Rheological behavior of block copolymers and block copolymer/homopolymer blends

A study of the rheological behavior of poly(styrene-*b*-isoprene-*b*-styrene) and polyethylene-*b*-poly(ethylene glycol) block copolymers and blends of their constituent components.

by

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Abstract

Block copolymers have an inherent ability to self-assemble into complex ordered patterns, referred to as phases. Transitions between different phases, order-order transitions (OOT), can be seen when block copolymers are exposed to temperature changes and shear forces. At sufficiently high temperature the ordered phase will disperse into a disordered state and an order-disorder transition (ODT) will occur. These transitions can be estimated by rheological measurements on block copolymers.

The rheological behavior of different phases has been investigated for two different block copolymer systems. The fist block copolymer poly(styrene-*b*-isoprene-*b*-styrene) (SIS) was studied in three different compositions with 14,17 and 22 wt. % polystyrene. The ODT temperature could be estimated for all three, whereas SIS with 17 wt. % polystyrene was the only one that indicated an OOT. The second system was a polyethylene-*b*-poly(ethylene glycol) (PbP) studied in two compositions with 50 and 80 wt. % poly(ethylene glycol). The only transition that could be estimated for this system was the ODT for PbP with 50 wt. % poly(ethylene glycol). It has been seen that both molecular weight and polydispersity plays a central role with regard to the rheological behavior.

Further on phase swelling and compatibilising effects were investigated by means of rheological measurements on blends of the block copolymers with varying fractions of the constituent homopolymer. The addition of homopolymer had a profound effect on the transitions in the SIS system. Different effects were seen depending on which of the two homopolymer that was added. The OOT was seen up to 30 wt. % homopolymer. At 70 wt. % of homopolymers the ODT was no longer observed and compatibilisation effects appeared. For the PbP/polyethylene blends it was noted that PbP has a softening effect on polyethylene.

Keywords: Block copolymer, rheology, poly(styrene-b-isoprene-b-styrene) , polyethylene-b-poly(ethylene glycol), transitions, phase swelling, compatibilisation.

Contents

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Lina Schäfer

Notations

Definitions

Fluctuations	- Oscillating effects at the interfaces.
Interface	- The surface between the domains and the matrix in a phase.
Segments	- A part of the chain where the properties are assumed to be near constant. [1]
Self-assembly	- Local interactions that cause a system to arrange itself into ordered/organized structures.

Abbreviations

DSC	Differential scanning calorimetry
ODT	Order-disorder transition
OOT	Order-order transition
PbP	Polyethylene-*b*-poly(ethylene glycol)
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PI	Polyisoprene
PS	Polystyrene
SAXS	Small-angle X-ray scattering
SCFT	Self Consistent Field Theory
SIS	Poly(styrene-*b*-isoprene-*b*-styrene) block copolymer
TEM	Transmission electron microscopy
WAXD	Wide-angle X-ray diffraction

1. Introduction

Polymers are large molecules composed of repeating units called monomer units. They can be both natural, for example cellulose, and synthetic, for example polystyrene.[2] Synthetic polymers are often referred to as plastics [3]. Plastics can provide different properties depending on the monomers, chain structure and additives, such as softeners or pigments. This opens the possibility to adjust plastics to meet certain needs [2,3]. Combining two or more different polymers into blends can be of interest to generate desirable properties, but very often the polymers are immiscible. In those cases the blends can separate into a two-system blend causing an undesired phase separation. One way to increase the level of miscibility is to add a block copolymer of the constituent polymers to the blend. [4,5] Block copolymers consist of blocks of two or more different monomers that are connected to each other. Due to the connection between the blocks large scale phase separation is impossible. The polymers in the blend will assemble close to the corresponding block and the block copolymer can act as a compatibiliser. [6,7] Block copolymer is a one-phase polymer due to the connection between the blocks that otherwise could be immiscible. This brings an inherent ability so self-assemble into ordered patterns, referred to as phases, on a microscale (~nm). These phases can for example be domains of spheres or cylinders of one block in a matrix of another block. In short terms the phase are determined by the composition (f), molecular weight (M_w), temperature (T) and interactions between the blocks [8]. When a block copolymer is exposed to changes in temperature and shear forces transitions between the phases can occur. It have been reported that the transition temperatures can be estimated by rheological measurements. [5] Several mechanical properties such as the storage modulus (G'), loss modulus (G''), complex viscosity ($\acute{\eta}$) and torque (Γ) can be measured by rheological techniques [9]. The measurements can be conducted in different ways with for instance varying or constant temperature, angular frequency (ω) and strain (γ).

The rheological behavior was studied for two block copolymer systems. The first one is an amorphous poly(styrene-*b*-isoprene-*b*-styrene) (SIS) triblock copolymer and the second one is a semicrystalline polyethylene-*b*-poly(ethylene glycol) (PbP). First it will be investigated how different phases affect the rheological behavior in the block copolymer systems. Compatibilising effects can be seen when block copolymer is added to a polymer blend. When the fraction of block copolymer increases the compatibilising effects will decrease and a phase swelling effects will appear instead. [4] This is due to that the homopolymer will assemble close to the corresponding block causing a swelling of the domains in the block copolymer [5]. Phase swelling and compatibilisation effects were studied on blends of block copolymer and their constituent homopolymer by rheological measurements.

1.1 Objective/aim

The objective of the study is to investigate how different phases in a block copolymer affect the rheological behavior. Further on phase swelling effects and the possibility of compatibilising effects will be investigated by conducting rheological measurements on blends of block copolymer and homopolymers.

1.2 Limitations

The materials that have been studied are the ones that have been available for this study. Further characterisation of the material, either than provided by the material supplier, has not been done. The study is limited to rheological measurements, complemented with differential scanning calorimetry (DSC) measurements in some cases.

2. Theory

2.1 Block copolymers

Block copolymers chains consist of long blocks of two or more different monomer units that are connected. They can have numerous architectures classified by the number of different blocks and topology, for example linear, branched and star. The blocks are often incompatible, like a system of oil and water. The connection between the blocks and the incompatibility brings an inherent ability for self-assembling into complex phases. [10] The blocks on their own often have different properties. For example one block may be amorphous and the other one semicrystalline. Another example is the glass transition temperature (T_g) or melting temperature (T_m) that can differ significantly from each other. [5,11] Block copolymers can bring useful mechanical properties but also drawbacks from a processing point of view, e.g. high viscosity and strong memory effects. [12] The composition, weight fraction of the blocks, influences properties like Young's modulus, toughness, thermal stability and melt viscosity [2,10,13].

2.1.1 Self-assembly in block copolymers

Due to the inherent ability to self-assemble block copolymers can adopt ordered phases on a micro scale (~nm). In short terms this phenomenon is driven by chemical incompatibilities and the connection between the blocks. The incompatibility causes the microphase separation whilst the connection prevent separation on a macroscale (>µm). [5,6,7] This chapter aims to give an elementary understanding of the different phases followed by basic physical theory in 2.2.

The classical ordered phases in block copolymer systems are; cubic packed spheres (spheres), hexagonal packed cylinders (cylinders), gyroid and lamellae, seen in Figure 2.1. Additional and more complex phases can also be adopted, discussed elsewhere [14,15]. Most often the matrix consists of the dominating block and the domains consists of the minor block.

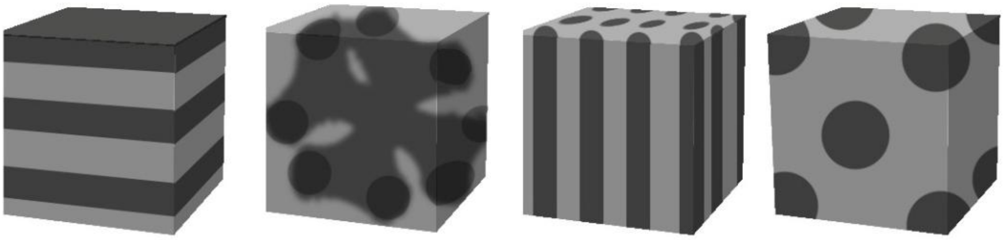

Figure 2.1: A schematic sketch of the classical phases in block copolymers. From the left: lamellae, gyroid cylinders and spheres.

The parameters that determine the phase are the volume fraction (f) of the blocks, the molecular weight (M_w), temperature (T) and the interactions between the blocks [8]. The interactions between the blocks are expressed by the temperature dependent Flory-Huggins interaction parameter (χ) [5].

In order to anticipate which phase that will be present at a certain point the physical behavior of a system needs to be identified. A successful way of doing this is by using the Self Consistent Field Theory (SCFT) on a Gaussian chain model further explained in 2.2. [16]

2.1.2 Transitions between ordered and disordered phases

A block copolymer can undergo order-order transitions (OOT) or/and an order-disorder transition (ODT). When an OOT occurs the system re-arranges between two ordered phases. In an ODT the system changes from an ordered phase to a disordered phase, in which the ordered phase becomes absent in the long range. [5,6] No further phase transition occurs when an ODT state has been reached. Both transitions can be realised by variations in temperature and/or shear forces. [5,6] It have been reported that the transitions can be estimated by analysing rheological data. [18,19,20]

Indication of an OOT can be given by a drop in G' [18,19]. In order to identify which phase that is present additional methods such as small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) needs to be used. [12,20,21]. In some cases the phase at a certain temperaure has been figured out by the shape of frequency sweep curves [5,22].

A common method for finding the T_{ODT} (order-disorder temperature) has been described by Han et al. [23,24,25]. The method suggests that plots of the loss modulus (G'') vs. the storage modulus (G') for a block copolymer system with an ordered phase show a temperature dependence whereas a disordered system is independent of temperature. The T_{ODT} is said to be reached when the curves at successively higher temperatures becomes linear and start to overlap. The difference between a block copolymer and a homopolymer can be seen in Figure 2.2. Han et al. [25] have also shown that plots of complex viscosity (ή) vs. the angular frequency (ω) give further indication that a disordered state has been reached (example in Figure 4.2). It is said that a block copolymer in an ordered phase has a higher melt viscosity than in the disordered state. Therefore a Newtonian behavior is not seen in an ordered phase, whereas it is seen for low ω (~0.5-10 rad/s) in the disordered state [20,25]. Completely

Newtonian behavior may not be seen in a polymer melt. However this method is not as convincing as the G'' vs. G' plots since it has been shown that isothermals lower than the expected T_{ODT} can show Newtonian behavior at sufficiently low ω even though domains of ordered phase still remains. [26] A significant loss in G' at a certain temperature can also be related to an ODT [19].

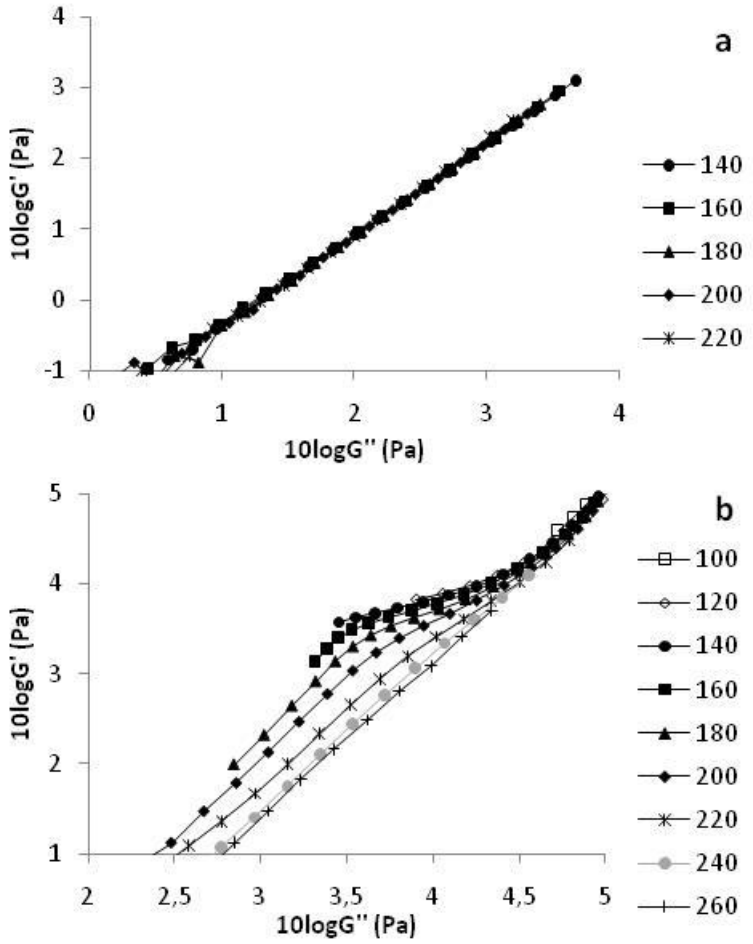

***Figure 2.2: Frequency sweep of a polyethylene homopolymer (a) and a poly(styrene-*b*-isoprene-*b*-styrene) block copolymer (b). The numbers in the legend refers to temperatures in °C. It is seen that the temperature independence for PE is seen at all isothermals. For the block copolymer the temperature independence starts at ~240°C when linearity is seen (grey curve). This is said to be the T_{ODT}* [23,24,25].**

2.2 Physical models of block copolymer self-assembly

In order to control transitions in block copolymers we need to know how the system behaves physically. It has been shown that the Gaussian chain model, supplemented with Self Consistent Field Theory (SCFT) calculations can provide good approximations [10,11,27]. This method gives the possibility to calculate composition profiles, equilibrium behavior and chain conformations in a system [14,18]. The SCFT is built on basic mechanical and thermodynamic laws but requires complicated numerical calculations. Only a brief review will be given here since this not is the focus of this study, an extended explanation can be found elsewhere [5,27].

The first step is to construct a model that can be approximated to behave like a polymer chain in a polymer melt. This model treats the chain as a long thin elastic thread consisting of a number of beams that are connected by springs, where each beam represents a sequence of segments. [2] In the SCFT the segments in the melt are thought of as completely isolated in a restricted area. Inside this area the segments can adopt a large number of configurations. Counting each and one of them is possible, but is unnecessarily complex. Instead a total sum of all the possible configurations for all segments is calculated by the partition function. [16] Minimising the free energy will generate the equilibrium phase for any given f, T and M_w . Therefore the SCFT can generate theoretical phase diagrams for block copolymer systems [5,6]. Every system requires a unique solution of the SCFT in order to predict the phase under certain circumstances. Studies have shown that theoretical phase diagrams calculated by the SCFT are supported by experimental results [10,16].

Even though the SCFT gives good approximations there are cases when the position of the segment cannot be estimated due to fluctuations in the interface. Local fluctuations of a low level may not affect the calculations, but when the interface may be less sharp on a larger scale, for example near a transition, the fluctuations may increase and can have an impact on the SCFT. [10,14,16,28] These effects can be integrated in the theory by mathematical additions, discussed elsewhere [16].

2.3 Compatibilising and phase swelling effects

From a thermodynamically point of view miscibility in homopolymer blends can only be achieved when the heat of mixing is negative [17]. However adding block copolymer to homopolymer blends can reduce the phase separation and increase the level of miscibility in the blend. Thus the block copolymer has a compatibilising effect in the blend. [5,6]

It is established that addition of homopolymer to a block copolymer system can cause changes of the transitions. This is caused by interactivities between the phase separation of the block copolymer and the homopolymer. The interactivities depend both on the composition and the M_w of the polymers. [5,7] Homopolymers with lower M_w than the corresponding block tend to solubilise into the corresponding domain and affect the separation on a micro scale. As the M_w of the homopolymer increases the separation enlarges and can affect on a macro scale. [5] Several studies have concluded that both OOTs and ODTs can be influenced by adding homopolymers or other block copolymers (for example adding a diblock to a triblock copolymer) to a block copolymer system [20,26,29]. For example Berglund et al. have shown that adding 19.5wt. % poly(styrene-*b*-isoprene) (SI) diblock to a SIS triblock decreased the T_{ODT} with ~20°C [26]. Such additions can be of interest in order to control the transitions. From for example a processing point of view a decrease of the T_{ODT} could reduce the processing temperature that in turn can reduce both plant costs and energy consumption.

3. Material and methods

3.1 Material

Two block copolymer systems and blends of those and their constituent homopolymers in different compositions have been studied.

An amorphous triblock poly(styrene-*b*-isoprene-*b*-styrene) (SIS) has been studied in three different compositions with 14, 17 and 22 wt. % of polystyrene (PS), here after called SIS14, SIS17 and SIS22. Further on a semicrystalline diblock polyethylene-*b*-poly(ethylene glycol) (PbP) has been studied in two different compositions, 50 and 80 wt.% poly(ethylene glycol) (PEG), indicated as PbP50 and PbP80. Polyethylene oxide (PEO) is often used as a synonym for PEG, but for low M_w PEG is mostly used [30]. Material characteristics are found in Table 3.1. Most of the information has been provided by the material supplier, Sigma-Aldrich [31].

Table 3.1: Material characteristics.

Material	**Composition**	**~ M_w (g/mol)**	**~M_n (g/mol)**	**Form**
SIS14	14 wt.% PS	~245 000[1] (½PS ≈17 150)	N.A.	pellets
SIS17	17wt.% PS	~160 000[2] (½PS ≈13 600)	N.A.	pellets
SIS22	22wt.% PS	N.A.	N.A.	pellets
PbP50	50 wt.% PEG	N.A.	~1 400	pellets
PbP80	80 wt.% PEG	N.A.	~2 250	pellets
Polystyrene (PS)	Homopolymer	~35 000	N.A.	pellets
Polyisoprene (PI)	Homopolymer	~38 000	N.A.	liquid
Polyethylene (PE)	Homopolymer	~24 000-25 000	~2 710-2 900	powder
PEG	Homopolymer	N.A.	~300	viscous liquid

The weight average molecular mass, M_w, and number average molecular mass, M_n, are defined as:

$$M_w = \frac{\sum w_i M_i}{W}$$

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{W}{\sum n_i}$$

were w_i is the mass and M_i is the relative molecular mass of the i^th^ fraction from a molecular distribution. W is the total weight ($\sum w_i$) and n_i is the number of molecules in the i^th^ fraction ($w_i = n_i M_i$). [2] Here M_w will be referred to as the molecular weight.

3.2 Preparation of polymer blends

This chapter describes the preparation methods for the blends. All studied samples and compositions are listed in 8.2.

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[1] Ref. [33]

[2] Ref. [33]

SIS and homopolymer blends were based on SIS17 and varying amount of homopolymers as seen in Table 3.2. The blends are named with the wt. % of homopolymers followed by A, B or C. The letters represents the following: A only contains PS, B only contains PI and C is a mix of 17 wt. % PS and 83 wt. % PI. The composition in C was chosen to be equal to the wt. % of PS in SIS17. The blends were prepared by solution blending in toluene stirred for 24h followed by evaporation. The evaporation started at room temperature for 1 week followed by vacuum oven drying at 40°C for 3 days. When no changes in weight could be seen the temperature was raised to 110°C for 2h in order to ensure no remains of the solvent. For immiscibility reasons the composition with 95 wt. % homopolymer was obtained by rapid precipitation in methanol (5/1 methanol/polymer solution). Less than 5 wt. % of the homopolymers (PS and PI) were dissolved in toluene and stirred for 24h before the precipitation step. [32] The precipitated solution was filtered and washed with methanol before evaporation in a vacuum oven at 40°C for 24h. The final blend was stored at room temperature.

Blends containing PbP and PE were produced by mechanical dry mixing and are listed in Table 3.3. Melting of the blends was obtained in connection to the hot pressing when producing samples for the measurements.

Table 3.2: Blends of SIS17 and homopolymers.
A= only PS, B=only PI and C a mix of 17 wt. % PS and 83 wt. % PI.

	Components wt. %		
Sample	**SIS17**	**PS**	**PI**
5A	95	5	0
15A	85	15	0
30A	70	30	0
50A	50	50	0
5B	95	0	5
15B	85	0	15
5C	95	0,85	4,1
15C	85	2,5	12,45
30C	70	5,1	24,9
50C	50	8,5	41,5
70C	30	11,9	58,1
95C	5	16,2	78,86

Table 3.3: Blends of PbP and PE.

	Components wt. %		
Sample	**PbP50**	**PbP80**	**PE**
PbP50,30	70	0	30
PbP50,50	50	0	50
PbP80,30	0	70	30
PbP80,50	0	50	50

3.3 Rheological measurements

Rheological measurements were conducted using an Anton Paar MCR 500 rheometer with a plate-and-plate mode (25 mm diameter plate and a gap of 1.8 mm or smaller). In order to prevent oxidation a constant nitrogen purge was applied. The temperature control was within ±0.5°C and the strain was fixed at different values within the linear viscoelastic regimes[3] of the samples. Due to instrument limitations the cooling rate after trimming the sample could not be controlled and measurements at temperatures lower than ~20°C were possible to conduct.

Two different types of measurements were conducted. 1) Temperature sweeps at a constant ω =1 rad/s and a temperature increase of 1°C/min. In order to compare the results, the same ω and temperature rate have been used for all samples. The temperature was varied from ~50 to 300°C depending on the sample. The samples were only used for one measurement. 2) Frequency sweeps with a ω ranging from 100 to 0.05 rad/s. The isothermals varied from ~50 to 260°C depending on the samples. The same sample was measured at several isothermals.

3.4 DSC measurements

DSC measurements were conducted with a TA Instruments DSCQ2000 V24.9 Build 121 using a DSC Standard Cell RC. A method from -90-200°C with a temperature increase of 5°C/min was used.

4. Results and discussion

4.1 Rheological behavior of different phases

4.1.1 Poly(styrene-*b*-isoprene-*b*-styrene) system

Both temperature and frequency sweeps have been conducted for all three SIS samples. In Figure 4.1 the result from the temperature sweep of SIS17 is seen. The overall trend is about the same for all three SIS (specific results of SIS14 and SIS22 can be found in 8.1.1). The differences between the samples are the values of G' and the positions of interesting features. SIS17 have two peaks that are not seen in SIS14 and SIS22, indicated by arrows in Figure 4.1. A similar drop seen in G' for SIS17 at ~180°C is also seen for SIS22 at ~280°C. SIS14 lack this feature and have a more gradual decrease in G'.

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[3] Controlled by rheological measurements (amplitude sweep with constant ω=1 rad/s and varying strain 0.01-100%).

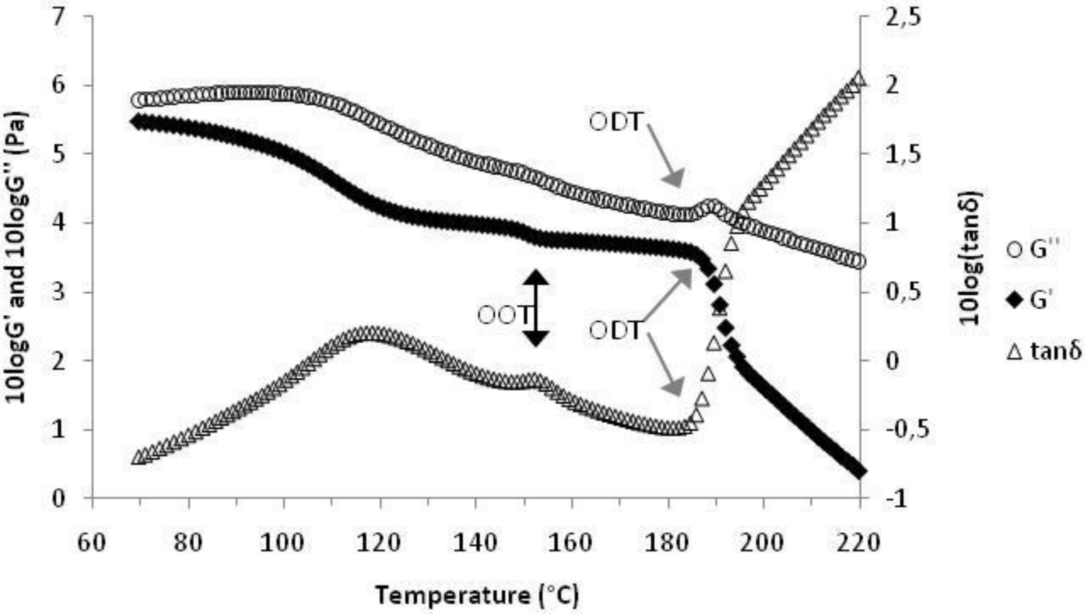

Figure 4.1: Temperature sweep of SIS17. The arrows indicate interesting features that is thought to be related to transitions. The black arrow indicates a possible OOT and the grey ones a possible ODT. The G'' curve has been offset to avoid overlapping.

Frequency sweeps of the complex viscosity (ή) of SIS17 at different isothermals is seen in Figure 4.2. Up to a certain point a viscoelastic behavior is seen and ή decreases with increasing T and ω. After this point, at ~220°C, a Newtonian behavior is seen instead and ή becomes independent of ω. This behavior is also seen for SIS14 at ~220°C (8.1.1). SIS22 does not show Newtonian behavior within the measured temperature range, but between ~240-260°C there is an indication of changes in the phase, seen in 8.1.1. Frequency sweeps above 260°C could not provide reliable results.

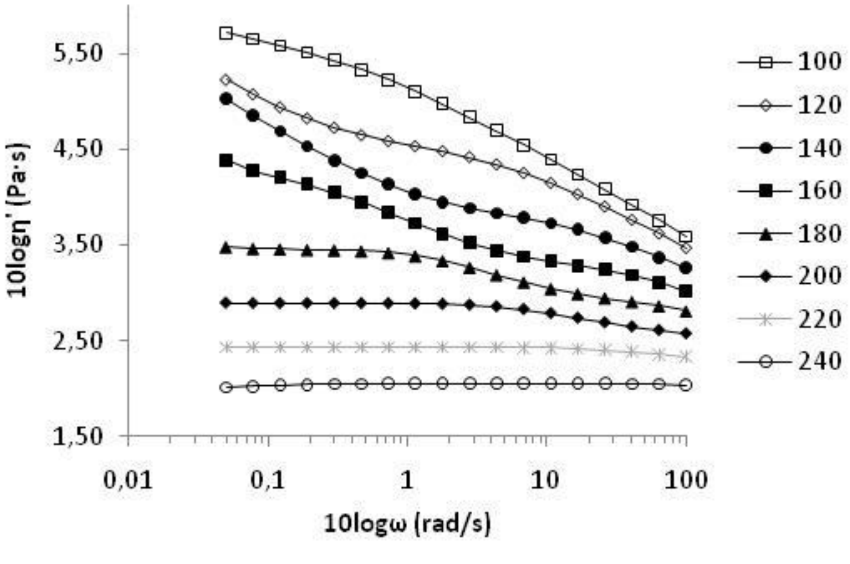

Figure 4.2: Frequency sweeps of the complex viscosity of SIS17 at different temperatures. The numbers in the legend refers to temperatures in °C. Newtonian behavior is seen at ~220°C (grey curve). At this point a disordered state is expected to be present.

Previous studies have defined the transitions in SIS systems using rheological methods mentioned in 2.1.2, combined with imaging instruments. Several studies have shown that material with about the same wt. % as SIS14 and SIS17 have spherical and cylindrical phases respectively [18,19,23,33,34]; hence this is assumed. It has been shown in other studies that a SIS with ~18-29 wt. % PS has cylindrical phase [13]; hence this is assumed for SIS22.

Further results and discussion have been divided into three regions: glass transitions, OOTs and ODTs.

Glass transitions. A standard PS usually has a T_g ~85-110°C, depending on the M_w [35]. The peaks in G'' (Figure 4.3) are close to this temperature and therefore it is assumed that this is the T_g of the PS blocks. The T_g seems to be slightly higher than for a standard PS and the peaks are broad. This could be explained by the fact that the blocks have restricted ability to move in comparison to a pure PS. SIS14 and SIS17 have similar T_g whereas it is higher for SIS22. Since SIS17 and SIS22 are suggested to have the same phase it would be reasonable that they behaved similar. On the other hand a higher PS content would probably need more time and higher temperature to reach a molten state, which would explain the higher T_g for SIS22. The M_w of the PS blocks will most likely have an effect on the T_g as well. The broadness of the peaks could also indicate that the samples have a wide polydispersity (M_w /M_n). A wide polydispersity could have an effect on both T_g and the transitions. SIS22 seems to have a narrower polydispersity than SIS14 and SIS17 since it has a narrower peak. Using this reasoning it appears as the composition and the M_w have a higher impact on T_g than the phase.

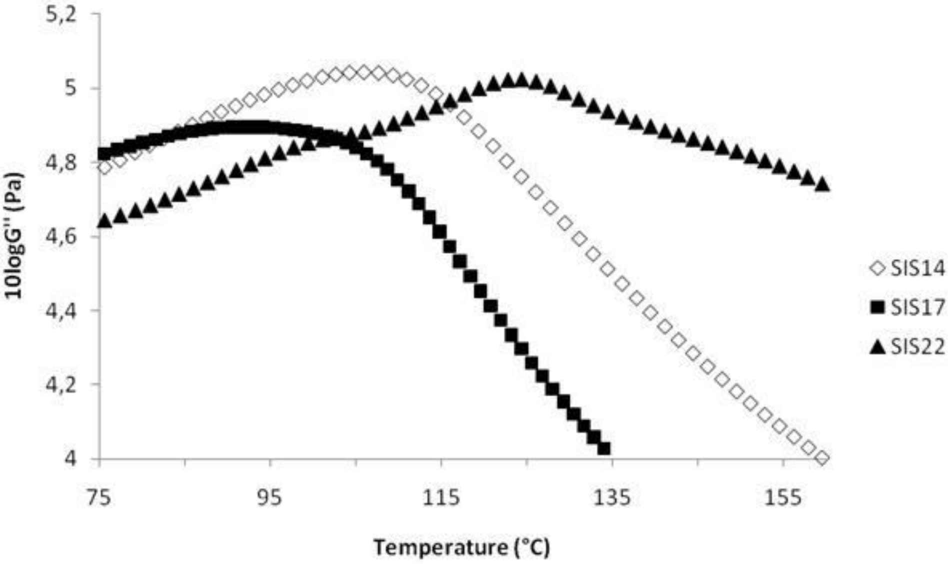

Figure 4.3: First region of the temperature sweeps showing possible glass transition for the PS blocks. SIS14 and SIS17 have similar T_g whereas SIS22 shows a higher T_g. It is also seen that the peaks are broad. This is believed to be an effect of wide polydispersity.

Order-order transitions. In the second region a possible indication of an OOT is seen for SIS17 at ~150°C (Figure 4.4). It has been suggested that at the temperature at which a minimum in G' occurs can signify an OOT [19], as seen for SIS17. Based on rheological results (with ω= 0.1 rad/s), Kim et al. found an OOT from cylinders to spheres for a SIS with 18.3 wt. % PS (M_w≈143 000 and a polydispersity index of 1.09) at ~181±1°C [18,36]. They saw a similar drop in G' as seen for SIS17. Further on it has been shown that SIS with ~18 and ~16 wt. % PS has a cylindrical and a spherical phase, respectively [13]. This would mean that SIS17 is very close to having spherical phase as a starting point. Based on this we believe that SIS17 undergoes an OOT from cylinders to spheres at ~150°C. An explanation for the difference in T_{OOT} (order-order temperature) could be that different ω has been used and due to the fact that SIS17 is closer to a spherical phase than the material they investigated. Differences in polydispersity are also believed to have an effect on the OOT and will be discussed later on. No photos of the samples could be obtained during this study, why there is no certainty of an OOT. There is a possibility that SIS17 could have domains of both cylindrical and spherical phase.

No potential indications of OOTs were seen for SIS14 and SIS22. The difference in wt. % of PS between SIS17 and SIS14 is small and SIS17 has the following transition order cylinders → spheres → disordered. Therefore it seems unreasonable that SIS14 would adopt any other phase before the ODT; hence it is believed that SIS14 goes directly from spheres to a disordered state and that no OOT occur. An OOT for SIS22 is neither rejected nor suggested based on the results. Comparable studies suggesting otherwise have not been found.

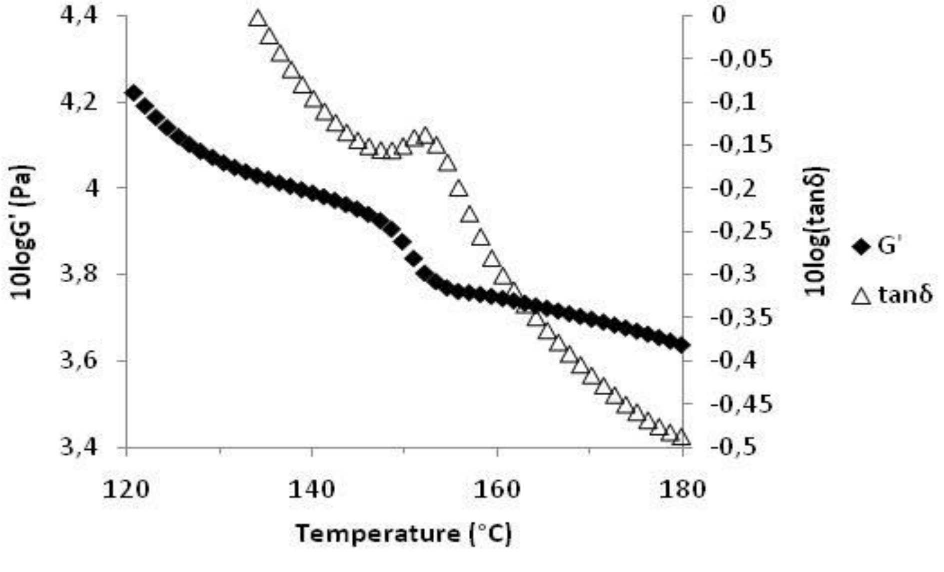

Figure 4.4: Temperature sweep of SIS17. There is a clear indication of a change in the sample at ~150°C. The transition is believed to be an OOT from cylinders to spheres.

Order-disorder transitions. For SIS17 the peak in G'' at ~190°C and the rapid decrease in G' at ~190°C (Figure 4.5) are believed to indicate an ODT onset. It may be reasonable that an ODT could continue during a large temperature interval since the material needs to undergo a major transition, requiring high chain mobility in order to reach a completely disordered state. This is why the indications at ~190°C are believed to be onsets. The frequency sweep clearly indicate that an disordered state have been reached at ~220°C (Figure 4.6), further confirmed by Newtonian behavior at the same temperature (Figure 4.2). Therefore it is believed that SIS17 has an ODT at ~220°C.

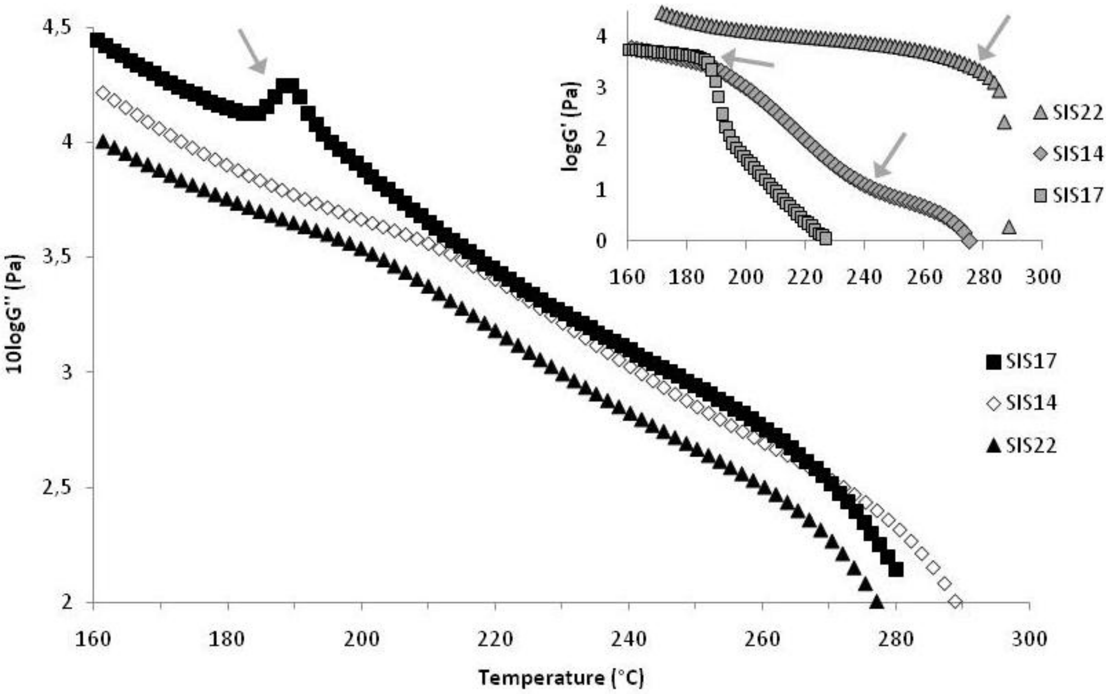

Figure 4.5: G'' and G' (insert) against temperature for all SIS. SIS17 shows a peak in G'' and a drop in G' at ~190°C.This is believed to be an indication of an ODT onset. For SIS22 a sudden drop in G' is seen at ~280C°, that could indicate an ODT onset. SIS14 has a plateau at ~240C° that could be related to an ODT. Arrows indicates the features that are believed to be related to the ODT.

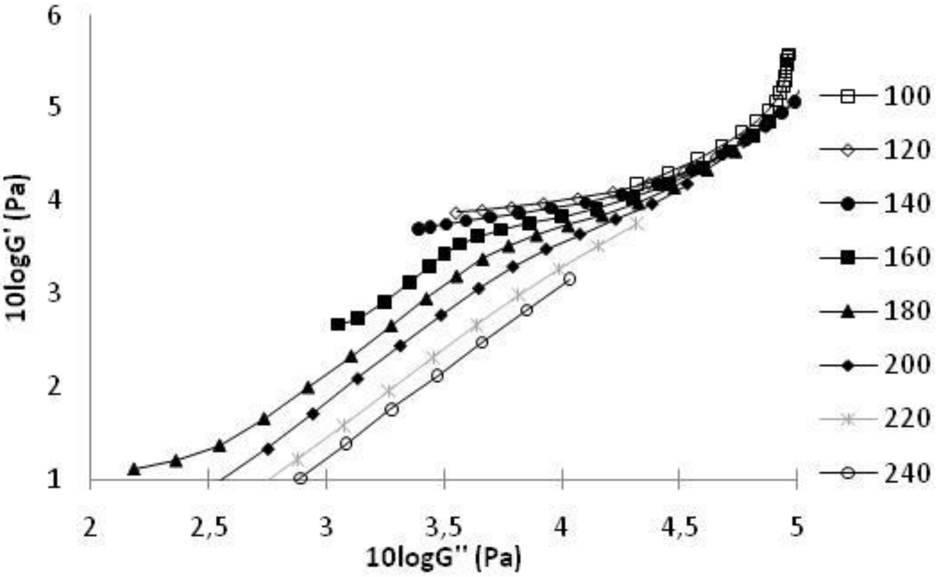

Figure 4.6: Frequency sweep of SIS17 at different isothermals. The numbers in the legend refers to temperatures in °C. At T=220 °C temperature independence is seen, marked with grey. This is believed to be the T_{ODT}.

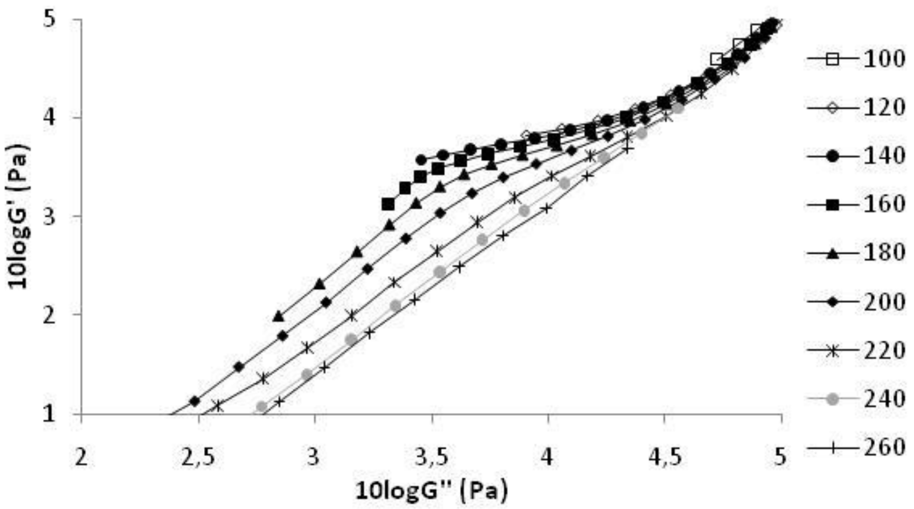

Figure 4.7: Frequency sweep of SIS14 at different isothermals. The numbers in the legend refers to temperatures in °C. At T=240 °C temperature independence is seen, marked with grey. This is believed to be the T_{ODT}.

For SIS14 the indications in the temperature sweep are less prominent, but the plateau at ~240°C is believed to be related to an ODT. The frequency sweep clearly indicates and ODT at~240°C (Figure 4.7) further confirmed by Newtonian behavior at the same temperature (seen in 8.1.1), hence T_{ODT}≈240°C is believed.

For SIS22 the frequency sweep (seen in 8.1.1) indicates an ODT above ~260°C and temperature sweep indicates an onset at ~280°C (Figure 4.5). Most likely there is an ODT above ~260°C, but this could not be confirmed with frequency sweep due to unreliable results above ~260°C. Winter et al. have studied a SIS (SIS56) with ~24.3 wt. % PS (M_n≈ 56 000 (g/mol) and M_w/M_n =1.1) suggesting an ODT at ~140°C [21]. Here an equal drop in G' is seen at ~140°C as seen for SIS22 at ~280°C (Figure 4.5). The drop could be related to an ODT which support that SIS22 becomes disordered above ~260°C. The large difference in T_{ODT} of 120° C probably depends on more factors than the difference in composition. Firstly, the rheological measurements have been conducted differently. Winter et al. conducted rheological measurement with ω=0.1 rad/s and a temperature increase of 2K/min. Secondly, SIS22 probably has a larger M_w than SIS56, based on the M_w of SIS14 and SIS17. Longer molecules would probably assemble in the centre of the domains and higher temperatures would be needed in order to reach sufficient mobility. The M_w of SIS22 is unknown why a direct comparison of the ODT is difficult.

The sudden drop in G' seen near the ODT for both SIS22 and SIS17 is absent for SIS14. It may be that the phase not is related to this behavior. It have been suggested that it is related to a certain fraction of the hard blocks, in this case the wt. % of PS [23]. In that case the limit from this fraction would be around 14 wt. % PS. With current results it is difficult to say if the composition is the only factor. According to earlier discussion the M_w and the polydispersity seems to have an effect on the mobility of the chains; hence they cannot be excluded in this case.

Summary. By using current results and information from previous studies the transitions for the SIS system are estimated, given in Table 4.1. Having established the transitions in the SIS system the overall rheological behavior can be discussed.

SIS17 is suggested to have a cylindrical phase up to ~150°C were it changes to spherical. This implies a similar behavior as SIS22 before the OOT and as SIS14 afterwards, which not is seen and will be further discussed. The ODT temperature for SIS17 and SIS14 is expected to be similar, which is observed.

Table 4.1: Suggested transitions for the SIS samples.

Sample	Phase[4]	~T_{OOT} (°C)	~T_{ODT} (°C)
SIS14	Spheres	not seen	240
SIS17	Cylinders	150°C, to spheres	220
SIS22	Cylinders	not seen	above ~260°C

When comparing a spherical and a cylindrical block copolymer system, Han et al. noticed that the spherical phase was more sensitive to variation in temperature [23]. Deformation tests on SIS with glassy PS have indicated that increased reinforcement in the polymer matrix is seen with increasing fraction of PS [13]. This could explain the behavior of SIS22. But it does not explain the fact that SIS14 show less temperature sensitivity than SIS17. SIS14 has ~1.5 times higher M_w than SIS17. Comparisons with an earlier study from Han et al. [23] were preformed in order to investigate how large effect the differences in M_w could have. They have conducted rheological measurements on Kraton 1107 which is a SIS triblock with ~14.2 wt. % PS, a spherical phase and a M_w ≈140 000 (g/mol) (close to SIS17). Kraton 1107 also contained ~20 wt. % diblocks and was suggested to have an T_{ODT}=230°C. The comparison is presented in Table 4.2 and Figure 4.8 . It is actually seen that Kraton 1107 and SIS17 behave quite similar. Thus it is believed that samples with the same phase can behave similar if the M_w is comparable. The polydispersity is unknown for the SIS samples, but by earlier reasoning it could be wide, which could be a further explanation for the similarity between SIS17 and Kraton 1107. If that is the case this could also be one explanation for the difference in T_{OOT} seen between SIS17 and in the SIS, with a narrow polydispersity, studied by Kim et al. [18,36] discussed earlier. Thus it is believed the M_w and the polydispersity have a large impact on the rheological behavior and the transition temperatures.

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[4] Under normal conditions; that is room temperature and no shearing.

Table 4.2: Comparison of frequency sweeps of SIS17 and SIS14 with Kraton 1107 at 180°C, which is above the T_{OOT} for SIS17. Kraton 1107 have ~14.2 wt. % PS and a M_w similar to SIS17. It is seen that SIS17 and Kraton behave quite similar. Data for Kraton 1107 are collected from a study by Han et al. **[23].**

~G''/ω at 180°C	0.4 rad/s	1 rad/s	10 rad/s	40 rad/s	100 rad/s
SIS17	3.1	3.4	4	4.5	4.75
SIS14	3.6	3.75	4.5	4.9	5
Kraton 1107	3.3	3.4	4.2	4.4	4.4

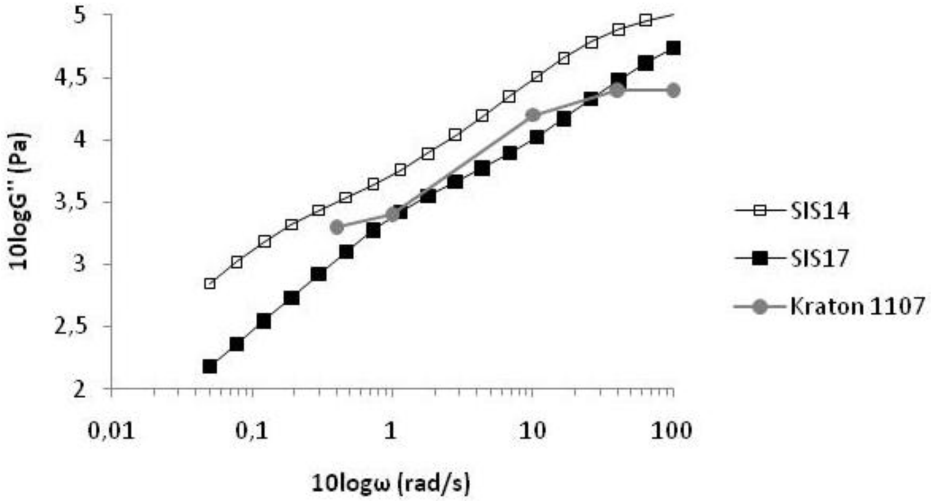

Figure 4.8: Frequency sweeps of SIS17 and 14 at 180°C. SIS14 and SIS17 are expected to behave similar above ~150°C since they both have spherical phase. This is not seen. Kraton 1107 behave more similar to SIS17, why it is believed that the M_w and polydispersity affect the rheological behaviour. Data for Kraton 1107 are collected from a study by Han et al. **[23].**

A parameter that not has been taken into consideration is the orientation of the PS domains. Whether the PS domains are isotropic or oriented could have had an impact on the rheological measurement especially for the cylindrical phase [13].

4.1.2 Polyethylene-*b*-poly(ethylene glycol) system

The PbP system is very different from the SIS system. First it is a diblock instead of a triblock and secondly it is a semicrystalline block copolymer that brings about a completely different behavior. Block copolymers that crystallise seem to be less studied than amorphous block copolymers and few comparable results have been found. Due to the complexity brought by the chain folding new properties are expected, why the interest in crystalline block copolymers has grown during the last years. [5,37]

Temperature and frequency sweeps have been conducted for both PbP50 and PbP80. Since the systems are semicrystalline DSC measurements have also been performed in order to obtain information regarding the T_m of the blocks.

Melting temperatures. In Figure 4.9 the DSC results for PbP50 are shown. The largest peaks are seen at ~30°C and ~100°C and are believed to be the T_m of PEG and PE blocks, respectively. Short chains may melt before long chains and this can cause broader melting/crystallisation peaks as seen in Figure

4.9. This indicates that PbP50 is an oligomer, which is reasonable since producing high M_w PbPs is difficult [37]. This is thought to have an effect on the self-assembly and rheological behavior. From the DSC results of PbP80, seen in 8.1.2, it is believed that the PEG blocks melts at ~55°C. Only a small sign of the melting of PE blocks is thought to be seen at ~90°C. DSC results of PE and PEG homopolymer (seen in 8.1.2) shows a $T_{m,PE}$≈130°C and $T_{m,PEG}$≈-10°C. A lower T_m for the blocks in the PbP than for the corresponding homopolymers can be expected [5]. It is seen that PEG has a very low M_n that explains the low T_m. It is believed that the PEG blocks have higher $M_n$and therefore the PEG is considered to be incomparable with the PbPs.

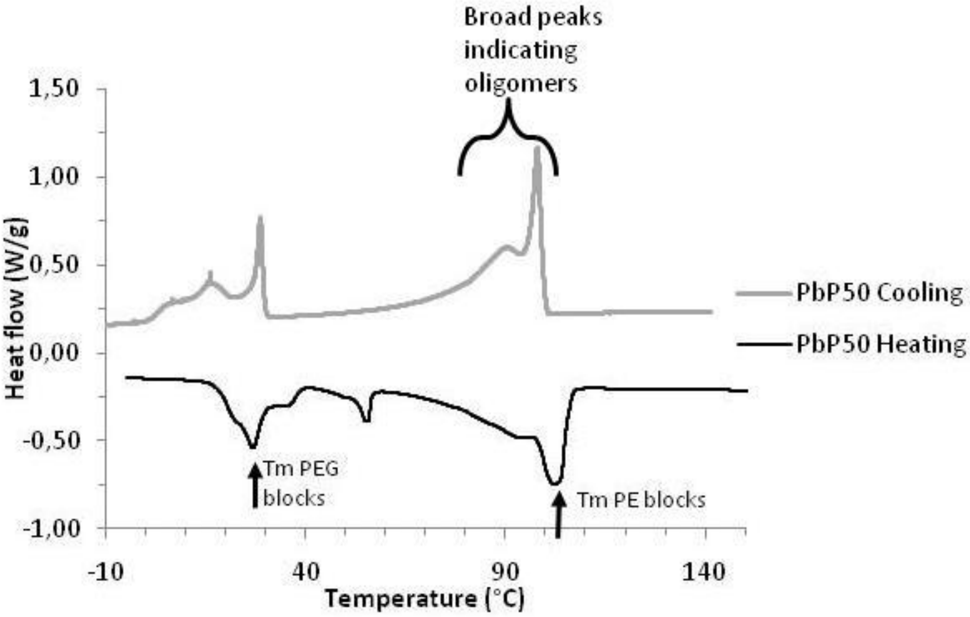

Figure 4.9: DSC measurement of PbP50. The peaks clearly indicate the melting/crystallization of the blocks in the block copolymer. The fact that several peaks are seen indicates that oligomers are present.

Transitions. The suggested melting temperatures for PbP50 have been confirmed by earlier studies of the same material [37]. In a study conducted by Sun et al. [37], it was shown by TEM that PbP50 had a lamellae phase at 0°C. Using wide-angle X-ray diffraction (WAXD) and SAXS they also saw that the PEG blocks were completely molten at 30°C while the crystals of the PE blocks were present up to ~97°C. At ~100°C the lamellae phase was still seen even though the sample was molten and at ~105°C a disordered state was seen. [37] The temperature sweep, Figure 4.10, of PbP50 shows a drop in G' and G'' at~ 90°C. This is believed to be correlated to the melting of PE blocks, also seen in DSC results. Further on PbP50 is believed to have a lamellae phase from room temperature up until ~100-105°C when an ODT occur. The ODT is indicated by a sudden drop in G' and G''. Based on the results from Sun et al. it is believed that PbP50 not undergo an OOT.

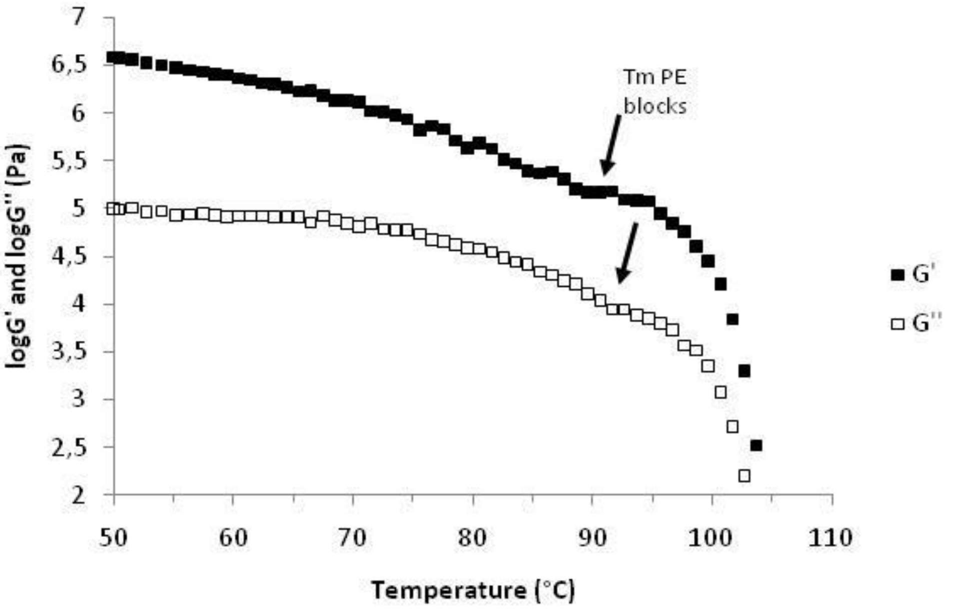

Figure 4.10: Temperature sweep of PbP50 showing both G' and G''. A small drop is seen in both curves at~90°C, marked by arrows. This is believed to be correlated to the melting of the PE crystals. The sudden drop at ~100°C is thought to be related to an ODT. G'' have been shifted vertically for clarity.

No comparable studies were found for PbP80 why the reasoning for PbP50 will be used here as well. PbP80 consists of 80 wt. % PEG, hence a lower G' than for PbP50 is expected. In the temperature sweep (Figure 4.11) drops in G' and G'' at ~62°C and $tan\delta$ at ~67°C are seen. This is probably the melting of the PEG blocks, which also is very close to the DSC result, seen in 8.1.2. The sample only allowed temperature sweeps up to ~83°C. At this temperature the PE blocks are not believed to be molten yet. If PbP80 follows PbP50 an ODT would be expected shortly after the melting of the PE blocks, at ~90°C. In a study from Cao et al. [38] it was shown that an OOT can occur even though PE crystals still remain. Therefore it is possible that a transition can occur after the melting of the PEG blocks. Cao et al. have also suggested that low M_w PE blocks with high mobility could be a trigging factor of an OOT and that the relative M_w of the blocks are expected to have an effect on the OOT as well [38]. This means that an OOT for PbP80 not can be excluded. According to the Flory-Huggins interaction parameter different lengths of PE and PEG chains may result in different phases, but it is not known yet whether the parameter can be applied for semicrystalline block copolymers [38]. This makes it even harder to speculate about the transitions. Lamellae phase is common for block copolymers with block that crystallise [5], but a lamellae phase cannot be verified in this case. Considering the information given by results and literature no transitions can be suggested for PbP80.

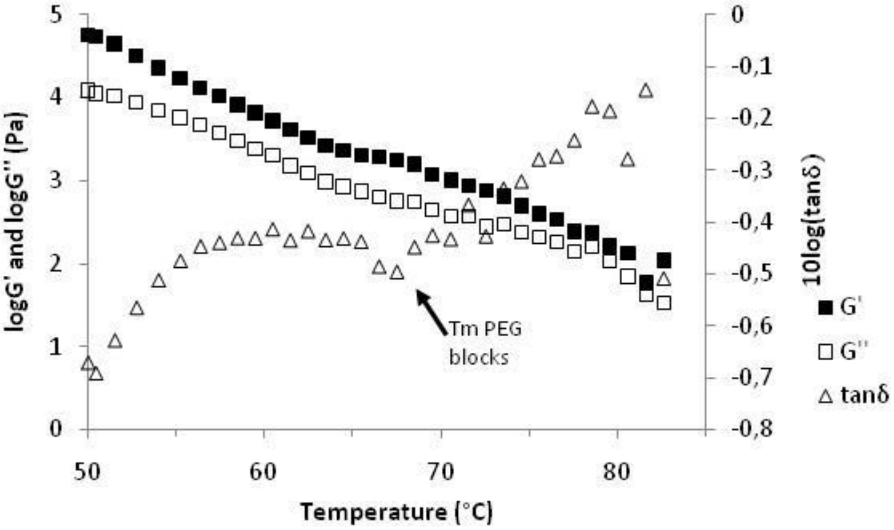

Figure 4.11: Temperature sweep of PbP80 showing G', G'' and tanδ. A small drop in G' and G'' is seen at ~62°C and for tanδ at ~67°C. This is believed to indicate the melting of PEG blocks.

The frequency sweeps of the PbPs did not provide with supportive information regarding the transitions. Measurements at higher isothermals than $T_m$of the PE blocks were not reliable and results could not be reproduced even though using the same pre-treatments. This is thought to be an effect of the crystalline behavior and/or a consequence of unbalanced chain folding caused by oligomers.

Summary. PbP50 is believed to have a T_{ODT}≈105°C, but no OOT. Results and literature have not provided enough information in order to suggest any transitions in PbP80. The T_m of the blocks can be seen in rheological measurements, confirmed by DSC results. Transitions seem related to the melting/crystallisation process of the PE blocks, but not completely dependent as it could be seen that ordered phases can be present even in the melt. It is believed that the $M_{w,}$ especially of the PE blocks, have an important role on the transitions and the rheological behavior in semicrystalline block copolymers, also suggested in other studies [37,38].

It could be discussed if rheological measurements on PbPs can provide with relevant information when studying transitions in semicrystalline block copolymers. It seems like other analysing instruments such as SAXS, WAXD, TEM, DSC and polarized light microscopy (PLM) are more suitable for this purpose. [5,37,38,39]

4.2 Phase swelling and compatibilising effects

4.2.1 Blends of poly(styrene-*b*-isoprene-*b*-styrene) and homopolymers

Varying wt. % of homopolymer was mixed with SIS17 in order to investigate the effects of phase swelling and compatibilisation of homopolymer blends. SIS17 were chosen since this SIS sample has provided most information. All measured samples are listed with both name and composition in 8.2. The results of the temperature sweeps will be presented first followed by the frequency sweeps. In order to highlight the important results a selection of the graphs are placed in this chapter. The rest can be found in 8.1.1.

Temperature sweeps. It has been established that an addition of homopolymer to a block copolymer system can affect the phase transitions [5,7]. Here it is seen that only a low amount of homopolymers (5 wt. %) seems to affects both the OOT and the ODT onset. The effect increases with increasing wt. % of homopolymers (Figure 4.12 and Figure 4.13).

The OOT onset seems highly affected by the homopolymers, Figure 4.12. B and C blends are seen to have a decreasing effect on the T_{OOT} while A has the opposite effect. The OOT onset is seen up to 30C and 30A (Figure 4.14 and Figure 4.16). Above this fraction of homopolymer it is not believed that the transition from cylinders to spheres not occur since the sample already could have a spherical phase or domains of both phases.

All three compositions induce the ODT. This becomes very distinct at 15 wt. % homopolymers when the difference of the drop in G' between SIS17 and the blends are ~20°C. For the C blends the ODT onset is seen up to 30 wt. % homopolymer (Figure 4.13). At 30A it is seen that the indications of the OOT and ODT have coincided completely (Figure 4.13 and Figure 4.14).

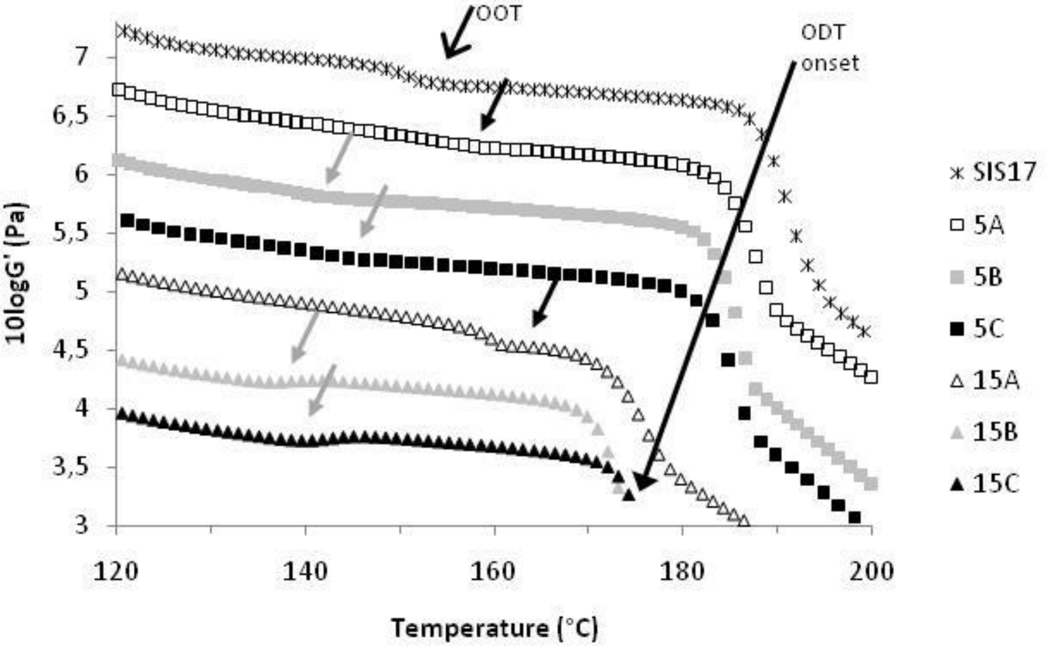

Figure 4.12: SIS17 is compared with blends of 5 and 15 wt. % homopolymer. It is seen that the OOT is shifted for the blends. The A blends seems to delay the OOT, short black arrows, while B and C blends seems to induce it, grey arrows. The ODT onset, long black arrow, is shifted to lower temperatures for all blends. All curves have been shifted vertically for clarity.

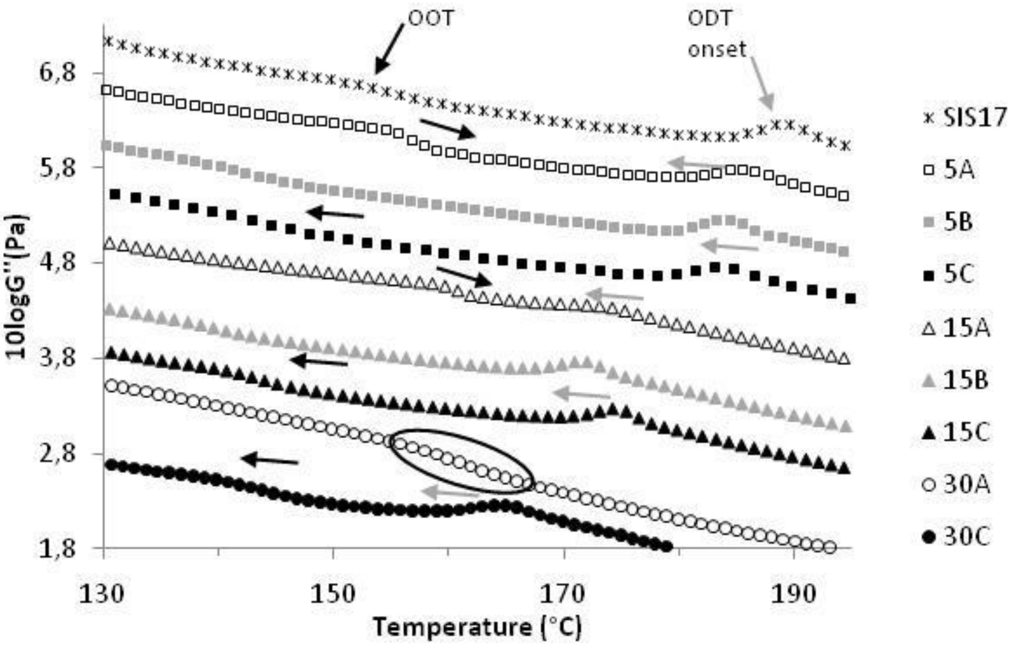

Figure 4.13: Temperature sweeps of SIS17 and blends up to 30wt. % homopolymer. The black arrows indicate the movement of the OOT and the grey arrows indicate the movement of the ODT onset. It is seen that the transitions are shifted towards each other for the A blends and apart from each other for the B and C blends. B and C blends behave very similar. At 30A the OOT and ODT onset have coincide, marked by the black circle. The curves have been shifted vertically for clarity.

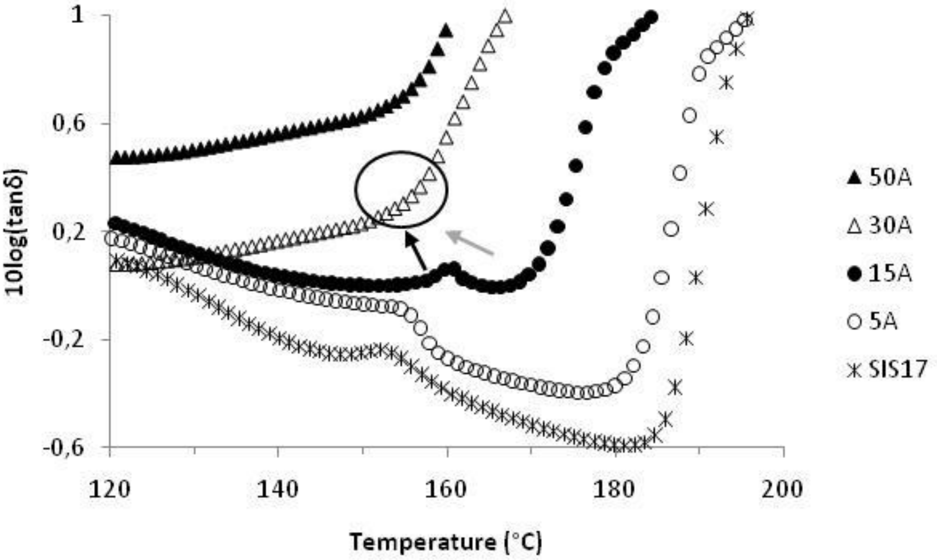

Figure 4.14: Temperature sweep of SIS17 and A blends. It is clearly seen that the OOT (black arrow) and ODT onset (grey arrow) are shifted towards each other as the wt. % of PS increases. At 30 wt. % PS they have coincided completely (black circle). The curves have been shifted vertically for clarity.

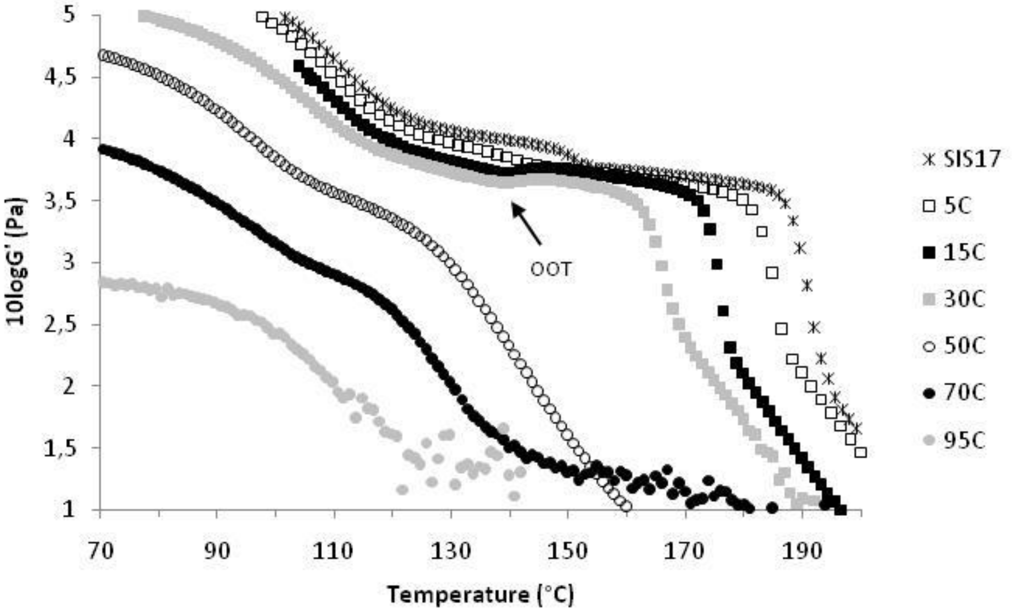

Figure 4.15: Temperature sweeps of SIS17 and C blends. Above 50 wt. % of homopolymer the OOT is not seen and SIS17 seems to lose the ability to control the rheological behaviour. The homopolymer starts to dominate more and compatibilising effects are started to be seen.

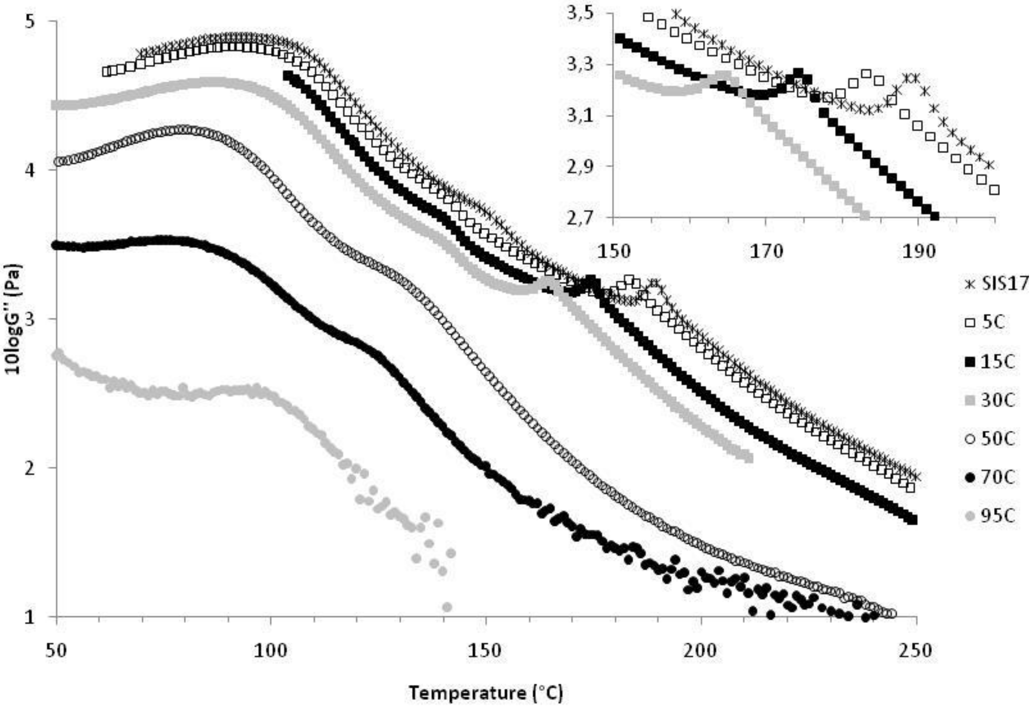

Figure 4.16: Temperature sweeps of SIS17 and C blends. The insert in the right corner is an enlargement of how the ODT onset is shifted with increasing fraction of homopolymer. At 50 wt. % it is no longer seen. Above this fraction SIS17 seems to lose the ability to control the rheological behaviour. The homopolymer starts to dominate more and compatibilising effects are starting to be seen.

Frequency sweeps. From the frequency sweeps the T_{ODT} and the Newtonian behavior have been estimated, presented in Table 4.3. All graphs are available in 8.1.1. The result clearly indicates that the ODT is induced by the homopolymers. At 5wt. % of homopolymer no difference is seen in T_{ODT}, but in the temperature sweep it is seen that the ODT onset was affected all ready at such low fractions. At 15 wt. % homopolymers it is seen that the T_{ODT} have decreased with ~20°C. The Newtonian behavior follows the decrease in T_{ODT} very well. At 70C and 95C it becomes hard to distinguish any temperature independence in the *G''* vs. *G'* curves and Newtonian behavior is not seen. This could imply that no clear ODT occurs above 70 wt. % of homopolymers. At this stage it is believed that the sample is macrophase separated with small domains of ordered/disordered block copolymer. SIS17 is believed to act as a compatibiliser.

Table 4.3: Table of possible ODTs and Newtonian behavior seen for SIS17 and its blends.

Sample	~T_{ODT} (°C)	Newtonian behavior (°C)
SIS17	220	220
5A	220	220
15A	200	200
30A	200	200
50A	180	180
5B	220	220
5C	220	220
15C	200	200
30C	200	200
50C	160	160
70C	Not seen	Not seen
95C	Not seen	Not seen

Transitions. It is seen that the OOT and ODT converges toward each other for the A blends and coincide at 30A, whereas both are induced for the B and C blends. The effect on the transitions of adding homopolymer to block copolymer system is said to depend very much on the M_w of the homopolymer, relative to the M_w of the blocks [34]. The M_w of the blocks in SIS17 is 13 600 for ½PS blocks and 132 800 for the PI blocks. This means that the $M_{w,PS} > M_{w,PS\ blcoks}$ and $M_{w,PI} < M_{w,PI\ blocks}$. Hashimoto et al. and Winey et al. [5] have compared the M_n of an added homopolymer with the M_n of the corresponding block in a block copolymer and indentified three general scenarios for binary blends, explained briefly below:

1. $M_n\ homopolymer < M_n\ block$
   The homopolymer is solubilised in the corresponding domain causing a phase swelling near the surface of the domains. This leads to a change in the interfacial area of the domains and the interface segregation may be affected, resulting in structural changes.
2. $M\ _n homopolymer \approx M_n\ block$
   The homopolymers are solubilised into the corresponding domain centres. Since they are more localized in the centre of the domains the phase swelling will not affect the interfacial area to the same extend, leading to less interference with the blocks in the matrix.
3. $M_n\ homopolymer > M_n\ block.$
   The homopolymer cannot solubilise completely in to the domains. Macrophase separation

occurs and small domains of microphase separated block copolymer may be present in the homopolymer matrix.

These scenarios can be related to the effects that are seen here. The M_w of the PI blocks is ~3 times larger than for PI, why scenario 1 is relevant. The added PI would probably assemble in the PI rich matrix. Swelling the matrix could cause a pressure, due to limited volume, on the cylinders trigging the transition to spheres. An increase of the interfacial curvature seems more beneficial than compression of the PS domains and stretching of the PI domains, thus the transition is seen earlier. This effect has also been seen in a study conducted by Mykhaylyk et al. [7] The PS on the other hand has a larger M_w than the corresponding blocks, why scenario 3 is relevant. Here it is seen that an addition of a homopolymer with larger M_w not necessarily leads to a macrophase separated system, at least not for all fractions. The long chains may partly be solubilised in to the centre of the domains and partly act as bridging blocks between the domains. In order to reach the OOT a larger movement of the chains could be expected and more energy needs to be provided. Thus the temperature needs to be higher in order for the OOT to occur. At larger fractions indications it is believed that the system becomes macrophase separated, with possible domains of ordered/disordered block copolymer.

The ODT is induced in both cases and at high fractions of homopolymer the C blends has the largest decrease in T_{ODT}. Earlier studies have shown that a decrease in T_{ODT} can occur when a sufficiently low M_w homopolymer (low enough to not cause instant macrophase separation) is added to the system [20], hence a decrease in T_{ODT} could be expected. The fact that the decrease is seen in both A and C blends could be explained by the phase swelling and larger interference of the interfaces as the temperature increases.

In this study 15 wt. % of homopolymers contribute with ~20°C lower T_{ODT}. Berglund et al. have conducted a study where a SIS with 14 wt. % PS and M_w ≈146 000 (g/mol) was mixed with SI diblock copolymer. It was shown that the diblock had an impact on G' and the ODT. An addition of 19.5 wt. % and 42.8 wt. % diblock with a M_w ≈72 000 (g/mol) resulted in a ~20°C and ~40°C lower T_{ODT}, respectively, compared to the pure block copolymer.[26] Thus it is believed that homopolymers have a larger effect on the transitions than the corresponding diblocks.

Summary. Phase swelling by addition of homopolymers have a profound effect on the transitions. The effect on the OOT and ODT increases with increasing fraction of homopolymers. The $M_w$of the homopolymer relative the M_w of the corresponding block is believed to be the dominating factor of the phase swelling. Adding the constituent homopolymer of the domains or of the matrix resulted in different behavior. The ODT was induced for all blends, while the OOT was induced for B and C blends and delayed for A blends. At 30A the OOT and ODT onset coincided and it is believed that macrophase separation started to dominate at this point. None of the transitions were seen in the temperature sweeps at 50A and 50B, but frequency sweeps indicated that the ODT still occurred. At high fractions (~70 wt. %) of homopolymers the ODT is believed to not occur. Instead it is believed that a macrophase separated system with domains of ordered/disordered block copolymer is present. Compatibilising effects started to appear at these fractions.

4.2.2 Blends of polyethylene-*b*-poly(ethylene glycol) and polyethylene

Since the frequency sweeps of the PbPs not were considered to be reliable only temperature sweeps were conducted for the blends of PbP and PE. Only PE homopolymers were used in these blends due to that the PEG was considered to not be comparable with the PbPs. Therefore the compatibilising effects have not been investigated.

The temperature sweeps of PbP50 and PbP80 with blends of 30 and 50 wt. % PE are seen below (Figure 4.17 and Figure 4.18). It is clearly seen that PE have an effect on the rheological behavior. Since the rheological measurements of pure PbP not provided with any information regarding the transitions it is impossible to know whether or how the addition of PE has affected the transitions. For both PbPs it is seen that adding PE both has an increasing effect on G' and the temperature sensitivity. For pure PbP50 and PbP80 the maximal temperatures before the measurements become unusable were ~105°C and ~83°C, respectively. Adding PE shows that this temperature can be delayed due to that the PE crystals holds the sample together up to ~130°C. The largest effect is seen when comparing PbP80 with PbP80-50PE where the difference is about ~50°C. According to the results is seem like PbP can be used as a softener in PE. Since the blends were made with mechanical dry mixing and only melted during the pressing of the samples a homogeneous blend may not have been reached. This could have caused less phase swelling effects in the samples. Melting or solution blending could have resulted in different behavior.

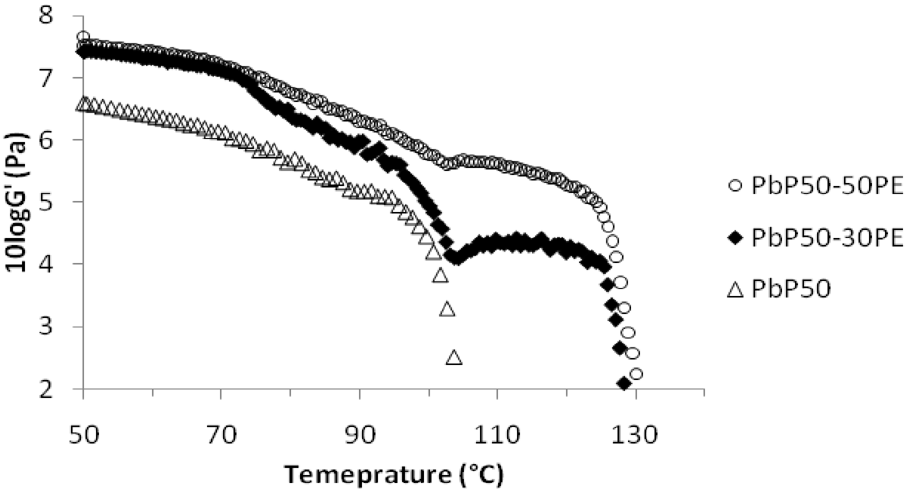

Figure 4.17: Temperature sweeps of PbP50 and in blends with 30 and 50wt. % PE. The effect from the added PE is clearly seen. G' of PbP50 completely drops at ~105°C whereas in the blends the PE can prolong this up to ~130°C when the PE crystals melt.

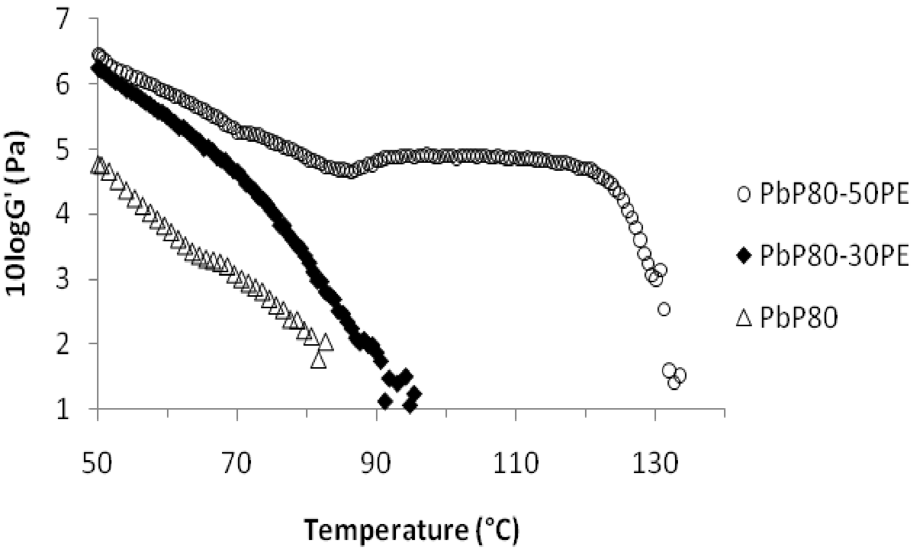

Figure 4.18:Temperature sweeps of PbP80 and in blends with 30 and 50wt. % PE. The effect from the added PE is clearly seen, foremost for 50 wt. % PE. G' of PbP80 drops at ~80°C whereas in the blends the PE can prolong this up to ~130°C when the PE crystals melt.

5. Conclusions

5.1 Rheological behavior of different phases

SIS system. For the SIS system rheological measurements can be used to indicate transitions, but in order to indentify the phase imaging instruments are needed. All three SIS samples are believed to undergo an ODT at SIS14~240°C, SIS17~220°C and SIS22 above 260°C. It is believed that SIS17 undergoes an OOT from cylinders to spheres at ~150°C and that SIS14 not have an OOT. Based on results and supportive literature an OOT could be identified for SIS22.

Samples with the same phase and a similar M_w exhibited a similar rheological behavior. The similarity seems to decrease with increasing difference in M_w. The overall rheological behavior appears to be strongly related to the M_w and polydispersity. It is believed that the phase, composition and the M_w are related to the transition temperatures. The polydispersity seems to affect block copolymers in nearly all aspects. The sudden drop in G' seen near the ODT for both SIS22 and SIS17, but absent for SIS14, could not be explained due to insufficient material characterisation.

PbP system. PbP50 is believed to have an ODT at ~105°C and no OOT. Based on results and supportive literature neither an ODT nor and OOT could be identified for PbP80. The T_m of the blocks and ODT can be seen in rheological measurements, but possible OOT could not be distinguished. The M_w, polydispersity and composition have a large effect on the crystalline behavior.

It is believed that the M_w, especially of the PE blocks, have an important role for the transitions and the rheological behavior. The transitions in semicrystalline block copolymers seem related to the crystallisation process of the blocks, but not dependent. Based on earlier studies it is believed that the chains adopt an ordered phase already in the molten state and that crystallisation of PE starts in the ordered phase. During this crystallisation other ordered phases can be adopted until the PEG blocks have crystallised.

The information provided by rheological measurement has not been sufficient in order to study the phase transitions in the PbPs. Other analysing instruments such as SAXS, WAXD, TEM, DSC and polarized light microscopy (PLM) appear more suitable for this purpose. [5,37,38,39]

5.2 Phase swelling and compatibilising effects

SIS system. Phase swelling by addition of homopolymers has a profound effect on the transitions. The effect on the OOT and ODT increases with increasing fraction of homopolymers. Addition of the constituent homopolymer of the domains or of the matrix resulted in different behavior. Addition of PI results in an induced OOT and ODT, while addition of PS results in a delay of the OOT and an induced ODT. The small amount of PS in the C blends did not differ from the B blends. For the C blends the OOT was seen up to 30 wt % homopolymer and above 70 wt. % homopolymer the ODT was no longer seen. At these addition levels compatibilising effects appear instead. The OOT and ODT coincide at 30 wt. % PS. When the transitions not were seen anymore it is believed that macrophase separation dominates and that small domains of ordered/disordered block copolymer may be present. Addition of the constituent homopolymer has a larger effect on the rheological behaviour than addition of the corresponding SI diblock. The M_w of the homopolymer relative the M_w of the corresponding block is a dominating factor with regard to the phase swelling.

Adding the corresponding homopolymer to an amorphous triblock copolymer system affects both the OOT and ODT. The ODT is induced when adding both the minor and major homopolymer, regardless the M_w.When adding the major polymer the OOT will be induced for both higher and lower M_w than the corresponding block. When adding the minor polymer with a lower M_W than the corresponding blocks the OOT is induced and adding a higher M_W delays the OOT. At a sufficiently large fraction or high M_w of the homopolymer macrophase separation will occur.

PbP system. From the results it is believed that PbP can be used as a softener in PE. The compatibilising effects could not be investigated in this study due to that the PEG not is comparable with the PbP. Since the blends were made with mechanical dry mixing the maximal phase swelling effects may not have been seen. Melting or solution blending could have resulted in a different behavior.

6. Recommendations

It have been seen that the M_w and polydispersity have an important role in case of rheological behavior. For further studies it is recommended to investigate to what extent differences in M_w and polydispersity affect the transitions and rheological behavior. Further material characterisation of the materials used here is necessary in order to analyse the results further.

In this study transitions and present phases have been estimated by comparing results with supportive literature. In order identify the present phase and the effect the phase swelling brings to the phase separation access to imaging instrument such as TEM is required.

For further investigation of transitions in PbP other or additional measurements than only rheology is recommended, as for example SAXS and TEM. If possible it is also recommended to investigate PbPs with higher M_n in order to minimise possible effects from oligomers.

7. References

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8. Appendix

8.1 Appendix I - Rheological and DSC measurements

8.1.1 Poly(styrene-*b*-isoprene-*b*-styrene) system

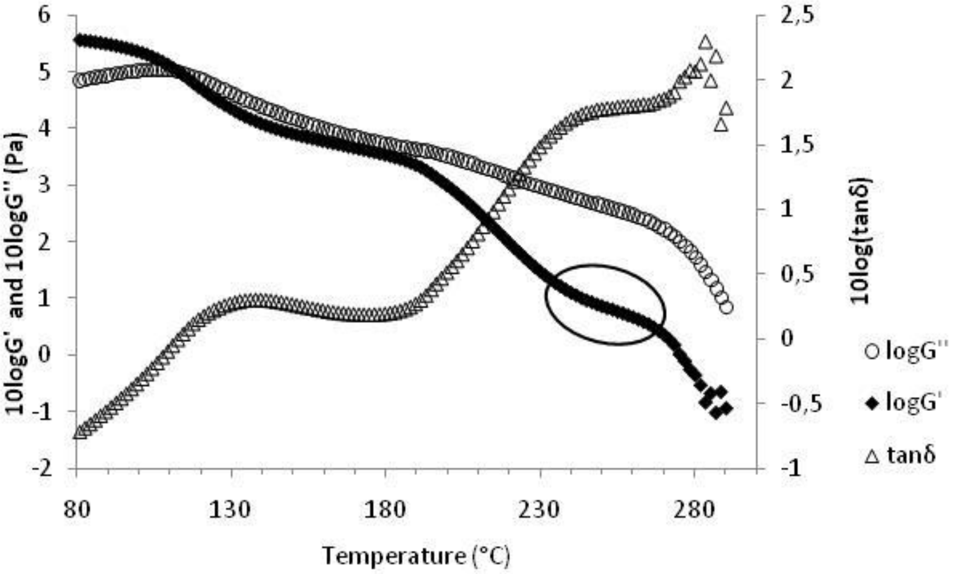

Figure 8.1: Temperature sweep of SIS14. No indication of an OOT is seen. At ~240°C a plateau is seen in G', black circle. This is believed to be related to an ODT.

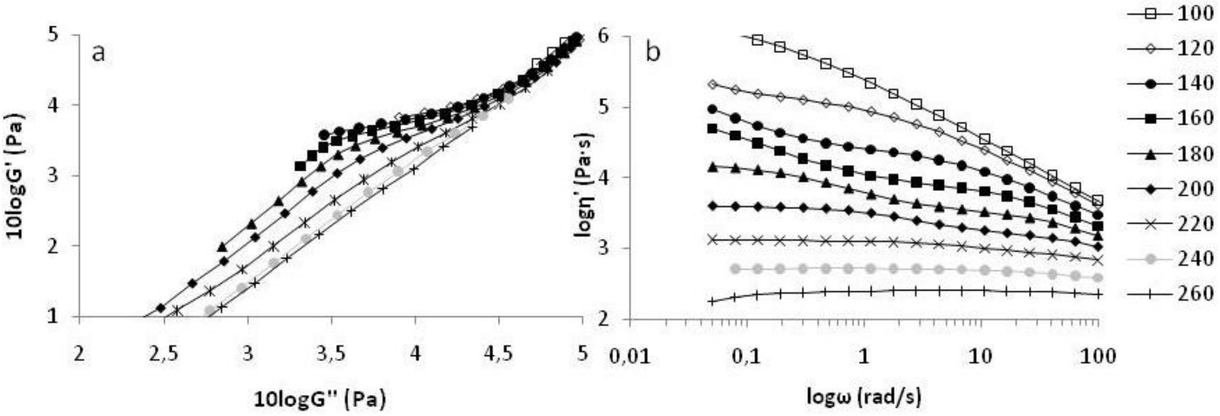

Figure 8.2: Frequency sweep of SIS14 at different isothermals. The numbers in the legend refers to temperatures in °C. At T~240 °C temperature independence is seen in a (grey curve). Newtonian behavior is seen at the same temperature in b (grey curve). This is believed to be the T_{ODT}.

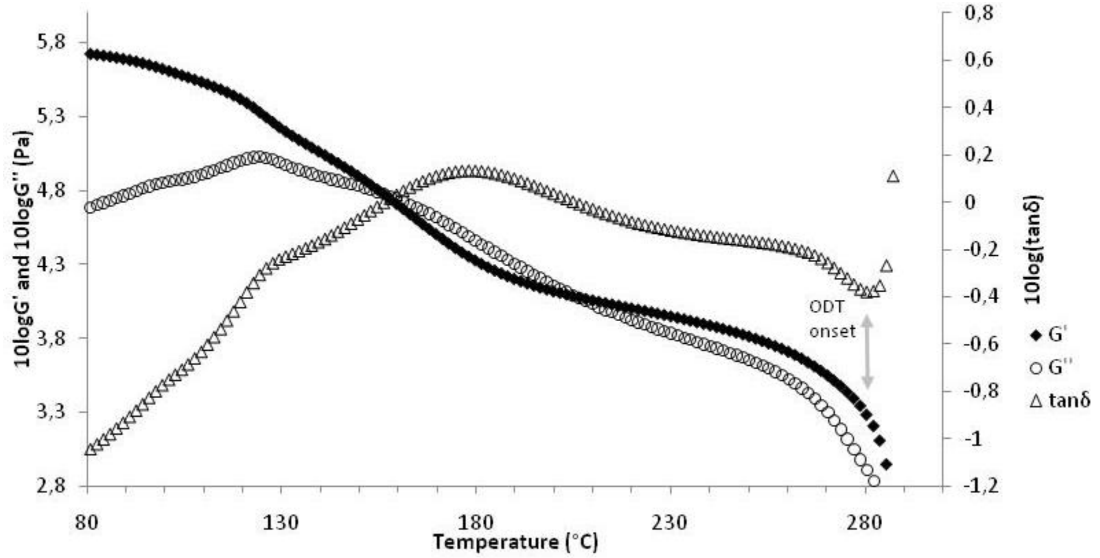

Figure 8.3: Temperature sweep of SIS22. No indication of an OOT is seen. At ~280°C there is a sudden drop in G' and G'' and a peak in tanδ (grey arrow). This is believed to be related to an ODT.

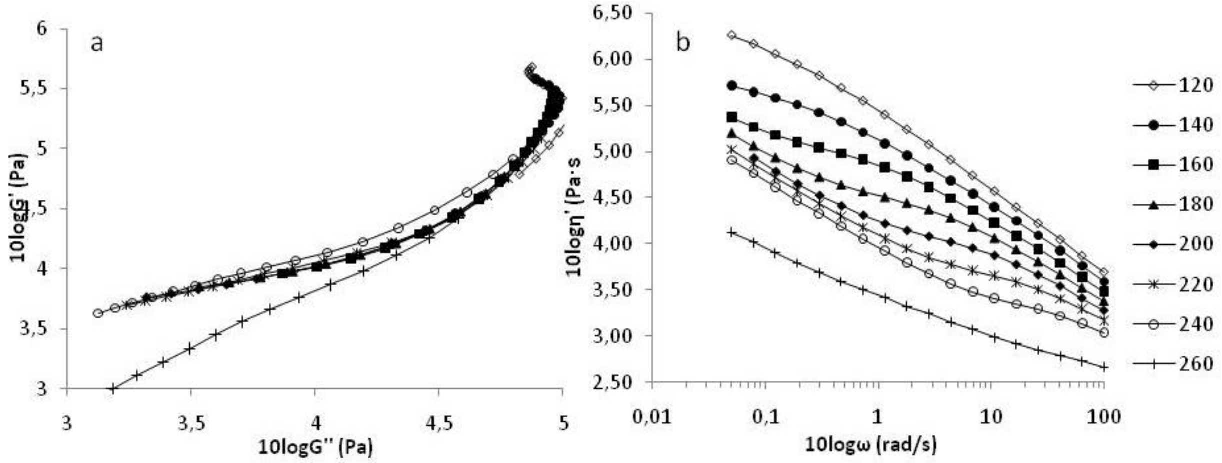

Figure 8.4: Frequency sweeps of SIS22 at different isothermals. The numbers in the legend refers to temperatures in °C. No clear temperature independence or Newtonian behavior is seen. At ~260°C it is seen that something is happening in the sample. It is believed that an ODT will occur above this temperature, which also is indicated in Figure 8.3.

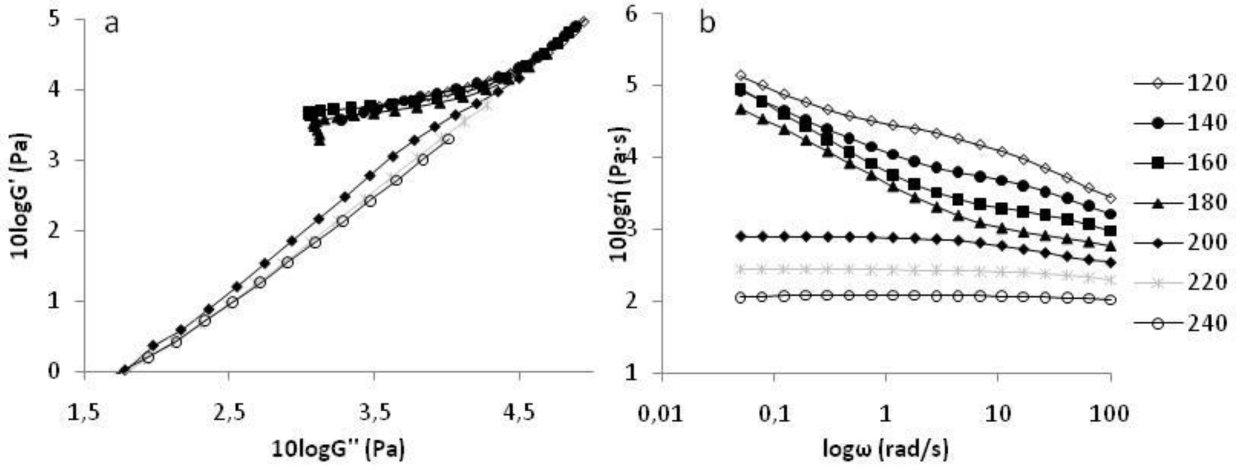

Figure 8.5: Frequency sweep of 5A at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~220°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

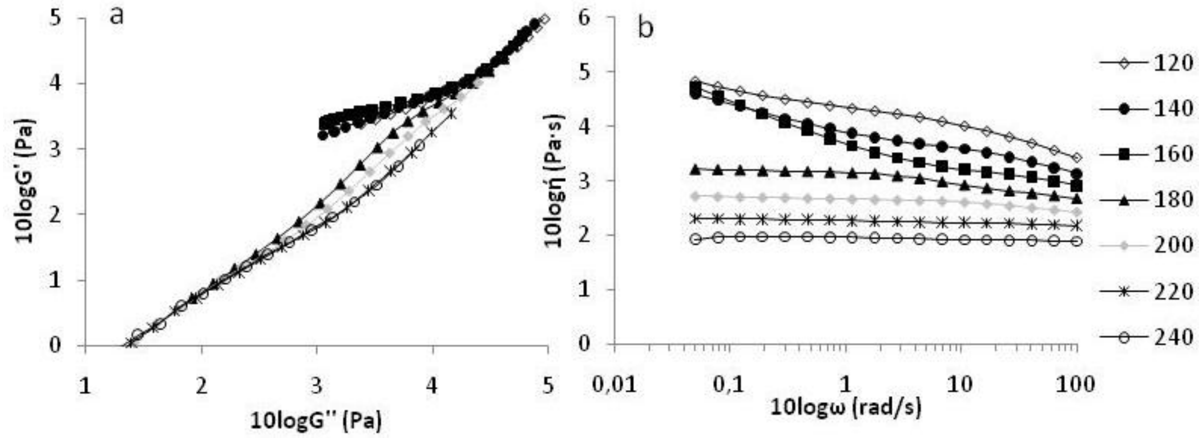

Figure 8.6: Frequency sweep of 15A at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~200°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

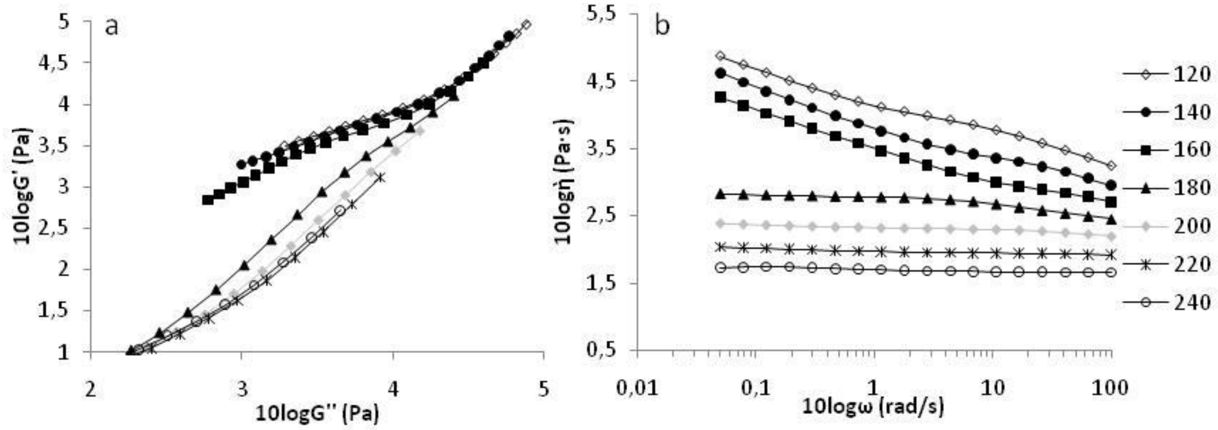

Figure 8.7: Frequency sweep of 30A at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~200°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

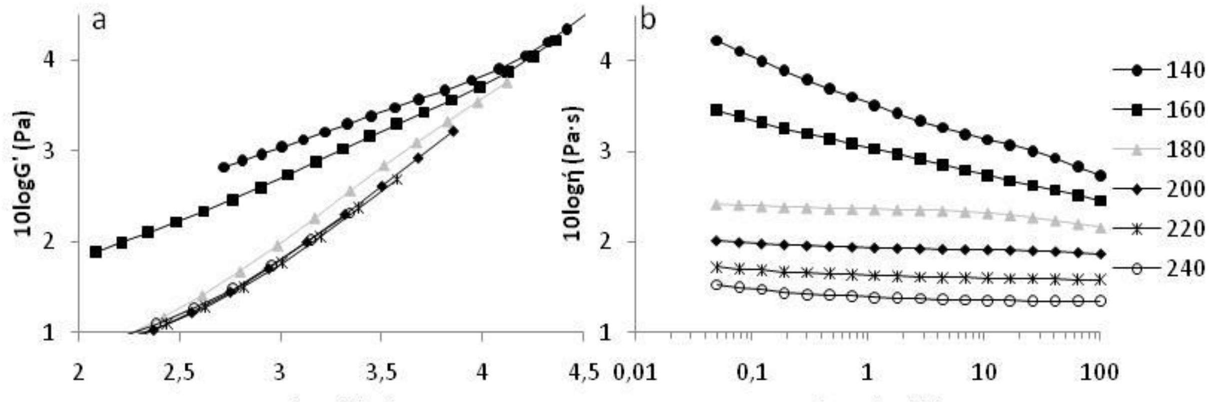

Figure 8.8: Frequency sweep of 50A at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~180°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

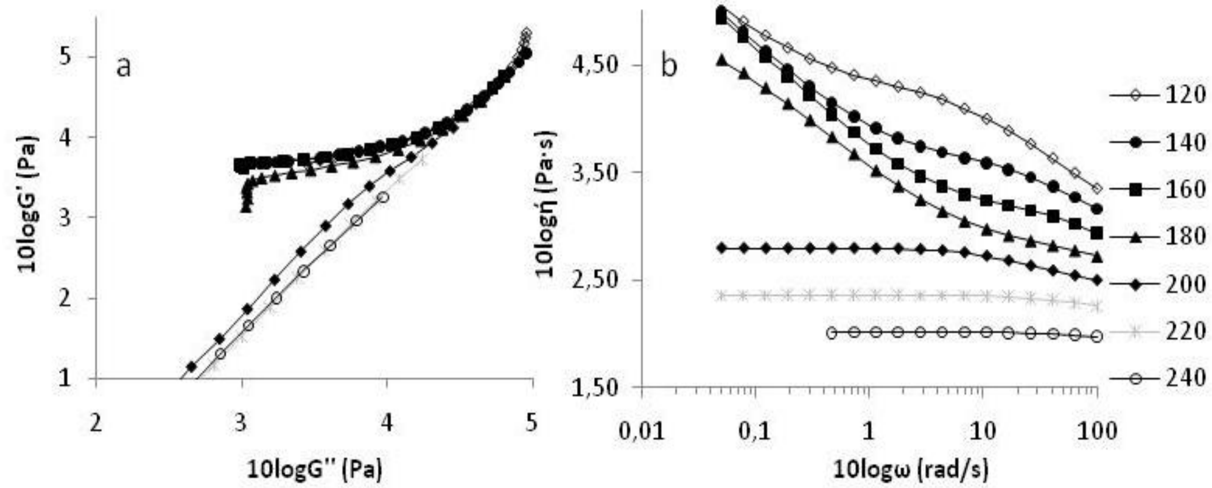

Figure 8.9: Frequency sweep of 5B at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~220°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

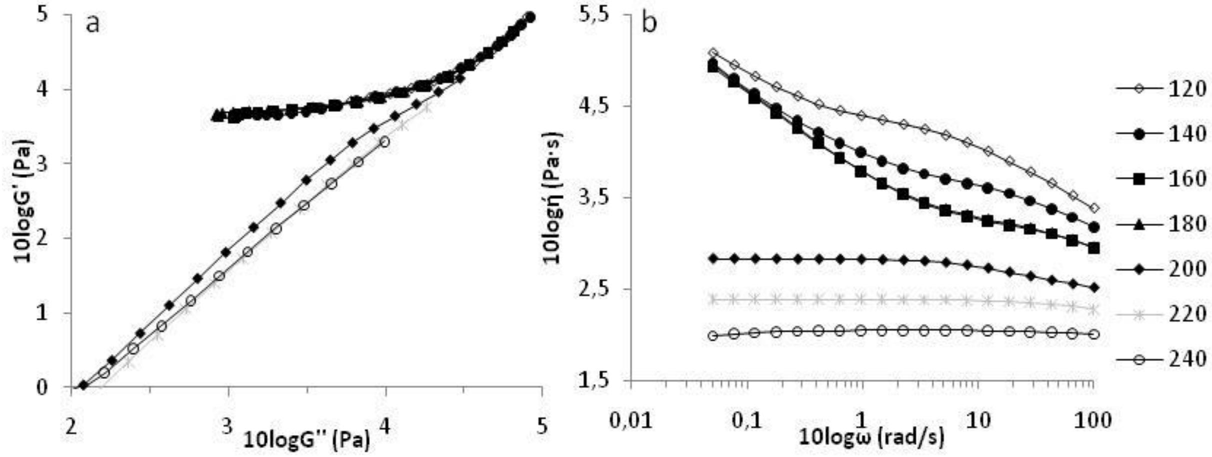

Figure 8.10: Frequency sweep of 5C at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~220°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

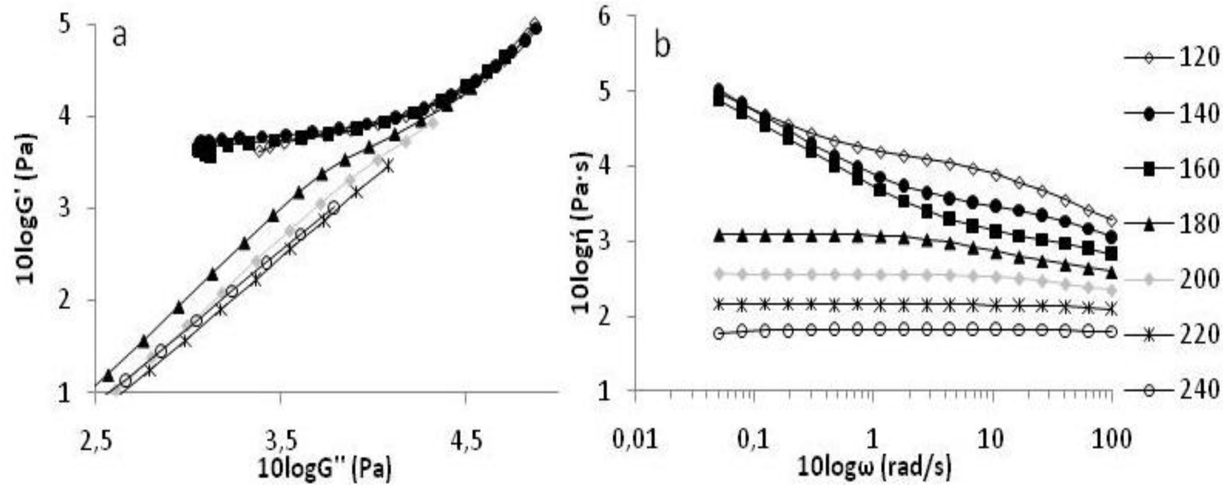

Figure 8.11: Frequency sweep of 15C at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~200°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

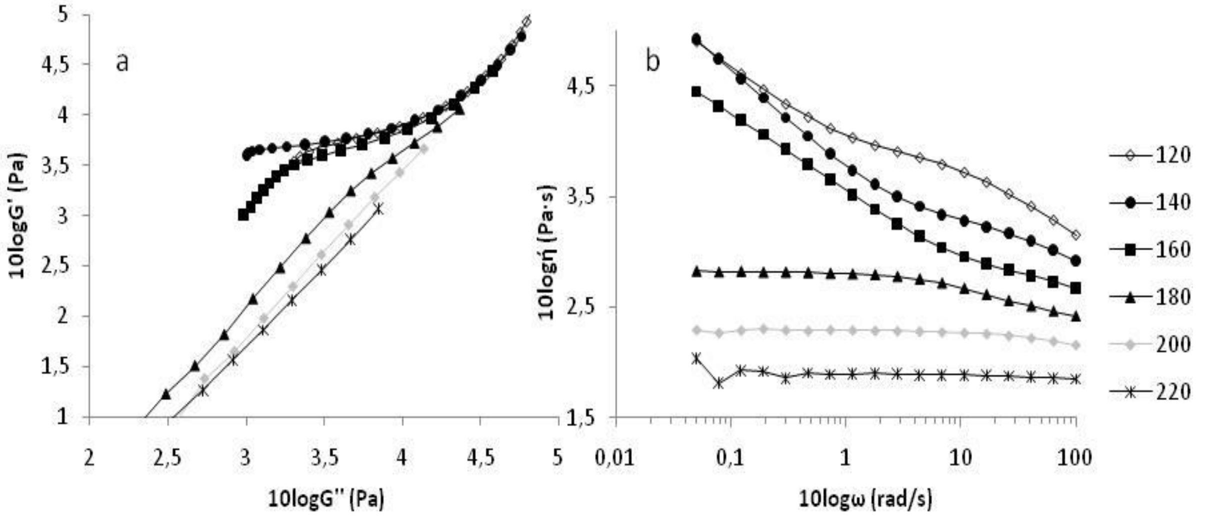

Figure 8.12: Frequency sweep of 30C at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~200°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

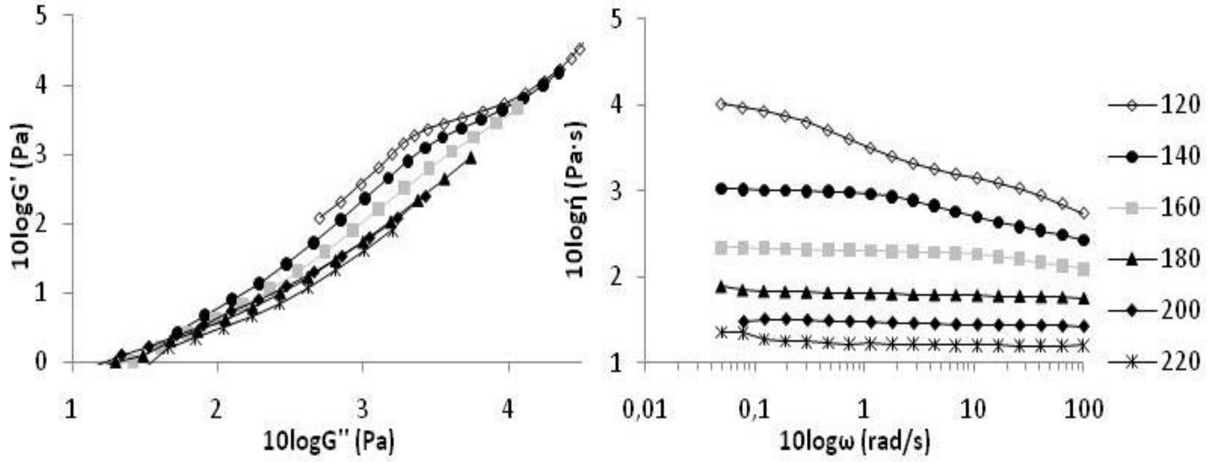

Figure 8.13: Frequency sweep of 50C at different isothermals. The numbers in the legend refers to temperatures in °C. Temperature independence is seen at ~160°C, grey curve in fig. a. Newtonian behavior for ω=0,05-10 rad/s is seen at the same temperature, grey curve in fig. b. This is believed to be the T_{ODT}.

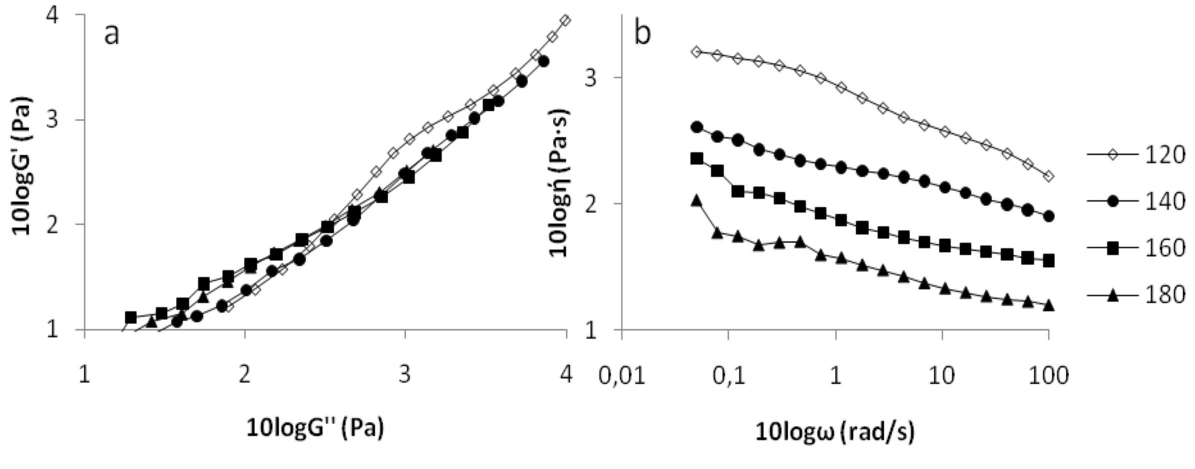

Figure 8.14: Frequency sweep of 70C at different isothermals. The numbers in the legend refers to temperatures in °C. At ~140°C the curves starts to become linear (a). This could be an indication of an ODT, but this is not verified by Newtonian behavior (b). Therefore it is believed that 70C not undergoes an ODT.

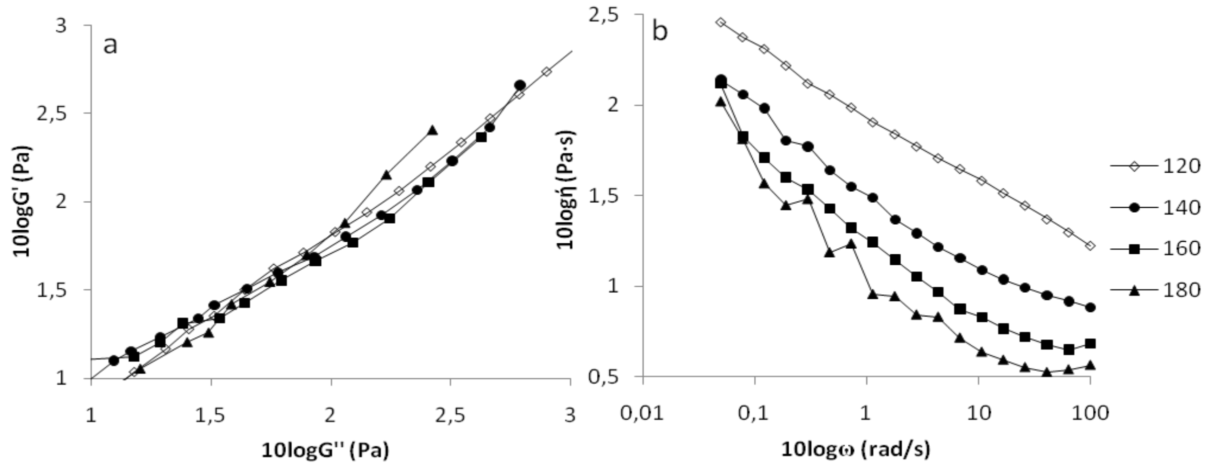

Figure 8.15: Frequency sweep of 95C at different isothermals. The numbers in the legend refers to temperatures in °C. No indications of an ODT is seen in either a or b. It is believed that 95C not undergoes an ODT.

8.1.2 Polyethylene-*b*-poly(ethylene glycol) system

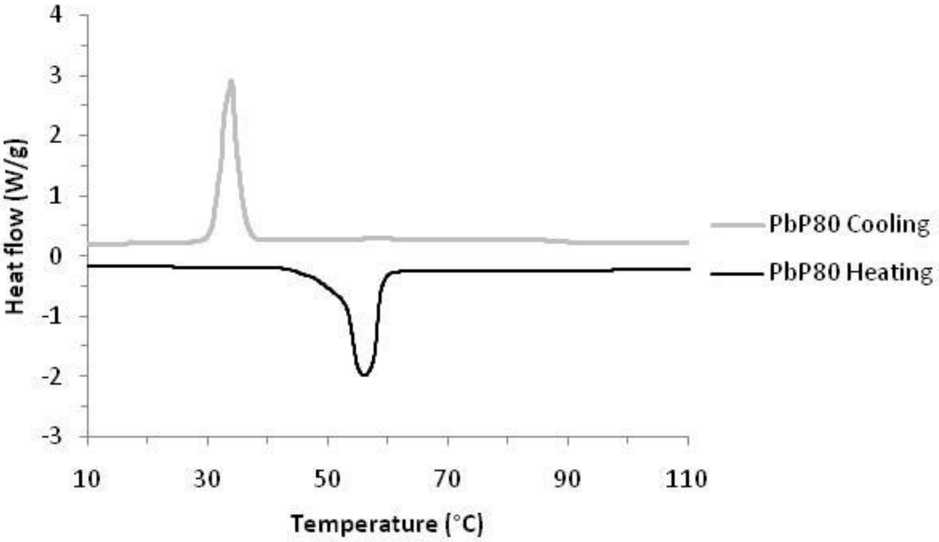

Figure 8.16: DSC scan of PbP80. The peak at ~60°C is believed to be the T_m of the PEG blocks. At ~90°C there is a small drop that is believed to be the T_m of the PE blocks.

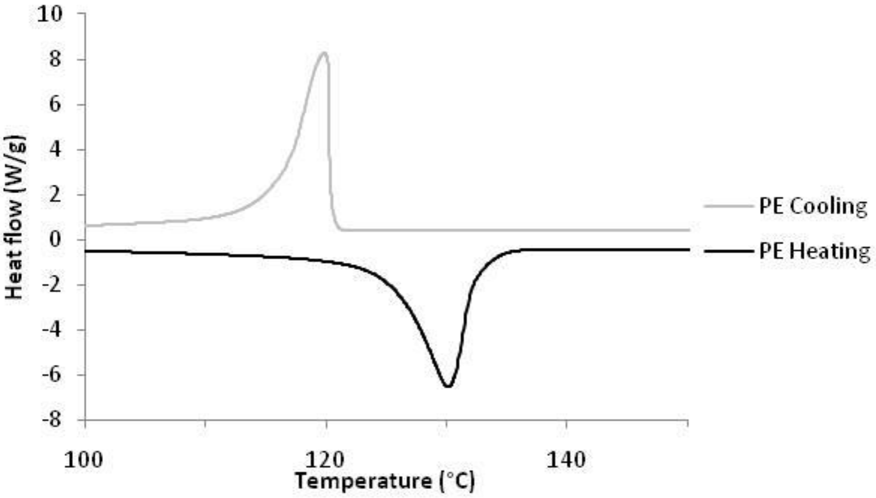

Figure 8.17: DSC scan of PE homopolymer. The peak at ~130°C is believed to be the T_m.

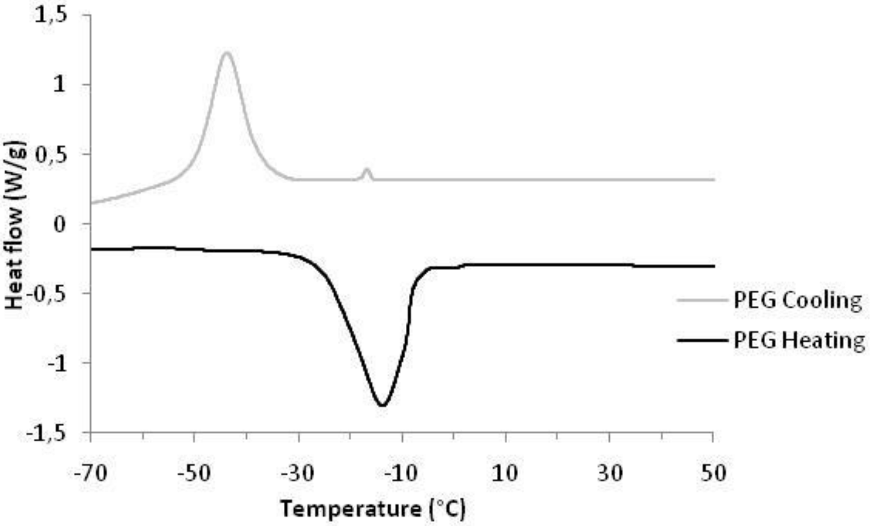

Figure 8.18: DSC scan of PEG homopolymer. The peak at ~-10°C is believed to be the T_m. This is very low why the PEG is considered to be incomparable with the PbPs.

8.2 Appendix II – Sample overview

Name	**Composition**
SIS-system	
PS	Polystyrene
PI	Polyisoprene
SIS14	Poly(styrene-*b*-isoprene-*b*-styrene) with 14wt. % PS
SIS17	Poly(styrene-*b*-isoprene-*b*-styrene) with 17wt. % PS
SIS22	Poly(styrene-*b*-isoprene-*b*-styrene) with 22wt. % PS
5A	SIS17 with 5wt. % PS
5B	SIS17 with 5wt. % PI
5C	SIS17 with 5wt. % homopolymer blend with 17wt.% PS and the rest PI
15A	SIS17 with 15wt. % PS
15B	SIS17 with 15wt. % PI
15C	SIS17 with 15wt. % homopolymer blend with 17wt.% PS and the rest PI
30A	SIS17 with 30wt. % PS
30C	SIS17 with 30wt. % homopolymer blend with 17wt.% PS and the rest PI
50A	SIS17 with 50 wt. % PS
50C	SIS17 with 50wt. % homopolymer blend with 17wt.% PS and the rest PI
70C	SIS17 with 70wt. % homopolymer blend with 17wt.% PS and the rest PI
95C	SIS17 with 95wt. % homopolymer blend with 17wt.% PS and the rest PI
PE-PEG system	
PE	Polyethylene
PEG	Poly(ethylene glycol)
PbP50	Polyethylene-*b*-poly(ethylene glycol) with 50wt. % PEG
PbP80	Polyethylene-*b*-poly(ethylene glycol) with 80wt. % PEG
PbP50,30	PbP50 with 30wt. % PE
PbP50,50	PbP50 with 50wt. % PE
PbP80,30	PbP80 with 30wt. % PE
PbP80,50	PbP80 with 50wt. % PE