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Polymer 40 (1999) 5919–5928

polymer

Phase behaviour and structure formation in the system syndiotactic polystyrene/cyclohexanol

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Received 2 October 1998; received in revised form 17 November 1998; accepted 17 November 1998

Abstract

Porous, membrane-like structures with different supramolecular organisation are prepared from solutions of syndiotactic polystyrene in cyclohexanol. Liquid–liquid (L–L) demixing leads to the formation of amorphous materials. They transform into the helix or γ-phase on heating above T_g. Further heating leads to a melting–recrystallisation process that transforms the γ-phase into the zigzag or β-phase. This structure formation prevents re-dissolution of the polymer and maintains the demixed state at temperatures far above the Θ-temperature of the polymer–solvent system. Elimination of the solvent at different temperatures leads to amorphous porous materials or porous materials with the polymer in the γ- or β-phase. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Phase behaviour; Syndiotactic polystyrene; Liquid–liquid demixing

1. Introduction

Thermally induced phase separation (TIPS) is an easy method for the production of porous materials. This structure formation from solution results from the interference of a liquid–liquid demixing process (L–L demixing) with a glass transition or crystallisation process [1]. Cooling of moderately concentrated solutions into the binodal or spinodal region leads to the formation of small domains of high and low polymer concentration in the initial stages of demixing. The combination of this L–L demixing and a vitrification of the concentrated domains or the crystallisation of the polymer in these domains will “freeze” the initially formed multidomain morphology. Elimination of the solvent will produce amorphous or crystalline porous materials. Their morphology depends on the experimental conditions such as overall initial polymer concentration, cooling rate, molecular mass of the polymer, concentration of the concentrated domains.

This procedure can be applied to any polymer solvent system provided that the glass transition–concentration relation or the crystallisation temperature–concentration relation and the L–L demixing domain are situated in the same temperature region [1–8].

The behaviour becomes more complex when polymers like syndiotactic polystyrene (sPS) are used. This polymer can adopt different molecular conformations in the ordered state [9–17]. Crystallisation from the melt or from solution under well-defined conditions leads to an all-*trans*, planar zigzag or T_4 conformation. Lamellar, folded chain crystals are produced and two major crystal modifications can be obtained: the α- and the β- modification. The polymer can also adopt a T_2G_2 helix conformation when crystallisation proceeds from solution. This can lead to the γ- and δ-modification. Some intermediate modifications have been reported, situated respectively between the glass and α-modification, and between the δ- and γ-modification [18–20]. It is clear that the interference of L–L demixing with such complex phase behaviour can lead to a wide variety of supramolecular organisations.

The purpose of this article is to investigate this process of interference and to study some of the properties of the obtained porous materials. Cyclohexanol (CH) was chosen for solvent and atactic polystyrene (aPS) will be used as the reference system. The Θ-temperature of the system aPS/cyclohexanol is 83.5°C [21]. Interesting aspects of the behaviour of this system have already been reported in the literature [22–23].

2. Experimental

The aPS used was a free-radical prepared sample with $M_n = 1.06 \times 10^5$ and $M_w = 2.80 \times 10^5$.

For practical reasons two different samples of sPS were

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PII: S0032-3861(98)00819-2

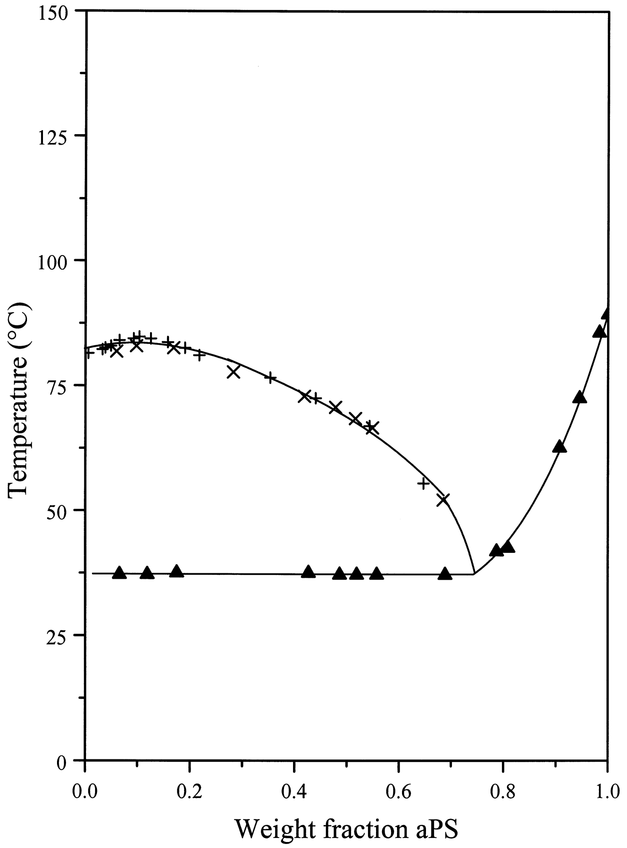

Fig. 1. Temperature–concentration diagram of aPS in cyclohexanol. ▲: glass transition temperature; demixing observed with: DSC, × and optical observations, +.

used. Both were supplied by DOW chemical, and have comparable molecular weights. The molecular weights were determined by GPC in 1, 2, 4-trichlorobenzene (135°C). The weight and number average molecular weights are 4.3×10^5 and 1.4×10^5 g/mol for the sPS used in the DSC measurements, and 4.5×10^5 and 1.1×10^5 g/mol for the sPS used in Wide Angle X-ray Scattering (WAXS), Fourier Transform Infrared (FT-IR) and Scanning Electron Microscopy (SEM). 99% pure cyclohexanol was obtained from Aldrich Chemie.

The thermal behaviour was studied by Differential Scanning Calorimetry (DSC) with a Perkin-Elmer DSC-2C for aPS in cyclohexanol and a DSC-7 of Perkin-Elmer for sPS in cyclohexanol. Scanning rates of 5°C/min were used. Samples were homogenised by a preliminary heating scan in DSC.

FT-IR measurements were performed on a FTIR 2000 of Perkin-Elmer (resolution 2 cm^{-1}) with the polymer solutions between two NaCl windows. Solutions were prepared in sealed glass tubes.

WAXS patterns were obtained using a Rigaku Rotaflex 200B rotating anode. Solutions with a weight fraction of 0.10 were prepared in sealed glass tubes and dried in vacuum after proper thermal treatment. The solutions with weight fraction 0.80 were given their thermal treatment in sealed DSC pans, which were then opened in order to measure the solution in WAXS (without drying).

SEM was performed with a Cambridge Stereoscan 200C at the Technical University of Eindhoven (The Netherlands). The samples were prepared in small glass tubes (3 mm inner diameter) and consequently dried in vacuum at room temperature and broken in liquid nitrogen.

3. Experimental results

3.1. *Atactic polystyrene/cyclohexanol: temperature–concentration relations*

When a solution of aPS in cyclohexanol ($w_2 = 0.10$) is quenched into liquid nitrogen and then brought to room temperature, an opaque, solidified situation is realised. Elimination of the solvent leads to a porous, membrane-like structure. Heating above 37°C turns the system into an opaque, viscous, demixed solution that becomes transparent and homogeneous above 80°C. Fig. 1 represents the temperature–concentration diagram of the system aPS/cyclohexanol, obtained through calorimetric and optical observations. Details on the experimental procedures can be found in [1]. Two concentration domains have to be considered.

$w_2 < 0.76$.

On cooling, an exothermic signal is recorded, characteristic of the L–L demixing in the system. The temperature at the onset of the exotherm is taken as the demixing temperature, T_d. This signal is followed by a shift in the baseline caused by the glass transition that takes place in the concentrated domains. On heating, the opposite transitions take place: a glass transition is followed by a remixing endotherm. The glass transition temperature (T_g) is taken as the temperature at the inflection point in the transition domain, recorded on heating. These temperatures are plotted in Fig. 1 as a function of polymer concentration, w_2.

Observations with the naked eye were also used for the localisation of the temperature at the onset of opalescence, T_{op}. They are also reported in Fig. 1. A good agreement with those determined by calorimetry is obtained. The line drawn by hand through the experimental points delimits the demixing domain. This L–L demixing is stopped at the temperature where this demixing curve intersects the T_g-concentration curve. The co-ordinates of this intersection point are 37°C and $w_2 = 0.74$.

In this concentration domain T_g is independent of the polymer concentration, a behaviour characteristic for the

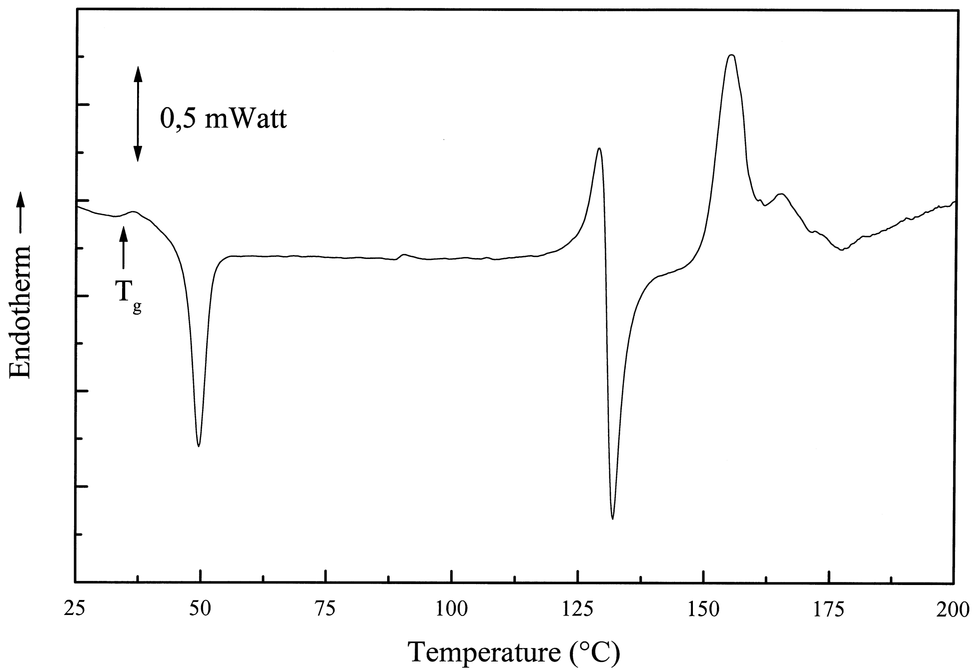

Fig. 2. DSC heating scan of sPS in cyclohexanol after quenching of the solution in liquid nitrogen ($w_2 = 0.10$).

interference of L–L demixing and a glass transition [1].

$w_2 > 0.76$.

In this high concentration region, no L–L demixing is observed anymore and only a T_g is recorded in a DSC scan. The concentration dependence of this transition temperature is also reported in Fig. 1.

3.2. Syndiotactic polystyrene-cyclohexanol: temperature–concentration behaviour

3.2.1. Macroscopic behaviour: optical observations

The behaviour of a solution of sPS is different from that of a solution of the atactic isomer and can be best illustrated by the optical observation of a solution with $w_2 = 0.10$.

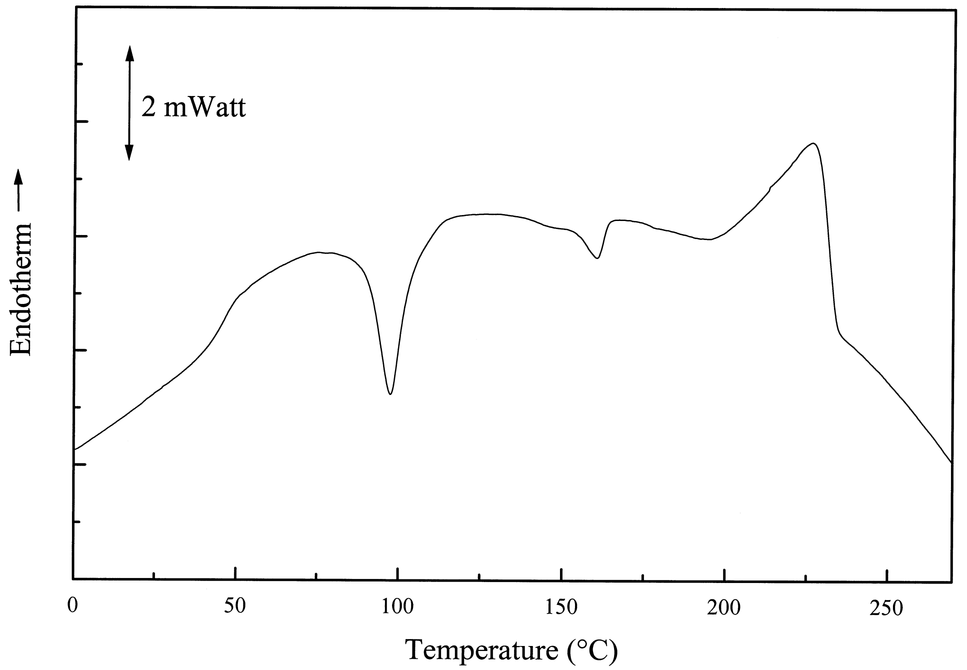

Fig. 3. DSC heating scan of sPS in cyclohexanol after quenching of the solution in liquid nitrogen ($w_2 = 0.81$).

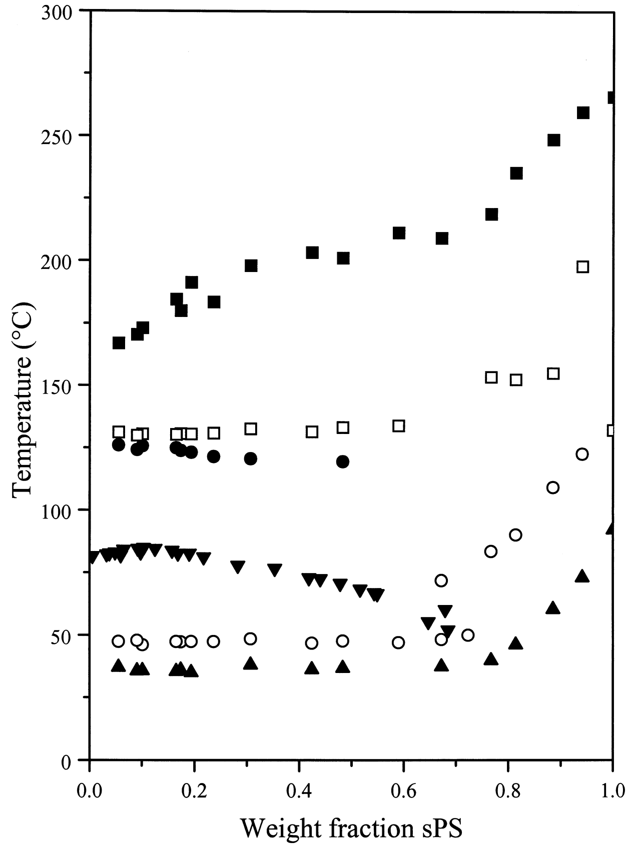

Fig. 4. Temperature–concentration diagram of sPS in cyclohexanol measured by DSC after quenching in liquid nitrogen. ○, □: exothermic signals; ●, ■: endothermic signals; ▲: glass transition temperature; ▼ (DSC), ▽ (optical): demixing of aPS in cyclohexanol.

Quenching in liquid nitrogen of such a solution results in a demixed, vitrified system similar to the one obtained with the atactic isomer. This solidified, demixed state is maintained up to more than 40°C above the Θ-temperature of 83.5°C [24]. The system weakens gradually at higher temperatures and turns into an isotropic solution around 170°C. When the homogeneous solution is cooled slowly to temperatures situated above 60°C, a suspension of crystals is formed. Fast cooling to a temperature between 40°C and 60°C results in a situation that can be compared with the one obtained after quenching in liquid nitrogen.

3.2.2. Temperature–concentration behaviour: quenched solutions

Thermal transitions that take place in solution are localised by DSC. Samples were quenched from the high temperature solute state into liquid nitrogen and then heated in DSC. The shape of the resulting scan depends on the overall concentration and two concentration domains ($0.00 < w_2 < 0.70$ and $0.70 < w_2 < 1.00$), have to be considered.

$w_2 < 0.70$.

A typical DSC scan obtained with a sample with $w_2 = 0.10$ is represented in Fig. 2. A glass transition (T_g) is observed at 36°C, and this transition is concentration independent. An exothermic transition sets in at about 10°C above the end of this concentration independent glass transition domain. At 120°C an endothermic signal sets in but transforms at 125°C into an exothermic signal. The temperatures at which these signals appear are also concentration independent. These

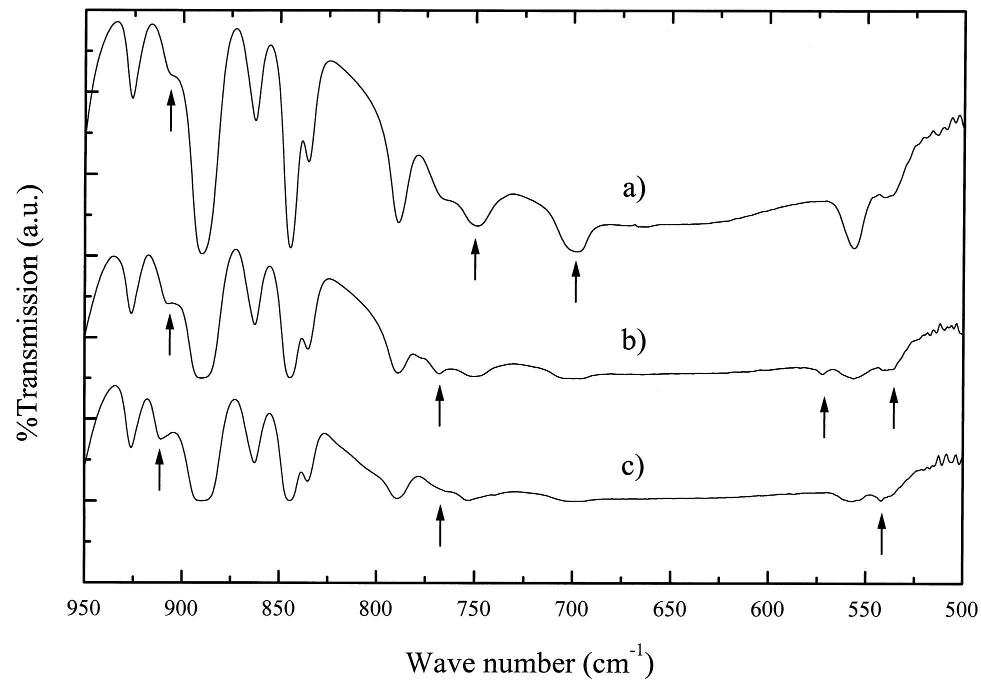

Fig. 5. FTIR-results of a solution of sPS in cyclohexanol $w_2 = 0.10$ quenched below room temperature and heated to (a) 20°C, (b) 90°C, and (c) 140°C.

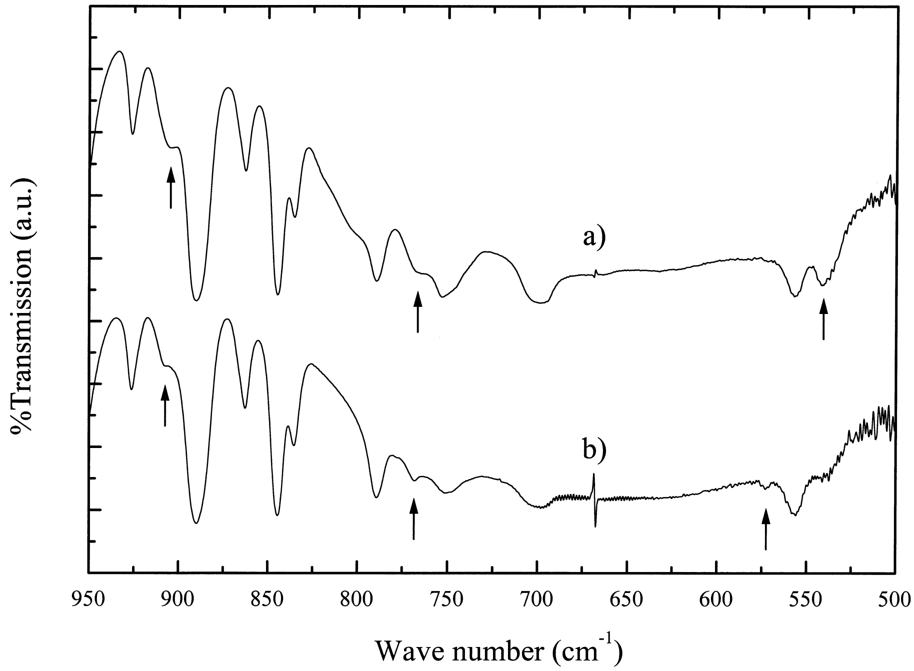

Fig. 6. FTIR-results of a solution of sPS in cyclohexanol $w_2 = 0.10$ quenched to 45°C and annealed at this temperature for (a) 20 min, and (b) 50 min.

signals are followed by a broad endothermic signal with a concentration dependent, final melting temperature.

$w_2 > 0.70$.

The behaviour of these solutions is different from the previous ones. A typical DSC scan is represented in Fig. 3 ($w_2 = 0.81$). The T_g increases with increasing polymer concentration and is followed by an exothermic signal. The temperature at the onset is situated about 25°C above this glass transition domain. This transition is followed by a less pronounced exothermic signal and then by a broad endothermic signal.

The measurements of both low and high weight fractions are represented in a temperature–concentration diagram (Fig. 4).

3.2.3. Temperature–concentration behaviour: slowly cooled solutions

Solutions that are cooled slowly behave in a different way. Cooling at 5°C/min in the DSC shows one exothermic signal. The temperature at the onset of this signal (called the crystallisation temperature or T_c) increases with increasing polymer concentration and is situated between 125°C (low concentration) and 240°C (high concentration). Heating results in a single melting endotherm with a melting temperature (T_m, temperature at the end of the melting peak) that increases with increasing polymer concentration.

3.3. Syndiotactic polystyrene/cyclohexanol: FT-IR analysis in the low concentration range

3.3.1. Isothermal observations

A solution of sPS in cyclohexanol ($w_2 = 0.10$) was quenched to below room temperature and then investigated by FT-IR at three different temperatures. The spectra in the frequency domain of interest are represented in Fig. 5.

At room temperature, the system shows the absorption characteristics of an amorphous, glassy material. The typical absorbances for this state are observed at 906, 749 and 697 cm^{-1}. No signals characteristic for the presence of any ordered conformation can be seen. When heated to 90°C, a FT-IR spectrum is recorded that is characteristic for a sample in which the helix-conformation predominates. Absorption bands characteristic for this molecular conformation appear at 908, 768, 572, 548 and 539 cm^{-1}. Heating to 140°C transforms this helix conformation into the zigzag-conformation with formation of the β-phase. Absorptions appear at 911 and 542 cm^{-1}, while the signal at 768 cm^{-1} disappears.

When the same solution ($w_2 = 0.10$) is cooled quickly to temperatures between 40°C and 60°C (above the glass transition temperature of the demixed system, 36°C), another modification appears. The infrared analysis shows characteristics of the meso-α-phase, an intermediate structure between the α-phase (less ordered zigzag) and the amorphous glass. The presence of this structure is supported by an absorption at 904.5 cm^{-1} that is observed at 906 cm^{-1} for

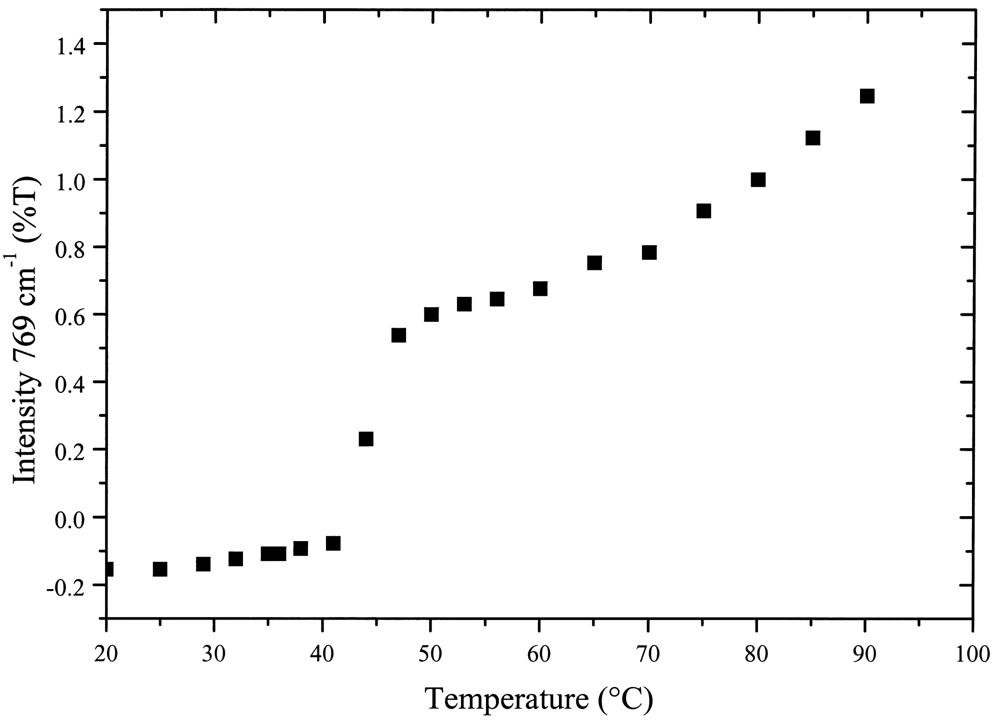

Fig. 7. Intensity of the helix specific infrared absorbance band at 769 cm^{-1} as a function of temperature of a solution of sPS in cyclohexanol $w_2 = 0.10$ after quenching below room temperature.

the completely amorphous state, at 911 cm^{-1} for the zigzag β-phase and at 902 cm^{-1} for the zigzag α-phase, and the signal at 741 cm^{-1}, typical for the zigzag phase, as can be seen in Fig. 6(a). When such a solution is annealed, for e.g. at 45°C for 50 min, a transformation into the helix-conformation takes place as illustrated by the appearance of absorptions at 908 and 768 cm^{-1} (Fig. 6(b)). This means that the initially formed

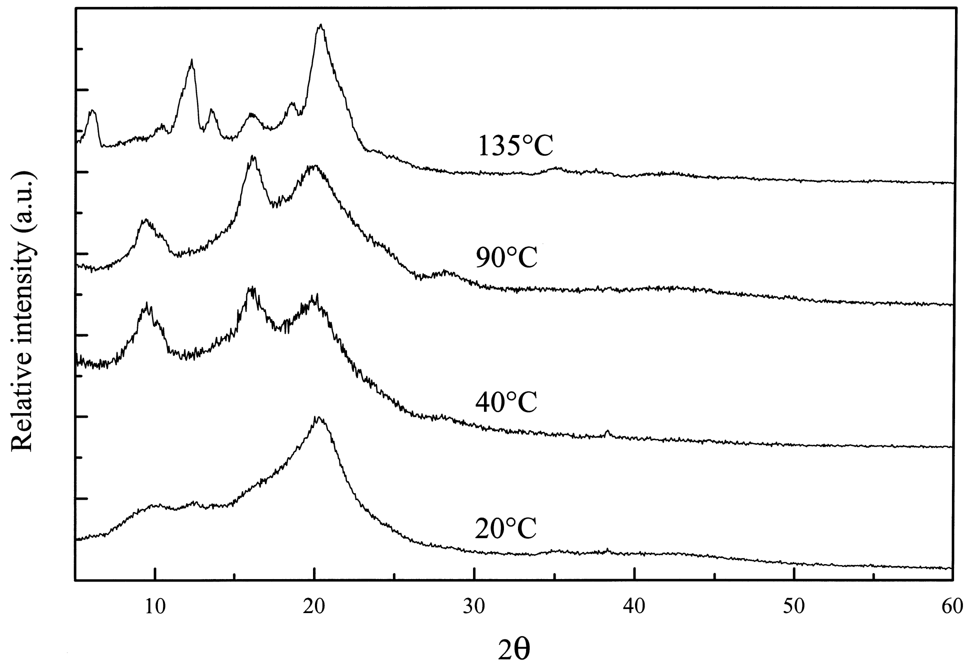

Fig. 8. WAXS patterns of sPS in cyclohexanol $w_2 = 0.10$ after quenching in liquid nitrogen, heating to the temperatures indicated and elimination of the solvent.

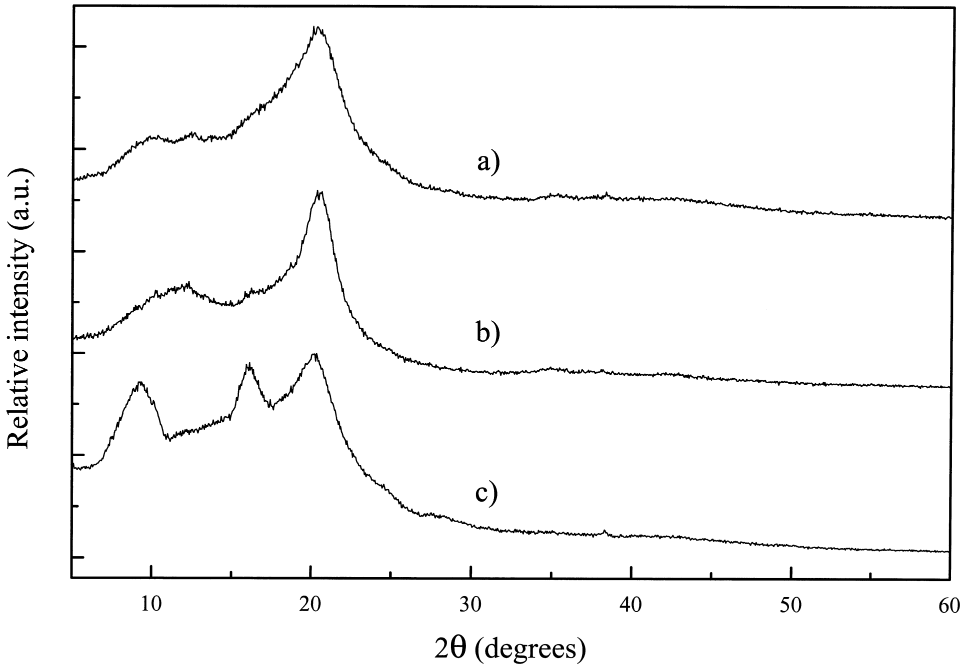

Fig. 9. WAXS patterns of sPS in cyclohexanol $w_2 = 0.10$: (a) after quenching in liquid nitrogen; (b) after quenching to 45°C; (c) after quenching to 45°C and annealing at this temperature for 50 min.

meso-structure slowly converts into the more stable helix-conformation during annealing at $T > T_g$.

3.3.2. Dynamic observations

Solutions were quenched to low temperature and then heated in the FT-IR spectrometer. The intensity of the signal at 768 cm^{-1}, characteristic for the helix conformation, was followed from 20°C to 90°C at a scanning rate of 0.5°C/min. The results are reported in Fig. 7. Below 40°C this signal appears only as a weak shoulder. Between 40°C and 50°C an important increase of the intensity is observed. This intensity increase continues when heated further above 50°C.

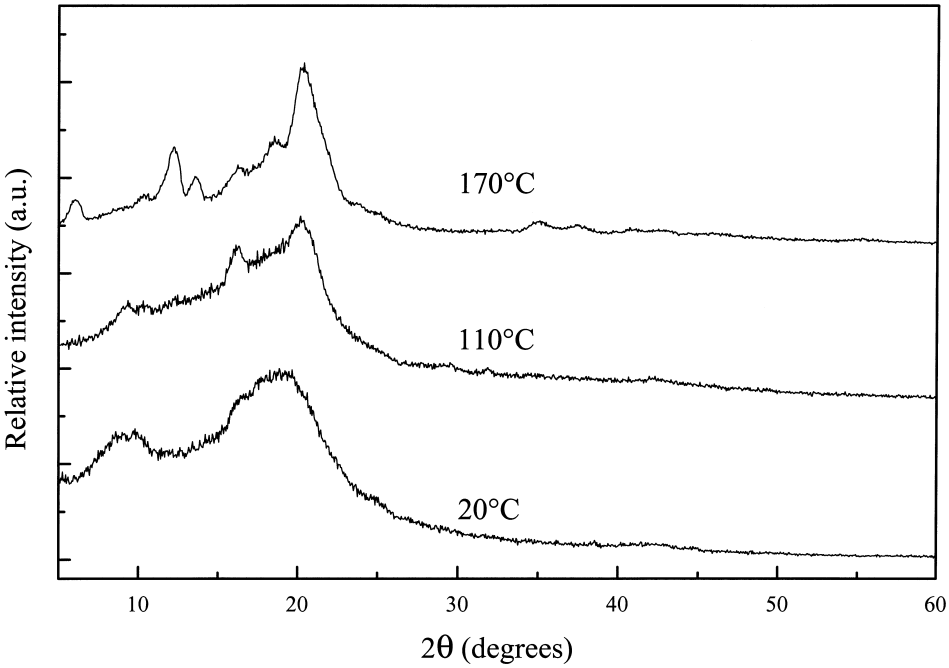

Fig. 10. WAXS patterns of sPS in cyclohexanol $w_2 = 0.80$ after quenching in liquid nitrogen and heating to the temperatures indicated.

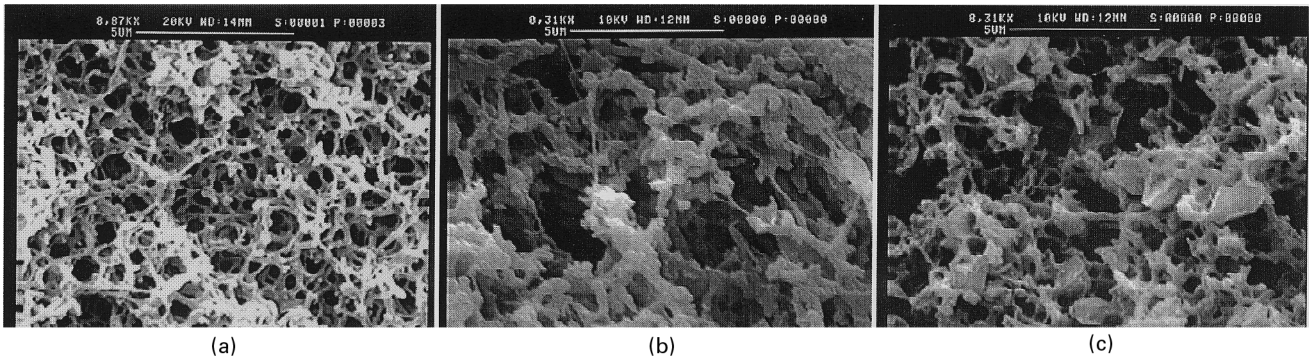

Fig. 11. SEM images of sPS in cyclohexanol $w_2 = 0.10$, quenched in liquid nitrogen: (a) heated to 20°C; (b) heated to 90°C; (c) heated to 120°C.

4. Wide angle X-ray scattering-analysis

$w_2 < 0.70$.

Further evidence for the nature of the different phases that are formed was obtained from WAXS-observations. The different structures were prepared in solutions with $w_2 = 0.10$ that were homogenised at 190°C and quenched in liquid nitrogen. Then they were annealed at room temperature, 40°C, 90°C and 135°C. The WAXS-patterns were recorded after elimination of the solvent. They are represented in Fig. 8.

Annealing at room temperature results in an amorphous, glassy sample with only the intense signal around $2\theta = 20.3°$, characteristic for the absence of any supramolecular order. Heating to 40°C generates diffraction peaks at $2\theta = 16.1°$ and 9.3°, characteristic for the presence of the γ-phase. At 90°C the same peaks are present, but their intensity has slightly increased. Annealing at 135°C transforms the γ-phase into the zigzag β-phase characterised by diffraction maxima at $2\theta = 6.0°$, 12.2°, 13.5°, 18.5° and 35.0°.

In a second series of experiments the solutions were cooled to temperatures between 60°C and T_g. The observed WAXS pattern is characteristic for the presence of the meso-α-phase (Fig. 9(a)). Annealing a sample at 45°C for 50 min leads to the helix-conformation as can be seen in Fig. 9(b).

$w_2 > 0.70$.

Samples with $w_2 = 0.80$ were quenched in liquid nitrogen and annealed at different temperatures. The WAXS patterns, recorded in the presence of the solvent, are represented in Fig. 10.

Annealing at room temperature results in an amorphous, glassy sample. Annealing at 110°C (temperature at the end of the first exotherm observed in the DSC) results in a pattern characteristic for the helix-conformation (γ-phase). At 170°C (temperature at the end of the second exotherm in the DSC), the WAXS-pattern corresponds to that of the zigzag-conformation (β-phase).

5. Scanning electron microscopy

A sample with $w_2 = 0.10$ was subjected to a SEM analysis. The sample was quenched in liquid nitrogen and heated to room temperature. Then the solvent was eliminated in vacuum at room temperature. A porous, membrane-like morphology is observed (Fig. 11(a)).

The sample was heated to 90°C in the presence of the solvent and the solvent was again eliminated at room temperature in vacuum. The SEM image shows a structure very similar to the one observed after the treatment at room temperature (Fig. 11(b)). This morphology is maintained even when the sample is first heated, in the presence of the solvent, to 120°C (Fig. 11(c)).

Annealing at higher temperature results in a degradation of the supramolecular organisation.

6. Discussion

The complex temperature–concentration behaviour of the system sPS/cyclohexanol (Fig. 4) can easily be understood from the combination of the data obtained by FT-IR, DSC and WAXS and the comparison with the behaviour of the atactic isomer.

6.1. Atactic polystyrene

When a solution of aPS in cyclohexanol is cooled quickly to room temperature, L–L demixing takes place and two phases of strongly different concentration are formed. The final equilibrium situation consists of two layers with different polymer concentration, dictated by the coexisting lines. However, this equilibrium state is seldom reached and most of the time, a system composed of a large number of small domains is obtained. Such a system slowly evolves towards this final equilibrium state. The onset of this L–L demixing can easily be observed by optical and calorimetric experiments. At moderate polymer concentration (e.g. $w_2 = 0.10$) the dilute phase is in excess so that the concentrated phase will be dispersed throughout the solution. At the concentration considered here, this concentrated phase

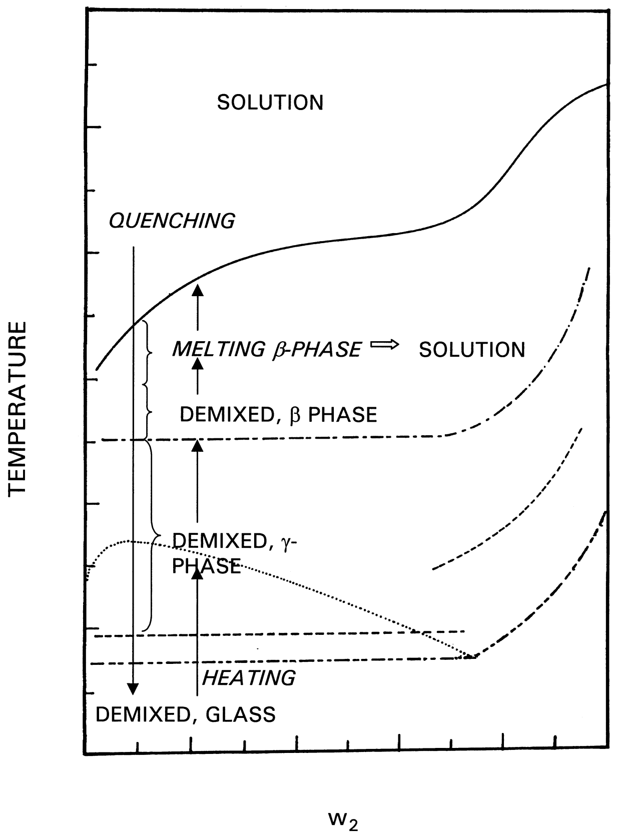

Fig. 12. Schematical phase diagram of sPS in cyclohexanol.

will be able to form a continuous, membrane-like texture through the solution. When this initial stage of demixing is cooled below the temperature at the intersection of the demixing domain and the T_g-w_2 line ($w_2 = 0.73$ at 36°C), the concentrated domains will vitrify and the solution as a whole solidifies. After elimination of the solvent, a porous material is obtained. The T_g of the concentrated domains will be dictated by the composition given by the coexisting curves. This composition in the case of aPS in cyclohexanol is independent of the overall concentration so that T_g is constant in the concentration domain under the demixing curve. This is not always the case and T_g can increase with decreasing overall polymer concentration when the position of the coexisting lines depends on this overall polymer content [7]. One can therefore use the concentration independence of T_g as a very good argument for the occurrence of L–L demixing, though this demixing cannot be directly observed by optical observations or calorimetry.

Samples heated above T_g return to the solute state once the demixing curve was crossed.

6.2. Syndiotactic polystyrene: temperature–concentration relations

L–L demixing cannot be observed directly in this system because of the interference with other thermal transitions that lead to structure formation. As a result of these transitions, the samples become opaque on cooling and the corresponding exothermic DSC signals are much larger than those related to L–L demixing. Evidence for the occurrence of such a demixing is nevertheless found in the invariant T_g in the concentration domain $0.00 > w_2 > 0.70$ when these solutions are quenched to low temperature. This corresponds exactly with the position of the demixing domain of aPS/cyclohexanol. Therefore, we represented in Fig. 4 the data obtained with the atactic isomer (Fig. 1).

The intersection of the demixing curve and the T_g-concentration relation is situated around 36°C and $w_2 = 0.70$. These values, very similar to those obtained with the atactic isomer, are independent of the overall polymer concentration. This means that the overall polymer concentration does not influence the position of the coexisting lines in the temperature range under consideration.

Elimination of the solvent from such a demixed, vitrified system results in an amorphous membrane.

When these demixed, vitrified systems are heated in the presence of the solvent, several transitions take place. Heating the system above 36°C will transform the polymer in the concentrated domains into the γ-phase with the polymer chains in a helix-conformation. This is reflected in the exothermic signal a few degrees above the glass transition domain (Fig. 2), the changes in the FT-IR spectrum around that temperature (Figs. 5 and 7) and the observation of the WAXS diffraction maxima characteristic of the γ-phase. Consequently, no remixing of the solution will take place and the multidomain morphology is maintained because of this supramolecular organisation (γ-phase). Elimination of the solvent transforms the system into a membrane in which the walls of the pores are in this γ- or helix phase.

The melting–recrystallisation around 125°C transforms the γ-phase in the zigzag β-phase and makes it possible to maintain this demixed, solidified situation in the high temperature region. After elimination of the solvent, a crystalline membrane (β-phase) is obtained.

Remixing of the system into a homogenous solution can only take place when the β-phase is completely molten. The corresponding final melting point depends strongly on the overall polymer concentration and is situated on the melting point-concentration line represented in Fig. 4.

These consecutive processes are schematically illustrated in the schematic phase diagram represented in Fig. 12.

Solutions with $w_2 > 0.70$ are situated outside the demixing domain and do not phase separate. Quenching below the T_g-curve results in formation of the amorphous glass. The sample has to be heated to at least 20°C above T_g in order to introduce a transition into the γ-phase. This difference with T_g is larger than in the L–L demixing domain where a difference of less than 10°C is sufficient. The reasons for this difference are not clear at the moment. One possible explanation could be the enhanced nucleation capability under the influence of L–L demixing. This influence of L–L demixing on the kinetics of crystallisation has been illustrated in the literature [3–4]. The temperature at which the transformation of helix into zigzag takes place increases with polymer concentration and this concentration dependence evolves parallel with the T_g-concentration relation.

6.3. Influence of the applied thermal treatment

A different behaviour is observed when the solutions are not cooled below the invariant T_g, and the resulting structure will depend strongly on the thermal procedure applied. Slow cooling results in the β-phase, while quenching in the temperature region $36°C > T > 60°C$ leads to the meso-α-phase that slowly transforms into the helix phase.

7. Conclusions

The complex phase behaviour of the system sPS-cyclohexanol allows the formation of different supramolecular organisations. When combining them with the process of L–L demixing, membranes can be formed in which the walls of the pores are glassy and amorphous, in the γ-phase or helix phase and in the β-phase or zigzag crystalline phase. The interference of this L–L demixing with these different processes of structure formation leads also to a thermal stability of the demixed system far above the Θ-temperature of the polymer–solvent system. The solvent free membrane is also thermally stable up to the melting point of the pure polymer.

Acknowledgements

This research was financed through a specialisation scholarship (JDR) of the Flemish Institute for the improvement of scientific research in industry (IWT) and a fellowship for JA from the National Fund for Scientific Research (NFWO). This project was supported by the Fund for Scientific Research Flanders (FWO) and Interuniversity Poles of Attraction, Belgian State, Prime Ministers office for Scientific Research, Technical and Cultural Affairs (IUAP IV, P4/11).

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