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Gelation Mechanism of Syndiotactic Polystyrene in Bromoform

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ABSTRACT: The gelation of sPS in bromoform was investigated with different techniques. Calorimetric results allowed to conclude that bromoform acts as a good solvent for sPS and that at low polymer concentration the formation of very strong, elastic gels is possible without interaction with the crystallization of the polymer. The conformational transition from coil into helix was followed by means of infrared measurements. The mobility change of the polymer chain during the transition was monitored by ^{1}H NMR. These results were compared with rheological measurements that detect the network formation. The results point to a two-step gelation mechanism where a single helix, formed in a first step, associates into multiple helices in a second step, thus forming the cross-links of the gel network.

1. Introduction

The physical gelation of solutions of stereoregular vinyl polymers has been studied intensively over the past decades.[1−9] Recent investigations seem to reveal a mechanism very similar to the one that is observed in solutions of biopolymers like carrageenans, gelatin, etc.[10−13] In these solutions the formation of a physical gel results from the intermolecular association of helical segments. Such a gelation process is initiated by an intramolecular coil-to-helix transition. This change in molecular conformation is then followed by an intermolecular association, which leads to the formation of a three-dimensional polymer network. The molecular continuity of the latter throughout the solution is at the origin of a physical gel. Very recently, this mechanism was also established for the gelation of stereoregular vinyl polymers like syndiotactic poly(methyl methacrylate) (sPMMA) and isotactic polystyrene (iPS).[14,15]

It also became clear that the formation of a supramolecular structure by intermolecular association can take place on different levels. A good illustration is found in the behavior of syndiotactic polystyrene (sPS). In dilute solutions with good solvents, the intermolecular association of the formed helices will be rather limited, and the growth of such a supramolecular organization will be stopped in the early stages of the process. The resulting gels will be transparent to slightly hazy. At higher concentrations, larger supramolecular structures are formed, and a well-defined wide-angle X-ray scattering (WAXS) pattern will be observed, characteristic for the presence of a three-dimensional crystal lattice.[16,17] Solvent molecules are generally trapped in the crystal lattice so that polymer−solvent clathrates are formed. Such a crystal structure is generally referred to as the δ-phase.[18] This structure-forming process differs from the well-known nucleation-controlled “classical” crystallization process of polymers. In the δ-phase the polymer chains adopt a T_2G_2 helix conformation which is different from the crystalline all-trans T_4 zigzag conformation, the thermodynamically most stable conformation of sPS.[16,18−20] In a “classical” crystallization the appearance of the latter conformation at these low polymer concentrations leads to a suspension of single crystals, with the formation of the so-called β-phase.[18] Several investigations have shown that the δ-phase represents a polymer−solvent compound. The number of solvent molecules involved is dependent on the solvent used. Evidence for this compound formation could be found in temperature−concentration diagrams in good solvents where the melting of the δ-phase shows the characteristics of an incongruently melting compound.[21−26]

The mechanism of gelation can be studied in the most efficient way in good solvents. At low polymer content only the δ-phase will be formed with no interference with the crystallization into the T_4 zigzag phase. However, in many of these solvents the use of for example rheology is very problematic as the melting point of the gel is generally very close to the boiling point of the solvent. As the purpose of this study is to approach the mechanism of gelation through infrared and rheological measurements, evaporation of the solvent during the experiments is then one of the major problems. Moreover, measurements have to be performed in the temperature region where conformational changes and intermolecular association proceed slow enough to allow their kinetics to be followed. Thus, a system with relatively slow gelation around room temperature would be ideal for the study intended. This is the case with low concentrated solutions of chloroform,

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which is known to be a very good solvent for sPS.[27] However, this system cannot be used in this investigation due to the low boiling point and high volatility of chloroform. Therefore, we have chosen bromoform with a boiling point of 149−150 °C. Another advantage of this solvent is the low amount of infrared absorption bands, which makes investigation of bands of the polymer in solution easier. To confirm the similarity of the solution behavior of sPS in this solvent and in for example chloroform, the temperature−concentration phase relations were also investigated. From such an investigation it is already possible to make conclusions about the molecular compound formation between the solvent and the polymer, an important characteristic of the gelation of sPS.

2. Experimental Section

Materials. The sample of sPS used for this study was obtained from Dow Chemical. The average molar masses are $\bar{M}_w = 4.5 \times 10^5$ and $\bar{M}_n = 1.1 \times 10^5$ g/mol. Bromoform (99+%) and bromoform-*d* (99%) from Aldrich Chemie were used. Homogeneous solutions were prepared by heating vacuum-sealed tubes to 150 °C. Their concentration is expressed in mass fraction of the polymer, w_2, except otherwise stated.

Methods. Calorimetric measurements were performed using a Perkin-Elmer DSC-7 at a scanning rate of 5 °C/min.

Fourier transform infrared measurements were performed on a Perkin-Elmer FTIR 2000. The samples were enclosed in a sealed liquid MIR-ATR tunnel reflection cell with a ZnSe crystal. By making use of this cell, measurements can be performed without evaporation of the solvent. An external circulation thermostatic bath was used to control the temperature. Cooling and heating measurements were performed at 0.7 °C/min.

High-resolution NMR experiments were performed on a Varian 500 Unity-Inova. Four different proton signals of the polymer are available, but none of them result in a singlet signal in the NMR spectrum because of ^{1}H−^{1}H coupling with neighboring protons. The coupling constant was therefore subtracted from the total line width, and the measurements were made with a lower sensitivity that resulted in a necessary additional subtraction of 3 Hz. Measurements were performed during cooling at 0.5 °C/min.

Rheological measurements were made with a strain-controlled rheometer, Advanced Rheometric Expansion System (ARES) of Rheometric Scientific. The solutions were measured between two parallel plates with a diameter of 25 mm. Dynamic shear measurements were performed with a frequency of 1 rad/s and a strain of 1%. Measurements during cooling and heating were performed at a rate of 0.7 °C/min.

3. Results

3.1. Gelation of Solutions of sPS in Bromoform. The system sPS/bromoform is extremely well suited for the formation of thermoreversible gels. The polymer cannot be dissolved in bromoform at room temperature, and homogeneous solutions can only be prepared by heating the polymer−solvent system to a temperature of 100 °C or higher, depending on the polymer content. Optical observations show that rigid, completely transparent gels can be formed very quickly by cooling solutions, with a polymer content as low as $w_2 = 0.001$, to room temperature.

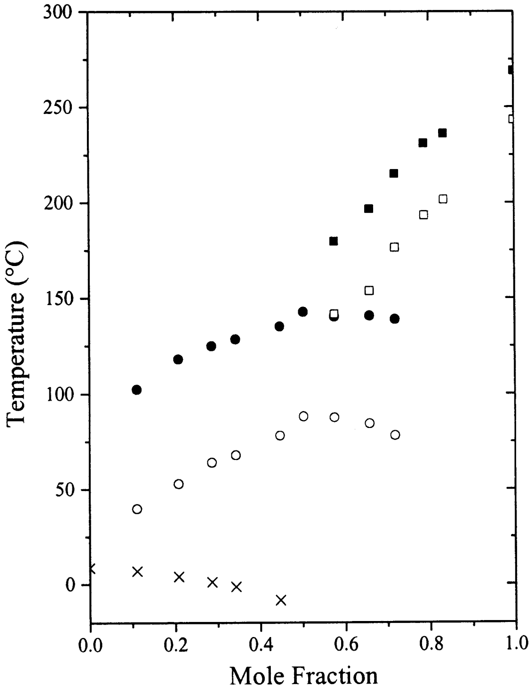

Figure 1. Temperature−concentration diagram of sPS in bromoform: ×, melting point bromoform; ○, gelation; ●, melting point gel; □, crystallization; ■, melting point crystals.

3.2. Temperature−Concentration Diagram. The temperature−concentration diagram of the system sPS/bromoform was constructed by using the data obtained from calorimetric observations. The homogenized samples were cooled to low temperature and then heated again in the DSC apparatus. The transition temperatures are presented in Figure 1 as a function of the mole fraction of monomer units of sPS. One can deduce that the mole fraction is related to the polymer mass fraction w_2 through the following equation:

$$\text{mole fraction monomer sPS} = \frac{1}{1 + \dfrac{M_{\mathrm{wm}}}{M_{\mathrm{wbf}}}\left(\dfrac{1 - w_2}{w_2}\right)}$$

with M_{wm} and M_{wbf} the molar masses of respectively the polystyrene monomer unit and bromoform. The mole fraction was used because the use of w_2 would give an erroneous image in the temperature−concentration diagram compared to diagrams in other solvents, due to the high molar mass of bromoform.

When the polymer concentration is low (mole fraction < 0.5), only one exotherm at low temperature is observed upon cooling; heating shows one endothermic signal. At intermediate concentrations two signals can be seen in both cooling and heating experiments. Finally, at high polymer concentrations only one exotherm and one endotherm are observed, situated at high temperature.

The resulting temperature−concentration diagram is very similar to the one obtained with the system sPS/chloroform and sPS in good aromatic solvents.[21,22,25,26] The shape of such a temperature−concentration diagram is characteristic for the formation of an incongruently melting polymer−solvent compound. From comparison with these other systems one can conclude that in the low concentration range only the δ-phase, responsible for the gel formation, is formed during cooling. The polymer chains adopt the T_2G_2 helix conformation, as can be concluded from the FTIR data. At intermediate concentrations the δ-phase has to compete with the formation of the crystalline β-phase with the molecules in the T_4 zigzag conformation. At the highest concentrations only this β-phase is formed.

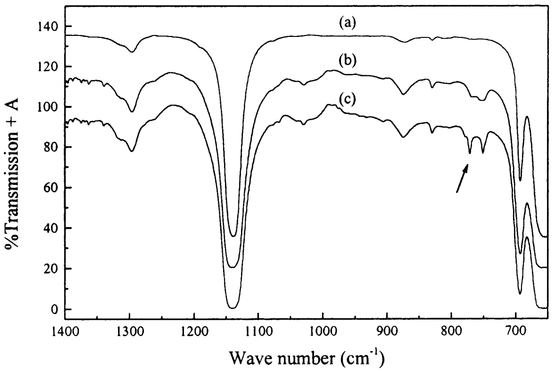

Figure 2. Infrared spectrum of bromoform (a) and a solution with $w_2 = 0.005$ before (b) and after gelation (c).

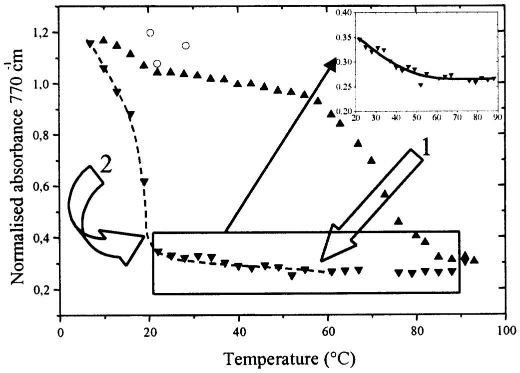

Figure 3. Normalized absorbance of the signal at 770 cm^{-1} during a cooling (▼) and subsequent heating (▲) experiment and values reached after isothermal gelation (○) with $w_2 =$ 0.005.

3.3. Conformational Changes: FTIR Observations. The occurrence of a specific molecular conformation is confirmed by FTIR observations. The transition from a coil to a T_2G_2 helix conformation leads to a number of new signals in the infrared spectrum. They are situated in the region of 500−600 cm^{-1} and at 770, 932, 943, and 1276 cm^{-1}.[28] The absorption at 770 cm^{-1}, caused by a combination of a skeletal mode and an in-plane ring mode, characteristic for the T_2G_2 conformation, is the most intense of these and will be used in our analysis.[29,30] A typical example of the infrared spectrum is represented in Figure 2 for a sample with $w_2 = 0.005$. The spectra were taken before and after gelation. As can be seen from the spectrum of bromoform, also represented in this figure, no peaks of the solvent are present in the direct neighborhood of the interesting signal. The relative absorbance of this signal will be used as a measure for the amount of helices present at a certain temperature and time.

Observations during a Cooling−Heating Experiment. The change in absorbance of the signal at 770 cm^{-1} was followed during a cooling-and-heating experiment at a constant scanning rate of 0.7 °C/min for $w_2 = 0.005$. The absorbance of this signal measured at different temperatures was normalized to the signal at 870 cm^{-1}, characteristic of bromoform and therefore independent of the polymer chain conformation. The temperature dependence of the absorbance is plotted in Figure 3. During cooling, no change is observed until the sample reaches 60 °C. Then a small but observable increase takes place upon cooling from 60 to 22 °C (see arrow 1 and data trend in the inset). This is followed by a very sharp increase from around 22 °C (see arrow 2). The intensity of the band mounts hereby by a factor of about 40 between 22 and 16 °C. Then a smaller increase is noticed upon further cooling. Reheating the sample leads to a limited decrease of the intensity up to 60 °C, followed by a total disappearance of the signal between 60 and 80 °C for the used concentration. Above 80 °C no conformational ordering of the polymer chains can be seen, indicative of a solution of random coils. From these results, we can conclude that there is a very pronounced hysteresis (of about 60 °C) between the cooling and the heating curves.

Isothermal Observations. From the above observations it is clear that between 60 and 22 °C the extent of helix formation in a dynamic cooling experiment remains very limited. However, in previous investigations on similar systems it was already shown that this behavior mainly results from the kinetics of coil-to-helix transformation.[5,14,15]

The coil-to-helix transformation in this temperature range can be followed in isothermal observations. For this purpose, the absorbance was followed as a function of time at different temperatures for a sample with $w_2 = 0.005$. The data, normalized to the signal at 870 cm^{-1}, are represented in Figure 4. They are a direct measure of the extent and kinetics of the coil-to-helix transition as they inform about the induction period, the time dependence, and the final level of conformational change. The values that can be reached in such an experiment coincide quite well with the absorbance data obtained during the heating experiment after continuous cooling, as can be seen in Figure 3.

(i) At 20.5 °C there is almost no induction period while a plateau value is reached after about 4000 s.

(ii) At 22.0 °C this induction period is around 200 s while the plateau value is reached only after 10 000 s.

(iii) Increasing the temperature results in a further lengthening of the induction period and the time needed to reach a plateau value.

3.4. Network Formation: Rheological Observations. *Observations during a Cooling−Heating Experiment.* The storage modulus (G') and the loss modulus (G'') were recorded during a cooling−heating experiment ($w_2 = 0.005$). The results are represented in Figure 5. For this purpose the sample was loaded at high temperature into the rheometer and cooled. As long as the temperature is higher than 20 °C, the values of G' and G'' are very low and G'' is always larger than G'. When 20 °C is reached, both parameters increase sharply and G' becomes much larger than G''. Within a few degrees, G' reaches 10^5 Pa, and an elastic gel is formed. On heating this gel, both G' and G'' decrease linearly by a factor of about 10 between 10 and 60 °C, G' still remaining larger than G''. Then the decrease with increasing temperature is much more pronounced, and a final melting temperature is reached around 85 °C. A hysteresis very similar to the one observed in the FTIR data is also present in these experiments. Anomalies at the lowest temperature are ascribed to the strong volume contractions in the gel upon cooling.

Isothermal Observations. The absence of gelation at $T > 20$ °C is not due to the thermodynamic impossibility of physical network formation but has to be ascribed mainly to kinetic effects. This was already clearly shown in a previous paragraph for the conformational transition. Therefore, the time dependence of the rheological characteristics of the solution was investigated in the same temperature range as the one that was used for

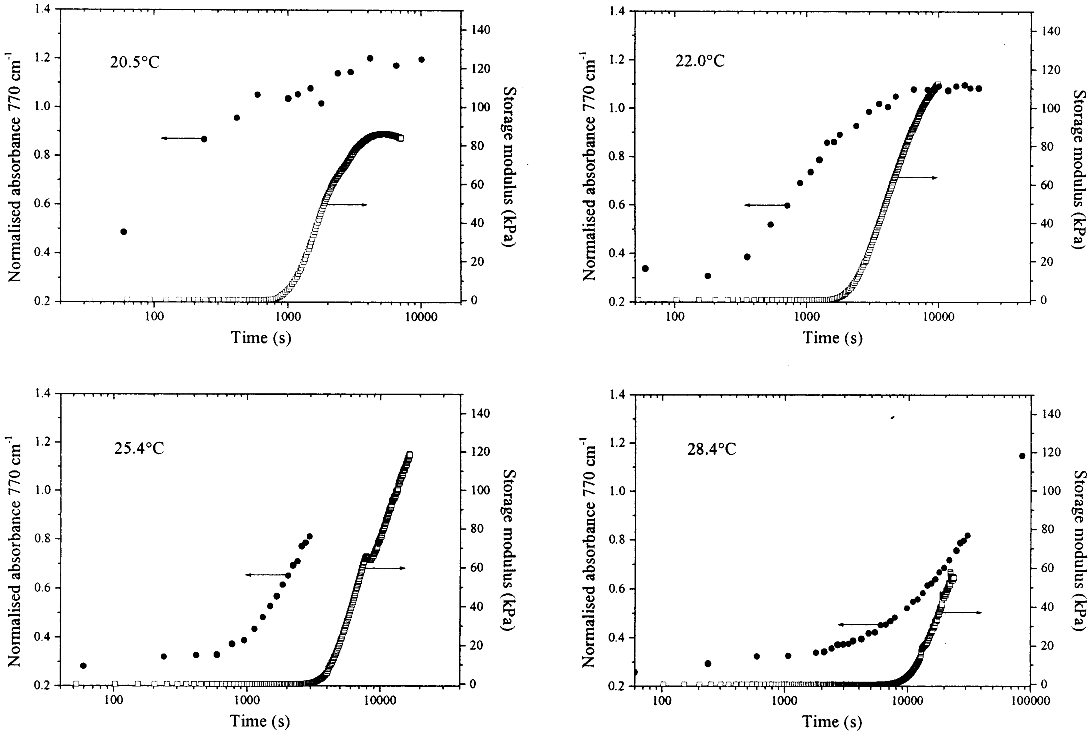

Figure 4. Normalized absorbance of the signal at 770 cm^{-1} (▼) and storage modulus (▲) during isothermal annealing of a solution with $w_2 = 0.005$ at different temperatures.

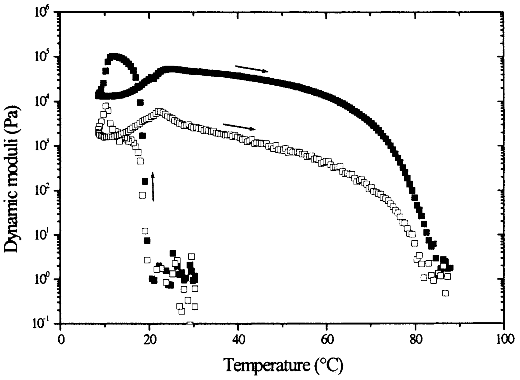

Figure 5. Storage (■) and loss (□) modulus during cooling and subsequent heating for $w_2 = 0.005$.

the FTIR experiments (w_2 = 0.005). The data are represented in Figure 4. Only the time dependence of G' is reported. At each temperature, an induction period is observed during which both G' and G'' are very low, G'' being larger than G'. This induction period increases with increasing temperature from 600 s at 20.5 °C to 5000 s at 28.4 °C. The resulting gel is very strong considering the low concentration. G' is around 10^5 Pa and independent of the gelation temperature. The obtained values for the dynamic moduli are comparable with the values found when the gel was formed during cooling (Figure 5). The gel is also very elastic, since the storage modulus G' is about 100 times higher than the loss modulus G''.

3.5. Temperature Dependence of the Molecular Mobility: ^{1}H NMR Measurements. The molecular mobility of the polymer chain can be investigated by ^{1}H spectroscopy. A change in the mobility of the polymer chains will have a direct effect on the area below the NMR signal of the protons of the polymer and on the line width of this signal, respectively decreasing and increasing when the mobility is lowered. The spectral line width at half-height, $\nu_{1/2}$, is inversely related to the transverse relaxation time T_2:

$$\nu_{1/2} \sim \frac{1}{T_2}$$

Upon cooling, the mobility of a polymer with random coils in solution decreases, and a linear increase is observed for the natural logarithm of the NMR line width of the polymer protons. A conformational transition or association will inevitably cause a second decrease of the mobility of the polymer chain and hence another increase in the proton line width. Subsequently two linear regions, with a higher slope at low temperatures, are observed upon cooling when a coil−helix transition is taking place. It should be noted that in our interpretation the presence of even a small fraction of chain segments of reduced mobility is supposed to affect the mobility of the whole chain in a given temperature interval of linear behavior. The temperature at the intersection of two linear regions corresponds to the onset of the formation of such a fraction of segments. This technique was already successfully applied in the system sPMMA/toluene, where the transition from (random) coil to helix upon cooling could be monitored.[14]

Observations during Cooling. A solution of sPS in deuterated bromoform (w_2 = 0.005) was investigated with this technique. The results obtained from a cooling experiment are presented in Figure 6 for the (−CH−) backbone proton, together with the results obtained with FTIR and rheology. A constant amount c was subtracted from the line width, accounting for the coupling constant and the lower sensitivity used in the measurement. The logarithm of this value as a function of temperature shows two changes in slope, one situated around 60 °C and the other one situated around 23.5 °C (see large arrows).

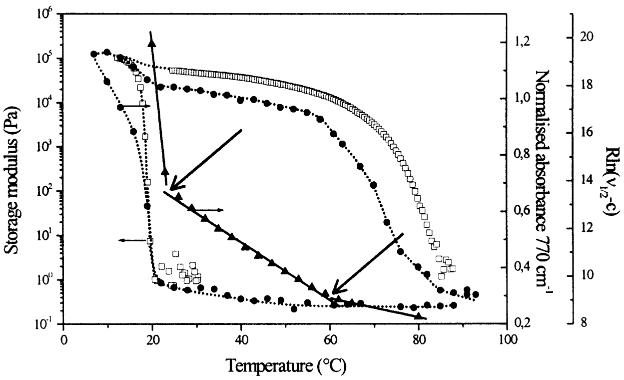

Figure 6. Combined results during cooling and subsequent heating of a solution with $w_2 = 0.005$: □, rheology; ●, infrared; ▲, ^{1}H NMR (−CH−).

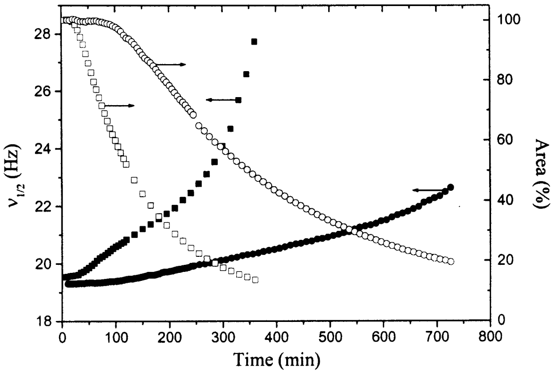

Figure 7. NMR results for the (−CH−) proton during isothermal annealing with $w_2 = 0.005$ at 28.4 °C (■, line width; □, area) and 31.0 °C (●, line width, ○, area).

The small but reproducible change at 60 °C clearly indicates that a change in molecular mobility sets in around this temperature. This is confirmed by the data obtained with FTIR observations. The latter ones show that in the temperature domain down to 22 °C a very small fraction of helices can already be formed. The linear slope of the line width data indicates that such a small fraction is indeed able to affect the overall mobility of the (largely disordered) chains with respect to the fully disordered conformation for $T > 60$ °C. The second change at 23.5 °C is the most pronounced and coincides relatively well with the dramatic increase of the intensity of the conformational band in the FTIR observations.

Isothermal Measurements. In the previous parts it was shown that kinetic measurements could be performed in the temperature domain situated just above the low-temperature transition. Isothermal experiments were carried out at 28.3 and 31.0 °C. The measurement at 28.3 °C allows us to compare the results with those obtained by FTIR and rheological observations. The line width and the area below the proton signal are plotted in Figure 7 as a function of time for a solution with $w_2 = 0.005$ for these two annealing temperatures. A very similar behavior is observed at both temperatures. The line width shows an induction period similar to the one observed by FTIR at the same temperature. This induction is followed by an important increase that proceeds in two steps. The decrease of the area under the ^{1}H peak shows the same time dependence, with a continuous decrease after the induction.

4. Discussion

4.1. Gelation and Phase Relations. The phase behavior of sPS in bromoform is very similar to the one observed with most other good solvents for polystyrene.[21,22,25,26] The temperature−concentration diagram is characteristic for the formation of a polymer−solvent compound so that we can propose that bromoform is intercalated between the polymer chains in the T_2G_2 conformation. Although the overall view of the temperature−concentration diagram is similar to that in other solvents, there exist some differences, notably in the melting and gelation temperature. These temperatures are between the values obtained for chloroform and aromatic solvents. The hysteresis between gelation and gel melting and the concentration dependence of these transitions however are also very similar to what is observed in the other solvents. This allows us to conclude that the system sPS/bromoform can be used as a model system for the gelation of sPS solutions, with the major advantage of the high boiling point of the solvent.

4.2. Gelation Mechanism. The combination of the experimental data obtained with different techniques allows for a detailed analysis of the gelation mechanism. The system shows large similarities with the gelation of sPMMA in certain solvents. Clear evidence is found for a two-step process as already proposed for sPMMA in earlier publications.[4,14] An equilibrium coil-to-helix transition precedes the intermolecular association that leads to the physical network formation. This conclusion is based on the following experimental facts obtained with different experimental techniques and under different experimental conditions.

i. Observations during Cooling. In a cooling experiment at constant rate, a small but observable deviation from the linear temperature−intensity relation of the FTIR conformational band (770 cm^{-1}) sets in around 60 °C, as can be seen in Figure 6. The intensity of this band continues to increase in a very limited way down to 25 °C. At lower temperature a much more dramatic change takes place. The broadening of the line width in ^{1}H NMR starts around 60 °C, increasing slightly with a decrease in temperature to 25 °C. No change in the rheological characteristics is observed until the temperature is below 25 °C. Then an important increase of both G' and G'' takes place with G' becoming rapidly much larger than G''. These observations are a first indication for the fact that in the temperature region 25 °C $> T >$ 60 °C the changes are predominantly limited to an intramolecular conformational change of coil into helix ("c" $\rightleftharpoons$ "h"). Of course, the formation of a very negligible amount of dimers at these high temperatures cannot be excluded. However, if present, it would only manifest as an increase of G''. Still, no increase could be observed under the actual experimental conditions.

Eventually, after a further decrease of temperature dimers ("d") and multichain association units ("m") can be formed (respectively 2"h" $\rightleftharpoons$ "d" and "d" + n"h" $\rightleftharpoons$ "m_{2+n}"). This intermolecular association causes the network formation with an increase of the dynamic moduli and the formation of a gel with $G' > G''$. This process can lead to the formation of a three-dimensional crystal structure in which solvent molecules are included in the lattice. For reasons of simplicity, in the following description only the three basic conformational entities will be considered, i.e., "c", "h", and "d". The formation of the conformationally ordered multichain

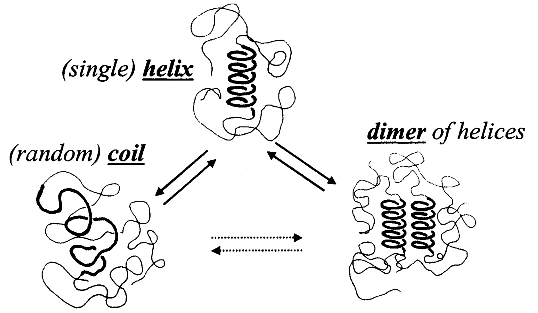

Figure 8. Possible scheme for the gelation of sPS in bromoform.

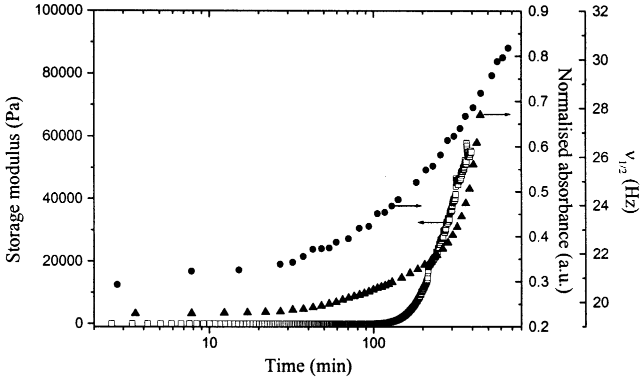

Figure 9. Combined results during isothermal annealing at 28.4 °C of a solution with $w_2 = 0.005$: □, rheology; ●, infrared; ▲, ^{1}H NMR (−CH−).

“m” units are considered just as a kinetically more hindered extension of the “d” ones.

ii. Isothermal Observations. Isothermal annealing (Figure 4) will result in a maximum value of coil-to-helix transformation, and the corresponding infrared intensity is situated in the vicinity of the intensity−temperature curve obtained on heating (Figure 3). The time dependence of G', indicating network formation, follows the same path, but an increase of this parameter is always observed to take place when already a certain amount of “c” conformations has been transformed into “h” conformations. This amount depends strongly on the annealing temperature and decreases rapidly with an increase in temperature of a few degrees. At 20 °C about 80% of the conformational change has taken place when the first increase of G' is observed. On the contrary, at 28.4 °C the network formation sets in when only a few percent of the total conformational change has taken place. Values between these two extremes are found for the intermediate temperatures. In Figure 9 a combination of the results obtained by rheology, FTIR, and ^{1}H NMR at 28.4 °C is presented. The ^{1}H NMR results lead to the same conclusion. The increase of the line width proceeds in two steps. The first rather limited change in the early stages of the experiment is mainly ascribed to the *intra*molecular conformational change, still in the absence of any significant *inter*molecular association. The much more pronounced increase at longer times is brought about by the occurrence of the transition from “h” to “d” and therefore by the network formation.

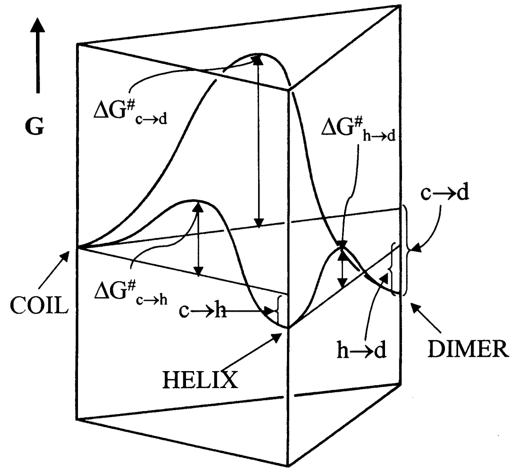

Figure 10. Schematical drawing of the thermodynamic stability of the different structures and the activation energy profiles between them.

Heating results in a very pronounced hysteresis for both the FTIR intensity and G'. Such a hysteresis effect could stem from a very high energetic barrier for the “c” ⇋ “d” transition in the cooling cycle, despite the expected order of stability [$G°_d(T) < G°_h(T) < G°_c(T)$]. This situation, both regarding the thermodynamic stability of the various forms and the corresponding activation energy profiles, is schematically represented in Figure 10. The “c” ⇋ “h” equilibrium is then the process that controls the gel formation upon cooling. It is kinetically required (and followed) by the intermolecular association leading to the more stable dimers and higher associates. The possibility of a separate detection of these intra- and intermolecular transitions is made possible through kinetic trapping in both dynamic and isothermal experiments.

These observations allow concluding to the following aspects of the gelation mechanism:

(i) The dominant equilibria in the course of the gelation are “c” ⇋ “h” and “h” ⇋ “d”. This is clearly illustrated by the data obtained from dynamic as well as isothermal experiments. An increase of G', characteristic for network formation, always sets in when already a certain fraction of helical content has been realized.

(ii) The formation of the “gel” crystal phase at high enough polymer concentration does not proceed through a nucleation controlled mechanism. The main difference between the two mechanisms is that in the former one the helix conformation represents by itself a stable structure. The system will increase further its stability through the formation of dimers and multimers, finally leading to a macroscopic 3D gel structure.

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