

Ordering and structure formation in triblock copolymer solutions. Part I. Rheological observations

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The linear viscoelastic properties of a poly(styrene)–poly(ethylene, butylene) triblock copolymer in the presence of a hydrocarbon oil have been investigated. The samples were followed rheologically, during annealing at different temperatures. In a relatively small temperature interval, $\tan \delta$ -curves, recorded at different frequencies, evolved in a pattern which is typical for a physical gelation. It allowed determination of the gel time. The kinetics of gel formation were found to be affected by the annealing temperature, and the rate was maximum at an intermediate temperature that depended on the polymer content of the sample. Increasing the polymer content shifted this maximum to higher temperatures. At lower temperatures, a glass transition of the polystyrene end-blocks was detected. The microphase separation temperature however, could not be determined. In addition, the influence of strain and the applicability of time–temperature superposition was analysed. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Block copolymers can be synthesized that form microphase separated structures. When microphase separation occurs, the micro domains may form a regular arrangement giving rise to a periodic structure, often referred to as a ‘macrolattice’ or ‘superstructure’^{1–3}. However, as the temperature is raised above a certain critical value, the micro domains disappear completely, giving rise to an isotropic phase with the different sequences interpenetrating each other. This state is in literature called the ‘disordered state’ as opposed to the microphase separated state, which is referred to as the ‘ordered state’^{1–5}. The lowest temperature at which a compositionally homogeneous phase is thermodynamically stable, is called the ‘order–disorder transition temperature (T_{ODT})’, or the ‘microphase separation temperature (T_{MST})’^{1–5}. In this study we prefer to use the term microphase separation to indicate the change from a microphase separated structure to a homogeneous one, in order to avoid any confusion with the transition indicating the ordering of microdomains in a superlattice. The microphase separation in block copolymers has been investigated in detail, and theoretical^{1,2,4,5} as well as experimental studies have been reported.

It is well established that a microphase separation affects the mechanical properties^{6–17}. The long relaxation modes, as observed in the dynamic moduli at low frequencies, drop significantly when heating through the microphase separation temperature^{6,11,12,14–16}. The change from Newtonian behaviour to non-Newtonian behaviour upon cooling has also been interpreted as a microphase separation^{7–10}.

Scattering techniques as well as electron microscopy have also been used extensively to study the structural changes occurring in block copolymer samples^{11,16,18–22}. Secondary peaks, showing long range order disappeared as T_{MST} was approached and the first order peak intensity dropped to a weak intensity level relevant to the broad scattering maximum from disordered melts^{11,16,20–22}.

Recently, attention was paid to the kinetics of phase separation and on the rate of ordering processes^{16,23–25}. Schuler and Stühn²⁴ observed two relaxation processes after a temperature quench from the homogeneous to the microphase separated state. A fast process related to the formation of concentration fluctuations and a slower process related to the arrangement of these structures into a macrolattice. Winter *et al.*¹⁶ showed that microphase separation occurred rapidly on cooling a triblock copolymer melt below T_{MST} while the growth of large scale spatial order ($\approx 1 \mu\text{m}$

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scale) needed long annealing times as shown with low frequency dynamic mechanical measurements. Recently, Floudas *et al.*²⁵ as well as Rosedale and Bates²³ reported similar changes in the low frequency rheological properties of diblock copolymers. In addition, the influence of annealing at temperatures below T_{ODT} has been discussed in literature^{16,26}.

The properties of block copolymers in the presence of solvents have been extensively studied in the literature. Especially in the low concentration regions, weight fractions below 0.002, the formation, dissolution and the aggregation of micelles has been discussed^{27–30}. In the higher concentration region^{31–39}, different research groups showed experimentally that the microphase separation temperature decreases on adding a solvent that is selective for one of the segments. In addition, Hashimoto *et al.*^{36,38}, Shibayama *et al.*³⁵ and Watanabe *et al.*^{31,32} investigated the influence of solvent on the micro domain structure and on the superlattice by rheological and scattering techniques. Their results indicate two thermal transitions on heating: (a) at lower temperatures a transition is observed, associated with a thermal destruction of the superlattice of the micro domains, while the nearest neighbour distance of the domains is preserved. This transition is referred to as the lattice disordering and is observed in SAXS as a sudden increase of the line profiles of the first order peak and an overlap or extinction of higher order peaks. (b) At higher temperatures an order–disorder transition occurs that invokes a dissolution of the micro domain structure, and corresponds to a disappearance of the first order scattering maximum itself.

In this study the linear viscoelastic properties of a poly(styrene)–poly(ethylene, butylene) triblock copolymer in the presence of a hydrocarbon oil ('extender' oil) are investigated as a function of temperature. Special attention will be paid to the time dependence of the viscoelastic functions. In a second part of this series, the morphology of these structures will be followed by SAXS, and the thermal transitions occurring in the same system as a function of temperature will be followed using calorimetry. These will be compared with the evolving rheological properties.

In two previous publications^{40,41}, the scattering curves of these triblock copolymers gels at room temperature have been analysed. A spherical domain morphology was observed, in which the microdomains adopt a hexagonal packing.

EXPERIMENTAL

Materials

The poly(styrene-*b*-ethylene, butylene-*b*-styrene) triblock copolymer (SEBS-94), supplied by Shell, contains 29% polystyrene. It has a total number average molecular weight of 94×10^3 and a polydispersity of 1.15. The polymer was used as-received.

The extender oil is a mixture of hydrocarbons having a number average molecular weight of 600. It selectively swells the ethylene–butylene phase of the copolymer. The samples used in this study contained between 6 and 50 wt% of triblock copolymer. All concentrations are expressed as wt%.

Sample preparation for rheology

Moderately concentrated samples (6–30%) were

prepared by mixing appropriate amounts of extender oil and polymer at a high temperature (150–180°C), using a mechanical stirring device. The mixing was stopped after a clear solution was obtained which was then cooled to room temperature.

Concentrated samples (40–50%) were prepared by solvent casting from toluene. Samples were dried at 100°C, for 5 days, under vacuum in order to remove all traces of toluene.

From these, sheets were moulded in a hydraulic press at 130°C and cooled rapidly in air to room temperature.

Rheological observation

Dynamic mechanical properties were measured in a Rheometrics Mechanical Spectrometer (RMS-800) using parallel plate geometry. The temperature control was accurate between ± 0.5 K. In order to analyse the measured data and to test the applicability of time–temperature superposition the interactive IRIS software was used. The kinetics of the gel formation was analysed with the GELPRO software (Mours and Winter)⁴². The following symbols were used: γ = strain amplitude; ω = frequency and δ = phase angle.

RESULTS

Sample with 20 wt% of polymer (SEBS-20%)

As-prepared sample. In the first experiments the sample was used without any specific thermal history. After preparation it was left at room temperature. Changes in the rheological behaviour were investigated during heating while measuring the evolution of G' and G'' (Figure 1A). At lower temperatures, the value of G' is significantly higher than G'' , a characteristic for highly elastic behaviour. On heating, two transitions are observed, each expressing itself in a maximum in G'' and a decrease in G' . The decrease in G' of the first transition starts around 55°C, while the crossover between G' and G'' is located at 105°C, at this temperature the system loses its elasticity and turns into a more liquid state.

After completion of this temperature sweep, the sample was annealed at 110°C for about 1 h. This treatment resulted in a pronounced increase of G' as is

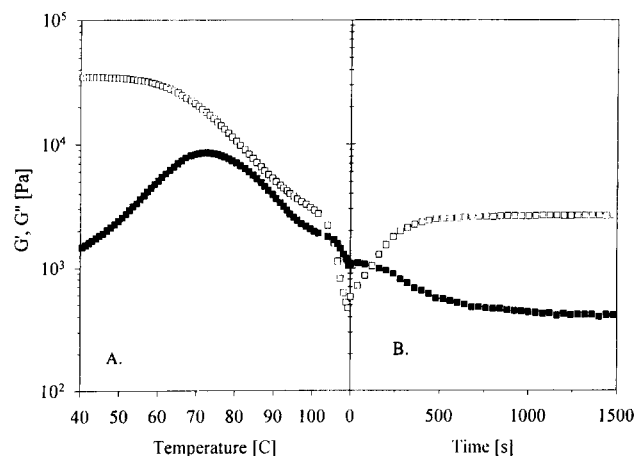


Figure 1 (A) The evolution of G' and G'' as a function of temperature (rate = 5 K min⁻¹, ω = 1 rad s⁻¹, γ = 0.04, \square = G' , \blacksquare = G'' , SEBS-20%). (B) The evolution of G' and G'' as a function of time (T = 110°C, ω = 1 rad s⁻¹, γ = 0.04, \square = G' , \blacksquare = G'' , SEBS-20%)

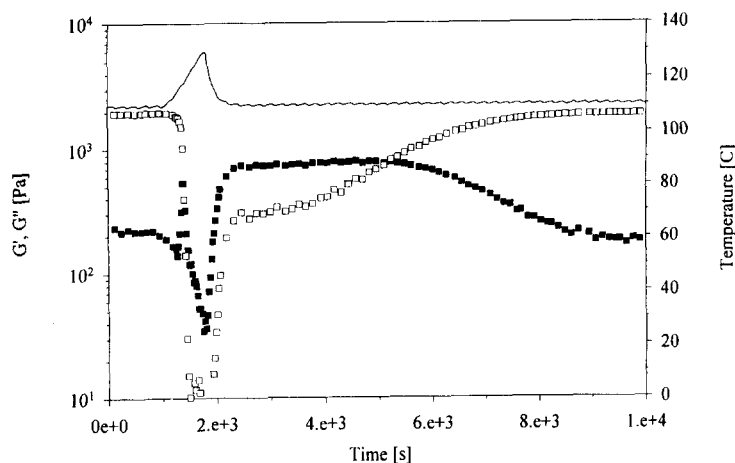


Figure 2 The evolution of G' and G'' as a function of time ($\omega = 1 \text{ rad s}^{-1}$, $\gamma = 0.04$, $\square = G'$, $\blacksquare = G''$, $— = T$, SEBS-20%)

illustrated in Figure 1B. The exact nature of this isothermal transition is studied in detail in the next section.

The transition is reversible. On further heating to 130°C, the gel-like structure starts to disappear at 118°C, and on cooling to 110°C it is slowly reformed, as is shown in Figure 2.

The reformation of a gel-like structure at higher temperatures can even be observed in the course of a heating scan, provided the heating rate is not too high. This is illustrated in a heating scan recorded at 2 K min^{-1} (Figure 3). If the heating rate is higher, for example 5 K min^{-1} , this reformation of a gel is not observed.

After heating an as-prepared sample to 140°C, and cooling it to room temperature, the gel-like behaviour is re-established during cooling, and at room temperature, the rheological properties of a heated gel are comparable to the properties of an as-prepared sample.

Detailed analysis of isothermal transitions. Gel formation. The isothermal transition was investigated in detail using rheology. In order to determine the instant of gelation, the sample was probed cyclically at different frequencies, and G', G'' -data were recorded continuously. Interpolation for each of the measured frequencies gave the evolution of the viscoelastic functions with time and this over the entire time range of the experiment. The results may be plotted as scans that represent the frequency dependence at a set of discrete times in between the first and the last frequency sweep.

Before starting the isothermal experiments the sample was first heated to 145°C, at this temperature the sample flows, in order to destroy any long range order. After a quick cool to the temperature of interest, the isothermal experiment was started and G' and $G''(\omega, t)$ -data were recorded. This procedure was used for the isothermal experiments described in this section.

In Figure 4 the evolution of $\tan \delta$ with time is shown for frequencies varying between 0.1 and 3.16 rad s^{-1} . The sample was probed isothermally at 112°C. $\tan \delta$ decreased from a relatively high to a relatively low value. The change was more pronounced for the lower frequencies. Moreover, all the $\tan \delta$ intersected each other at the same time, $t = 5500 \text{ s}$. This phenomenon is known from chemical gelation where a frequency independent $\tan \delta$ indicates that the critical gel is formed^{43,44}. However, in a physical gelation, the frequency

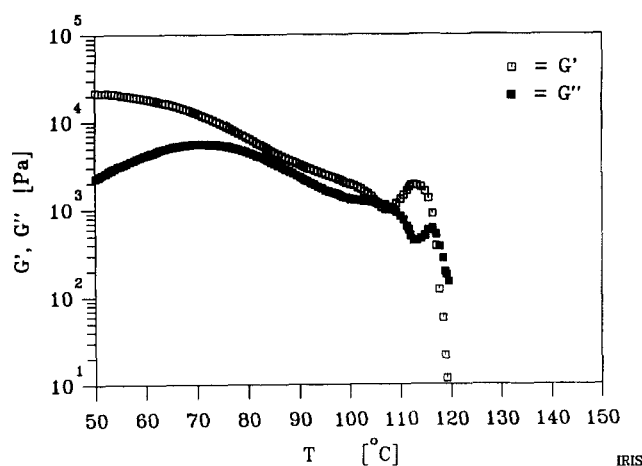


Figure 3 Temperature sweep of an as-prepared sample ($\omega = 1 \text{ rad s}^{-1}$, $\gamma = 0.04$, rate = 2 K min^{-1} , SEBS-20%)

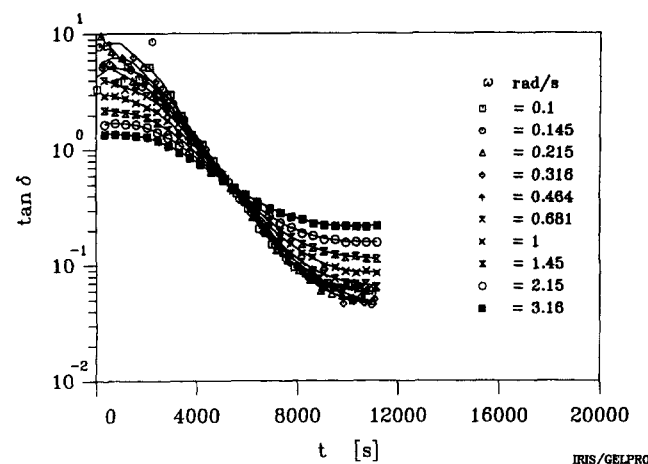


Figure 4 The evolution of $\tan \delta$ as a function of time. The frequency is indicated ($T = 112^\circ\text{C}$, $\gamma = 0.04$, SEBS-20%)

region that can be measured is limited^{45,46} because the use of time-temperature superposition is not possible, and often, the physical process will evolve with time, which implies that measurements at very low frequencies cannot be performed.

In Figure 5 $\tan \delta$ as a function of frequency is plotted after different annealing times. The lower frequency range shows the transformation from liquid behaviour to

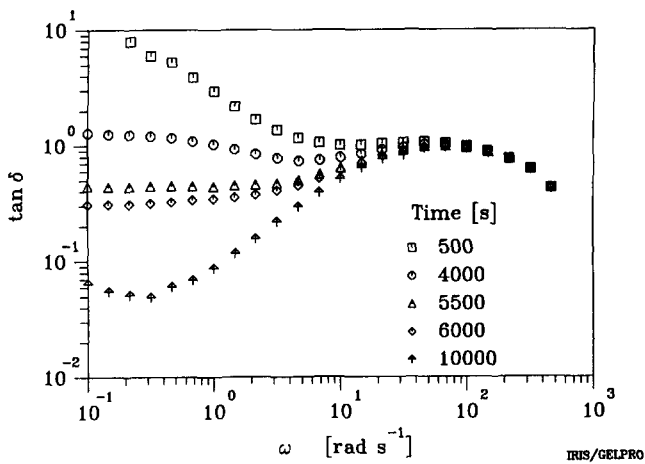


Figure 5 $\tan \delta$ as a function of frequency. The curves are measured after different annealing times as is indicated ($T = 112^\circ\text{C}$, $\gamma = 0.04$, SEBS-20%)

solid behaviour, while the higher frequency range is not affected by the whole transition. At 112°C a frequency of 0.1 rad s^{-1} is the lowest frequency accessible to our instrument. The torque values are too low for measurements at lower frequencies.

The same behaviour is seen in the evolution of G' and G'' with frequency. In *Figure 6*, frequency sweeps G' and G'' are presented for the liquid (A), critical gel (B) and solid state (C). Again only the lower part of the frequency window shows the changes. At the critical gel-state, G' and G'' are linear and parallel with the frequency ($\omega \leq 10^1$). At the gel point, G' is already larger than G'' , this is typical for a physical gelation.

Breaking and recovery of the formed structure. The effect of strain on the formed gel, the recovery after the application of high strain and the influence of strain during the gel formation were studied.

A gel was formed at 112°C and subjected to oscillatory strain at increasing strain amplitude (at 112°C). The linear viscoelastic region extends to strain amplitude values 0.04. At higher strains the structure starts to break, resulting in an increase in G'' and a decrease in G' . This indicates that the physical gel which was formed isothermally has very weak cross-links between the chains. If the strain stability of this sample at 112°C is compared with its strain stability at room temperature, the structure at room temperature is stable up to strain amplitude values of 1.

In *Figure 7* the recovery of G' and G'' after breaking the gel by applying a high strain, $\gamma = 2$, is shown. The temperature is 112°C during the whole experiment. The time needed to reform this gel is approximately equal to the time which was needed to form the original gel.

In *Figure 8* the gel formation is followed, while probing the sample at different strain amplitudes, again at 112°C . At $\gamma = 2.8$, the first part in this figure, the rate of gel formation is nearly zero, and G' and G'' are independent of time. In the second part of the figure, a strain of 1 was applied to the system, and this resulted in an increase of G' and G'' with time, and a gel formation took place. In the third part, the strain was lowered to 0.02, which is in the linear viscoelastic range of the gel formed. In this region the increase of G' and G'' is more pronounced and the gel is formed within

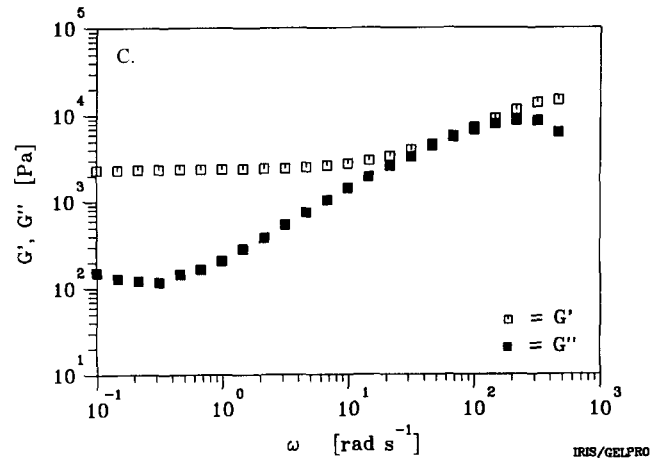
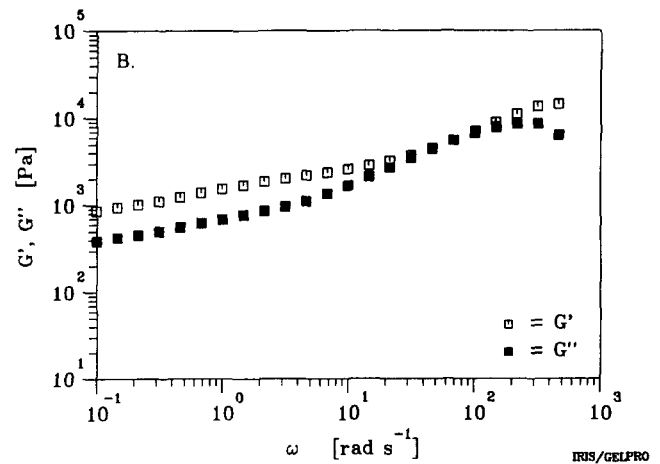
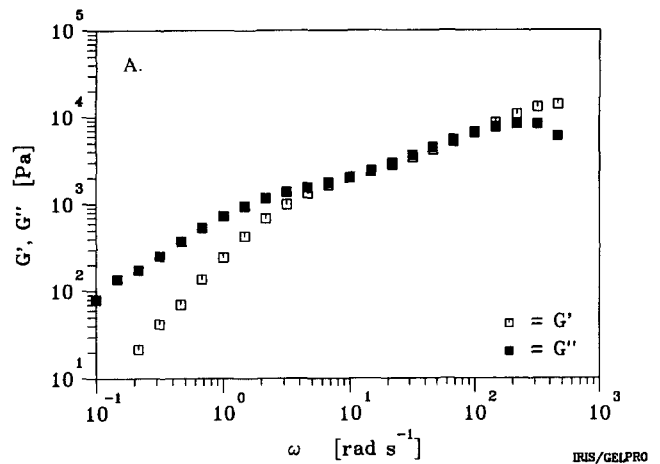


Figure 6 G' and G'' as a function of frequency ($T = 112^\circ\text{C}$, $\gamma = 0.04$, SEBS-20%). (A) after 500 s; (B) after 5500 s; (C) after 10000 s

10000 s. This indicates that high strain oscillatory movements prevent the gel formation.

Influence of the gelation temperature. In this section isothermal changes of the viscoelastic functions, recorded at temperatures between 84°C and 113°C are discussed. The time sweeps were similar to those recorded at 112°C . Again the $\tan \delta$, recorded at different frequencies, cross each other after a certain time, the critical gel time. However, the frequency window, in which the gel formation is observed, shifts to lower frequencies as the temperature decreases. The time needed to reach the critical gel state is strongly temperature dependent (*Figure 9*). The rate of gel formation is highest at 96°C

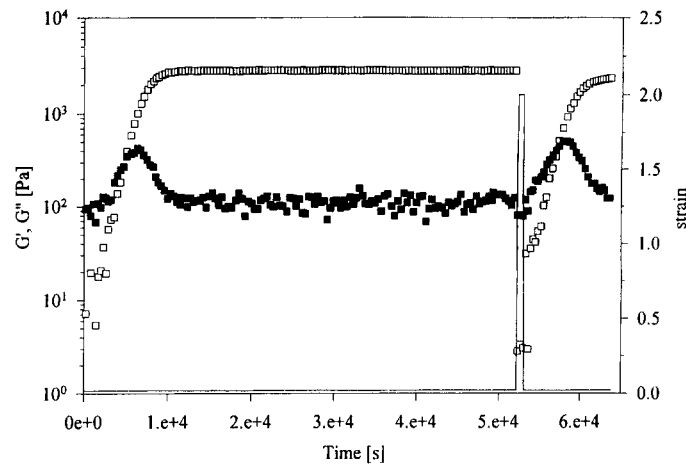


Figure 7 G' and G'' as a function of time at strain $\gamma = 0.02$ and $\gamma = 2$ ($\square = G'$, $\blacksquare = G''$, $\text{—} = \gamma$, $\omega = 0.1 \text{ rad s}^{-1}$, $T = 112^\circ\text{C}$, SEBS-20%)

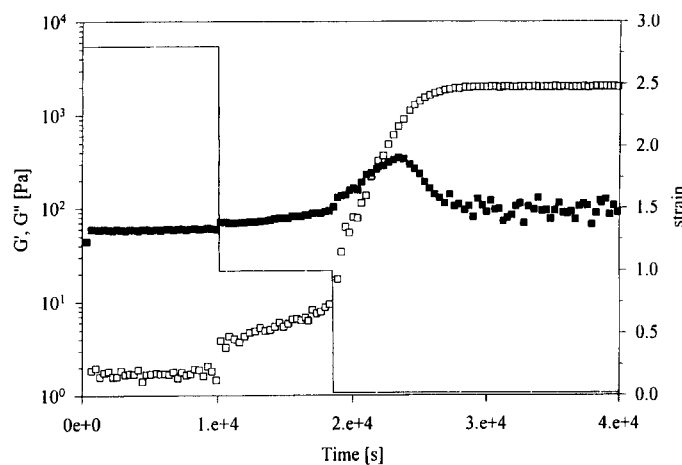


Figure 8 G' and G'' as a function of time at strain $\gamma = 2.8$, $\gamma = 1$ and $\gamma = 0.02$ ($\square = G'$, $\blacksquare = G''$, $\text{—} = \gamma$, $\omega = 0.1 \text{ rad s}^{-1}$, $T = 112^\circ\text{C}$, SEBS-20%)

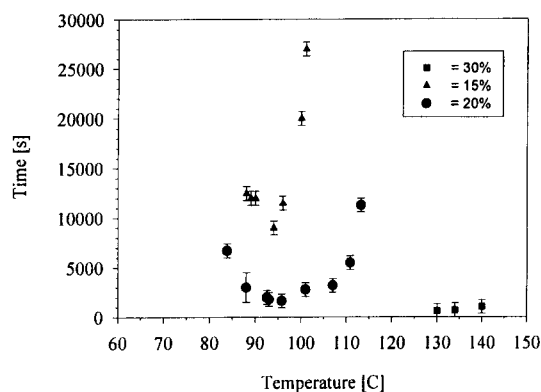


Figure 9 The time needed to form a critical gel is plotted as a function of temperature for different concentrations

and, hence, the time needed to reach the critical gel state goes through a minimum at this temperature.

At temperatures between 84 and 90°C, we had difficulties to determine the exact rate of gelation, because the gel formation was fast compared to the time needed to record the corresponding frequency sweeps. The main problem is the very long recording time which is needed at low temperatures. The reason for this is the shift of the frequency region, in which gelation can be observed, to lower and lower frequencies, when the temperature is lowered. Measurements at lower

frequencies are more time consuming. The time needed to measure a single frequency sweep, however, should be short compared to the time needed to form the critical gel. This is not always possible. At 88°C for example, the gel was formed before the first frequency sweep was performed and it was not possible to measure the gel point accurately. Therefore large error bars are included in *Figure 9* for the measurement at this temperature.

Time-temperature superposition. Frequency sweeps, measured isothermally at different temperatures, can be superimposed into a master curve, measured at one temperature and extending over a large frequency range, provided phase transitions or structural transitions are absent. In this sample three possibilities exist. Frequency sweeps measured before, after or at the critical gel formation can be used to create master curves.

A master curve, composed of frequency sweeps recorded without annealing, is represented in *Figure 10*. Only the evolution of G' is shown. The high frequency ranges superimpose, while in the lower frequency ranges G' drops significantly on heating between 78°C and 132°C. This is an indication that a phase, or structural transition occurs.

Figure 11 shows a master curve, composed of frequency sweeps, measured after isothermal annealing was completed. The different frequency sweeps nearly overlap. In the lower frequency range a small decrease in

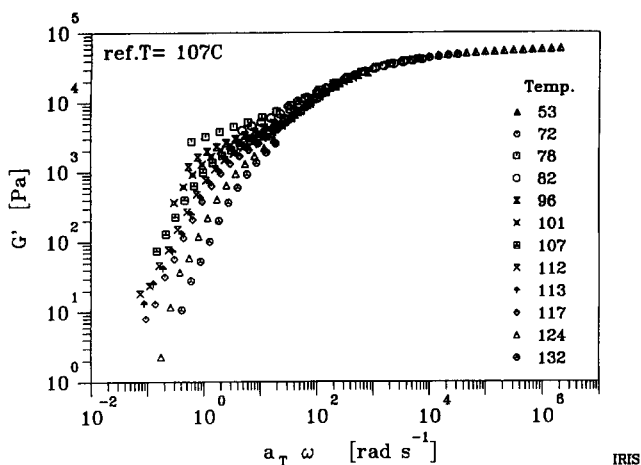


Figure 10 Master curve composed of frequency sweeps measured without annealing, only G' is shown ($\gamma = 0.04$, SEBS-20%)

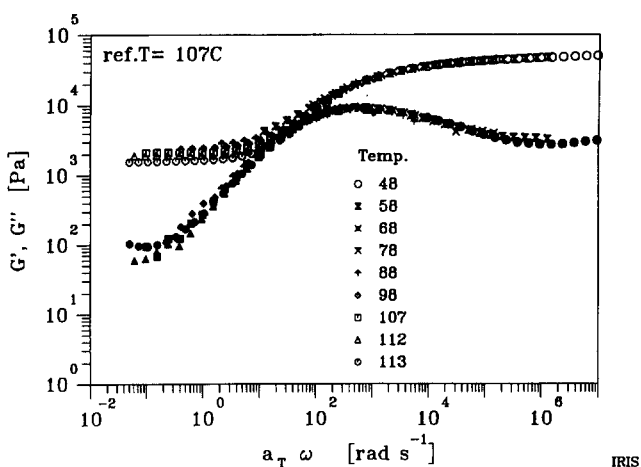


Figure 11 Master curve composed of frequency sweeps measured after annealing. Open symbols refer to G' , filled symbols to G'' ($\gamma = 0.04$, SEBS-20%)

G' is observed between 78°C and 113°C. In this master curve the decrease in G' is much less compared to the drop of G' observed in the same temperature interval in the master curve measured before annealing.

The shift factors used in the two superpositions are plotted as a function of temperature, Figure 12. In the two cases the high frequency range was used to determine the superposition. This high frequency range is not sensitive to time effects, therefore the shift factors, used in the two superpositions are equal.

Influence of polymer concentration. The triblock copolymer concentration has an influence on the isothermal gel formation. The temperature–concentration diagram, Figure 13, indicates the temperatures at which isothermal transitions were observed (open triangles) and the temperatures at which isothermal transitions were not observed (filled triangles) for different concentrations of polymer. The experiments show that a minimum concentration of polymer is needed in order to observe rheologically an isothermal gelation. For a 12% sample no rheological changes were observed during annealing between 75°C and 105°C and 80°C. A 15% sample however, showed isothermal changes at temperatures between 101°C and 80°C. At higher

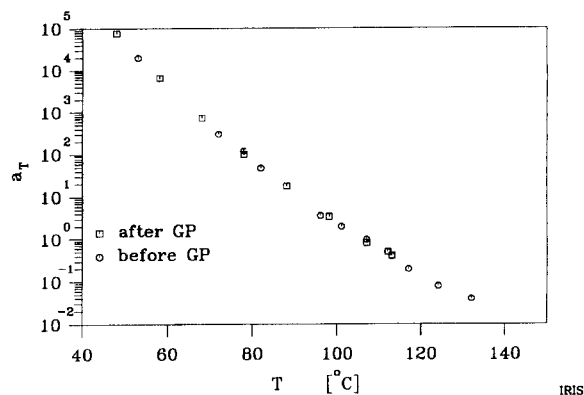


Figure 12 Shift factors used to compose master curves, without annealing and after annealing

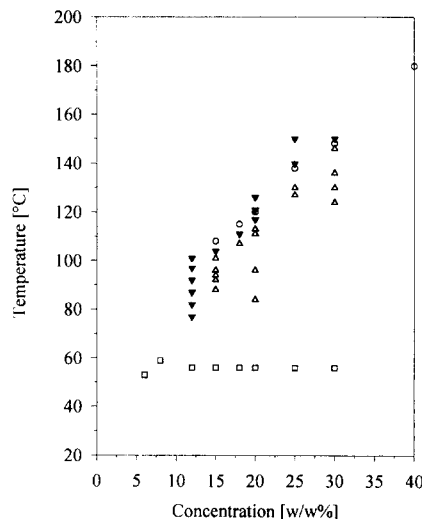


Figure 13 Temperature–concentration diagram for SEBS-extender oil: indicating positions at which time influence (Δ) were observed, respectively not observed (\blacktriangledown), and based on temperature sweeps of annealed samples (glass transition, \square ; onset of flow, \circ)

temperatures, isothermal changes were no longer observed. This diagram indicates, for different concentrations, an upper temperature limit for isothermal effects to take place. Above this temperature the isothermal transitions are no longer observed. This upper limiting temperature increases linearly with concentration.

In Figure 9, the time needed to form a critical gel is shown as a function of temperature for three different concentrations. The 20% sample and the 15% sample show a minimum as a function of temperature. In a 30% sample the gel formation is so fast that it was not possible to measure directly if there is a minimum gelation time.

Temperature sweeps, measured rheologically, were investigated in detail. The first decrease in G' can be explained by a glass transition (T_g) of the end block. This was confirmed by calorimetric techniques and is discussed in Part II of this series. For the lower concentrated samples, 6–8%, T_g is the only transition observed. On heating, these samples start flowing at T_g . In concentrated gels, two transitions were observed: a glass transition at lower temperatures followed by the onset of flow at higher temperatures. The temperature, at which the sample starts flowing, depends on the thermal history. Annealing will increase the flow temperature.

Glass transition and flow transition temperatures, deduced from heating scans of annealed samples, are also indicated in Figure 13.

DISCUSSION

At room temperature the triblock copolymer samples, investigated in this study, have the characteristics of elastic materials; G' is nearly independent of frequency, and G'' is much lower than G' . This indicates that at room temperature a physical network is present. As more extender is added to the system, the plateau modulus decreases. This is in accordance with literature³² data. In SAXS experiments, it was shown that the investigated triblock copolymer samples have a macro phase separated structure at room temperature with spherical polystyrene domains, and that long range order between the microdomains is present, showing a hexagonal packing.

Glass transition of the polystyrene phase

On heating these gels, the mechanical properties change drastically. At relatively low temperatures (60–70°C), G' starts to decrease, indicating a softening of the gel-like structure. This is ascribed to the occurrence of a glass transition in the polystyrene domains and this will be confirmed by d.s.c. (Part II). We associated the softening in rheology with a glass transition of the polystyrene domains.

The glass transition of homo polystyrene of comparable molecular weight, however, is expected around 86°C⁴⁷. There are two possible effects that explain the relatively low temperatures found in these gels: (a) The influence of the block copolymer structure can induce a lowering of T_g due to partial mixing of the polystyrene and the rubbery segments^{48,49}. (b) The penetration of a small fraction of extender oil in the polystyrene phase will lower the T_g .

The extender oil is a very poor solvent for polystyrene. A separate study on this system⁵⁰ however, has revealed an upper critical solution temperature and a maximum in the demixing curve at 135°C for a PS sample with $M_n = 2000$ and $M_w/M_n = 1.05$. By increasing the molecular weight of PS to the value of the PS segments in the block copolymer, this maximum in the demixing curve increased drastically. From the study of this phase behaviour we can nevertheless conclude to the presence of a few percent of oil in the polystyrene phase. The plasticizing effect of this oil can easily account for the observed decrease in T_g .

Transitions at higher temperatures

Different methods^{6–17} have been proposed to determine T_{MST} from rheological data. The temperature where the storage modulus, especially if measured at low frequencies, shows an abrupt drop as a function of temperature^{14,23} has been used to localize T_{MST} . However, Han and coworkers¹² showed that shear experiments in oscillatory flow are not suited for the determination of T_{MST} for highly asymmetric block copolymers. Therefore in our samples, with a spherical morphology, this approach cannot be used.

The applicability of time–temperature superposition has also been used to localize T_{MST} ^{14,17,23}. As long as the copolymer remains either phase-mixed or completely phase-demixed, data taken over a range of temperatures,

can be time–temperature superimposed. If on the other hand, the copolymer undergoes a transition from the ordered to the disordered state the dynamic mechanical data cannot be made to overlap. This method is successfully applied by Resole and Bates²³. They find a low temperature region and a high temperature region where overlap between different frequency sweeps is possible. In the intermediate temperature region, overlap was not possible because the system evolved from a phase separated into a homogeneous state. If we want to apply these criteria to our triblock copolymer solutions, we observe a low temperature region where overlap is possible, at least in the annealed samples. No overlap can be found however, in the high temperature region. We can therefore conclude that at least in the investigated temperature region, no isotropic solution can be obtained but that the system gradually evolves with increasing temperature towards this isotropic state.

On heating the as-prepared samples in a rheometer, G' and G'' will cross at temperatures above the glass transition, the system will lose its elasticity and become a viscous liquid. The onset of flow in rheology can be extended to higher temperatures if the samples are annealed at adequate temperatures above the glass transition. During this isothermal annealing, the sample changes from liquid into a gel-like material. However, in order to clearly circumscribe this transition, information on the morphology of the samples is needed, and this will be discussed in Part II.

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