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**Long Time Stress Relaxation of a triblock copolymer with asymmetric  
composition**

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For Peer Review

## Abstract

The long-time stress relaxation was examined for poly(styrene)-poly(ethylene-*co*-butylene)-polystyrene triblock copolymer with asymmetric composition in the microphase separated state. Stress relaxation data from a parallel plate rheometer were extended to very long times by using a newly built compression instrument. Three properties were measured, the relaxation time spectrum, the equilibrium modulus, and the instantaneous modulus. Relaxation experiments over several months (without zero drift) allowed determination of extremely long relaxation times as found in soft solids and in liquids near the gel point. In this way, we can distinguish solid from liquid behavior within the experimental time frame. The BCC lattice structure of the test polymer behaves as liquid except at low temperature where an equilibrium modulus was observed in an experiment that lasted over a period of four months. The corresponding instantaneous modulus was observed to be constant for the same material and for the same time period.

Keywords: stress relaxation, equilibrium modulus, triblock copolymer, microphase separation

## Introduction

Block copolymers microphase separate below a certain temperature, called “microphase separation temperature” ( $T_{MST}$ ), and form ordered domains the morphology of which depends on the temperature, volume fractions, and the compatibility between the blocks. The phase behavior of block copolymers is well understood (Fredrickson and Bates, 1999). Less clear is the dynamics of such block copolymers, especially near their

ordering transitions. Many studies in the literature have addressed the question whether microphase separated block copolymers behave as a solid or not. The rheological signature of a solid is a true plateau in  $G'$  at low frequency (or a finite equilibrium modulus over longer times). Kossuth *et al.* (1999) claim that only those block copolymers that form the cubic phases upon microphase separation show such true plateau in  $G'$  at lower frequencies. Defects in the lattice order will cause this plateau not to extend to zero frequency as it can be found with perfect crystals. Other block copolymer morphologies, such as cylinders and lamellae, are not able to exhibit a true plateau in  $G'$  at low frequencies (Koppi *et al.*, 1992, Rosedale and Bates, 1990, Kawasaki and Onuki, 1990, Ryu *et al.*, 1997). On the other hand, experiments on a triblock copolymer, styrene-isoprene-styrene with cylindrical domains, after flow induced ordering showed a plateau in  $G'$  at low frequencies (Winter *et al.*, 1993).

For a polymer with two distinct blocks in particular, when the composition of the two blocks is highly asymmetric, spherical domain morphology is obtained and the spheres of the shorter blocks arrange on a body centered cubic (BCC) lattice in a continuous matrix formed by the major block. The ordering of the microspheres on cubic lattice occurs only below a certain temperature that is called “lattice ordering temperature”,  $T_{LOT}$  (Shibayama *et al.*, 1983, Kim *et al.*, 1999). This temperature is substantially lower than the  $T_{MST}$ . At all temperatures between  $T_{LOT}$  and  $T_{MST}$ , the microspheres of the block copolymer assume liquid-like short-range order in the continuous matrix of the major phase (Shibayama *et al.*, 1983, Kim *et al.*, 1999, Sakamoto and Hashimoto, 1998). Additional temperature effects enter when the block

copolymer is cooled below one of the microphase separated domains's glass transition temperature,  $T_g$ .

The solidification in such cubic phase block copolymers may occur because of any of the following three mechanisms: 1) lattice ordering, 2) formation of a physical network due to the tie molecules (for tri-blocks or multi-blocks), and/or 3) formation of a "soft glass" (disordered solid state). Each mechanism is associated with a particular nano-scale structure that depends on thermal and mechanical history. Kleppinger *et al.* (1998) state that below  $T_g$  the nanospheres act as physical cross-links, i.e. bridging is supposed to be the solidifying mechanism. On the other hand, Kim *et al.* (1999) have observed that between  $T_g$  and  $T_{LOT}$ , the interdomain bridging due to tie molecules between nanospheres does not result in solidification. Without the lattice order, their material behaved as a liquid.

Throughout the literature, there is a controversy over the block copolymers being solid or liquid especially at long times (or at very low deformation rates). At low deformation rates, BCC-nanophase block copolymers have sometimes been described as viscoelastic solids having a yield stress and an equilibrium modulus (Hashimoto *et al.*, 1983, Watanabe and Kotaka, 1984). Sebastian *et al.* (2002) studied the steady shear rheology of the cubic phases of di- and tri-block copolymer melts and found that, at very low shear rate (shear stress), these materials flow with a Newtonian viscosity rather than showing a yield stress. However, the BCC lattice is preserved during the flow at these low shear rates, which was confirmed by SAXS. This may be explained with a defect mediated flow mechanism (as in metals and ceramics) that gives rise to Newtonian creep at low deformation rates (Kossuth *et al.* 1999).

It should be noted that most of the above studies were carried out in the melt state or in the strongly diluted state avoiding the material states that relax very slowly. Even then, there seems to be a controversy about the solid or liquid behavior. It is nearly impossible to investigate the behavior when the relaxation mechanisms slow down to an extent that they occur outside a reasonable experimental window.

In view of this, there is a definite need to devise an experiment that measures the long relaxation times and conclusively discerns whether physical gels, such as microphase separated block copolymers, are true solids or still liquids. In this paper, a new technique has been used to accomplish this task, at least for time scales of several months. The experiments focus on the relaxation modulus that will be measured in a clearly defined stress relaxation experiment. For this purpose, the test sample gets deformed by a strain  $\gamma$  and held in the strained state ( $\gamma(t)=\gamma_0=\text{constant}$ ) for extended times while the resulting stress  $\tau(t)$  is measured. The stress is largest when the strain is first introduced and decays with time. The relaxation modulus

$$G(t) = \frac{\tau(t)}{\gamma_0} \quad (1)$$

is the material property that expresses this phenomenon of stress relaxation, both for liquids and for solids as well. A special case of the relaxation modulus is the “linear relaxation modulus” which is measured when the strain in the sample is very small so as not to disturb the equilibrium structure of the sample. It is defined as

$$G^0(t) = \lim_{\gamma_0 \rightarrow 0} \frac{\tau(t)}{\gamma_0} \quad (2).$$

Stress relaxes quite rapidly in low molecular weight liquids as long as the molecules do not associate by some long-range interaction. Less clear is the experiment

for structured fluids such as gels, associative networks, microphase separated block copolymers, colloidal solutions that form physical gels. Fast dynamics is associated with small-scale relaxation processes (small molecules, molecular strands, subunits of molecules) and, vice versa, slow dynamics belongs to macromolecular motions or long-range correlation of supermolecular motions (physical aggregation, for instance). This viscoelastic nature of polymers (and other complex fluids) requires a further effort when performing a relaxation experiment that covers a sufficiently wide time window.

The relaxation modulus  $G^0(t)$  is chosen here for a second reason. The stress in an equilibrated material is fully defined by the classical theory of linear viscoelasticity of Boltzmann (see Ferry (1980), for instance). In this theory,  $G^0(t)$  has great significance since it is the only material function required (at constant density) to calculate the stress  $\tau(t)$  as a function of any strain history  $\gamma(t;t') = \int_{t'}^t dt'' \dot{\gamma}(t'')$  for  $-\infty < t' < t$  as long as the memorized strain does not exceed the “linear viscoelastic limit”. This can be expressed in a memory integral

$$\tau(t) = \int_{-\infty}^t dt' G^0(t-t') \dot{\gamma}(t') = \int_{-\infty}^t dt' \left( \frac{\partial G^0(t-t')}{\partial t'} \right) \gamma(t;t') \quad (3).$$

The variable  $(t-t')$  denotes the distance to a strain-event in the past at  $t'$ , where  $t$  is the current time and  $t'$  is the instant in past. The linear relaxation modulus  $G^0(t)$  governs shear experiments equally well as extensional experiments. The conversion from one to the other requires geometry factors (Trouton factor, see Bird *et al.*, 1987 for instance).

A fundamental difference between a solid and a liquid is that the stress in a solid (at constant strain) decays to a finite value over a period of time while, for a liquid, it decays to zero. Only the solid has a long-time modulus that is finite.

$$\lim_{t \rightarrow \infty} G^0(t) = \begin{cases} 0 & \text{(liquid)} \\ G_e & \text{(solid)} \end{cases} \quad (4).$$

The long-time modulus of the solid is called “equilibrium modulus”,  $G_e$ . This difference in relaxation behavior serves as a useful criterion to distinguish solids from liquids. In comparison, the liquid has a finite viscosity in steady shear flow, while the steady shear viscosity is undefined for a solid (no steady shear flow can be achieved for a solid below yield stress or within the “linear viscoelastic region”).

The modulus is often expressed in a discrete spectrum

$$G^0(t) = G_e + \sum_{i=1}^{\infty} g_i e^{-t/\lambda_i} \quad (5).$$

Two contributions are clearly separated: a constant equilibrium modulus  $G_e$  (solids only) and a transient part that governs the relaxation dynamics. If the experimental time is very long as compared to the longest relaxation time, the measured value of  $G^0(t)$  approaches the equilibrium modulus  $G_e$  of the material.

This study concerns materials that relax very slowly; their study requires very long experimental times in the order of the longest relaxation time are. However, we also consider the other extreme of an experiment that is short enough so that any relaxation is still negligibly small. We introduce a characteristic shortest relaxation time,  $\lambda_{\min}$ , that is required for allowing any significant short-time dynamics to occur. If a meaningful  $\lambda_{\min}$  exists for a given material, then it is possible to devise a short time experiment (relatively



speaking) in which the experimental time is much shorter than  $\lambda_{\min}$  and the measured stress is governed by the instantaneous modulus,  $G^0(0)$

$$G^0(0) = G_e + \sum_{i=1}^{\infty} g_i \quad (6).$$

In this application (experimental time  $\ll \lambda_{\min}$ ), the instantaneous modulus is equal to the “incremental modulus” (Horst et al., 2003).

The conventional technique of measuring  $G^0(t)$  is the “dynamic mechanical spectroscopy”. Several advantageous specifics come together in mechanical spectroscopy: oscillatory shear in commercial rheometers has advanced to a highly accurate level, the spectroscopic character of the experiment results in high resolution over a wide range of time scales, and oscillatory data can be converted easily from the frequency to the time domain (Baumgärtel and Winter, 1989). The time domain of the  $G(t)$  data corresponds to the inverse of the frequency domain of the experiment. Typically, the frequency domain can be widened by “time-temperature superposition” (whenever it applies). However, even at this rather advanced state of mechanical spectroscopy, the extremely low frequency behavior that corresponds to the long time behavior of the sample cannot be measured accurately. Typical problems arise from insufficient resolution of low stress levels and from long time zero drift of the transducers that are used to measure the relaxing stress in conventional measuring devices.

In this study we utilize a recently built stress relaxation apparatus (called the “relaxometer” hereafter) for relaxation experiments that may last for several months. The special features of the relaxometer are high resolution of the stress measurements and complete elimination of the zero drift problems (Horst et al., 2003). The instrument has been specifically designed for stress measurement in soft materials. Here we apply the

instrument, for the first time, for distinguishing liquid from solid behavior of a soft polymer on both sides of its liquid-solid transition. In addition, we measure the relaxation time spectrum and, whenever possible, the instantaneous modulus. A microphase separated block copolymer was chosen as model system. The material is especially interesting for this study since it is a physical gel that may flow at long times even if it looks like a solid during the short exposure time of mechanical spectroscopy. The data from the stress relaxation experiment are compared with the data from mechanical spectroscopy.

### Materials

For studying the long-time behavior near the liquid-to-solid transition, we selected a poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] tri-block copolymer (SEBS), supplied by Shell (commercial name Kraton G1650). It contains about 29wt% polystyrene and has a number average molecular weight  $M_n = 94000$  and a polydispersity index of 1.15. The midblock of the polymer was selectively swollen with an extender oil (commercial name Fina Vestan) having a number average molecular weight of 600. All the samples used in this study contain 20wt% of the tri-block copolymer (termed as SEBS20 henceforth). The microphase separation temperature is about 120 °C whereas the glass transition temperature of the polystyrene phase is about 60 °C. (Soenen *et al.*, 1997)

### Sample Preparation

The details of the sample preparation are discussed elsewhere (Soenen *et al.*, 1997). Basically, a mechanical stirring device was used to dissolve the polymer in the oil at high temperatures (150-180°C). The samples used in all of the experiments were first annealed at 100°C. Fig 1 shows SAXS profile of SEBS20 after annealing. The SAXS

profile was recorded at room temperature. It is evident from the position of the primary and secondary peaks that the morphology corresponds to that of the BCC lattice. However, it should be noted that the annealed sample contains grains, which have different orientations of the lattice directrices, and does not have a highly ordered long-range structure. Hence, the X-ray pattern showed concentric rings.

### **Experimental Apparatus and Protocol**

Two types of experiments were carried out: dynamic mechanical spectroscopy and stress relaxation in a newly developed compression device (Relaxometer).

For dynamic mechanical spectroscopy in an ARES rheometer (Rheometric Scientific, now TA Instruments), a disk-shaped sample was first heated to 150°C and held there for 10 minutes. Then it was cooled to 100°C and annealed at this temperature for 2 hours for development of BCC structure and then subjected to oscillatory shear at different temperatures at and below the annealing temperature.

The second instrument is the Relaxometer (Horst *et al.*, 2003). Its design is dedicated to stress relaxation experiments on soft solids. Its mode of operation depends on the characteristic material time scales. For slowly relaxing materials (for the material in this study at temperatures at or below 50°C for), a relatively thick sample (about 10 mm in height) is mounted into a compression jig (with bolts and suitable spacers) so that it gets compressed between two parallel surfaces. During the entire experiment, the sample will be held at constant compression strain. In order to measure the restoring force in the sample, the initial compressive strain (due to spacers and bolts in the jig) is modulated with an incremental strain while measuring the force response. The total force gives the compression modulus and the slope of the stress-strain curve gives the

instantaneous modulus  $G^0(0)$ . Stress experiments get repeated periodically over long periods of time that may last several months.

The compression strain imposed by the relaxometer,  $\varepsilon = \varepsilon_0 H(t - t_0) + \Delta\varepsilon^i H(t - t_1)$ , consists of two contributions that get applied at different times as expressed by a Heaviside function  $H(x)$ . Time  $t_0$  is the time when the sample is loaded into the compression jig and the initial strain  $\varepsilon_0$  is introduced. The incremental strain of magnitude  $\Delta\varepsilon^i$  at time  $t_1$  has the purpose of probing the residual stress in the sample and of measuring the incremental modulus. The total strain is kept small so that the sample remains in the equilibrium state where the linear viscoelastic relations are valid. For the compression experiment in the relaxometer, eq. 3 simplifies to

$$\begin{aligned}\sigma(t) &= \int_{-\infty}^t dt' \left( \frac{\partial E(t-t')}{\partial t'} \right) \varepsilon(t; t') \\ &= \int_{-\infty}^{t_0} dt' \left( \frac{\partial E(t-t')}{\partial t'} \right) \{\varepsilon_0 + \Delta\varepsilon^i\} + \int_{t_0}^{t_1} dt' \left( \frac{\partial E(t-t')}{\partial t'} \right) \Delta\varepsilon^i \\ &\approx \varepsilon_0 E(t - t_0) + \Delta\varepsilon^i E^i(t)\end{aligned}\quad (7)$$

where  $\sigma(t)$  is the compression stress at  $t > t_1$ . The stress in the sample has two contributions that are additive. This experiment measures both the relaxation modulus  $E(t)$  as well as the incremental modulus  $E^i(t)$  that is related to the incremental strain as

$$E^i(t) = \lim_{\Delta\varepsilon^i \rightarrow 0} \frac{\Delta\sigma(t)}{\Delta\varepsilon^i}\quad (8)$$

This incremental modulus agrees with the initial tensile modulus  $E(0)$  under a condition that the time after the imposition of the incremental strain,  $t - t_1$ , is much smaller than all relaxation times  $\lambda_j$  of the material. However, this agreement is not found if the condition is not fulfilled.

Conventionally, the modulus is expressed in relation to the shear experiment even if it was measured in compression (application of Trouton factor of 3). The corresponding shear moduli are

$$\text{relaxation modulus} \quad G^0(t) = E(t)/3,$$

$$\text{and instantaneous modulus} \quad G^0(0) = E^i(0)/3.$$

Throughout the remainder of the paper we will use that convention.

The time for one stress measurement is about 90 s, which is very small as compared to the fastest relaxation mode for SEBS at low temperatures, as will be seen below. Thus, the incremental modulus measured in all the low temperature experiments is nearly equal to the instantaneous modulus,  $G^0(0)$ . The behavior of the instantaneous modulus is discussed further below.

The focus of this study is on the slow relaxation processes. In comparison, for the experiments at higher temperatures, stress relaxation in SEBS samples is relatively fast and can be measured directly. A compression strain is applied and kept constant throughout the experiment while the resulting force is recorded as it decays in time. This is compared to the classical compression experiment in a commercial rheometer where the sample is lifted by a piston and compressed to a given extent without any need of spacers or bolts.

There are some practical problems in determining the exact compressive modulus in low temperature experiments in the relaxometer. First of all, no sample is exactly flat and rather has a wavy surface. Because of this, the exact thickness of the sample before and after the compression is very difficult to determine. Several methods were employed to overcome this difficulty. Here we use the relaxation modulus from dynamic

mechanical measurements and match the short time modulus from the relaxometer (after dividing by the Trouton factor of 3). The initial stress from the relaxometer divided by the short time relaxation modulus gives the strain that was used in the subsequent relaxometer experiments. There are other methods to determine the thickness of the sample before and after the compression. One of them is the measurement of normal force. These techniques were employed in high temperature experiments in order to determine the thickness and the strain level in the sample. In such a case, it is possible to compare the data from the relaxometer with the dynamic data from the rheometer.

### Results and Discussion

The structured samples (Fig. 1) were studied with small amplitude oscillatory shear at seven different temperatures, viz. 25, 40, 50, 60, 70, 85 and 100°C, at frequencies ranging from  $10^{-4}$  to  $10^2$  rad/s, see Fig 2. The same strain amplitude of  $\gamma_a=0.04$  was chosen for all experiments. This strain amplitude was confirmed to be well inside the linear viscoelastic range of the SEBS samples (see below). Although these experiments cover six decades in frequency, the frequency window is still too small to explore all the interesting phenomena. Especially missing are the relaxation phenomena that occur at very long times and are not accessible to the dynamic mechanical experiments. For example, at 100°C, the expected plateau in  $G'$  at lower frequencies attributed to the BCC lattice occurs over a wide frequency range with a value of about 3000 Pa. However, experiment does not extend to low enough frequencies to include the very slow relaxation modes. This can be clearly seen for the relaxation modulus in Fig 3. Similar phenomena were observed at 85°C. At 70°C, the plateau in  $G'$  begins to appear at low frequencies. At 50°C, the similar plateau in  $G'$  or the minimum in  $G''$  at low frequencies is not seen at

all in the experimental window. At 25°C, the relaxation process is slowed down so that a second plateau in  $G'$  with a magnitude of about 30000 Pa becomes accessible in the experimental window extending up to the lowest frequency. This is the rubbery plateau ( $G_N$ ) observed at higher frequencies than the BCC plateau as discussed by Kossuth *et al.* (1999). The second crossover at low frequency between  $G'$  and  $G''$  is seen only at 100 °C and that too at the lowest frequency that is  $10^{-4} \text{ s}^{-1}$ . At all temperatures, the dynamics includes very slow modes.

An attempt to shift all the dynamic data to 100°C, using time-temperature superposition, demonstrates that time-temperature superposition does not apply to this material in the experimental temperature range (Fig 4). With a change in temperature, the mechanisms of molecular motion and supramolecular motion may shift and each mechanism has different kinetics of relaxation. Thus, it is not possible to obtain the entire relaxation spectrum by conventional techniques. Additional long-time experiments are required.

The limit of linear viscoelasticity as observed in strain sweeps at different frequencies, Fig 5a and Fig 5b, is quite different for the two temperatures, 85°C and 25°C. At low frequencies, the strain levels used at 25°C are definitely within the linear viscoelastic range whereas the strain levels used at 85°C are very close to the linear viscoelastic limit.

Long time relaxation experiments were carried out in the Relaxometer at four different temperatures: 85°C, 70°C, 50°C and 25°C. The strain levels in the relaxometer experiment were:  $\varepsilon_0 = 0.08$  at 70°C,  $\varepsilon_0 = 0.063$  at 85°C,  $\varepsilon_0 = 0.063$  at 50°C, and  $\varepsilon_0 = 0.122$  at 25°C. The strain is defined with respect to the initial thickness of the sample. The

experiments have the purpose of measuring the relaxation modulus (relaxation times and, possibly, the equilibrium modulus of eq. 4). The results of the relaxation experiments are shown in Figs. 6 to 9. The data is plotted on both log-log scale as well as log-linear scale so that the short time as well as the long time behavior can be clearly seen. At the three highest temperatures, 85, 70, and 50°C, the stress relaxes completely within a finite time (of the order of about  $10^5$  s), a time scale that certainly is too long to be accessible in conventional rheometry devices. It was surprising to see that the stress relaxes completely even at 50°C, a temperature that is below the glass transition temperature  $T_g$  of the BCC nanospheres. At 25°C, however, the stress in the sample does not decay to zero even after a time span of the order of  $10^6$  s (about 4 months). This shows that the material has a finite equilibrium modulus ( $G_e=7460$  Pa) at room temperature and hence exhibits solid behavior.

The figures also show the relaxation modulus calculated from the dynamic mechanical data taken in the ARES rheometer at these temperatures. The compressive modulus (normalized by a factor of three) and the shear modulus obtained from the dynamic mechanical data are in fair agreement with each other. However, the time range of overlap is limited. Table 1 shows the spectrum of relaxation times at room temperature. These were obtained by the X-method of Tobolsky and Murakami (1959). In the X method, one first starts with the relaxation data at long time and subtracts the equilibrium modulus (if applicable). Then, this data at long times is plotted on log-linear scale of modulus versus time. Its long-time tail is fitted to find the longest relaxation mode,  $g_1 e^{-t/\lambda_1}$ . After this, the relaxation modulus data is modified by subtracting the longest mode. The remainder,  $G(t) - g_1 e^{-t/\lambda_1}$ , is fitted to find the second largest mode,



$g_2 e^{-t/\lambda_2}$ . This procedure gets repeated until all modes down to the shortest mode are obtained. Table 1 gives the equilibrium modulus and the relaxation spectrum at 25°C where the sample was found to exhibit solid behavior.

The dynamics at 25°C is sufficiently slow to allow measurement of the instantaneous modulus,  $G^0(0)$ . The shortest relaxation mode is about  $\lambda_{\min} = 50,000$  s. The experiment for measuring the instantaneous modulus requires about 90 s which is very small as compared to  $\lambda_{\min}$ . For a small incremental strain, the measured incremental modulus should be equal to the instantaneous modulus  $G^0(0)$  of eq.6. This is true as long as the initial compressive strain as well as the incremental strain is within the linear viscoelastic region, which is indeed the case. Fig 6b shows the time behavior of the instantaneous modulus on a linear time scale. The instantaneous modulus was found to be nearly constant even though the stress in the material (and hence  $G(t)$ ) is decaying. It can also be seen from Fig 4b that the measured value of the instantaneous modulus is approximately 33000 Pa whereas the value calculated from the relaxation spectrum of Table 1 is 32270 Pa. Thus, the two values are in excellent agreement. For SEBS20, the measurement of instantaneous modulus is possible only near room temperatures. This is because at elevated temperatures, the relaxation process is accelerated and it is not possible to perform a measurement such that the experimental time is very small as compared to  $\lambda_{\min}$ . In such a case, the measured incremental modulus will not be equal to the instantaneous modulus.

The relaxation pattern and the equilibrium modulus observed at room temperature for SEBS20 can be due to several reasons, for example, the short time behavior can be attributed to the dynamics of the matrix phase governed either by the entanglement of the

midblock chains or by the bridging chains of midblock from one PS nanosphere to another or by both and long time behavior due to dynamics of spherical domains with BCC structure. We studied SEBS20 as a model material representing a class of soft solids with several transition mechanisms. It would be interesting to study the relaxation of the corresponding diblock copolymer containing similar blocks and with similar composition of microphases. This will be the focus of future work.

### **Conclusions**

In experiments that last over a period of four months, the room temperature SEBS sample shows a true solid behavior when subjected to a constant strain that is within linear viscoelastic region. The equilibrium modulus at room temperature is found to be about 7500 Pa for a sample that contains 20% polymer. The instantaneous modulus at room temperature was observed to be constant over the entire time span. However, for the same material at elevated temperatures, the stress and hence the modulus decays to zero over a long period of time showing liquid behavior. This is true even at 50°C which is lower than the glass transition temperature of polystyrene phase that forms the nanospheres. The time scales of stress relaxation are very large (of the order of  $10^6$  s) which is a typical characteristic for a “soft solid”. The modulus data from the relaxometer is in good agreement with the dynamic data obtained from the commercial rheometer.

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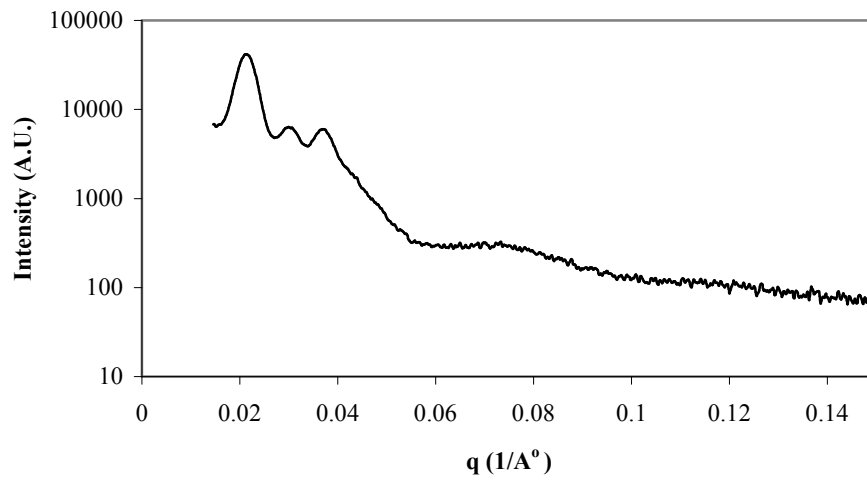
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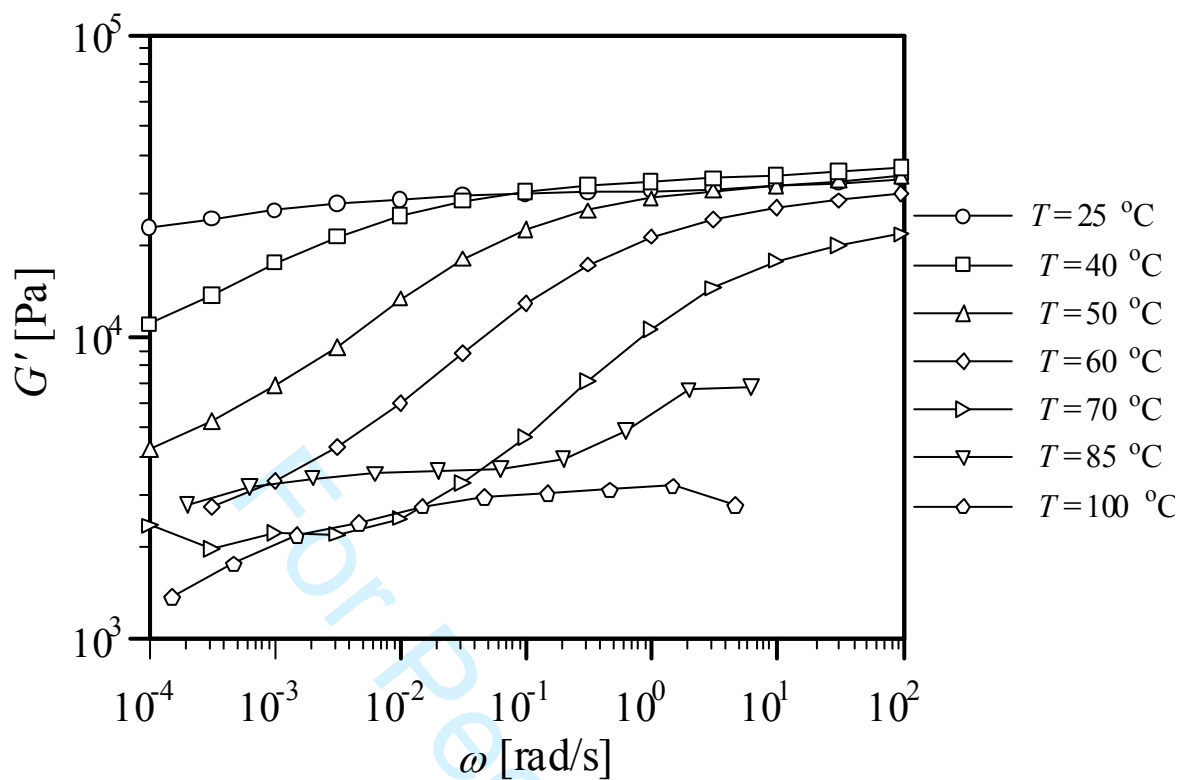
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Table 1 Spectrum of relaxation times for SEBS20 at 25 °C  
(with  $G_e = 7460$  Pa)

$g_i$ (Pa)	$\lambda_i$ (s)
1320	$2 \times 10^6$
6890	$1 \times 10^6$
16600	$5 \times 10^4$

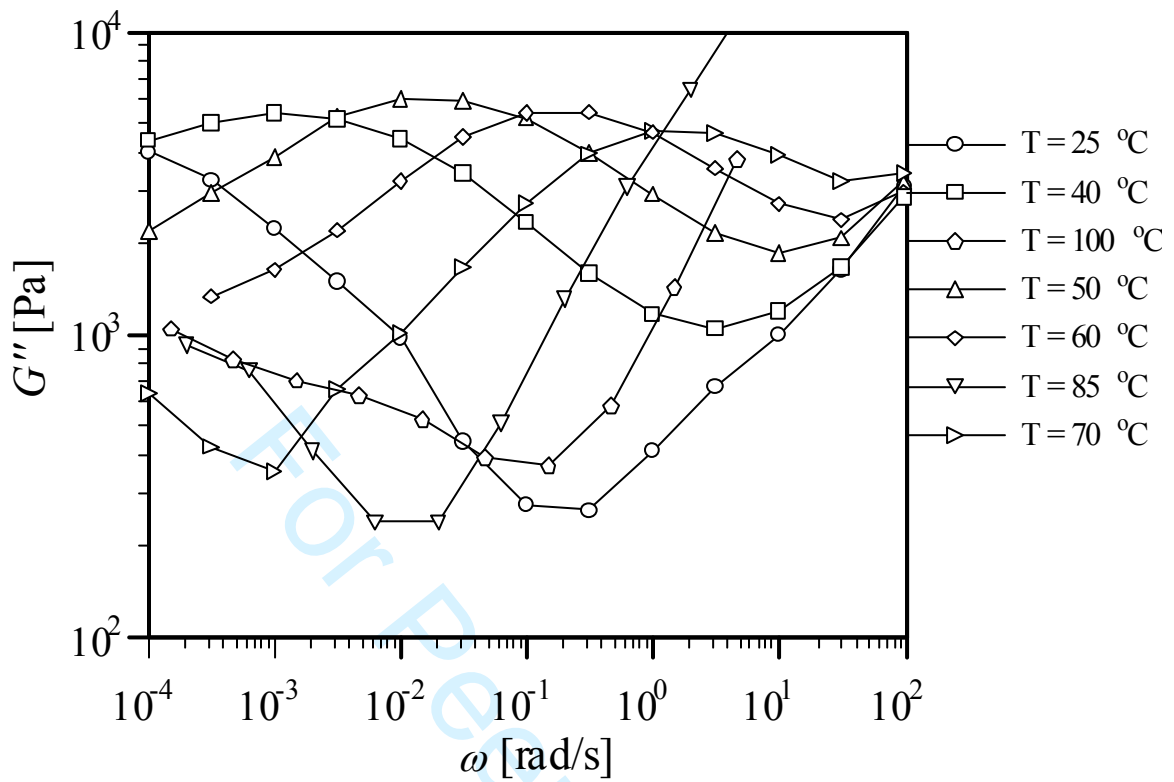


**Fig 1 SAXS profile of SEBS20 annealed at 100 °C and recorded at room temperature**

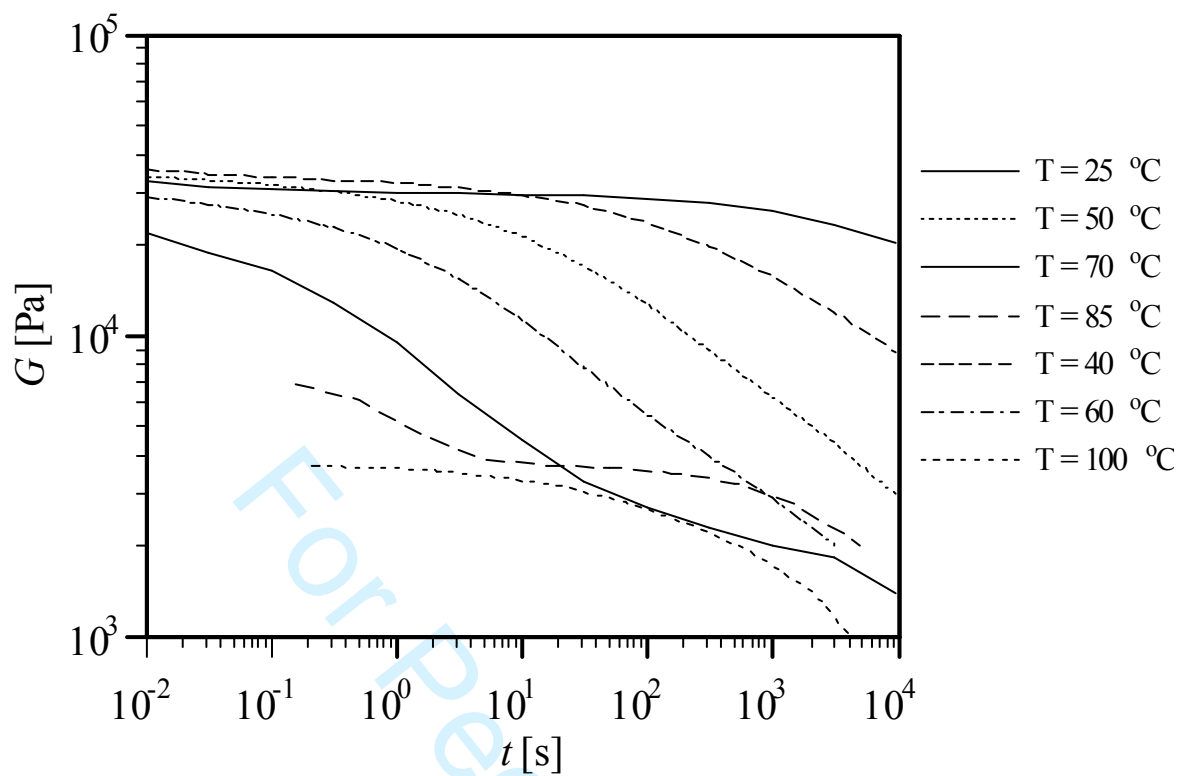


**Fig 2a** Storage modulus of SEBS20 that was first annealed at  $100\text{ }^\circ\text{C}$  for structure development and then probed at seven different temperatures





**Fig 2b** Loss modulus of SEBS20 that was first annealed at 100 °C for structure development and then probed at seven different temperatures



**Fig 3** Relaxation modulus of SEBS20 that was first annealed at 100 °C for structure development and then probed at seven different temperatures

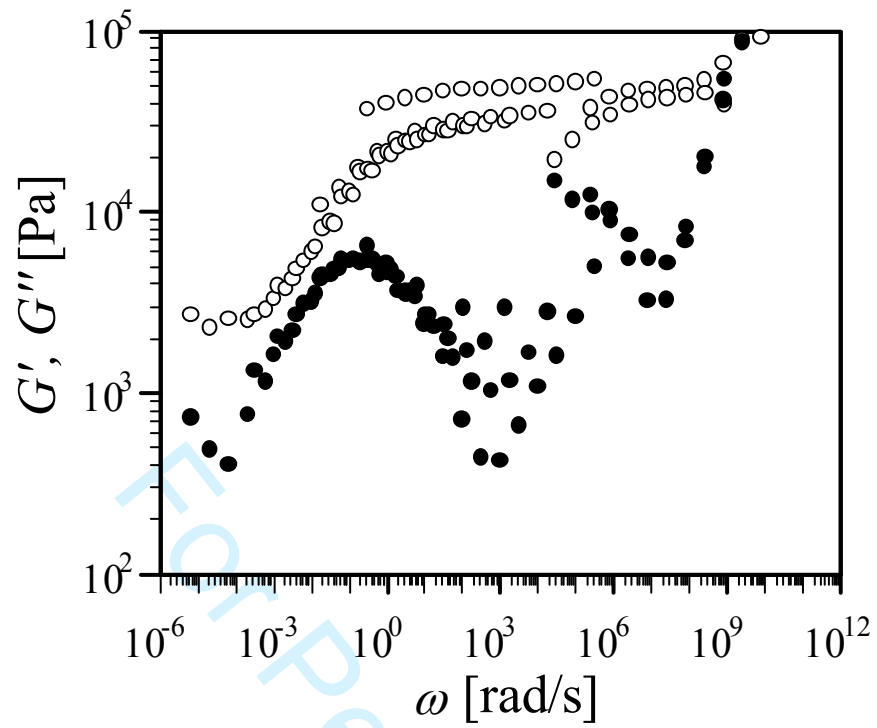


Fig 4 Time-temperature superposition attempt of the dynamic data of Fig 2

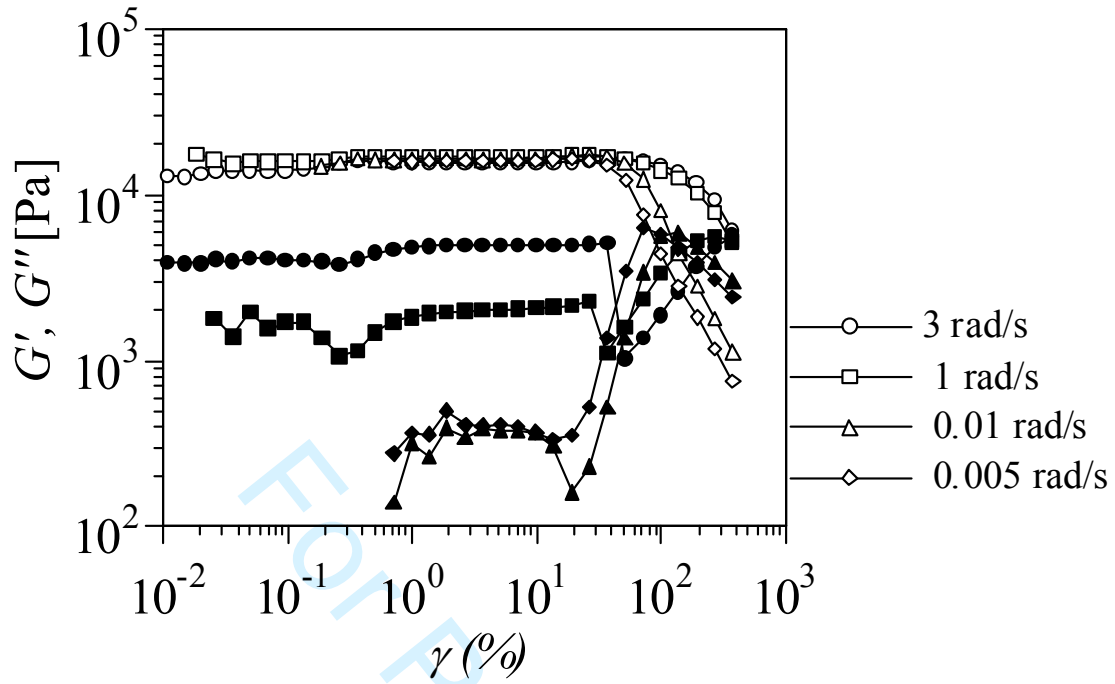


Fig 5a Strain sweep at 25 °C for SEBS20 annealed at 100 °C for different frequencies

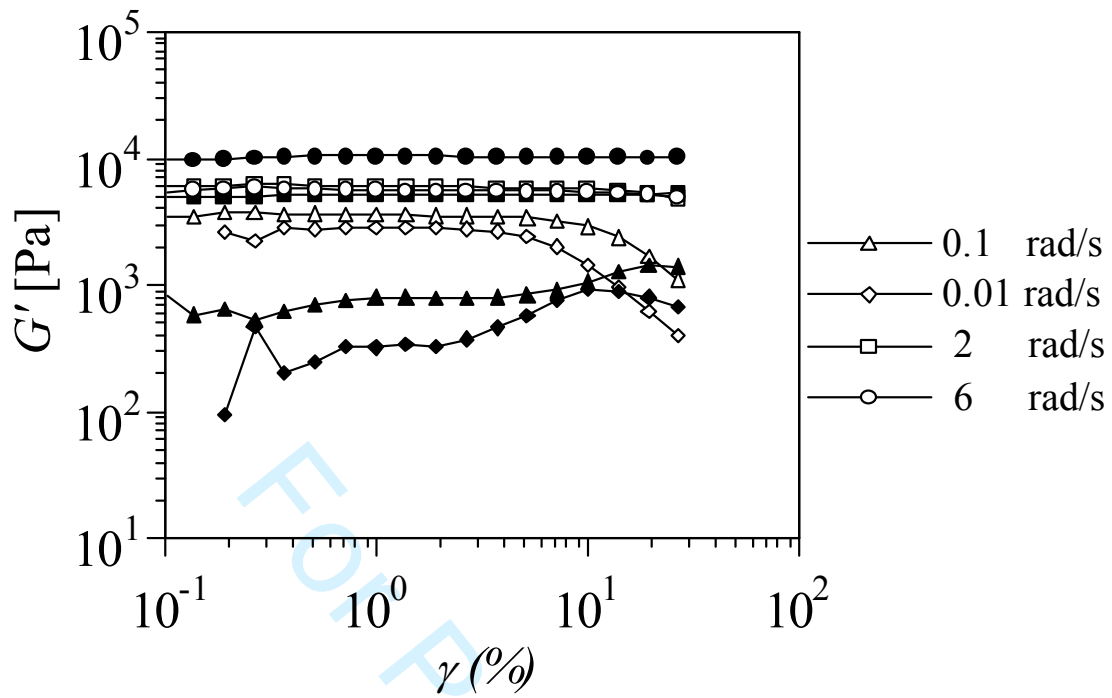
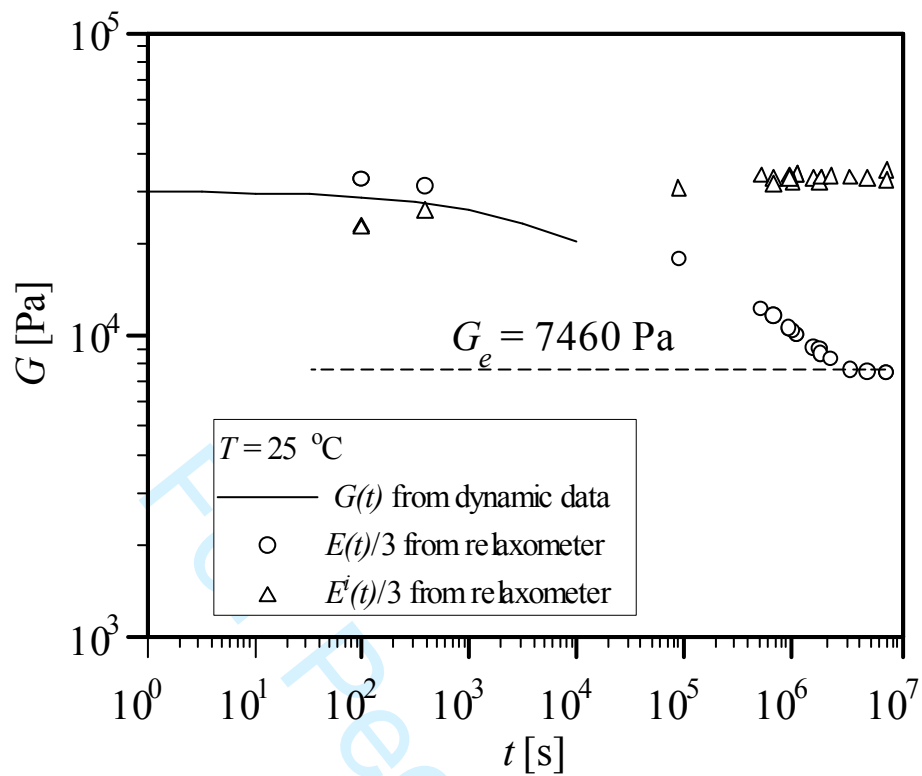
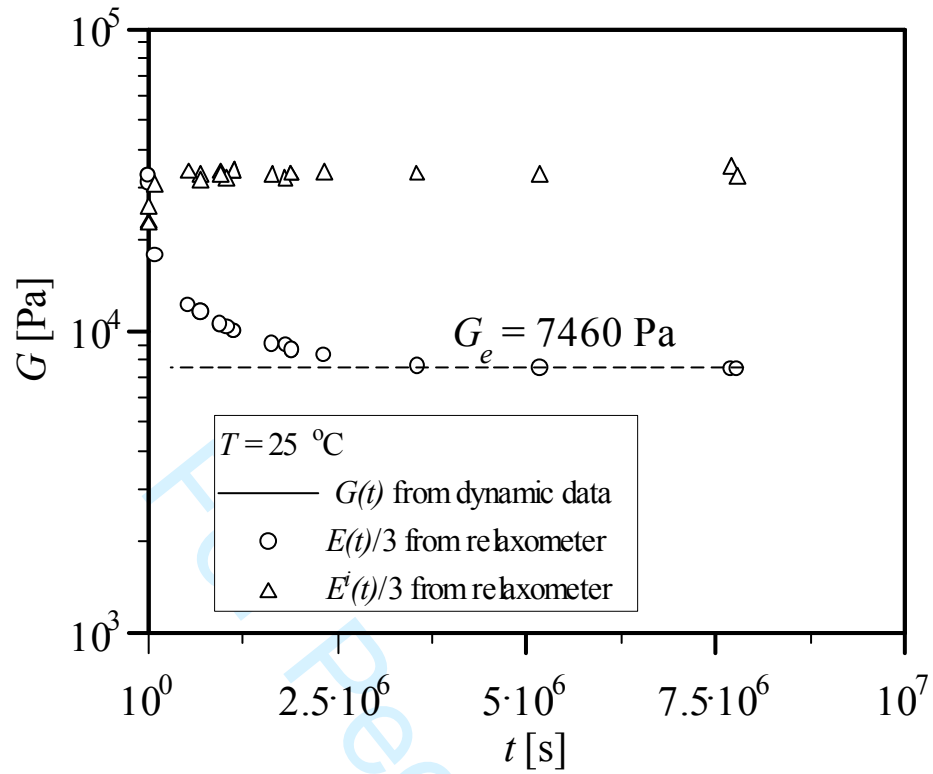


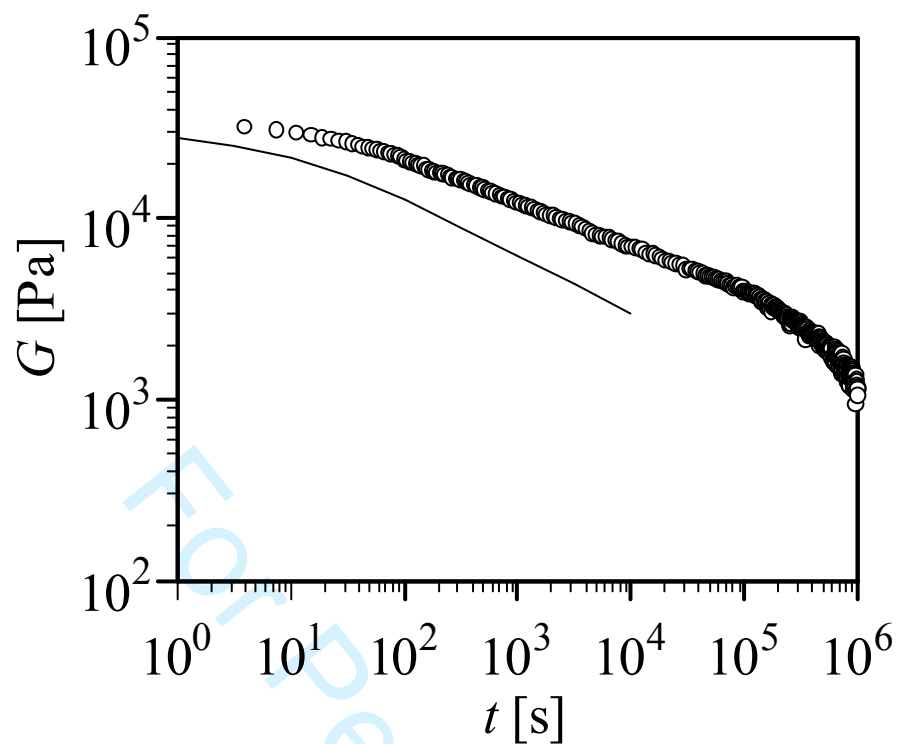
Fig 5b Strain sweep at 85 °C for SEBS20 annealed at 100 °C for different frequencies



**Fig 6a** Relaxometer data at 25 °C showing decaying modulus as well as the incremental modulus (dashed line represents  $G_e = 7460$  Pa)

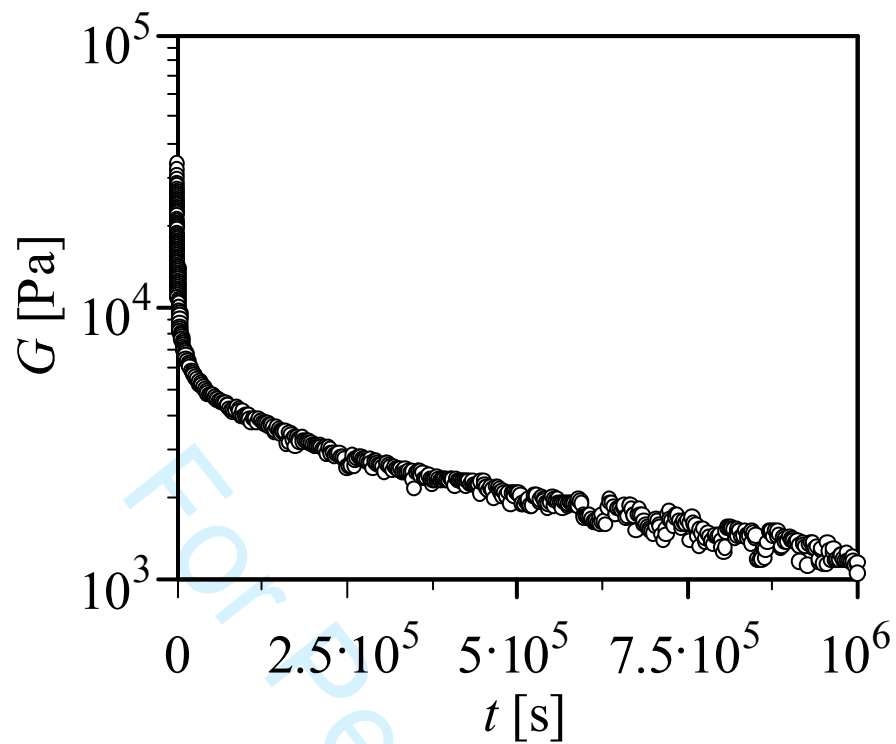


**Fig 6b Relaxometer data at 25 °C on a linear scale (same data as in Fig 6b) showing a nearly constant incremental modulus. The relaxation modulus approaches a value of 7460 Pa at long times**

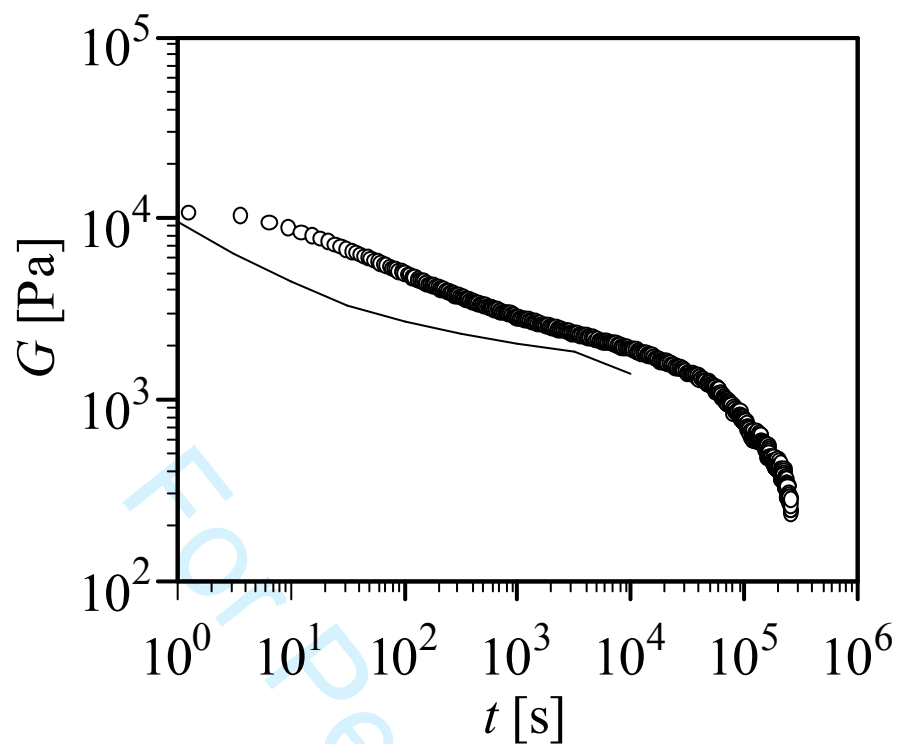


**Fig 7a Comparison of relaxometer data and dynamic data for SEBS20 at 50 °C (sample initially annealed 100 °C). Solid line represents  $G(t)$  calculated from the dynamic data and circles represent data from the Relaxometer.**

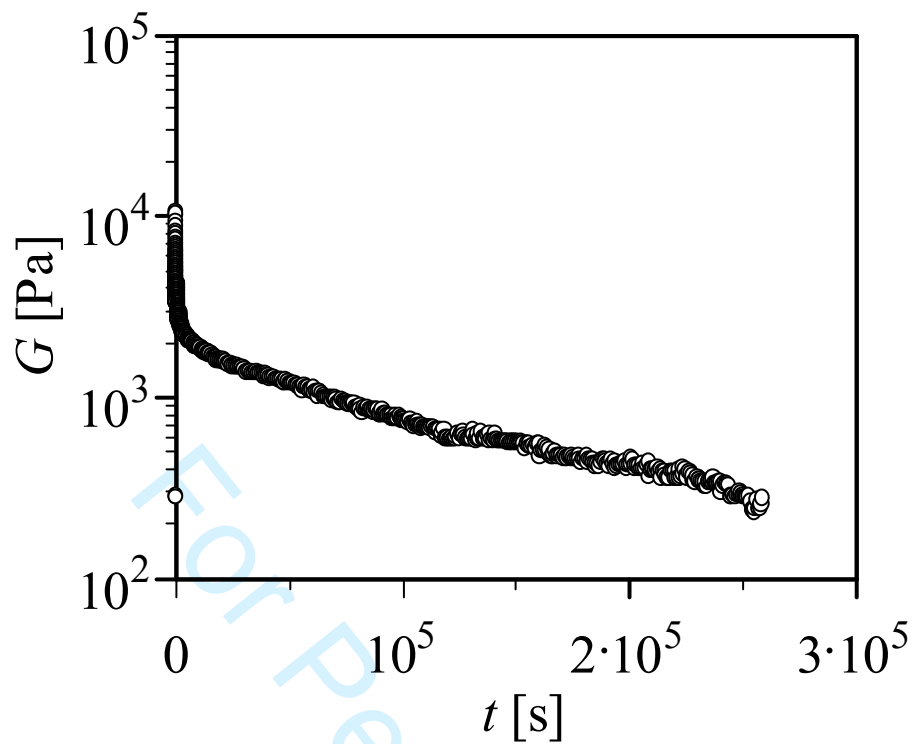




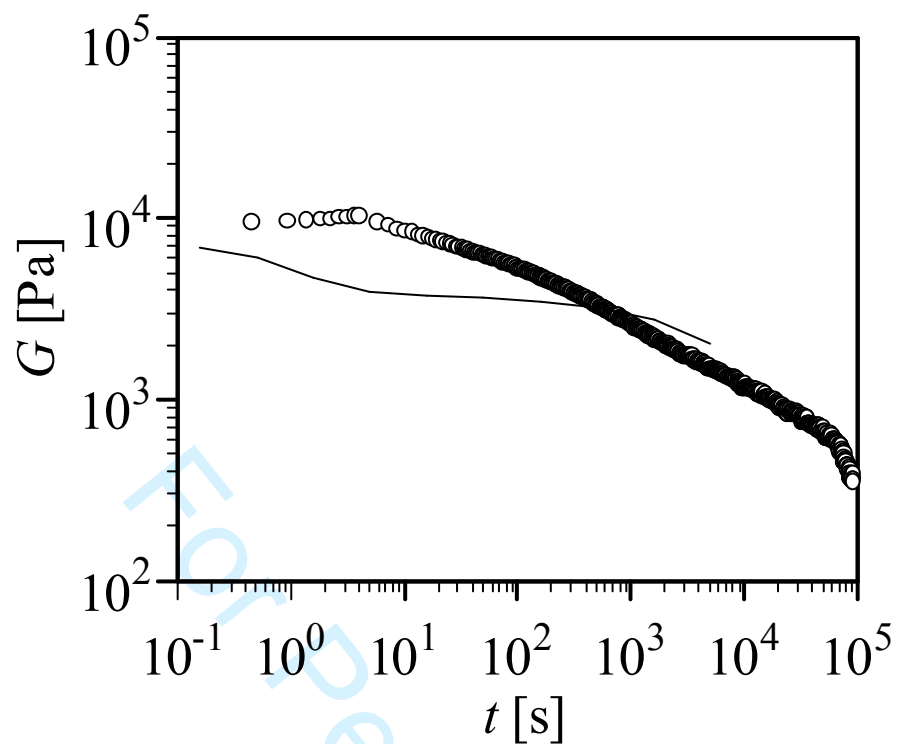
**Fig 7b** Relaxometer data of Fig 7a plotted in semi-log format to demonstrate the long time behavior



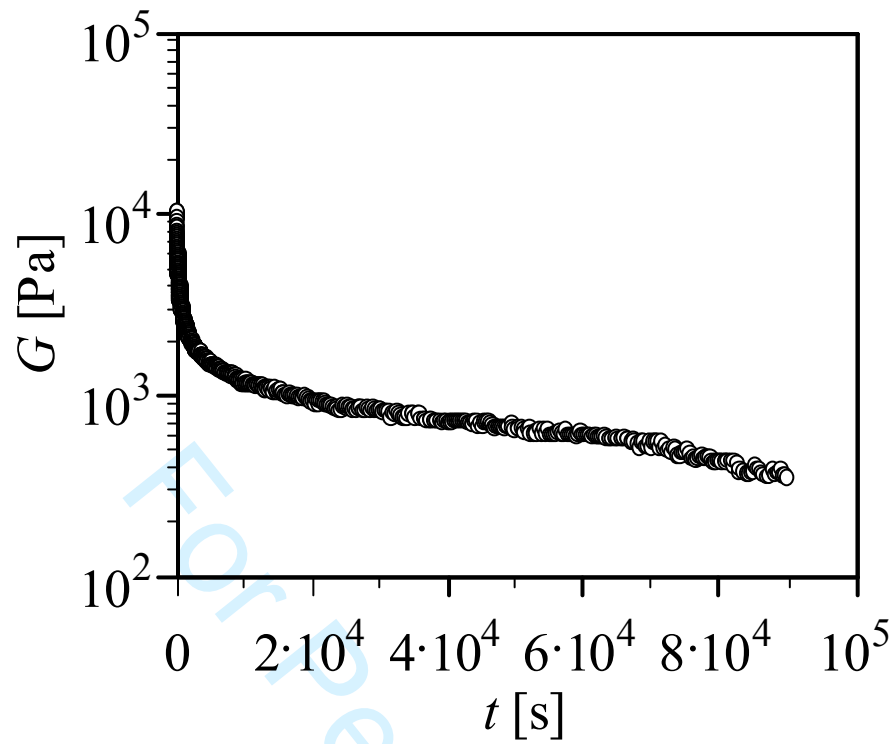
**Fig 8a Comparison of relaxometer data and dynamic data for SEBS20 at 70 °C (sample initially annealed 100 °C). Solid line represents  $G(t)$  calculated from the dynamic data and circles represent data from the Relaxometer.**



**Fig 8b** Relaxometer data of Fig 8a plotted in semi-log format to demonstrate the long time behavior



**Fig 9a Comparison of relaxometer data and dynamic data for SEBS20 at 85 °C (sample initially annealed 100 °C). Solid line represents  $G(t)$  calculated from the dynamic data and circles represent data from the Relaxometer.**



**Fig 9b** Relaxometer data of Fig 9a plotted in semi-log format to demonstrate the long time behavior