodating 1 *trans*-decalin molecule per monomer unless one accepts a very high density (~ 2 g/cm^3). Clearly, this issue has to be settled either by considering another lattice, but also by exploring the diffraction at smaller angles in order to find out whether a diffraction maxima corresponding to larger spacings exists.

Effect of the Path for Reaching a T,C Coordinate

In the case of toluene all the data points gathered for solvent-induced samples are virtually the same as those obtained from solution-cast samples[6,7] (see Figure 9). Clearly, the melting behaviour and correspondingly the nature of the phases does not depend significantly upon the path followed to reach a given C_{pol}, T coordinate: starting from concentration C_{pol} and cooling to temperature T is equivalent as starting from temperature T and reaching concentration C_{pol} through solvent diffusion. It is also worth mentioning that this statement also applies to the latent heats ΔH associated with the different thermal events: they correspond within experimental uncertainties to those measured from solution-cast samples. The systems therefore behave as if they were at equilibrium, which emphasizes that rules established by Gibbs from *equilibrium thermodynamics* still hold to describe systems that are not strictly speaking at equilibrium.

The terminal concentration reached by the system depends upon the exposure temperature: the higher the exposure temperature T_{expo}, the lower the polymer fraction (shown in the phase diagram of Figure 10 by means of arrows). The variation of C_{pol} vs T_{expo} appears to be linear, which implies that polymer concentration lower than $C_{pol} \approx 0.48$ cannot be reached this way without melting and dissolving into the solvent the initially-solid polymer sample. Indeed, at a temperature $T_{expo} \approx 130°C$, the liquid phase is obtained in sealed vessel (total dissolution of the polymer).

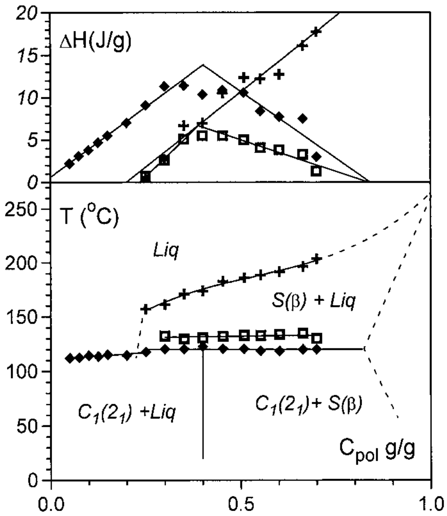

Fig. 7. Temperature-concentration phase diagram sPS/*trans*-decalin. (♦)= incongruent-melting of the compound (compound⇒ β-phase), (□) exothermic event; (✚) terminal melting (β-phase). From reference 21.

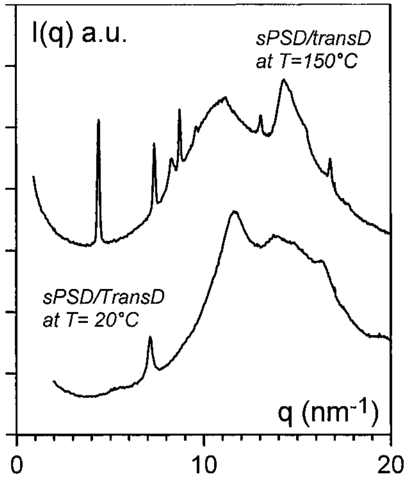

Fig. 8. Neutron diffraction patterns (both sPS and *trans*-decalin are deuterated). Lower pattern system at 20°C, upper pattern after heating at 150°C, namely above the transformation compound⇒ β-phase.Polymer concentration C_{pol}= 0.35 w/w. From reference 21.

In the case of benzene, polymer concentrations higher than those achieved by Daniel et al. from solution-cast systems[7] have been obtained. It appears that the data points obtained from the solvent-exposed samples complete the phase diagram established for solution-cast samples in the range of high polymer concentrations. This also suggests that the melting events and the corresponding phases are independent of the processing path.

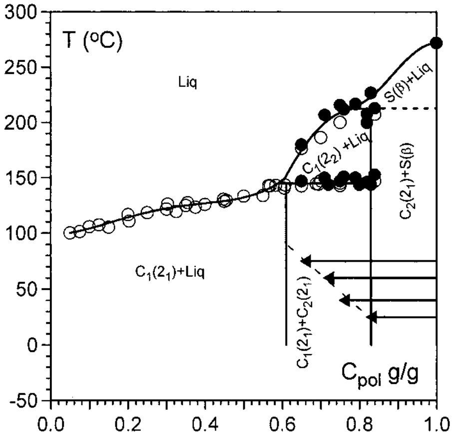

Fig. 9. Temperature-concentration phase diagram for sPS/toluene systems. The open symbols stand for measurements carried out on samples prepared from homogeneous solutions (From reference 7), the black symbols for samples prepared through diffusion of toluene in a solid polymer matrix at various exposure temperatures. Two compounds are identified. The arrows indicate the polymer concentration reached by the samples for different exposure temperatures T_{expo}.

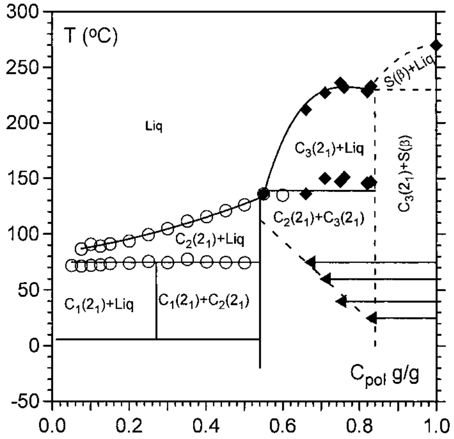

Fig. 10. Temperature-concentration phase diagram for sPS/benzene systems. The open symbols stand for measurements carried out on samples prepared from homogeneous solutions (From reference 6), the black symbols for samples prepared through diffusion of benzene in a solid polymer matrix at various exposure temperatures. Three compounds are identified. The arrows indicate the polymer concentration reached by the samples for different exposure temperatures T_{expo}.

Concluding Remarks

Carbonnel and coworkers[22] as well as Koeningsveld and coworkers[23] have already emphasized that Gibbs phase rules can be applied to mesomorphic systems in spite of an apparent non-equilibrium state. Here, additional arguments have been provided for supporting the use of temperature-phase diagrams and Tamman's diagrams in the characterization of polymer-solvent compounds. In addition, it has been shown that the path taken for reaching a T, C coordinate has virtually no influence on the thermal behaviour: the phase diagrams obtained from solution-cast samples and from solvent-exposed samples are superimposable. All these points highlight the powerful predicting potential of T-C phase diagrams, especially for detecting new phases and suggesting the occurence of new molecular structures.

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