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Phase Behaviour and Structure Formation in Solutions of Vinyl Polymers [and Discussion]

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Phase behaviour and structure formation in solutions of vinyl polymers†

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The supramolecular structure formation in solutions of syndiotactic polystyrene is discussed from the viewpoint of the temperature–concentration behaviour of this system. The phase diagrams that result from these investigations localize the different temperature–concentration domains in which the β-phase (planar zigzag chain conformation) and the δ-phase (helix chain conformation) are formed. The study of these diagrams informs also on the relationship between the different phases and the nature of the supramolecular structure that is formed. The shape of the diagrams is characteristic of the formation of an incongruent melting compound (δ-phase) between the polymer and the solvent. The formation of this compound at not to high polymer concentrations leads to the formation of thermoreversible gels. The solvent quality has a different influence on the stability of the β- and the δ-phase. An increase of the solvent quality lowers the melting point of the β-phase, but increases the stability of the δ-phase. The diagrams are interpreted on the basis of schematized equilibrium diagrams.

1. Introduction

The thermoreversible gelation of solutions of stereoregular vinyl polymers has been reported almost as early as their synthesis. The intermolecular complex formation between isotactic and syndiotactic sequences of poly(methyl methacrylate) is an illustrative example of this type of supramolecular structure formation in solution (Fox 1957). Many other systems have been studied ever since and most of the information has been brought together in different review publications (Keller 1983; Spevacek 1987; Guenet 1992). These investigations have revealed the complex morphological behaviour of these polymers and their ability to adopt different molecular conformations. The important role of the solvent in the formation and stabilization of some of these structures has been emphasized many times. Different mechanisms of supramolecular structure formation have been proposed.

Structure formation by folded chain crystallization has been well understood and thermoreversible gels made by this mechanism are generally opaque and paste-like. The crystal structure and molecular conformation are mostly those encountered in melt crystallized samples.

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The formation of almost transparent gels with polymer-solvent systems has been a subject of great interest in the last decades. Their formation mechanism, however, has not been well understood up to now but it seems to differ in many aspects from the one described above. The molecules mostly adopt a molecular conformation that differs from the one encountered in the melt crystallized samples. The resulting supramolecular organization cannot be formed from the melt and the presence of the solvent is a necessary condition.

An interesting example is syndiotactic poly(methyl methacrylate) (sPMMA). This polymer does not crystallize from the melt but thermoreversible gels can be obtained in different solvents. The inclusion of solvent molecules in the supramolecular organizations that form the physical cross-links has been reported (Bosscher 1982; Kusuyama 1982, 1983). Evidence for a two-step mechanism has been presented for the gelation of this polymer in *o*-xylene and toluene (Berghmans 1986, 1992). An intramolecular coil to helix transition precedes the intermolecular association that leads to the gel formation.

The gelation of solutions of stereoisomers of polystyrene and especially the behaviour of the syndiotactic isomer (sPS), has also received much attention during the last years. Although the synthesis of syndiotactic polystyrene has been reported only recently (Ishihara 1986), many studies have already been devoted to the complex morphological behaviour of this polymer (Immirzi 1988; Vittoria; 1988; Chatani 1988; Kobayashi 1989; Guerra 1990; Gomez 1990; Kobayashi 1990; Prasad 1990; Rappacciuolo 1991; de Rosa 1991; Chatani 1992). The polymer chain can adopt an all trans planar zigzag conformation (T_4) and a helix conformation (T_2G_2). The polymer can crystallize in four major crystalline modifications. In the α- and β-modification, the chains adopt a T_4 conformation. These two forms can be further subdivided in modifications, characterized by a differing degree of structural order. The γ- and δ-modifications are characterized by a T_2G_2 conformation.

The α- and the β-modification are found back in the well-known folded chain crystallization from the melt of from solution under certain circumstances. The δ-modification can only be prepared in presence of a solvent and its exact crystalline structure depends on the solvent. The participation of the solvent and the formation of a molecular compound has been illustrated (Immirzi 1988; Vittoria 1988, 1990; Chatani 1992, 1993; Deberdt 1993, 1994). Complete elimination of this solvent results in the formation of the γ-phase.

2. Phase behaviour and the phase rule

The formation and coexistence of different phases has to obey the phase rule that has been derived from general thermodynamic principles by J. W. Gibbs more than a century ago. This rule establishes the general relation between the degrees of freedom (F), the number of components (C) and the number of phases (P):

$$F = C - P + 2.$$

In a multicomponent system the degrees of freedom are pressure, temperature and concentration. Interesting information concerning a multicomponent system can therefore be obtained from the study of the phase behaviour. The experimentally obtained transition temperatures can be brought together in a temperature–

concentration diagram. The shape of this diagram can provide very valuable information on the nature of the phases that are formed, their thermal stability and their interrelation. This information, in combination with structure analysis by spectroscopic and scattering techniques, can be of great help in the understanding of the supramolecular structure formation in a system (Point 1985, 1992)

This approach that refers to equilibrium situations, can also be used when polymers are involved in spite of the fact that polymers cannot be considered as single components. Their molecular mass distribution makes them a constituent, composed of a many components of different molecular mass. Polymer crystallization never leads to equilibrium structures and the stability of the crystalline phase and therefore its melting point is strongly influenced by the crystallization and melting conditions. It has nevertheless become clear from our experimental investigations that phase diagrams, constructed on the basis of these non-equilibrium data, give a very good qualitative picture of the behaviour of a system that contains a polymer.

The structure formation in solutions of stereoregular vinyl polymers will be approached from the point of view of the phase behaviour and will be illustrated in detail by the behaviour of solutions of sPS.

3. Phase behaviour of sPS-solvent systems

(*a*) *Qualitative observations*

sPS cannot be dissolved in any good solvent for the atactic isomer. Structure formation takes place very quickly on cooling and almost transparent, themoreversible gels are formed at relatively low polymer concentrations. The polymer chains adopt a helix conformation and the δ-phase is formed. Cooling of a solution of sPS in chloroform (polymer mass fraction, $w_2 = 0.03$) results in the formation of a slightly hazy gel that melts around 70 °C. These gels can also be formed in poor solvents like decalin.

(*b*) *Study of the phase behaviour*

The phase behaviour of sPS in presence of a solvent has been investigated by differential scanning calorimetry (DSC) (Deberdt 1993, 1994). The data obtained by this technique are combined with those obtained from wide angle X-ray scattering (WAXS) experiments and infrared analysis. Phase diagrams, representing the relationship between the melting temperatures and polymer concentration are constructed. Data on the concentration dependence of the glass transition temperature (T_{g}) are also included. The polymer concentration is given in weight fraction, w_2.

An important consequence of the dynamic character of the DSC measurements is that non-equilibrium values are obtained for the different transition temperatures. These transitions temperatures will be influenced by the scanning rate and this rate dependence will add to the non-equilibrium character of polymer crystallization, already mentioned earlier. The data reported in this paper have been obtained at a scanning rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$ and have not been corrected for their non-equilibrium character. The discussion will therefore be limited to a qualitative comparison between experimental data and equilibrium situations.

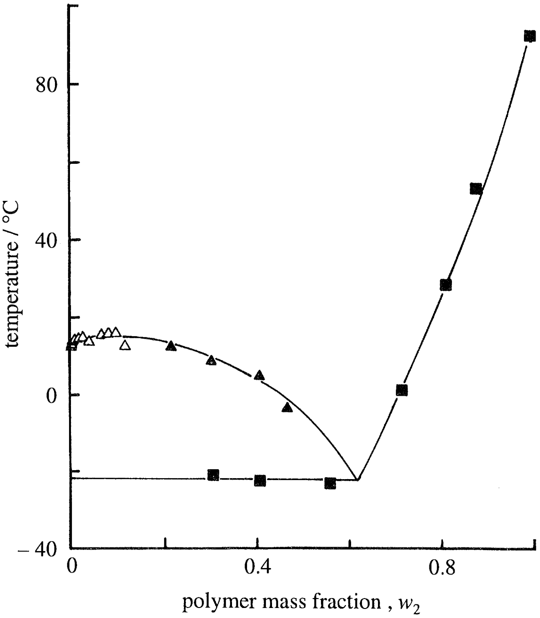

Figure 1. Phase diagram of the system aPS–TD. (△) Liquid–liquid demixing, optical observations. (▲) Liquid–liquid demixing, DSC observations. (■) T_g.

(c) *Phase behaviour of the system sPS–*trans*-decalin*

(i) *Liquid–liquid phase separation*

The different isomers of decalin and their mixtures are poor solvents for polystyrene. This is illustrated by the phase diagram of the atactic isomer (aPS) dissolved in *trans*-decalin (TD), represented in figure 1. Liquid–liquid phase separation takes place at a polymer mass fraction $w_2 < 0.62$. At higher polymer concentrations, only the T_g of the polymer-solvent system is recorded. The interference of these two transitions at $w_2 = 0.62$ and -21 °C results in the vitrification of the concentrated phase and can lead, with a polymer of narrow molecular mass distribution, to an invariance of T_g within the concentration range of the demixing domain. This combination of transitions, discussed in detail in the literature (Arnauts 1987, 1990, 1993; Vandeweerdt 1991; Hikmet 1988) is an interesting route for the formation of amorphous, porous materials.

The behaviour of the syndiotactic isomer is much more complex. It has not been possible to observe this liquid–liquid demixing for the system sPS–TD. Cooling of moderately concentrated solutions always results in crystallization and/or gelation, even when the samples are quenched in liquid nitrogen.

(ii) *Supramolecular structure formation*

A DSC scan, recorded at low polymer concentration is very instructive with respect to this structure formation and illustrates the complexity of the situation. Cooling of a solution with for instance $w_2 = 0.29$, results in the appearance of two exothermic signals (figure 2). The first one corresponds to the formation of the β-phase. The phase formation is stopped, however, at 75 °C, although only part of the polymer has been crystallized. This is unusual as the decrease in temperature,

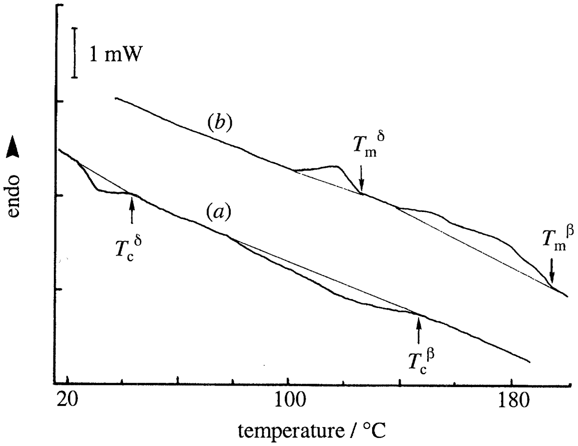

Figure 2. DSC Thermogram of the system sPS–TD; scanning rate: 5 °C min^{-1}; $w_2 = 0.29$. (*a*) Cooling, (*b*) heating.

corresponding to an increase of the degree of undercooling, normally leads to an increase of the rate of crystallization. The crystallization of the β-phase should not be interrupted and should go to completion. No structure formation, however, takes place between 75 °C and 37 °C, temperature at which the formation of the δ-phase sets in. This clearly indicates that the formation of the β-phase can only take place above a certain temperature, and that, at lower temperature, the formation of the δ-phase takes over. Annealing at high temperature results therefore in the formation of only the β-phase. The resulting thermoreversible gels are paste-like. Quenching to room temperature results in the formation of only the δ-phase and slightly hazy thermoreversible gels are formed at not to high polymer concentrations.

The difference in stability between both phases is illustrated by the their melting points in the presence of the solvent. The β-phase is the most stable phase over the whole concentration range: its melting point is always superior to that of the δ-phase. These melting points (respectively T_m^β and T_m^δ), together with the temperatures of formation of both phases (respectively T_c^β and T_c^δ), are represented in figure 3.

The melting point-concentration relationship of the β-phase can be considered as characteristic for the melting of crystals in the presence of a poor solvent. The melting point of the δ-phase is not influenced by the polymer concentration.

The δ-phase is not formed at high polymer concentrations when the samples are cooled in the DSC and a quantitative transformation of the polymer into the β-phase takes place. The δ-phase can only be formed when a sample, quenched into the glassy state, is heated above its T_g. This δ-phase transforms into the β-phase by a mechanism of melting-recrystallization. The extent of overlapping of the two phenomena depends on the scanning rate and this overlapping makes the exact location of the melting point of the δ-phase difficult. The data clearly show, however, that this phase transformation proceeds always in the same temperature region.

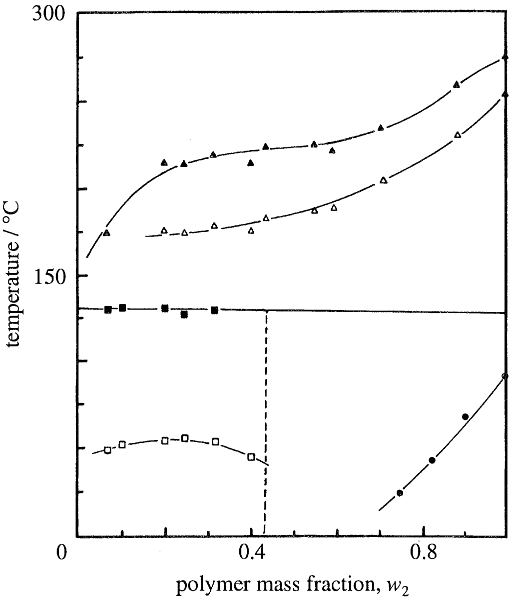

Figure 3. Phase diagram of the system sPS–TD. ▲, T_m^β; △, T_c^β; ■, T_m^δ; □, T_c^δ; •, T_g. Proposed 1/1 molar composition of the compound sPS–TD.

(*d*) *Phase behaviour of the system sPS–*o*-xylene*

An increase of the solvent quality from TD to *o*-xylene (*o*-X) has a pronounced influence on the solution behaviour of sPS. The phase diagram of this system is represented in figure 4. The β-phase cannot be formed anymore at low polymer concentration and at the scanning rate used to construct this phase diagram and only the δ-phase is formed. Slightly hazy thermoreversible gels are formed. At intermediate polymer concentrations, both phases are formed successively and the resemblance with the behaviour in TD is striking. The formation of the β-phase in a system with $w_2 = 0.63$ is stopped at 145 °C and no structure formation takes place until the solution has been cooled to 53 °C. At that temperature, the formation of the δ-phase takes over. At high polymer concentration, only the β-phase is formed. The δ-phase can only be formed in this concentration region when the samples are first quenched to below their T_g and then heated. The melting point of the δ-phase is then invariant and represents the transition into the β-phase and a polymer solution by a mechanism of melting-recrystallization. This invariant melting point is superior to the one observed in the presence of TD. In the low concentration region the melting point of the δ-phase is variant. The melting point of the β-phase is always variant and is always situated at higher temperatures than the melting point of the δ-phase in the same concentration range.

4. Quantitative interpretation of the phase diagrams

(*a*) *Phase diagram of a two-component system*

The phase diagrams, reported in this paper, have to correspond to one of the possibilities offered by a two-component system. It is well known that polymers

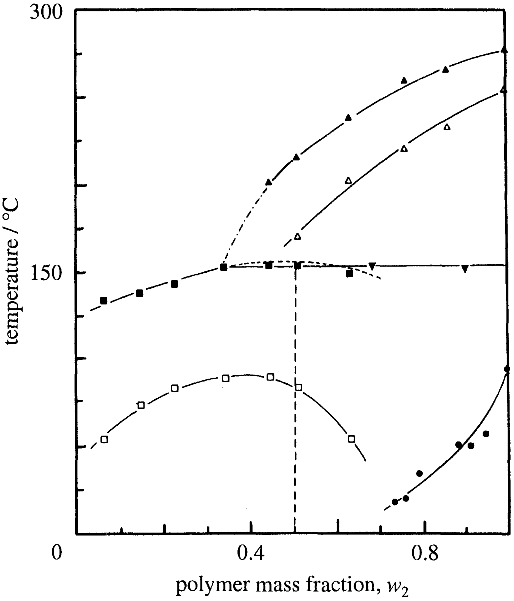

Figure 4. Phase diagram of the system sPS–*o*-X. ▲, T_{m}^{β}; △, T_{c}^{β}; ■, T_{m}^{δ}, after cooling at 5 °C in the DSC; ▼, T_{m}^{δ}, after quenching and heating at 5 °C in the DSC; ☐, T_{c}^{δ}; ●, T_{g}. Proposed 1/1 molar composition of the compound sPS–*o*-X.

cannot be considered as a single component because of their molecular mass distribution, and therefore they have to be referred to as a multicomponent constituent. Their behaviour can nevertheless be discussed in a qualitative way as if they were only a single component and this approach will be followed in this paper. Thus the discussion on the behaviour of a 'two-component system' will be applied in a qualitative way to the behaviour of a system constituted of a solvent and a polymer with a molecular mass distribution. First, equilibrium temperature–concentration relationships will be discussed in general. Then the experimental diagrams will be compared with these idealised equilibrium diagrams.

(*b*) *The melting of a two-component system*

The melting of a system composed of two components, mutually soluble in all proportions in the melt, is characterized by an eutectic behaviour. If one of the components is a low melting solvent (component 1 or **1**), only one branch of the eutectic diagram will be observed (figure 5*a*) and the liquidus of the high melting component (component 2 or **2**) will approach the solvent axis at low concentration and extend to the melting point of the solvent. An equilibrium is established between the melt or solution (L) and the crystalline phase of **2**. The formation of a stable compound (C) between the two components will manifest itself in a maximum in the temperature–concentration diagram at the composition of this compound (figure 5*b*). The temperature at this maximum corresponds to the congruent melting point of this compound. The left-hand side represents the melting point depression of the compound in the presence of the solvent. The right-hand side represents the eutectic behaviour of the system C–**2**. This

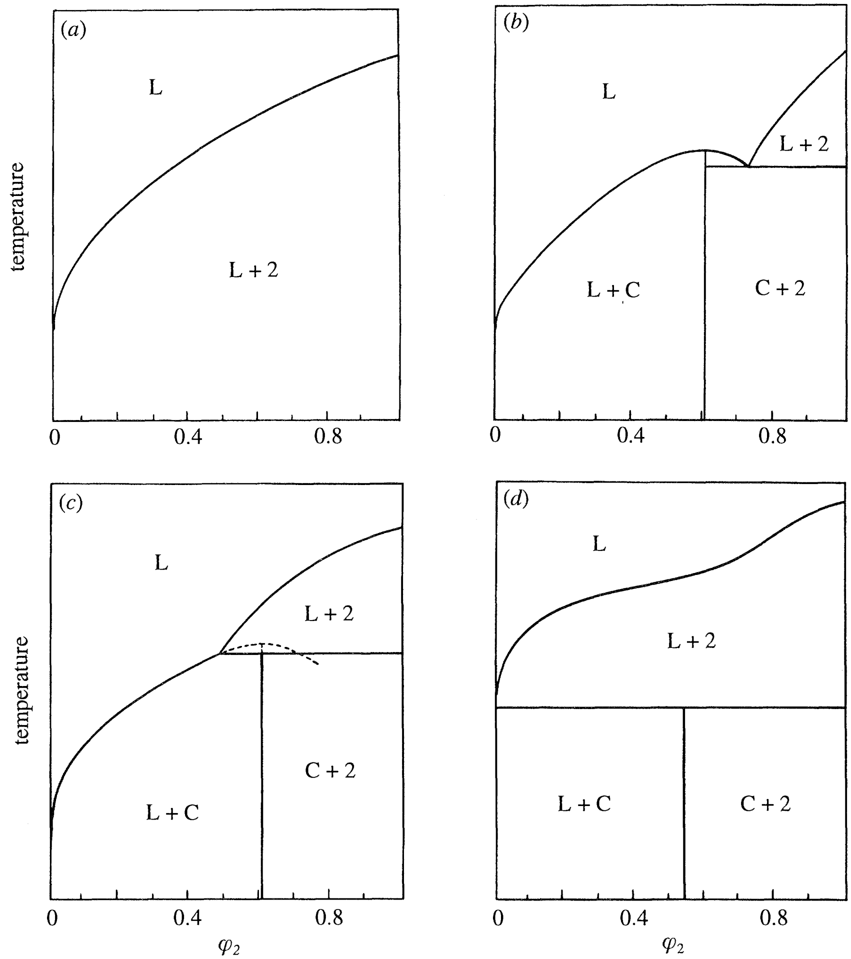

Figure 5. Schematized phase diagrams of two-component systems, representing the melting point–concentration relation of a component with high melting point in presence of a solvent: L, solution of melt; C, compound; 2, high melting component; z^2 is the volume fraction. (*a*) Melting point depression of 2 by the addition of 1. (*b*) Congruent melting of the compound formed by the two components. (*c*) Incongruent melting of the compound formed by 1 and 2. (*d*) Incongruent melting of a compound formed by 1 and 2. The melting point of 2 is superior to that of 1 over the whole concentration range.

results, at constant pressure, in an invariant situation at the eutectic temperature because of the coexistence of three phases: L, C and **2**.

When the compound decomposes on heating before it reaches its melting point, incongruent melting is observed. The situation is represented in figure 5*c*. The left-hand side represents the liquidus of the compound, in equilibrium with the solution, L. The high temperature part at the right-hand side corresponds to the melting of **2** and represents the equilibrium L–**2**. At lower temperatures, an equilibrium C–**2** is installed. In between these domains, an invariant situation at constant pressure is realized by the coexistence of three phases L, C and **2** as a consequence of the transformation of C into **2** and L.

(*c*) *Interpretation of the phase diagram of the system sPS–*o*-X*

The phase diagram of sPS–*o*-X agrees very well with the diagram of figure 5*c* and one should therefore conclude to the formation of a compound, the δ-phase, between the solvent and sPS. This compound formation has already been reported for the system sPS–toluene and its crystal structure has been been studied by WAXS (Chatani 1993).

Up to now, no information is available concerning the exact molar composition of the compound sPS–*o*-X and therefore a molar ratio of its constituents (chain repeating unit-solvent molecule) of 1/1 or $w_2 = 0.50$ (dotted line in figure 3) has been arbitratily put forward. This is realistic in view of the shape of the phase diagram. Cooling in the low concentration region establishes an equilibrium between the δ-phase or compound and the solvent. This structure formation is at the origin of the formation of thermoreversible gels. At intermediate concentrations, the β-phase is formed first but only to a certain extent and then the δ-phase is formed at lower temperature. The initially formed β-phase should transform into the δ-phase on cooling but this type of peritectic reaction is difficult even with low molecular mass substances. No evidence has been found for this transformation and the presence of both phases is revealed by the melting behaviour of the system. At even higher polymer concentration, cooling results in the complete transformation of the polymer in the β-phase. No peritectic reaction takes place on further cooling.

When samples with this high polymer concentration are quenched in liquid nitrogen, a glassy amorphous system is obtained. Heating of a quenched, amorphous sample in this high concentration region should result in the formation of the δ- and β-phase, in equilibrium with each other. All the solvent is taken up by the δ-phase and the remaining, solvent free polymer should crystallize as the β-phase ($w_2 = 1.00$). But this does not take place as the elimination of the solvent brings the polymer in the glassy domain where it freezes as an amorphous glass. At higher temperatures the δ-phase melts and transforms into a solution and the β-phase. The presence of these three phases results in an invariant situation. Then the β-phase melts on further heating (variant situation).

(*d*) *Interpretation of the phase diagram sPS–TD*

The behaviour in TD is different and the corresponding phase diagram cannot be directly related to the diagram represented in figure 5*c*. But it nevertheless corresponds also to the phase behaviour of an incongruent melting system. The melting point of the β-phase is always superior to that of the δ-phase and this shifts the intersection point of the liquidus of the β-phase to the pure solvent axis (figure 5*d*). Complete transformation into the β-phase can always take place on cooling at any concentration. This situation is easily realized at high concentrations and/or at the scanning rates used in the DSC. At lower concentration it only takes place when the solutions are cooled very slowly or annealed at high enough temperatures. Above 75 °C, an equilibrium is established between the solution (L) and the β-phase (**2**). At lower temperature, a solvent-polymer compound can be formed and the molar ratio of its constituents (chain repeating unit-solvent molecule) has been arbitrarily put equal 1/1. This ratio corresponds to $w_2 = 0.43$ (dotted line in figure 2). Two concentration regions have to be considered. When the low concentrated samples are cooled quickly, the crystallization into the β-

phase can be overruled and an equilibrium between the δ-phase (compound) and the solvent is established. Heating transforms the δ-phase into the β-phase by a melting-recrystallization mechanism. During this transformation, the compound coexists with the solvent and the β-phase and this three phase equilibrium results in an invariant situation at 127 °C. At high polymer concentration the problem is similar to that encountered in the system sPS–o-X. Cooling at not to high rates establish an equilibrium between the solution and the β-phase. Quenching results in amorphous, glassy samples that transform in the δ-phase on heating. The absence of the β-phase at low temperature is the consequence of the presence of the glassy region. At higher temperature, transformation of the δ-phase into the β-phase takes place by a mechanism of melting-recrystallization.

(*e*) *Coil–helix transition*

When the crystallization of the β- and the δ-phase take place during the same cooling experiment, no structure formation takes place in the temperature region between these two thermal transition. This peculiar behaviour can be interpreted by the two-step mechanism already proposed for the behaviour of the system sPMMA–o-X and sPMMA–toluene. The mechanism of supramolecular structure formation is initiated by an intramolecular coil to helix transition. The solvent is expected to take part in this transformation. This change in conformation makes any further crystallization into the β-phase impossible. The equilibrium constant that governs this equilibrium increases with decreasing temperature (Berghmans 1986, 1992). The formation of the δ-phase necessitates a second step of intermolecular association and this step can only take place at much lower temperature at the scanning rate used. A sufficient degree of intramolecular coil–helix transformation is needed to allow the intermolecular step to take place. This degree of intermolecular transformation will only be reached at low temperature or high degree of undercooling. The formation of this δ-phase by isothermal annealing can proceed at higher temperatures but always below the lower temperature limit for the formation of the β-phase. The participation of the solvent in the formation of the δ-phase leads to the formation of a polymer- solvent compound.

(*f*) *Relative stability of the phases*

The study of the phase behaviour in these solvents reveals a difference in solvent quality dependence of the melting point of the β- and δ-phase. The β-phase becomes less stable when the solvent quality is increased and this is expected from general thermodynamic principles. The melting point depression of this phase, at the same solvent content, is larger in o-xylene than in TD. The stability of the δ-phase on the other hand increases with increasing solvent quality. The invariant melting point that reflects the decomposition of this phase and its transformation into the solution and the β-phase, increases with increasing solvent quality. This invariant temperature is situated at 127 °C in TD and at 155 °C in o-X. One can therefore state that the solvent quality has an opposite effect on the stability of the β- and the δ-phase. An increase of the solvent quality from o-X to TD decreases the stability of the β-phase, but increases the stability of the δ-phase. This phase stability inversion explains the difference in solubility between sPS and aPS and the formation of thermoreversible gels with a relatively high melting point in a good solvent like chloroform.

5. Conclusions

The investigation of the phase behaviour of solutions of sPS has revealed the following interesting points:

1. The temperature–concentration phase diagrams of solutions of sPS in TD en *o*-X are characteristic for the formation of a polymer-solvent compound, the δ-phase. This phase is responsable for the formation of slightly hazy, thermoreversible gels. The data obtained by this thermodynamic approach confirm the conclusions that were reported in the literature on the basis of structure analysis by X-ray scattering.

2. The formation of this compound seems to take place by a two-step mechanism. Cooling results first in intramolecular coil–helix transition, while intermolecular association takes place in a second step at much lower temperature.

3. The solvent quality influences in a different way the stability of the β- and δ-phase. An increase of solvent quality decreases the melting point of the β-phase at constant solvent content. The melting point of the δ-phase or compound and its decomposition temperature increase with increasing solvent quality.

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Discussion

A. Keller (*University of Bristol, U.K.*). Gelation does not directly follow from the phase diagrams shown. Clearly, gel formation is the consequence of the establishment of connectedness hence of geometry, and does not directly follow from thermodynamics. How does the establishment of such connectedness relate to the phase transformatons indicated by the phase diagrams?

Various helical chain conformations have been referred to. Was the reference to chain conformations as in the different crystal forms, or do the helices and the corresponding conformational transformations have an existence of their own when not part of the crystal?

H. Berghmans. Gel formation takes place in moderate polymer concentration, e.g. 10% polymer by mass. The connectedness that is responsible for this physical network formation depends on the experimental conditions.

1. Decalin at high temperature: the polymer crystallizes in the zigzag conformation (β-phase). A paste-like gel is obtained.

2. Decalin, fast cooling to room temperature: an almost transparent gel is formed, in which the molecules adopt the helix conformation (δ-phase). For this gel formation, a two step mechanism is proposed and this proposition is based on data obtained from the gelation of syndiotactic poly(methyl methacrylate) (see Berghmans 1986, 1992) and isotactic polystyrene (A. Jacobs, Ph.D. thesis, Leuven (1991)). Cooling will result in a coil-to-helix transformation and these helices associate to form the physical network points. The intermolecular connection will lead to the formation of the almost transparent gels. This mechanism is similar to the one that seems to be operative in the formation of carrageenan gels, for example.

There is no doubt concerning the zigzag conformation. The polymer chains adopt this conformation in the lamellar crystals that are formed by crystallization from the melt. The formation of paste-like gels confirms that this conformation also leads to the formation of lamellar crystals in solution.

The formatin of the helix conformatin, however, is a more complex problem and neccessitates further experimental investigation. But the data actual available suggest that these helices can have an existence on their own. The interruption of the crystallization into the zigzag conformation on cooling decalin solutions with formation of the δ-phase (unless the sample is cooled to low temperature) suggest that an intramolecular transformation takes place from coil to helix which prevents any further crystallization into the β-phase. This molecular transformation is also responsible for the absence of any liquid–liquid demixing. This intrinsic stability of these helices does not necessitate any further large scale agglomeration. The intermolecular association of only a few sequences suffices for the formation of a physical gel network and therefore a transparent gel. This is illustrated by the fact that a rigid, transparent gel can be formed with a solution containing a mass fraction of 0.3 syndiotactic polystyrene with a molecular mass of 1.3×10^6. These structures can grow further in order to increase their stability. This increase in size makes the gels hazy.

R.W. Cahn (*University of Cambridge, U.K.*). Many of the configurations you describe appear to be metastable, at any rate not in full equilibrium. To what extent is it feasible to establish phase diagrams of polymer mixtures that could properly be described as equibrium diagrams?

H. Berghmans. The data are non-equilibrium for different reasons. First, polymer crystallization never results in the formation of equilibrium crystal structures. Important limitations result from the folded chain crystallization mechanism that leads to the formation of a crystal morphology with varying crystal thickness. The lamellar thickness and therefore the corresponding melting point, depend on the crystallization conditions. Equilibrium melting points can therefore only be obtained by an extrapolation method. A second important reason is the dynamic character of the experimental methods. The data have been obtained by differential scanning calorimetry at a scanning rate of 5 °C min^{-1}. This dynamic aspect necessitates another extrapolation to zero scanning rate. This was not done in the data presented here. But from our investigation on different systems, it became clear that these non-equilibrium diagrams can be used to get a qualitative picture of the phase behaviour. One should, however, be very careful in using these data for the calculation of fundamental thermodynamic parameters.

It is possible, in view of the comments given above, to observe a different phase diagram. In *o*-xylene, no crystallization into the β-phase takes place at low concentration when crystallization is performed on cooling. When crystallization is performed by annealing at high temperature, the β-phase can be formed over the whole concentration range. Only a narrow temperature window, very close to the melting point of the β-phase, is available for this isothermal crystallization. This shows that the β-phase is the most stable phase over the whole concentration range if it has been prepared under the right conditions, close to equilibrium conditions. Under dynamic conditions, this β-phase becomes less stable than the β-phase at low polymer concentrations.