Solvent Quality and Phase Stability in Syndiotactic Polystyrene–Solvent Systems

T. Roels, F. Deberdt, and H. Berghmans*

Laboratory for Polymer Research, Katholieke Universiteit Leuven, Celestijnenlaan, 200F, B-3001 Heverlee, Belgium

Received May 24, 1994; Revised Manuscript Received July 30, 1994[®]

ABSTRACT: The phase behavior of syndiotactic polystyrene in solvents with different qualities has been investigated. The concentration dependence of the melting points of the β- and δ-phases has been measured, and the experimental data have been used to construct the corresponding liquidi. The different solvents can therefore be classified in order of increasing solvent quality for polystyrene: decalin < 1,2,4-trichlorobenzene < *o*-xylene < 1,2-dichlorobenzene < chlorobenzene < chloroform. The stability of the β-phase increases with decreasing solvent quality. The opposite influence of this solvent quality is observed for the δ-phase. This solvent quality induced inversion of the phase stability explains the peculiar behavior in good solvents like chloroform and the formation of thermoreversible gels in these solvents. The study of the phase behavior and the analogy with the melting behavior of mixtures of low molecular mass substances reveal the formation of an incongruent melting polymer–solvent compound. A two-step mechanism composed of a coil to helix transition followed by an intermolecular association is proposed.

Introduction

Syndiotactic polystyrene (sPS) crystallizes from the melt or, under the correct crystallization conditions, from solution, with formation of a crystalline phase in which the polymer chains adopt an all-trans zigzag conformation. Different modifications of this crystalline structure have been reported, and the reader is referred to the literature for detailed information.[1-10] Distinction between these modifications can be made by X-ray scattering analysis. Calorimetric investigations by differential scanning calorimetry (DSC) cannot distinguish between these different modifications, and melting experiments show only one melting domain. The occurrence of different melting endotherms has been ascribed to recrystallization during heating.[11] We will therefore not distinguish between the α- and the β-phases and their modifications, and the phase in which the polymer chains adopt this zigzag conformation will be called the β-phase.

The polymer chains can also adopt a T_2G_2 helix conformation, and the formation of the corresponding crystalline structure, called the δ-phase, can only take place in the presence of a solvent. Elimination of the solvent results in formation of the γ-phase.

The addition of a solvent influences in a different way the stability of the β- and the δ-phase.[12,13] The study of the phase behavior of the systems sPS–decalin and sPS–*o*-xylene reveals that the melting point of the β-phase increases with decreasing solvent quality, while the melting point of the δ-phase increases with increasing solvent quality. The formation of an incongruent melting compound between the polymer and the solvent has been proposed.[12,13] This specific role of the solvent has already been stressed by different authors.[1,2,10,14-16] Experimental evidence obtained from a detailed X-ray analysis of the system sPS–toluene has been presented recently.[15] This important role of the solvent will be further investigated in this paper.

Experimental Details

Syndiotactic polystyrene was supplied by Dow Chemical, USA. The number-average and mass-average molecular masses, determined by GPC in 1,2,4-trichlorobenzene at 135 °C, are 14.3×10^4 and 42.9×10^4.

The thermal behavior was studied by differential scanning calorimetry (DSC2 and DSC7, Perkin-Elmer). A cooling and heating rate of 10 °C/min was used. Wide-angle X-ray scattering (WAXS) patterns were obtained using Cu Kα radiation and recorded with a Philips PW 1792 flat-film camera. Thermogravimetric analysis (TGA) was carried out with a Setaram TGDSC 111 instrument.

Solvents were obtained from Baker (chlorobenzene and 1,2-dichlorobenzene), Janssen Chimica (1,2,4-trichlorobenzene), and Aldrich Chemie (1,2,4,5-tetrachlorobenzene).

The polymer mass fraction, w_2, is used to express the polymer concentration.

Experimental Results

Investigation of the Phase Behavior. The phase behavior of the different sPS–solvent systems was investigated by differential scanning calorimetry. Temperature–concentration phase diagrams are constructed by plotting the melting point of the polymer, deduced from a DSC thermogram recorded on heating, as a function of polymer concentration. The temperature at the end of the melting endotherm has to be taken as the melting point when working with a system composed of two constituents, polymer and solvent.[17] No corrections were made for the dynamic character of the experimental method and the nonequilibrium character of the experimental data. Therefore these phase diagrams can only be used in a qualitative way. It has nevertheless been shown that the shape of these nonequilibrium diagrams reflects very well the equilibrium behavior.[12,13,17] A detailed discussion based on a comparison with equilibrium diagrams has been published recently.[18]

The conclusions drawn from these temperature–concentration data are supported by WAXS analysis and infrared (IR) observations. This combination of experimental techniques allows for the characterization of the different phases involved. A detailed description of the experimental method has been given in previous papers.[12,13]

Phase Behavior of sPS–Solvent Systems. The solution behavior of sPS is complex: at room temperature, this polymer is not soluble in good solvents for atactic polystyrene. Thermoreversible gels can be formed with dilute solutions ($w_2 < 0.01$) of a polymer with a high

---

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-6216$04.50/0

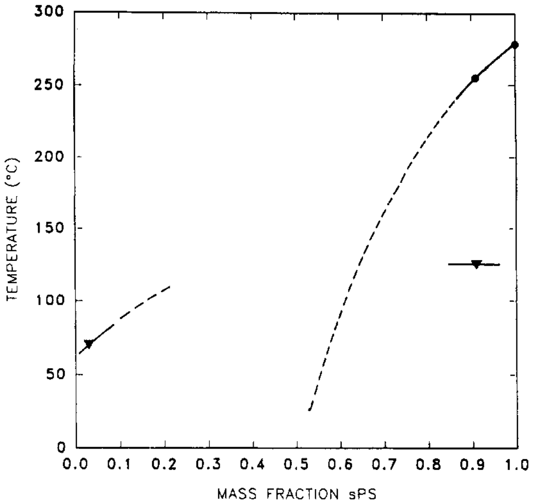

Figure 1. Schematic drawing of a possible temperature–concentration diagram of sPS/chloroform: (●) melting of β-phase; (▼) melting of δ-phase.

molecular mass[19] in tetrahydrofuran, chloroform, chlorobenzenes, etc. To understand this peculiar behavior, the temperature–concentration diagrams in some of these solvents were investigated.

Phase Behavior in Chloroform. Semicrystalline sPS crystallized from the melt in the β-phase swells in chloroform at room temperature and the β-phase dissolves. This solvent treatment however will not lead to the formation of a homogeneous solution but to the formation of the δ-phase. A thermoreversible gel is obtained at low polymer concentration. A detailed analysis of the phase behavior is very difficult because of the low boiling point of the solvent. Only a few melting points have been localized experimentally.

At low polymer concentration, the melting of the δ-phase takes place around 70 °C. In the high-concentration region, the vapor pressure of the solvent becomes very low and the melting behavior could be studied in hermetically sealed DSC pans. A melting point depression of 25 °C for the β-phase is recorded when a mass fraction solvent of 0.09 is added. This melting point depression is far superior to the one observed under analogous conditions with other solvents such as chlorobenzene. The corresponding metastable liquidus of the β-phase will reach room temperature at relatively high polymer mass fraction. This explains the swelling behavior in the solvent. During the swelling at room temperature, the liquidus of the β-phase is crossed and melting of this phase takes place. Then the much more stable δ-phase, with its melting far above room temperature, is formed. This results in a thermoreversible gel at moderate polymer concentrations. A schematic drawing of a possible phase diagram is presented in Figure 1. The formation of the δ-phase is not observed in *o*-xylene where the metastable liquidus of the β-phase reaches the pure solvent axis above room temperature.

Phase Behavior in Chlorobenzenes. The melting point depression in different chlorobenzenes is much less pronounced than in chloroform. The behavior in chlorobenzene (Figure 2) is very similar to that observed in *o*-xylene. The same melting point–polymer concentration relationship is found for the β-phase, and the invariant incongruent melting of the δ-phase takes place at the same temperature. We refer the reader to ref 13 for a detailed discussion of such a system.

The introduction of one additional chlorine atom in the solvent has only a limited influence on the melting behavior. The melting line of the β-phase in 1,2-dichlorobenzene is shifted to higher temperature by only a few degrees. The melting of the δ-phase is not influenced (Figure 3).

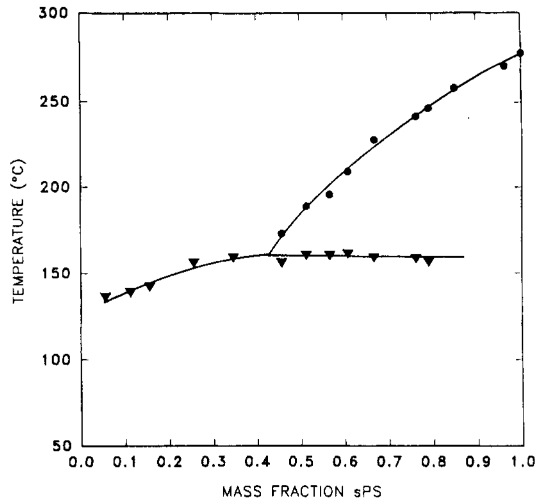

Figure 2. Temperature–concentration diagram of sPS/chlorobenzene: (●) melting of β-phase; (▼) melting of δ-phase.

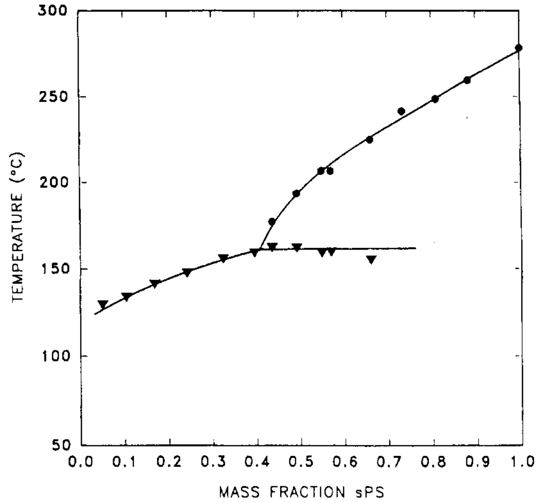

Figure 3. Temperature–concentration diagram sPS/1,2-dichlorobenzene: (●) melting of β-phase; (▼) melting of δ-phase.

The shift to higher temperatures in the melting line of the β-phase in 1,2,4-trichlorobenzene is more pronounced, and the intersection with the melting line of the δ-phase is situated at lower polymer mass fraction (Figure 4). The incongruent melting of this δ-phase takes place at lower temperature. One can therefore conclude that there is an increase of the stability of the β-phase and a decrease of the stability of the δ-phase.

The introduction of an additional chlorine atom in the solvent increases further the stability of the β-phase. The melting behavior of this phase in 1,2,4,5-tetrachlorobenzene approaches that of the system sPS–decalin.[12] However, the melting of the δ-phase is no longer observed because of the high melting point of the solvent. The phase diagram represents the eutectic melting of the system 1,2,4,5-tetrachlorobenzene–sPS (β-phase) (Figure 5).

Phase Behavior in *o*-Xylene. The phase behavior in this solvent has been discussed in detail in a previous paper.[13] The phase diagram (Figure 4, ref 13) is similar to the one observed in chlorobenzene and 1,2-dichlorobenzene.

Phase Behavior in *trans*-Decalin. The behavior in this poor solvent has also been discussed in detail in a previous paper,[12] and the corresponding phase diagram is

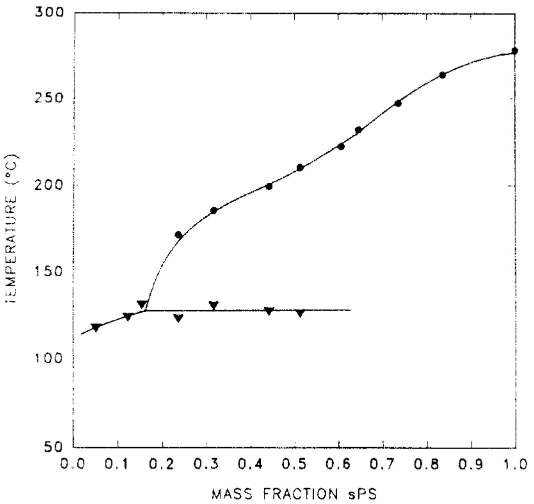

Figure 4. Temperature–concentration diagram sPS/1,2,4-trichlorobenzene: (●) melting of β-phase; (▼) melting of δ-phase.

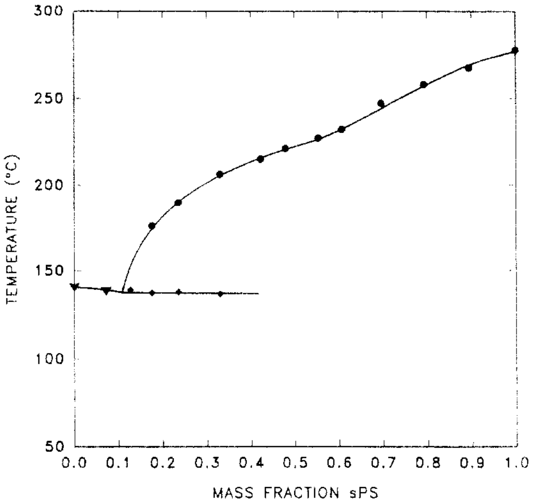

Figure 5. Temperature–concentration diagram sPS/1,2,4,5-tetrachlorobenzene: (●) melting of β-phase; (◆) eutectic melting; (▼) melting of the solvent.

presented in Figure 13 of ref 12. The liquidus of the β-phase is situated at higher temperature than reported for the system sPS–1,2,4,5-tetrachlorobenzene. The incongruent melting of the δ-phase in *trans*-decalin takes place around the same temperature as the one found in 1,2,4-trichlorobenzene.

Discussion

The phase diagrams of the different sPS–solvent systems represent only one side of a eutectic melting diagram. An exception has to be made for the system sPS–1,2,4,5-tetrachlorobenzene. The high melting point of the solvent leads to a eutectic behavior and to the absence of the formation of the δ-phase. This diagram will therefore be left out of the discussion.

The shape of the phase diagrams is characteristic for the formation of an incongruent melting compound. However, the change in these diagrams with solvent quality is not fully in agreement with general thermodynamic considerations. We will therefore discuss the melting behavior of the β- and the δ-phases separately.

Melting of the β-Phase. A schematic representation of a melting system composed of two components with a large difference in melting point is shown in Figure 6. In the absence of a liquid–liquid (L–L) demixing, a negatively curved liquidus is observed (1). When a metastable L–L demixing domain approaches the liquidus, this liquidus starts to show an inflection point (2). The liquidus becomes horizontal where it is touched by the L–L demixing curve (3).[20] Detailed inspection of the experimental data and their relation with Figure 6 leads to two important remarks.

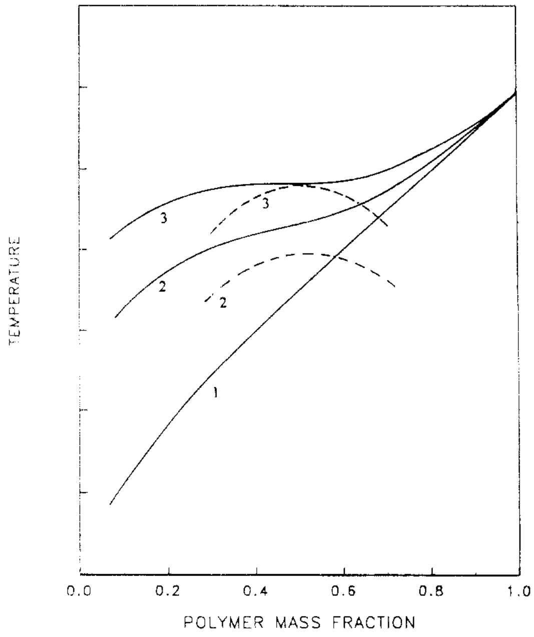

Figure 6. Schematic representation of the influence of the position of a L–L demixing (- - -) on the shape of the liquidus (—) of a polymer–solvent system. The solvent quality decreases from 1 to 3.

(1) To observe the L–L demixing phenomenon and explain the liquidus of the β-phase in sPS–decalin, the maximum in the L–L demixing curve has to be situated at $w_2 = 0.50$. This is not possible in polymer–solvent systems where the maximum and the critical point are close to the solvent axis.

We also do not expect this shape of liquidus when the liquid–liquid demixing domain is situated at temperatures far below the liquidus, and this is to be expected for the system sPS–decalin. It was not possible however to localize experimentally a liquid–liquid demixing for the system sPS–decalin. We only can estimate its position on the temperature scale from experimental data reported for the atactic isomer.[21-23] This however is too far below the liquidus of the β-phase so that it cannot influence this liquidus in such a way as to originate this specific S-shaped curve.

(2) The liquidus is curved upward at the high polymer content side and this results in an S-shaped curve, not predicted by theory.

This very specific S-shaped curve can also be obtained under rather different conditions. The investigation of the eutectic melting of mixtures of water and aliphatic alcohols leads to very analogous phase diagrams. An illustration is given in Figure 7 for the systems water–methanol, water–ethanol, and water–2-propanol.[24] It is well known that the increase of the contribution of the hydrocarbon group in an alcohol will increase the difference between water and the alcohol and make the alcohol less hydrophilic. This could then, in view of the discussion in this paper, be interpreted as a decrease of the solvent quality of the alcohol for water. This decrease in solvent quality results in an increase of the melting temperature at constant composition of the solution. The sigmoidal shape could then be ascribed to the occurrence of a liquid–liquid demixing. This demixing however is never observed, but the shape of the liquidus of water nevertheless changes

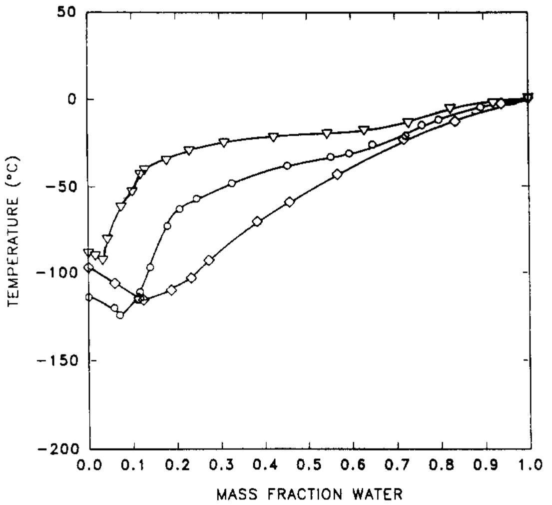

Figure 7. Liquidi of the systems water–methanol (◇), water–ethanol (○), and water–2-propanol (▽).[22]

from an almost continuous decrease of the melting point with increasing alcohol content (methanol–water) to a more and more pronounced S-shaped liquidus with increasing hydrophobic character of the alcohol. This shape is ascribed to the occurrence of specific interactions between both components, leading, at lower temperature, to the formation of an incongruent melting compound.

The striking analogy between the phase behavior of the system water–aliphatic alcohols and the β-phase of sPS in the presence of a solvent firmly supports the proposition of compound formation (δ-phase) between the polymer and the solvent.

An important increase of the melting point at constant concentration is observed when passing from chloroform, a very good solvent for polystyrene, to decalin, a solvent in which liquid–liquid demixing could take place just below room temperature. We can therefore classify the different solvents used in this work, in order of decreasing solvent quality for polystyrene. The melting point at constant concentration, or the width of the concentration domain where the β-phase is formed, can be used as a criterion: chloroform > chlorobenzene > 1,2-dichlorobenzene > *o*-xylene > 1,2,4-trichlorobenzene > 1,2,4,5-tetrachlorobenzene > *trans*-decalin.

Melting of the δ-Phase. The experimental evidence brought in this paper and the experimental data found in the literature on low molecular mass compounds clearly support the proposed formation of an incongruent melting compound. The shape of the corresponding melting line and the interference with the melting line of the β-phase are strong arguments in favor of this proposition. The stability of this compound increases with increasing solvent quality. This results in a phase stability inversion, induced by the quality of the solvent. In decalin the β-phase is the most stable phase over the whole concentration range. This β-phase dissolves easily in chloroform by swelling at room temperature and represents the stable phase at high polymer concentrations. At lower polymer content, the β-phase becomes metastable and the δ-phase becomes stable. The peculiar swelling behavior in chloroform and the impossibility of preparing solutions of sPS in any good solvent for polystyrene have to be explained by this phase stability inversion, induced by a change in solvent quality.

Composition of the Compound. From the phase behavior it was not possible up to now to obtain the exact composition of the compound. Literature data on the system sPS–toluene propose the formation of a compound that contains 17% solvent. This solvent content was proposed because it was difficult to eliminate it from samples dried at room temperature. The conclusion looks attractive but could lead to erroneous conclusions. Drying of a sample at room temperature brings the system, by a horizontal shift through the phase diagram, into the high-concentration region where the sample is in its glassy state. Complete elimination of the solvent from this glassy state is very difficult, even when atactic polystyrene is involved.[13] Therefore the composition of the compound has been arbitrarily put equal to a (styrene repeating unit)/(solvent molecule) ratio of 1/1.

Mechanism of Compound Formation. A two-step mechanism for the formation of the polymer–solvent compound (δ-phase) has been proposed. In a first step the polymer chain changes its conformation from a random coil to a helix. These helices agglomerate in a second step to form the δ-phase. The role of the solvent is presently unclear. Its presence is necessary and evidence has been found for its participation in the compound formation. The absence of any specificity suggests that the solvent does not bind in a stable manner to the polymer chains but acts as a solvating agent which makes the formation of the helix and its stabilization possible.

Up to now no direct experimental evidence has been obtained, and the proposed mechanism is deduced from indirect experimental evidence. The best illustration is found with the system sPS–decalin for which the β-phase is stable and the δ-phase is metastable at any concentration. In the low-concentration region, the formation of the δ-phase competes with the formation of the β-phase. An increase of the cooling rate promotes the formation of the metastable δ-phase at the expense of the stable β-phase.[12,13] This stable β-phase cannot be formed below a certain temperature limit, and this inhibition can only be explained by a change in the molecular conformation in solution. This makes the crystallization of the random coil into the zigzag conformation impossible. We therefore propose that, below a certain temperature limit, a change from a random coil conformation into a solvated helix takes place. This coil to helix transformation is characterized by a temperature-dependent equilibrium constant. A decrease of temperature will shift the equilibrium toward the helix side. Once a large enough helix content has been realized, intermolecular association betweeen the helices takes place, resulting in the formation of the δ-phase. Therefore only the δ-phase is formed when the solutions are cooled quickly. Slow cooling or isothermal annealing at high enough temperature will allow the β-phase to be formed. Both phases can be formed at not too high cooling rates.

Conclusions

The complex phase behavior of sPS–solvent systems is explained by the formation of two different phases.

The β-phase can be considered as a "classical" crystalline phase whose stability increases with decreasing solvent quality. This phase represents the stable phase in poor solvents for polystyrene such as decalin. The δ-phase is characterized as a polymer-solvent compound with a stability that shows an opposite solvent quality dependence and represents the stable phase in good solvents for polystyrene such as chloroform. Therefore, a change in solvent quality results in an inversion of the stability of these two phases. Phase diagrams characteristic for the formation of an incongruent melting compound, are obtained in solvents with intermediate quality. This complex phase behavior also explains the difficulties encountered in the formation of homogeneous solutions.

A two-step mechanism for the formation of the δ-phase is proposed. The random coils transform into a helix and the solvent acts as a stabilizing element in this transition. Solvent molecules are taking part in the formation of this supramolecular organization of this compound.

This δ-phase is responsible for the formation of thermoreversible, almost transparent gels in moderately concentrated solutions.

Acknowledgment. The authors are indebted to the IWONL and DSM, Geleen, The Netherlands, for a fellowship to F.D. and T.R. Financial support by the National Fund for Scientific Research and the Ministry of Scientific Programmation through IUAP-16 is gratefully acknowledged. The authors also wish to thank Dow Chemical, USA, for supplying the sample.

References and Notes

(1) Immirzi, A.; de Candia, F.; Ianelli, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 761.
(2) Vittoria, V.; de Candia, F.; Ianelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765.
(3) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1989**, *22*, 4377.
(4) Guerra, G.; Vitagliano, V.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.
(5) Petraccone, V.; Auriemma, F.; Dal Poggetto, F.; De Rosa, C.; Guerra, G.; Corradini, P. *Makromol. Chem.* **1993**, *194*, 1335.
(6) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78.
(7) Prasad, A.; Mandelkern, L. *Macromolecules* **1990**, *23*, 5041.
(8) Rapacciuolo, M.; De Rosa, C.; Guerra, G.; Mensitieri, G.; Apicella, A.; Del Nobile, M. A. *J. Mater. Sci. Lett.* **1991**, *10*, 1084.
(9) De Rosa, C.; Guerra, G.; Petraccone, V.; Corradini, P. *Polym. J.* **1991**, *23*, 1435.
(10) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Ijitsu, T.; Yukinari, T. *Polymer* **1992**, *33*, 488.
(11) Arnauts, J.; Berghmans, H. *Polym. Commun.* **1990**, *31*, 343.
(12) Deberdt, F.; Berghmans, H. *Polymer* **1993**, *34*, 2192.
(13) Deberdt, F.; Berghmans, H. *Polymer* **1994**, *35*, 1694.
(14) Vittoria, V.; Russo, R.; de Candia, F. *Polymer* **1991**, *32*, 3271.
(15) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620.
(16) Kobayashi, M.; Kozasa, T. *Appl. Spectrosc.* **1993**, *47*, 1417.
(17) Aerts, L.; Berghmans, H. *Bull. Soc. Chim. Belg.* **1990**, *99*, 931.
(18) Berghmans, H.; Deberdt, F. *Philos. Trans. R. Soc. London* **1994**, *398*, 117.
(19) Deberdt, F.; Berghmans, H., unpublished results.
(20) Bakhuis Roozeboom, H. W. *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*; Druck und Verlag von Friedr. Vieweg & Sohn: Braunschweig, 1918, 19 Heft 2, Teil 2, pp 129–135.
(21) Arnauts, J.; Berghmans, H. *Polym. Commun.* **1987**, *28*, 66.
(22) Arnauts, J.; Berghmans, H. *Physical Networks*; Burchard, W., Ross-Murphy, S. B., Eds.; Elsevier Applied Science: Dordrecht, 1990; Chapter 3, pp 35.
(23) Arnauts, J.; Berghmans, H.; Koningsveld, R. *Makromol. Chem.* **1993**, *194*, 77.
(24) Ott, J. B.; Goates, J. R.; Waite, A. B. *J. Chem. Thermodyn.* **1979**, *11*, 739.