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# Analysis of glass transition and relaxation processes of low molecular weight polystyrene-*b*-polyisoprene diblock copolymers

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## Abstract

The objective of this study is to analyze the glass transition temperature and relaxation processes of low molecular weight polystyrene-*block*-polyisoprene diblock copolymers with different compositions, synthesized via anionic polymerization. Thermal properties were investigated by differential scanning calorimetry and dynamic mechanical thermal analysis, while the morphologies at room temperature were investigated by transmission electron microscopy and small angle X-ray scattering. The  $\chi N$  values indicate that the diblock copolymers lie near the weak segregation regime. Three different experimental techniques were applied to determine the dynamic properties, i.e. linear viscoelastic shear oscillations, creep recovery experiments and dielectric spectroscopy. The rheological experiments were performed above the order-disorder transition temperature where the diblock copolymers behave like a Maxwell fluid. Our results indicate that the presence of the polyisoprene segments strongly influences the monomeric friction coefficient and the tendency to form entanglements above the order-disorder temperature. Consequently, the zero-shear rate viscosity of a diblock copolymer is much lower than the zero-shear rate viscosity of the neat polystyrene block (the polystyrene precursor of the polymerization procedure). Dielectric spectroscopy enables the analysis of relaxation processes below the glass transition of the polystyrene microphase. Frequency sweeps indicate the dynamic glass transition of the polyisoprene blocks, which are partly mixed with the polystyrene blocks, which are always the majority component in the block copolymers of this study.

**Keywords** Diblock copolymers, Dynamic-mechanical analysis, Creep recovery, Dielectric spectroscopy, Glass transition

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## Introduction

Anionic polymerization opened an attractive opportunity for combination of different types of polymers to synthesize block copolymers [1]. In this way, it is possible to combine hydrophilic and hydrophobic as well as hard and soft blocks, respectively. Phenomena like microphase separation lead to complex relations between the molecular structure and the end-use properties of block copolymers [2-5]. Several experimental techniques are available to provide information about the viscoelastic and dielectric behavior of block copolymers. Rheological studies [6-8] and broadband dielectric spectroscopy [9-15] give information on the dynamics on different length scales from the macromolecular size down to the segmental structure which are essential for material application and processing. Therefore, an almost complete characterization of relaxation processes for a variety of block copolymers with similar chemical and molecular characteristics is possible.

Nowadays, block copolymers are widely used as additives in plastic technology [7,16], since they have unique properties, which result from their ability to self-assemble into different microphase morphologies [1,2,17]. Various works were accomplished with the focus on the analysis of rheological and dielectric properties of block copolymers as well as on relations between morphology and molecular architecture [18-20]. The phenomenon of microphase separation depends on many factors, such as the chemical type of the monomers that a specific block copolymer consists of, the relative amounts of the different blocks, the degree of polymerization, and the temperature. The end-use properties of block copolymers do not only depend on molecular weight and composition, but the morphology also has a strong impact on different properties (e.g., on mechanical properties) [21].

Several scientific studies on diblock copolymers, in particular on polystyrene-*block*-polyisoprene (PS-*b*-PI) diblock copolymers, have been carried out, focusing on the viscoelastic properties, relaxation times spectra, morphology influence, etc.. Winey et al. [22,23] studied low molecular weight PS-*b*-PI diblock copolymers with a volume fraction of 50% and a majority of 1,4-polyisoprene. They proved that shear deformation influences the morphology as well as its alignment. The work of Förster et al. [24] described new morphologies (especially the hexagonally perforated lamellae) and the phase behavior of PS-*b*-PI diblock copolymers near the order-disorder temperature, also for diblock copolymers with a majority of the 1,4-PI microstructure. In their work, a tentative phase diagram for the examined polymers was presented. A follow up work from Khandpur et al. [25] examined PS-*b*-PI diblock copolymers with different volume fractions,

expanding the tentative phase diagram. Additionally Bates et al. [26] worked on numerous block copolymer systems and studied in detail the parameters that influence the phase behavior near the order-disorder transition. Furthermore, in the case of PS-*b*-PI block copolymers, Floudas et al. [27] investigated the ordering kinetics in block copolymer blends as well as the order-disorder transition and its dependence on the degree of polymerization. Schwab et al. [28] studied the order-disorder transition for an asymmetric PS-*b*-PI diblock copolymer, finding a stable state of liquid-like order between the disordered state at elevated temperatures and the bcc ordered spheres. Finally, besides the viscoelastic properties studies on diblock copolymers, in the works of Neumann et al. [29-31] the properties of polyisoprene-*block*-polybutadiene-*block*-polystyrene triblock copolymers were examined, proving similarities to the diblock copolymers. Apart from the above mentioned works, dielectric spectroscopy of PS-*b*-PI diblock copolymers revealed the dependence of relaxation processes on the molecular weight and the morphology [20,32]. Recently, broadband dielectric spectroscopy studies on P2VP homopolymers led to valuable information about the change of polymer properties on the nanometer scale [33], while same work has been done for polyisoprene (cis-1,4 microstructure) [34] and PS-*b*-PI diblock copolymers [35] providing information about the relaxation processes and the polymer properties.

In this work, glass transition and relaxation processes of PS-*b*-PI diblock copolymers were studied. The diblock copolymers were of low molecular weight, below the entanglement molecular weight of each block [36]. As expected from the chosen synthesis conditions, the polyisoprene blocks mainly consist of 1,2- and 3,4-microstructure [37]. This combination led to diblock copolymer systems with reduced brittleness in comparison to neat polystyrene. Samples with a small volume fraction of polyisoprene were synthesized in order to examine the viscoelastic properties of asymmetric diblock copolymers. The molecular weight was varied in order to vary the tendency towards microphase separation. The in depth examination of the viscoelastic properties as well as the relaxation processes gave an overview of the influence of molecular weight and composition of the diblock copolymers on the thermal and viscoelastic properties in the low molecular weight regime. Such materials are used for fabrication of composite materials, therefore an “a priori” knowledge of their properties can lead to fabrication of nanocomposites with tailored properties. Furthermore, the viscoelastic properties of the neat polystyrene precursors were compared with those of the diblock copolymers, indicating the changes caused by the addition of the polyisoprene block.

## Experimental

### Synthesis

Diblock copolymers of the PS-*b*-PI type were synthesized via anionic polymerization under an inert atmosphere from high purity argon [38]. The complete preparation regarding the synthesis of the aforementioned diblock copolymers was done under high vacuum techniques, in high performance pyrex glass reactor. Styrene (Sigma-Aldrich, USA, 99%) was purified from aluminum oxide (Macherey-Nagel, Germany) and di-*n*-butylmagnesium (Sigma-Aldrich, USA, 1.0 M solution in heptane) under high vacuum. Isoprene (Sigma-Aldrich, USA, 99%) was also purified from calcium hydride (Sigma-Aldrich, USA, >90%) and twice from *n*-butyllithium (*n*-BuLi, Sigma Aldrich, USA, 1.6 M solution in hexane). The solvent used was tetrahydrofuran (THF, Th. Geyer, Germany, 99.9%), refluxed and distilled from sodium metal, titrated with *sec*-butyllithium (*s*-BuLi, Sigma Aldrich, 1.4 M solution in cyclohexane).

The synthesis started with the polymerization of styrene with *s*-BuLi, in THF at -78 °C for approximately 2 hours. A small aliquot was removed from the polymerization reactor and terminated with degassed methanol (Sigma-Aldrich, USA, 99.8%), for molecular characterization of the first block. Afterwards, the purified isoprene was added to the mixture and the temperature was increased up to -10 °C. Isoprene polymerization was finished after 4 hours and the polymerization was terminated using degassed methanol. The polymer was precipitated in methanol containing a very small amount of stabilizer BHT (2,6-Di-*tert*-butyl-4-methylphenol, Sigma-Aldrich, USA) in order to prevent oxidation or crosslinking. Finally, the samples were dried and kept in vacuum at 35 °C. The nomenclature given to the synthesized samples was PS<sub>x</sub>PI<sub>y</sub><sup>z</sup> where x: wt% polystyrene, y: wt% polyisoprene, z:  $\bar{M}_n^{PS-b-PI}$  in kg/mol.

### Molecular Characterization

Molecular characterization was accomplished with the use of gel permeation chromatography (GPC), in order to obtain the polydispersity index and the molecular weight of the synthesized polymer, as well as proton nuclear magnetic resonance (<sup>1</sup>H-NMR). GPC measurements were performed at room temperature in THF as it is described elsewhere [39]. <sup>1</sup>H-NMR was accomplished with the Avance 300 spectrometer (Bruker GmbH, Germany), equipped with a 300 MHz magnet and a triple resonance inverse (TXI) probe. The experiment was done at room temperature with deuterated chloroform as solvent and tetramethylsilane as internal standard.

### *Thermal Characterization*

The thermal properties of the block copolymers were studied by differential scanning calorimetry (DSC) experiments and dynamic mechanical thermal analysis (DMTA). The instrumentation used for the DSC experiments was the calorimeter DSC 1 (Mettler-Toledo, Greifensee, Switzerland). It is known that polyisoprene exhibits glass transitions at approximately -60 to -50 °C for the 1,4 microstructure and at -30 °C to 0 °C for the 3,4 microstructure. On the other hand, the glass transition of polystyrene is expected around 100 °C. Therefore the temperature range was set to -100 °C up to +150 °C in an argon atmosphere. In addition, a heating and cooling rate of 10 K/min were used in order to obtain accurate values. A faster rate would have reduced the resolution and a slower rate would have led to a wider thermal transition, yielding a less precise calculation of the glass transition temperature. For the experiment approximately 10 mg of the polymer were placed in an aluminum pan of 10 µl. The samples were first heated up to 150 °C to erase the thermal history of the sample and then cooled down to -100 °C. In the third interval, the sample was again heated up to 150 °C. The second heating interval provided the data for the  $T_g$  determination.

Dynamic mechanical thermal analysis (DMTA) experiments were performed in order to determine the glass transition temperature of the polystyrene block and compare it with the DSC data, as well as to probe the order-disorder transition during cooling from 200 °C to 50 °C, with a temperature cooling rate of 1 K/min, a frequency of 1 Hz and a strain amplitude  $\gamma_0$  of 1%. The use of 10 K/min cooling rate (rate used for the DSC experiments) is a very fast rate and the observation of the transitions would be impossible because of temperature gradients. The measurements were performed using an ARES rotational rheometer (Rheometric Scientific, Piscataway (NJ), USA) with a plate-plate geometry. Cylindrical specimens of 8 mm diameter and 2 mm thickness were prepared. Initially the bulk polymer powder was dried in the oven overnight. Then the sample was compression molded at 135 °C for approximately 7 min, applying a force of approximately 60 kN and vacuum of  $10^{-2}$  atm. Before the measurement, the samples were annealed at the starting temperature for 7 min. The linear viscoelastic range was also checked via an amplitude sweep in the range of 0.5-5% and a frequency of 1 Hz.

As the sample preparation for rheological experiments demanded high temperatures during compression molding, the samples were examined through thermogravimetric analysis (TGA) for checking their thermal stability. For these experiments the instrumentation used was the TG 209 F1 Iris (Netzsch, Selb, Germany). The temperature range was from 25 °C up to 500 °C, with a heating

rate 10 K/min in nitrogen gas flow. Approximately 5 mg of polymer was used for the TGA experiments.

### *Morphological Characterization*

Morphological characterization of the diblock copolymers was accomplished via transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). The (TEM) experiments were done using a Tecnai G2 F20 electron microscope (FEI, Eindhoven, The Netherlands), operated at 200 kV, in bright field mode. Polymer films were cast from toluene solutions and slowly dried in presence of solvent vapor in a desiccator for a time period of approximately 2 weeks. Toluene was chosen as it is a rather non-selective solvent for this diblock copolymer system. Then the films were annealed at 100 °C under vacuum for one week. Ultra-thin sections of about 50 nm were cut with a Leica Ultramicrotome EM UCT (Leica Microsystems, Wetzlar, Germany) equipped with a diamond knife. In order to increase the electron density contrast between the two blocks, polyisoprene was selectively stained by OsO<sub>4</sub> vapour.

SAXS experiments were accomplished with the use of an Incoatec (Geesthacht, Germany) X-ray source I $\mu$ S with Quazar Montel optics. Focal spot size at sample was 1 mm<sup>2</sup> and the wavelength  $\lambda$  used was 0.154 nm. The distance between the sample and CCD detector (Rayonix SX165) was 1.6 m. The exposure time was 1 h. For the SAXS experiments parts of the unstained films prepared for the TEM experiments were used. SAXS data are presented as scattering intensity  $I$  as a function of scattering vector  $q = (4\pi/\lambda)\sin\theta$  with  $\theta$  being half of the scattering angle. In addition, the calculated curves after fitting of the SAXS data with the best structural model are plotted. The fit was done with the use of the software *Scatter*, version 2.5 [40] using the models for the structure of hexagonally packed cylinders and double gyroid inside the “1D calculation of crystal scattering part” of the software. The fit procedure was performed using a simplex algorithm, followed by a Marquardt algorithm, both part of the software “Scatter”. The fit parameters were: lattice constant, domain size, relative displacement, cylinder radius, standard deviation of radius and primary intensity. Fixed parameters were: baseline, Gaussian peak shape, cylinder length. The brittle sample - films were placed in specific holders and stabilized with Kapton<sup>®</sup> tape.

### *Rheological Characterization*

A rotational rheometer MCR502 (Anton Paar GmbH, Graz, Austria) was used for the shear rheology experiments. Cylindrical specimens with 8 mm diameter and 2 mm thickness were

prepared with the same method described for the DMTA measurements. It should be mentioned at this point that the samples were very brittle due to the low molecular weight and the high weight fraction of polystyrene. Rheological tests were done for comparison using the polystyrene homopolymer precursors. A parallel plates geometry tool for 8 mm cylindrical specimens was used and the gap for the measurements was set to 2 mm. The melting - annealing time was 7 min. The measurements were performed at constant temperature, i.e. 110 °C, 120 °C, 140 °C and 160 °C, under a nitrogen atmosphere, in order to avoid sample degradation. The samples PS<sub>69</sub>PI<sub>31</sub><sup>7.5</sup> and PS<sub>79</sub>PI<sub>21</sub><sup>17</sup> were also measured at 100 °C.

First rheological tests were carried out as a function of the angular frequency  $\omega$  in the dynamic mode. The angular frequency was varied between  $10^{-2}$  and  $10^2$  rad/s, starting from the highest frequency. Strain sweep experiments were carried out prior to the frequency sweep experiments in order to determine the linear viscoelastic regime. The strain amplitude  $\gamma_0$  was 4% in case of the PS<sub>92</sub>PI<sub>08</sub><sup>32.2</sup> diblock copolymer and 5% for all other diblock copolymers. In addition, the viscoelastic behavior of the diblock copolymers at larger times was examined using creep experiments at the same temperatures. Creep experiments also allow the investigator to determine directly the recoverable part of deformation. Similar to the frequency sweeps, the linear viscoelastic range for each sample was checked by amplitude sweeps as a function of shear stress prior to the creep experiments. The shear stress in the creep interval was 50 Pa and 0 Pa in the recovery interval. The creep time was 1000 s or 3600 s, which is much larger than the longest relaxation time of the polymers at 110 °C and higher temperatures.

### *Dielectric Spectroscopy*

Dielectric spectroscopy measurements were performed using an Alpha-AN high resolution dielectric analyzer (Novocontrol Technologies GmbH, Hundsangen, Germany). Films were directly cast on a brass plate from solution in chloroform, giving films of approximately 120  $\mu\text{m}$  thickness, after drying overnight in air. A second brass plate was placed on top of the sample. Afterwards the two brass plates containing the sample were inserted in the spectrometer. The diameter of the brass plates was 40 mm. The temperature of the frequency dependent measurements ranged from -50 °C to +90 °C, in increments of 20 °C. The frequency ranged in the interval of  $10^{-3}$  Hz up to  $10^6$  Hz.

## Results and Discussion

The results of molecular characterization by means of GPC and  $^1\text{H-NMR}$  are presented in Table 1(a). The outcome of the synthesis was low molecular weight diblock copolymers of polystyrene and polyisoprene. The calculated results for the value of  $\chi N$  are given in Table 1(a), through the use of [41]

$$\chi = 66/T - 0.0937 \quad (1)$$

It should be noted that the equation for the interaction parameter  $\chi$  is an experimental equation describing the dependence of the polymer – polymer interaction as a function of temperature  $T$ . In literature a variety of different equations are given [25,27]. Equation 1 refers to samples synthesized in the same manner (majority of polyisoprene 1,2- and 3,4-microstructure). In Table 1(a) the thermal characterization by means of DSC and DMTA is presented. The glass transition temperature of the polystyrene block was approximately 85 °C. The only exception is the  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  diblock copolymer with a glass transition at a lower temperature (56 °C). At approximately 10 °C a second glass transition was observed, which results from the partial miscibility of the two blocks. This glass transition was 22 °C for the  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  diblock copolymer because of the low molecular weight and thus the higher miscibility of the PS and the PI blocks.

**Table 1** (a) Molecular and thermal characteristics of the diblock copolymers of this study. The weight fraction of polyisoprene is denoted by  $f_{PI}$ . (b) Parameters  $c_1$  and  $c_2$  of the WLF equation (6).

(a)

Sample	$\bar{M}_n^{PS^a}$ [g/mol]	$\bar{M}_n^{PI^b}$ [g/mol]	$\bar{M}_n^{PS-b-PI^b}$ [g/mol]	PDI <sup>a</sup>	$\chi N^c$	$f_{PI}^d$	$T_g^{PS^e}$ [°C]	$T_g^{MIX^e}$ [°C]	$T_g^{PS^f}$ [°C]
PS <sub>69</sub> PI <sub>31</sub> <sup>7.5</sup>	5200	2300	7500	1.09	6.99	0.31	56	22	56
PS <sub>79</sub> PI <sub>21</sub> <sup>17</sup>	13400	3600	17000	1.30	15.15	0.21	85	8	87
PS <sub>75</sub> PI <sub>25</sub> <sup>19.6</sup>	14600	5000	19600	1.09	17.77	0.25	84	7	88
PS <sub>78</sub> PI <sub>22</sub> <sup>20.6</sup>	16100	4500	20600	1.09	18.33	0.22	85	10	86
PS <sub>92</sub> PI <sub>08</sub> <sup>32.2</sup>	29700	2500	32200	1.40	26.83	0.08	89	-	94

(b)

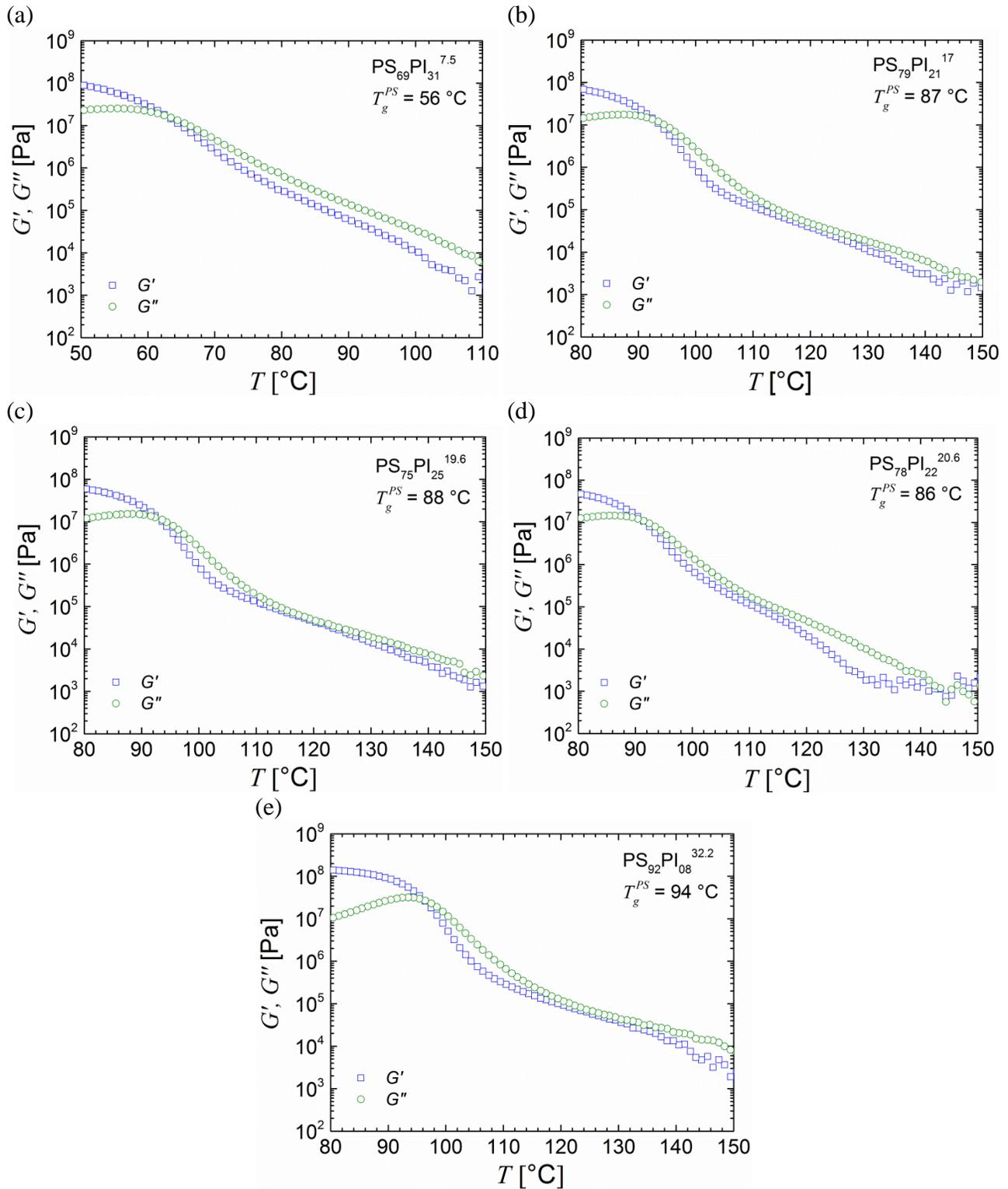
Sample	$c_1^g$	$c_2^g$	$c_1/c_2$
PS <sub>69</sub> PI <sub>31</sub> <sup>7.5</sup>	0.77	31.32	0.025
PS <sub>79</sub> PI <sub>21</sub> <sup>17</sup>	7.18	68.33	0.105
PS <sub>75</sub> PI <sub>25</sub> <sup>19.6</sup>	11.65	95.09	0.123
PS <sub>78</sub> PI <sub>22</sub> <sup>20.6</sup>	6.16	60.99	0.101
PS <sub>92</sub> PI <sub>08</sub> <sup>32.2</sup>	4.14	23.06	0.180

<sup>a</sup> Determined by GPC. <sup>b</sup> Determined by GPC and <sup>1</sup>H-NMR. <sup>c</sup> Determined from the total degree of polymerization  $N$  of the diblock copolymer and the Flory-Huggins interaction parameter  $\chi = 0.083$  (at 100 °C). <sup>d</sup> Determined by <sup>1</sup>H-NMR. <sup>e</sup> Determined by DSC. <sup>f</sup> Determined by DMTA. <sup>g</sup> Results of least-squares fit of Eq. (6) to the shift factor in Fig. 5. Only the  $G''$  values were used for the fit to the data of PS<sub>78</sub>PI<sub>22</sub><sup>20.6</sup>.

This thermal transition can be explained by the fact that the phase separation of the two different blocks is not strong, leading to partial mixing of the polyisoprene and polystyrene blocks. In case of the diblock copolymer (PS<sub>92</sub>PI<sub>08</sub><sup>32.2</sup>) having a large fraction of polystyrene, no second glass transition temperature was observed. Since the polyisoprene content is too low, the glass transition temperature for the polyisoprene was not visible.

Prior to the discussion of the DMTA results, the TGA analysis of the diblock copolymers is worth to be mentioned. Our results show that thermal degradation occurred only at elevated temperatures, starting above 240 °C and concluding above 400 °C. The fact that a stabilizer was used during precipitation in methanol is one reason for not observing any crosslinking effect of the polyisoprene block. Furthermore, the nitrogen atmosphere in the rheological experiments prevents cross-linking of the polymers.

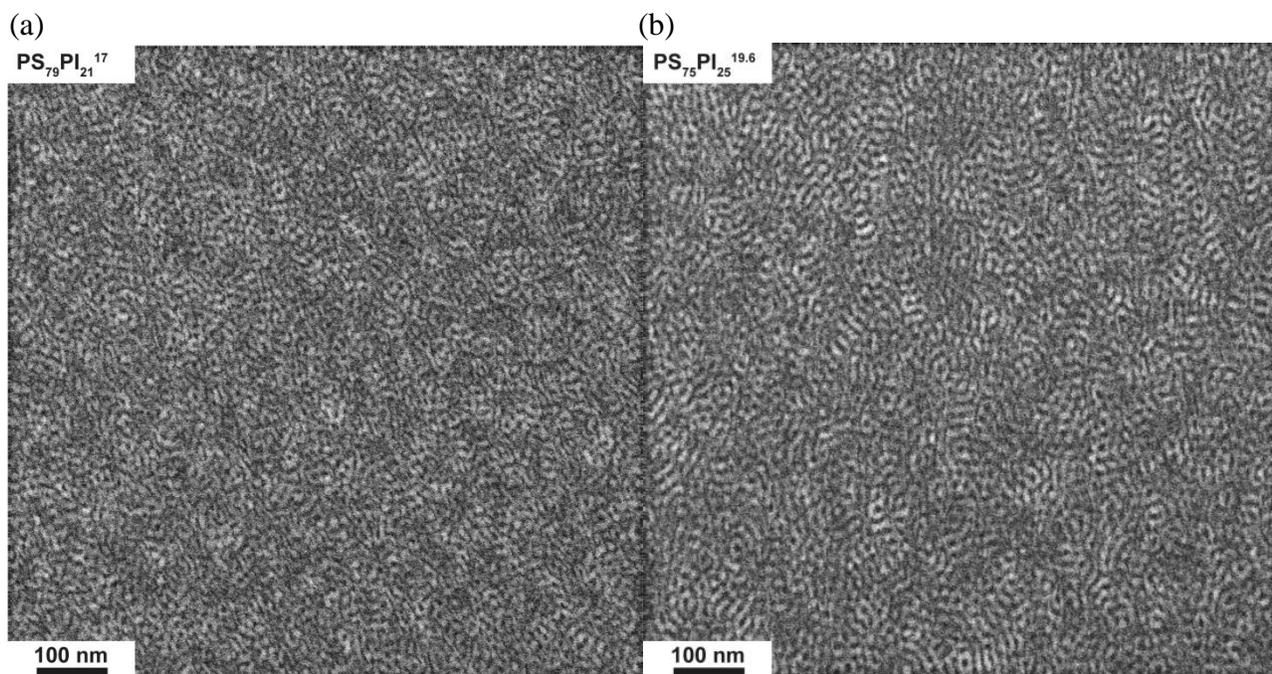
From the DMTA experiments the glass transition temperature of the polystyrene block was determined. The scattering of the storage modulus  $G'$  at high temperatures (Fig. 1) is caused by the limit of torque resolution of the rheometer. The  $T_g$  value corresponds to the temperature which is associated with a maximum of the loss modulus  $G''$  [42]. The values of the glass transition temperature of the polystyrene microphase are in agreement with the DSC data (see Table 1(a)). For the examined diblock copolymers the glass transition temperature was approximately 87 °C, with the exception of the  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  diblock copolymer where due to the low molecular weight and the partial miscibility of the blocks, the glass transition occurs at a lower temperature (56 °C). Another reason which could cause the decrease of glass transition temperature is the butyl groups from the initiator, which also could act as a plasticizer in the case of low degree of polymerization [43,44]. The DMTA graph of the diblock copolymer  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  exhibits a very low loss modulus  $G''$  because of the low molecular weight. Generally, the DMTA graphs reveal almost no rubbery plateau above the glass transition temperature. A cross-over of  $G'$  and  $G''$  is not visible, particularly in the case of the  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  diblock copolymer. Due to the higher molecular weight, only the diblock copolymer  $\text{PS}_{92}\text{PI}_{08}^{32.2}$  depicts a very small entanglement plateau in the DMTA graph. Furthermore, DMTA curves indicate no order-disorder transition. Different heating/cooling rates do not influence the observation of this transition. The onset of microphase separation would have been identified by a rapid change of the slope in the temperature interval of the order – disorder transition. The DMTA data show that the polystyrene microphase, which is the majority component, strongly influences and dominates the viscoelastic behavior of the diblock copolymer. This result is in agreement with the work of Han et al. [45]. Additionally, the glass transition temperature of the diblock copolymers depends on the molecular weight as well as on the molecular composition.



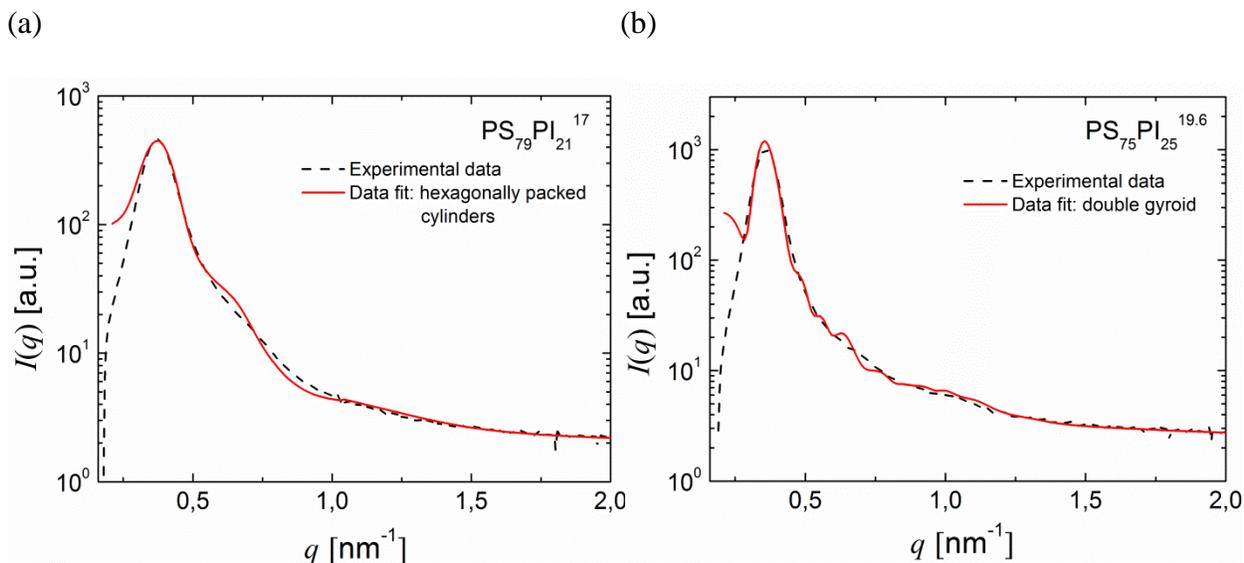
**Fig. 1** Results of DMTA experiments for (a)  $PS_{69}PI_{31}^{7.5}$ , (b)  $PS_{79}PI_{21}^{17}$ , (c)  $PS_{75}PI_{25}^{19.6}$ , (d)  $PS_{78}PI_{22}^{20.6}$  and (e)  $PS_{92}PI_{08}^{32.2}$ . The storage and the loss moduli ( $G'$  and  $G''$ ) are shown as functions of temperature ( $T$ ). The frequency was 1 Hz and the cooling rate was 1  $^{\circ}K/min$ .

### *Morphological Properties*

TEM micrographs and SAXS data are presented in Figs. 2 and 3 respectively. It needs to be mentioned that morphological characterization was done at room temperature. The results do not correspond to the morphology of the diblock copolymers in the melt. Since the relaxation times of the diblock copolymers of this study are very short and the samples were cooled down slowly after annealing, the morphologies presumably represent the equilibrium at the glass transition temperature of the polystyrene or polystyrene-rich microphase.



**Fig. 2** Transmission electron micrographs of two diblock copolymers of this study: (a) PS<sub>79</sub>PI<sub>21</sub><sup>17</sup> and (b) PS<sub>75</sub>PI<sub>25</sub><sup>19.6</sup>. The bright areas correspond to the polystyrene microphase.



**Fig. 3** SAXS patterns for the examined diblock copolymers: (a)  $\text{PS}_{79}\text{PI}_{21}^{17}$  and (b)  $\text{PS}_{75}\text{PI}_{25}^{19.6}$ . The intensity  $I$  is given as a function of the magnitude  $q$  of the scattering vector. The dashed and the solid lines correspond to the experimental curves and the fitted models, respectively.

Due to the low molecular weight and the composition of the examined diblock copolymers, no long range order was found. This is in agreement with the calculated  $\chi N$  values which indicate that the samples are near the limit of weak segregation limit. In more detail the samples  $\text{PS}_{69}\text{PI}_{31}^{7.5}$ ,  $\text{PS}_{79}\text{PI}_{21}^{17}$ ,  $\text{PS}_{78}\text{PI}_{22}^{20.6}$  and  $\text{PS}_{92}\text{PI}_{08}^{32.2}$  exhibited microphase separation, but a regularly ordered structure was not observed. As representative TEM micrograph and SAXS pattern, the data of the sample  $\text{PS}_{79}\text{PI}_{21}^{17}$  are given in Fig. 2(a) and Fig. 3(a), respectively. In the TEM micrograph the polyisoprene (dark phase) in the matrix of polystyrene (bright phase) is observed. The respective SAXS pattern in Fig. 3(a) confirms the weak order, since very broad peaks are observed. Upon the models for different microphase structures in diblock copolymers, the overall SAXS curve could be fitted best with a model of hexagonally packed cylinders. However, as mentioned before, clear peaks shown by the model could not be seen experimentally. Thus the structure is highly distorted, if not even disordered, as could be expected from the low  $\chi N$  value. Through this model the lattice constant and the nearest neighbor distance were calculated and are found equal to 17.9 nm. The displacement from the optimal structure is 16%, relatively high since the peaks are very weak and the diameter of the cylinders is 4.8 nm with a standard deviation of 19%.

On the contrary, the sample  $\text{PS}_{75}\text{PI}_{25}^{19.6}$  depicts a more pronounced order. In the transmission electron micrograph Fig. 2(b) a bi-continuous structure is observed. From the SAXS data (Fig. 3(b)) broad peaks are visible (experimental data), indicating weak order. In this case, the model for the

double gyroid structure led to the best fit, although many individual peaks of the fit are not observed experimentally. Through the calculated model the lattice constant is 44.2 nm and the nearest neighbor distance 38.3 nm. The domain size is very small as a result of the very weak peaks. The displacement from the ideal structure according to the model is 10%, which indicates a more elaborated order and is lower than in the case of the previously mentioned diblock copolymer. The diameter of the gyroid phase is 6.5 nm with a standard deviation of 11%. The morphological characterization of the diblock copolymers of this work differs from literature [24,46,47]. Förster et al. [24] examined copolymers with a majority of 1,4-polyisoprene near the weak segregation regime. In our study, the majority is associated with 1,2- and 3,4-polyisoprene microstructure, near the limit of weak segregation. Our results on the PS<sub>75</sub>PI<sub>25</sub><sup>19.6</sup> block copolymer indicate the existence of the double gyroid structure in lower weight fractions of polyisoprene, expanding their experimental phase transition diagram. On the other hand, Hasegawa et al. [47], working on a diblock copolymer system similar to ours, without temperature annealing treatment, identified the double gyroid structure at a polyisoprene weight fraction of 35% and a total diblock copolymer molecular weight of 96 kg/mol. A hexagonal cylindrical structure was observed for a polyisoprene weight fraction of 26% and a total molecular weight of 22 kg/mol. On the contrary, in this work, the double gyroid structure was obtained at 25% polyisoprene weight fraction for the sample PS<sub>75</sub>PI<sub>25</sub><sup>19.6</sup>. The observation of different microphase-separated structures appears due to the fact that the samples belong to the weak segregation regime, a regime where the morphologies observed could not be accurately predicted.

### *Rheological Characterization*

The analysis of the data from the frequency sweeps at different temperatures led to master curves using the method of time-temperature superposition with the software LSSHIFT (Freiburg Materials Research Center, Freiburg, Germany). Furthermore, creep recovery experiments were performed in shear. The creep and the recovered creep compliance  $J(t)$  and  $J_r(t')$  were calculated taking into account the deformation caused by the response of the material to the applied stress. The time-dependent creep compliance  $J(t)$  is defined by the equation

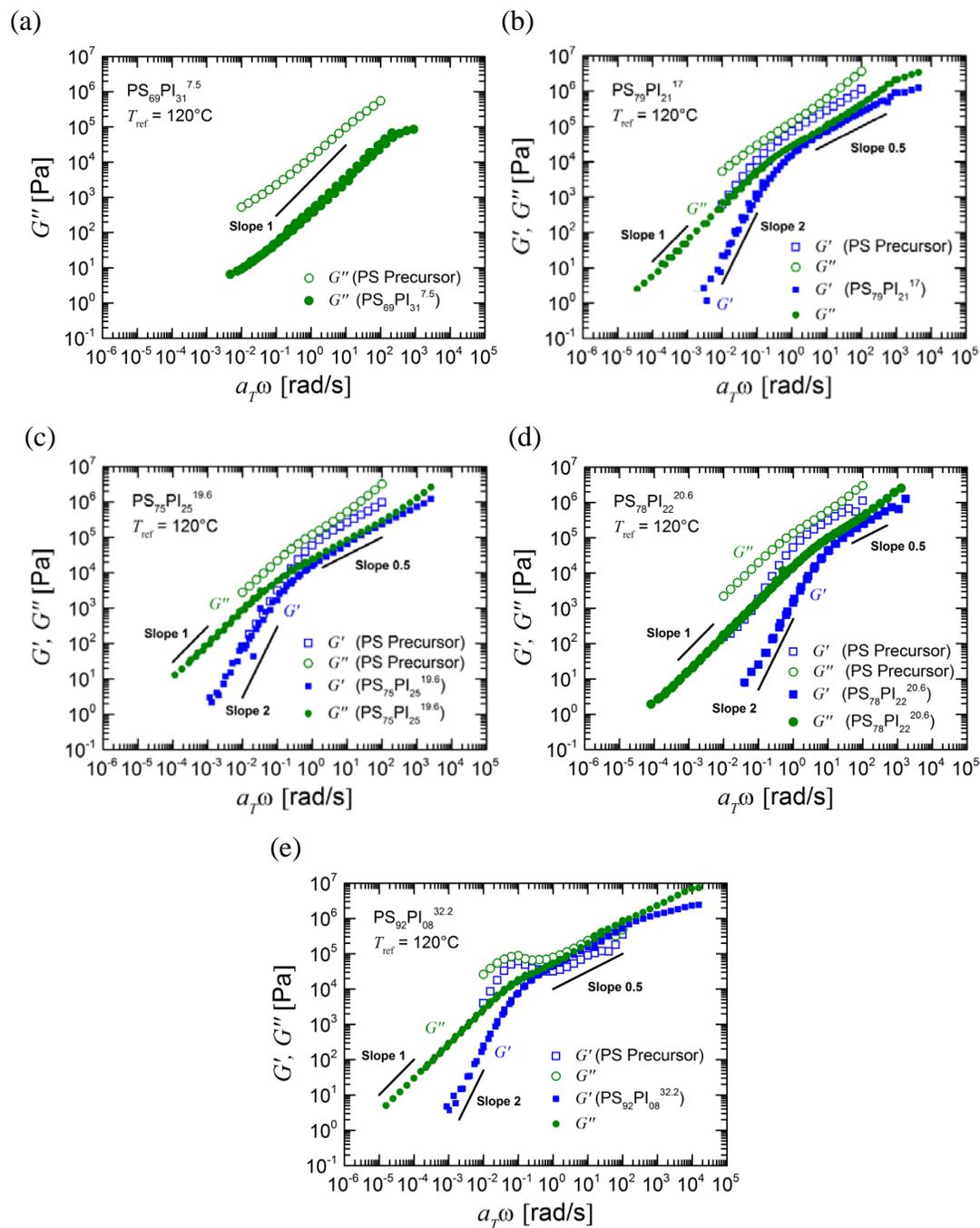
$$J(t) = \gamma(t)/\sigma_{xy} \quad (2)$$

with the shear strain  $\gamma(t)$  and the constant creep stress  $\sigma_{xy}$  in the creep interval. The recovered creep compliance, which is proportional to the recovered strain, was calculated using

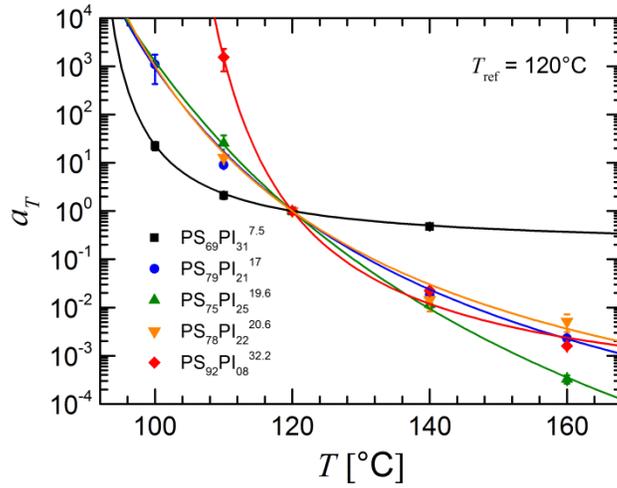
$$J_r(t') = [\gamma_{max} - \gamma(t')]/\sigma_{xy} \quad (3)$$

where  $\gamma(t')$  and  $\gamma_{max}$  denote the shear strain at time  $t'$  and  $t = t_{max}$ , respectively. The recovery time  $t'$  in the recovery interval ( $t \geq t_{max}$ ) is given by  $t' = t - t_{max}$ , and the creep time is denoted by  $t_{max}$ . Creep recovery experiments are described in detail, e.g., in Ref. [48].

The results of the rheological investigations are shown in Figs. 4 to 6. The master curves of the experiments in the oscillatory mode are presented in Fig. 4 for all examined diblock copolymers. In Fig. 5 the time-temperature shift factor  $a_T$  as a function of temperature is shown. The reference temperature was 120 °C, which is above the order-disorder transition temperature. In Fig. 6, creep and creep recovery data of two selected polymers are presented at a temperature of 120 °C in order to compare the creep data with the frequency sweeps.



**Fig. 4** Master curves created with the method of data superposition from frequency sweeps for the samples (a)  $\text{PS}_{69}\text{PI}_{31}^{7.5}$ , (b)  $\text{PS}_{79}\text{PI}_{21}^{17}$ , (c)  $\text{PS}_{75}\text{PI}_{25}^{19.6}$ , (d)  $\text{PS}_{78}\text{PI}_{22}^{20.6}$  and (e)  $\text{PS}_{92}\text{PI}_{08}^{32.2}$  and their polystyrene precursors. The reference temperature was  $T_{\text{ref}} = 120^\circ\text{C}$ . The dynamic moduli of the polystyrene precursors are also shown (open symbols). The values of the storage modulus  $G'$  in (a) were beyond the limit of rheometer resolution and hence are not shown. For the same reason the data in (d) only include the  $G'$  measurements at  $110^\circ\text{C}$  and  $120^\circ\text{C}$ . In (a) and (b) data at  $100^\circ\text{C}$  are also included.



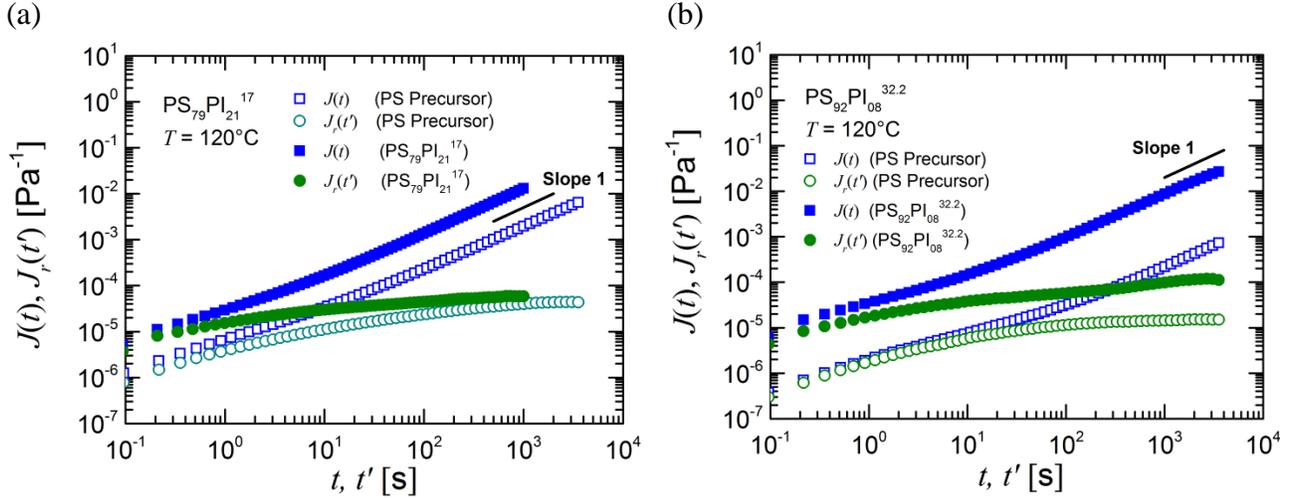
**Fig. 5** Shift factor  $a_T$  of the diblock copolymers for the reference temperature  $T_{\text{ref}} = 120$  °C, cf. also Table 1(b).

The master curves in Fig. 4 correspond to the viscoelastic behavior of Maxwell fluids since the characteristic power-laws for  $G'$  and  $G''$  (slopes 2 and 1, respectively) are observed for these low molecular weight polymers at low frequencies in the double-logarithmic presentation. In the limit of low frequencies, it is possible to calculate the zero-shear rate viscosity  $\eta_0$  and the elastic equilibrium compliance  $J_e^0$  :

$$\eta_0 = G''/\omega \text{ for } \omega \rightarrow 0 \quad (4)$$

$$J_e^0 = G'/(\omega\eta_0)^2 \text{ for } \omega \rightarrow 0 \quad (5)$$

where  $\omega$  denotes the angular frequency. The master curves in Fig. 4 do not show an entanglement plateau in agreement with the results of the DMTA experiments. In the frequency range around  $\omega = 100$  rad/s,  $G'$  and  $G''$  attain the slope 0.5 on a double-logarithmic scale which corresponds to the Rouse behavior at the glass-rubber transition. Furthermore the comparison of the dynamic moduli of the polystyrene precursor and the corresponding diblock copolymer in the frequency range around  $\omega = 100$  rad/s reveals an increase of loss tangent  $\tan \delta = G''/G'$  for the diblock copolymers, i.e.  $G'$  and  $G''$  attain similar values in comparison to the polystyrene precursor. This increase of elasticity is caused by the larger chain length of the block copolymer when compared to the precursor leading to a more pronounced tendency to entanglements. On the other hand, the absolute value of the dynamic moduli is reduced by the presence of the “soft” polyisoprene segments.



**Fig. 6** Creep ( $J(t)$ ) and recovered creep ( $J_r(t')$ ) compliance as a function of time  $t$  and recovery time  $t'$ , respectively, with shear stress  $\sigma_{xy}$  of 50 Pa, creep time of 1000 s and 3600 s, respectively, and temperature of 120 °C. The diblock copolymers are (a) PS<sub>79</sub>PI<sub>21</sub><sup>17</sup> and (b) PS<sub>92</sub>PI<sub>08</sub><sup>32.2</sup>. The results for the polystyrene precursors are also shown.

The shift factor  $a_T$  in Fig. 5 strongly depends on the composition of the diblock copolymer. In case of the diblock copolymer PS<sub>69</sub>PI<sub>31</sub><sup>7.5</sup> the polyisoprene fraction is relatively large, which leads to a high viscosity reduction. Consequently, the temperature dependence of  $a_T$  is less pronounced than for the other diblock copolymers because the influence of the polystyrene component (with a larger  $T_g$  value and thus a stronger temperature dependence) is decreased. The shift factors of PS<sub>79</sub>PI<sub>21</sub><sup>17</sup>, PS<sub>75</sub>PI<sub>25</sub><sup>19.6</sup> and PS<sub>78</sub>PI<sub>22</sub><sup>20.6</sup> attain similar values because of their similar composition. The block copolymer with the largest molecular weight and the largest polystyrene fraction (PS<sub>92</sub>PI<sub>08</sub><sup>32.2</sup>) is characterized by a large value of  $a_T$  at 110 °C because of the highest glass transition temperature, see Table 1. The temperature dependence of the shift factor  $a_T$  of amorphous polymers can be generally described by the Williams-Landel-Ferry equation

$$\log(a_T) = -c_1(T - T_{\text{ref}})/[c_2 + (T - T_{\text{ref}})] \quad (6)$$

with the parameters  $c_1$  and  $c_2$ .  $T$  is the temperature of the experiment and  $T_{\text{ref}}$  the reference temperature [49]. Using a least-squares fit, the material parameters  $c_1$  and  $c_2$  were obtained for the reference temperature 120 °C, cf. Table 1(b). A clear trend in the data can be seen by comparing the values of  $c_1/c_2$ . The value of  $-c_1/c_2$  is proportional to the logarithm of the shift factor  $\log(a_T)$  in the vicinity of the reference temperature and thus equals the slope of  $\log(a_T)$  at the reference

temperature. Below the reference temperature, the shift factor attains the lowest value for PS<sub>69</sub>PI<sub>31</sub><sup>7.5</sup> (lowest  $T_g$  and highest PI content) and the largest value for PS<sub>92</sub>I<sub>08</sub><sup>32.2</sup> (largest  $T_g$  and highest PS content) in agreement with the fact that a stronger temperature dependence is observed closer to the glass transition temperature, i.e. for PS<sub>92</sub>I<sub>08</sub><sup>32.2</sup>. The value of  $10^{-c_1}$  indicates the shift factor at large temperatures. The diblock copolymer PS<sub>69</sub>PI<sub>31</sub><sup>7.5</sup> attains a shift factor close to unity because of its weak temperature dependence, since its glass transition temperature attains the lowest value among the diblock copolymers of this study. The other four diblock copolymers attain roughly similar  $c_1$  values.

**Table 3** Zero-shear rate viscosity  $\eta_0$  and elastic equilibrium compliance  $J_e^0$  based on the analysis of the master curve and of the creep recovery experiments at a temperature of 120 °C. The empty entries marked with “-” means that no analysis was possible.

Samples	$\eta_0$ [Pa s] (Master curve)	$J_e^0$ [Pa <sup>-1</sup> ] (Master curve)	$\eta_0$ [Pa s] (Creep)	$J_e^0$ [Pa <sup>-1</sup> ] (Creep)
PS of PS <sub>69</sub> PI <sub>31</sub> <sup>7.5</sup>	2.27 x 10 <sup>4</sup>	-	-	-
PS <sub>69</sub> PI <sub>31</sub> <sup>7.5</sup>	2.91 x 10 <sup>2</sup>	-	4.37 x 10 <sup>2</sup>	-
PS of PS <sub>79</sub> PI <sub>21</sub> <sup>17</sup>	5.32 x 10 <sup>5</sup>	2.2 x 10 <sup>-5</sup>	5.82 x 10 <sup>5</sup>	4.3 x 10 <sup>-5</sup>
PS <sub>79</sub> PI <sub>21</sub> <sup>17</sup>	5.31 x 10 <sup>4</sup>	7.8 x 10 <sup>-5</sup>	7.82 x 10 <sup>4</sup>	5.9 x 10 <sup>-5</sup>
PS of PS <sub>75</sub> PI <sub>25</sub> <sup>19.6</sup>	2.75 x 10 <sup>5</sup>	1.1 x 10 <sup>-5</sup>	3.05 x 10 <sup>5</sup>	-
PS <sub>75</sub> PI <sub>25</sub> <sup>19.6</sup>	1.03 x 10 <sup>5</sup>	7.7 x 10 <sup>-5</sup>	1.44 x 10 <sup>5</sup>	-
PS of PS <sub>78</sub> PI <sub>22</sub> <sup>20.6</sup>	2.22 x 10 <sup>5</sup>	3.1 x 10 <sup>-5</sup>	3.24 x 10 <sup>5</sup>	-
PS <sub>78</sub> PI <sub>22</sub> <sup>20.6</sup>	1.77 x 10 <sup>4</sup>	1.6 x 10 <sup>-5</sup>	3.99 x 10 <sup>4</sup>	-
PS of PS <sub>92</sub> PI <sub>08</sub> <sup>32.2</sup>	-	-	5.02 x 10 <sup>6</sup>	1.7 x 10 <sup>-5</sup>
PS <sub>92</sub> PI <sub>08</sub> <sup>32.2</sup>	2.93 x 10 <sup>5</sup>	2.6 x 10 <sup>-5</sup>	1.54 x 10 <sup>5</sup>	7.1 x 10 <sup>-5</sup>

Creep experiments allow the calculation of the zero-shear rate viscosity and the elastic equilibrium compliance. Figure 6 presents two examples of creep recovery experiments. The slope of the creep compliance at large times is proportional to  $1/\eta_0$  and equals unity on a double-logarithmic scale which indicates terminal flow behavior of the polymer. In particular, the creep time  $t_{max}$  was larger than the largest retardation time of the diblock copolymers. The equilibrium

compliance  $J_e^0$  is defined by the steady-state value of the recovered creep compliance  $J_r(t')$  at large recovery times  $t'$ . The creep experiments also reveal that the diblock copolymers of this study behave like Maxwell fluids. In Table 3, the results regarding the zero-shear rate viscosity  $\eta_0$  and the equilibrium compliance  $J_e^0$  from the master curve with reference temperature 120 °C are summarized.

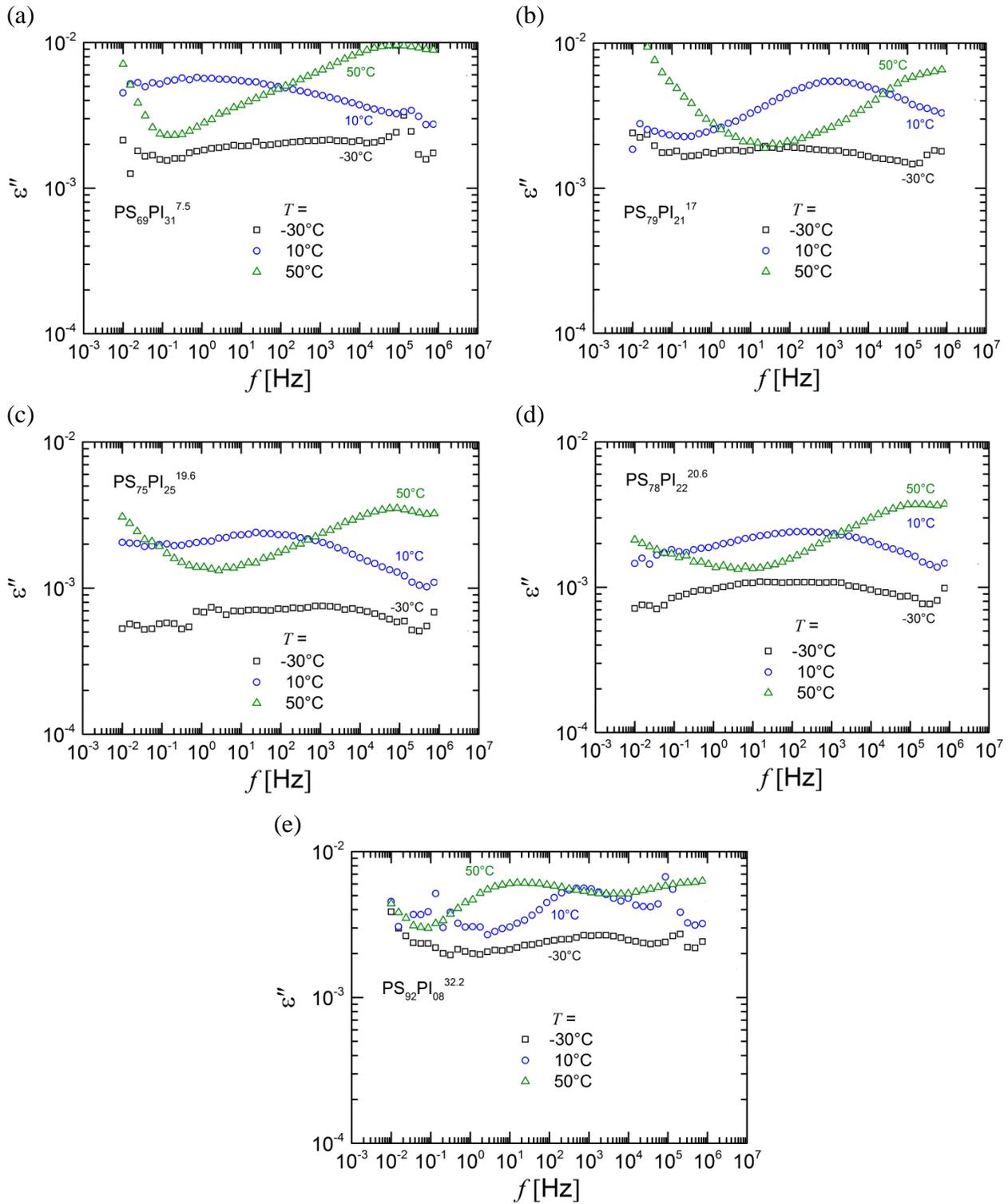
The viscosity of the  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  diblock copolymer was very low because of the low molecular weight. Accordingly, the elastic equilibrium compliance could not be determined neither in oscillation nor in creep due to the limit of rheometer resolution and the drift in the creep experiment, respectively. On the contrary, the diblock copolymer  $\text{PS}_{92}\text{PI}_{08}^{32.2}$ , which has the largest molecular weight and the largest fraction of polystyrene, has the largest viscosity. The comparison of this diblock copolymer viscosity with its polystyrene precursor reveals that the presence of polyisoprene segments, although even at a small weight fraction, reduces the viscosity, implying a lower monomeric friction coefficient. The same behavior is also observed for the three other diblock copolymers. The zero-shear rate viscosity is strongly reduced by the presence of the polyisoprene segments. On the contrary, the elastic equilibrium compliance is influenced to a lower extent, see the data in Table 3.

### *Dielectric Spectroscopy*

The results of the dielectric spectroscopy experiments are presented in Fig. 7 for the five diblock copolymers of this study. In this figure, the dielectric loss  $\varepsilon''$  of the diblock copolymers is shown as a function of frequency for three temperatures (-30 °C, 10 °C and 50 °C) below the order-disorder transition temperature. Figure 7(a) presents the data for  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  which has the lowest molecular weight among the five samples. At low temperatures (i.e. in the range of -50 °C to approximately 0 °C) no relaxation process can be seen because of the very low content of 1,4-microstructure in the polyisoprene block. Therefore a normal mode relaxation could not be observed, as in studies of block copolymers with a larger content of 1,4-microstructure [11,32]. The data for  $T = 10$  °C show a very broad relaxation peak. This broad relaxation peak can be attributed to the segmental relaxation of the polyisoprene microphase. At a measurement temperature of 50 °C, a pronounced increase of  $\varepsilon''$  is observed at low frequencies, which is caused by ionic conductivity.

The sample  $\text{PS}_{79}\text{PI}_{21}^{17}$  does not show any pronounced relaxation process at -30 °C (Fig. 7(b)). However, the peak of segmental relaxation at 10 °C is more pronounced than for  $\text{PS}_{69}\text{PI}_{31}^{7.5}$ ,

because of the larger molecular weight and the larger value of  $\chi N$  (less miscibility between the polystyrene and polyisoprene domains). Furthermore, the increase of ionic conductivity at low frequencies at 50 °C starts at higher frequencies than for the sample  $\text{PS}_{69}\text{PI}_{31}^{7.5}$  because of the larger polystyrene fraction. Similar trends can be seen for the samples  $\text{PS}_{75}\text{PI}_{25}^{19.6}$  and  $\text{PS}_{78}\text{PI}_{22}^{20.6}$  in Fig. 7(c) and (d). The results for the sample with the lowest fraction of polyisoprene ( $\text{PS}_{92}\text{PI}_{08}^{32.2}$ ) are shown in Fig. 7(e). The peak of the segmental relaxation of the polyisoprene phase can be clearly seen at the measurement temperature of 10 °C.



**Fig. 7** Dielectric loss  $\epsilon''$  for the examined block copolymers as a function of frequency  $f$  at three different temperatures ( $-30^\circ\text{C}$ ,  $10^\circ\text{C}$  and  $50^\circ\text{C}$ ). The samples are (a)  $\text{PS}_{69}\text{PI}_{31}^{7.5}$ , (b)  $\text{PS}_{79}\text{PI}_{21}^{17}$ , (c)  $\text{PS}_{75}\text{PI}_{25}^{19.6}$ , (d)  $\text{PS}_{78}\text{PI}_{22}^{20.6}$  and (e)  $\text{PS}_{92}\text{PI}_{08}^{32.2}$ .

## Conclusion

In this study, polystyrene-*block*-polyisoprene diblock copolymers near the weak segregation limit were investigated. Thermal characterization by means of differential scanning calorimetry revealed two glass transitions for each block copolymer. Since polystyrene forms the majority component, the glass transition of the polyisoprene block was difficult to detect. Dynamic-mechanical-thermal analysis also proved the  $T_g$  value of the polystyrene phase. Morphological characterization at room temperature revealed the structuring of the block copolymers after film casting and annealing.

Despite the low molecular weight, dynamic heterogeneity on a local (segmental) scale was observed even in the disordered state. However, no long-range order was present in these samples. The observation of the double gyroid structure for a diblock copolymer near the weak segregation regime and a total molecular weight below the molecular weight for entanglements gave significant information regarding the microphase transition. From the morphological characterization it is observed that although the phase diagram does not predict microphase-separated morphologies, weakly ordered microstructures are observed.

Rheological characterization was performed using frequency sweeps and creep recovery experiments in shear above the order-disorder transition temperature. The disordered diblock copolymers behaved as Maxwell fluids. This result implies that the samples of this study essentially behave like one phase systems with viscoelastic properties that are derived from the composition of the two blocks. The order-disorder transition temperature of these block copolymers is close to the glass transition temperature of polystyrene. The presence of “soft” polyisoprene segments yields a reduction of the average monomeric friction coefficient and to more pronounced elasticity because of the larger chain length and the larger tendency towards entanglements. On the other hand, dielectric spectroscopy gave the possibility of studying the relaxation properties of these diblock copolymers in the non-melt state. The results of dielectric spectroscopy gave further indication of the glass transition of the polyisoprene domains in the temperature interval around 10°C. Consequently, the analysis and comparison of the three different techniques for viscoelastic and thermal characterization of diblock copolymers reveal that the dilution effect caused by the partial miscibility of the polystyrene and the polyisoprene domains can be described by effective parameters for the thermal and viscoelastic properties of the block copolymer. These effective

values of glass transition temperature and viscosity depend on the molecular weight and composition of the diblock copolymer.

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