

RESEARCH ARTICLE | MAY 22 2015

# Analysis of stability and viscoelastic properties of melts of polystyrene-*block*-polyisoprene diblock copolymers in oscillatory shear and creep-recovery experiments **FREE**

Ulrich A. Handge; Taida Gil Haenelt; Prokopios Georgopoulos; Clarissa Abetz; Sofia Rangou; Doreen Alisch; Ulla Vainio; Andreas Meyer; Volker Abetz



AIP Conf. Proc. 1664, 170001 (2015)

<https://doi.org/10.1063/1.4918519>



20 July 2024 02:29:18

## AIP Advances

Why Publish With Us?

- 25 DAYS**  
average time to 1st decision
- 740+ DOWNLOADS**  
average per article
- INCLUSIVE**  
scope

[Learn More](#)

# Analysis of Stability and Viscoelastic Properties of Melts of Polystyrene-*block*-Polyisoprene Diblock Copolymers in Oscillatory Shear and Creep-Recovery Experiments

Ulrich A. Handge,<sup>a</sup> Taida Gil Haenelt,<sup>a,b</sup> Prokopios Georgopoulos,<sup>a</sup> Clarissa Abetz,<sup>a</sup> Sofia Rangou,<sup>a</sup> Doreen Alisch,<sup>b</sup> Ulla Vainio,<sup>c</sup> Andreas Meyer,<sup>b</sup> Volker Abetz<sup>a,b</sup>

<sup>a</sup>*Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Strasse 1, 21502 Geesthacht, Germany*

<sup>b</sup>*Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany*

<sup>c</sup>*Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Strasse 1, 21502 Geesthacht, Germany*

**Abstract.** In this study, the rheological properties of polystyrene-*block*-polyisoprene (PS-*b*-PI) diblock copolymer melts with different types of morphology are analysed. Using the technique of anionic polymerization three different PS-*b*-PI diblock copolymers with a spherical, cylindrical and lamellar morphology, respectively, were synthesised. The objective of our study was to determine the viscous and elastic properties of these PS-*b*-PI diblock copolymers and to investigate the influence of morphology on the viscoelastic properties at short and long times. The analysis of our experiments reveals that morphological changes take place in the melt which lead to changes of the dynamic moduli. Furthermore, all three diblock copolymers of this study reveal a non-terminal behaviour in oscillatory shear flow in the microphase-separated state. Our creep recovery experiments indicate that microphase-separated diblock copolymers are characterised by a pronounced recoverable deformation.

**Keywords:** Diblock copolymers, Microphase separation, Shear rheology.

**PACS:** 83.80.Uv, 83.85.Vb, 83.85.Tz

## INTRODUCTION

Block copolymers are a versatile class of nanostructured materials. Below the order-disorder transition temperature (ODT) microphase separation yields a variety of complex nanostructures which strongly influence the rheological properties of these materials in melt processing [1]. A complete understanding of stability, elastic and viscous properties is necessary in order to tailor polymer processing. Therefore a series of investigations was devoted to the rheological properties of diblock copolymers in oscillatory shear flow. These studies have shown that diblock copolymers in the microphase-separated state are characterized by a non-terminal behaviour at low frequencies [2]. Han et al. investigated the applicability of different methods in order to determine the ODT via rheological experiments [3]. Furthermore, it was shown that orientation phenomena take place in large amplitude oscillatory shear flow [4]. The works of Sebastian et al. [5,6] reveal that the lattice structure of an ordered polystyrene-*block*-polyisoprene diblock copolymer melt can be broken up in steady shear. This shear-induced disordering is reflected in the rheological quantities. The ordering dynamics of polystyrene-*block*-polyisoprene diblock copolymers was investigated in Ref. 7. After a quench from above ODT, the ordering dynamics is characterized by a two-step process. In contrast to shear oscillations in the linear or in the nonlinear regime, shear experiments at a constant applied shear stress (creep experiments) have been performed to a much lesser extent. These experiments allow the determination of the elastic properties of diblock copolymers (i.e. the recoverable part of deformation) and give much insight into the interplay of microstructure and rheology.

The objective of this work is to study the influence of molecular structure on the rheological properties. In particular, we focus on the elastic properties of diblock copolymers in the microphase-separated state. Creep-recovery experiments allow for the determination of the recoverable part of deformation as a function of creep stress. In this work, shear creep recovery experiments of diblock copolymers with different types of morphology were performed and discussed. Polystyrene-*block*-polyisoprene (PS-*b*-PI) diblock copolymers were chosen as model systems. First the stability and the linear viscoelastic properties of these materials in shear oscillations were discussed. Then creep recovery experiments were analyzed. Morphological investigations were carried out in order to detect morphological changes during the rheological experiments.

## Experimental

### Materials

Three asymmetric polystyrene-*block*-polyisoprene diblock copolymers were synthesized using the technique of sequential anionic polymerization of styrene and isoprene in tetrahydrofuran. The initiator was *sec*-butyllithium. The results of the molecular characterisation of the three diblock copolymers are presented in Table 1. The molecular weight of the polystyrene precursor of the polymerization procedure ranges between 40 000 and 50 000 g/mol for all three different diblock copolymers. This yields a roughly equal number of entanglements of the polystyrene chains for all block copolymers of this study.

**TABLE (1).** Properties of the diblock copolymers of this study. The notation  $S_xI_y^z$  for the three diblock copolymers implies x wt% of styrene and y wt% of isoprene. The number average of the molecular weight in kg/mol is denoted by z.

Polymer	Styrene Content [wt%]	Isoprene Content [wt%]	$M_n$ [g/mol]	$M_w$ [g/mol]	Morphology
$S_{86}I_{14}^{47}$	86	14	47 000	54 000	Spherical
$S_{78}I_{22}^{63}$	78	22	63 000	68 000	Cylindrical
$S_{59}I_{41}^{82}$	59	41	82 000	89 000	Lamellar

### Rheological Experiments

Cylindrical samples with a diameter of 8 mm and a thickness of 2 mm were used for the rheological experiments. The samples were prepared by compression moulding at a temperature of 135 °C for 23 min. A rotational rheometer (MCR 502, Anton Paar GmbH, Graz, Austria) was used with a plate-plate geometry in a nitrogen atmosphere. The gap between the lower and the upper plate was set to 1.9 mm.

The stability of the samples was studied using time sweeps with a constant angular frequency of 0.1 rad/s and a strain amplitude of 4%. The measurement temperature of the stability tests was 180 °C which was in all cases below the order-disorder transition temperature of the diblock copolymers. Shear oscillations at five different temperatures (120, 140, 160, 180 and 200 °C) in the linear viscoelastic regime were performed with the strain amplitude equal to 4%. Master curves of the dynamic moduli  $G'$  and  $G''$  were obtained using the time-temperature superposition principle. The reference temperature was 120 °C. In order to determine the elastic properties of the diblock copolymers in the melt, creep-recovery experiments were performed at a temperature of 180 °C. The creep and the recovery time were both 10000 s. In the creep interval a creep stress of 50 Pa was applied. In the subsequent recovery interval, the stress was set to zero and the recoverable deformation was measured. Further creep experiments with a creep stress of 500 Pa and 5000 Pa, respectively, were also performed.

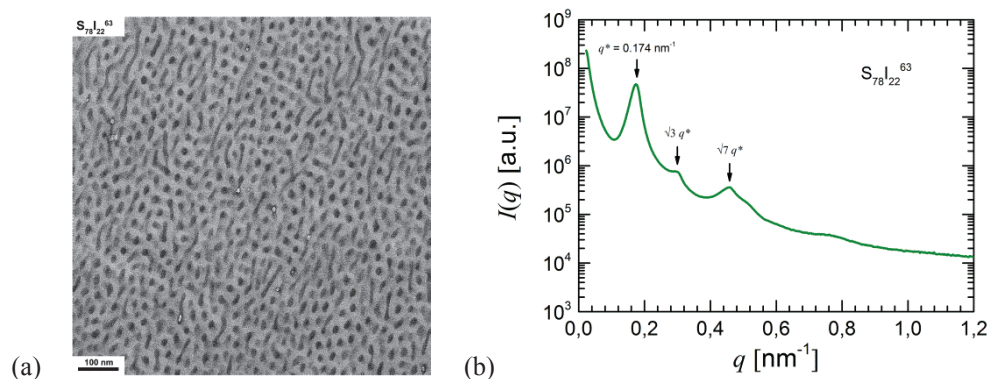
### Morphological Investigations

Compression moulded samples and solution cast films of the three diblock copolymers were used for microscopic investigations. Ultrathin sections were obtained by an ultramicrotome equipped with a diamond knife. The ultrathin sections were stained with osmium tetroxide vapor. A transmission electron microscope FEI Tecnai G2 F20 (FEI, Eindhoven, The Netherlands) was used for the investigations. The acceleration voltage was 200 kV. The brighter areas in the transmission electron micrographs correspond to the polystyrene phase and the dark regions to the polyisoprene phase.

Small angle X-ray scattering (SAXS) measurements were carried out at bioSAXS beamline P12 at the PETRA III synchrotron of DESY in Hamburg at an X-ray energy of 10 keV. Compression-moulded samples were used for the experiments. The samples were investigated before and after selected rheological experiments. The sample-to-detector distance was 3065 mm and the scattering was detected using a Pilatus 2M area detector.

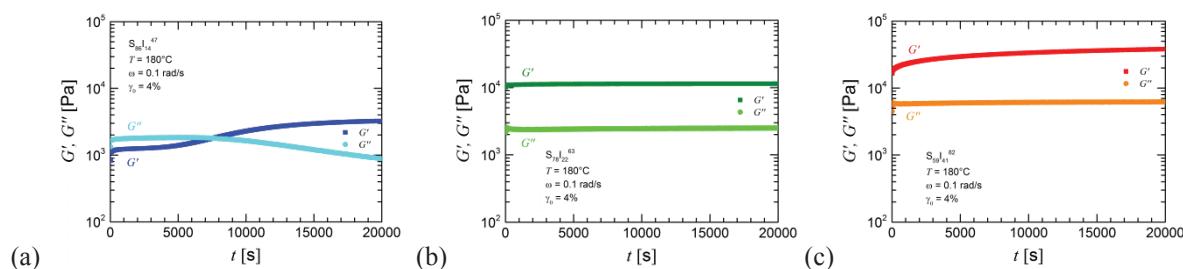
## RESULTS AND DISCUSSION

The morphological investigations using transmission electron microscopy and SAXS experiments revealed that the three different compositions of the diblock copolymers led to different morphologies, i.e. a spherical ( $S_{86}I_{14}^{47}$ ), a



**FIGURE 1.** (a) Transmission electron micrograph of a compression moulded sample of the diblock copolymers  $S_{78}I_{22}^{63}$  of this study. The bright phase is the polystyrene phase and the dark phase corresponds to the polyisoprene phase. (b) SAXS pattern of a sample of the diblock copolymer  $S_{78}I_{22}^{63}$  after a time sweep with  $\omega = 0.1$  rad/s and  $\gamma_0 = 4\%$  at  $180^\circ\text{C}$  for 20000 s.

cylindrical ( $S_{78}I_{22}^{63}$ , see Fig. 1) and a lamellar ( $S_{59}I_{41}^{82}$ ) morphology. Because of the sample preparation technique (compression moulding) and the relatively long relaxation times of the polymer chains in the melt state, deviations from a perfectly long-range ordered structure were observed. First, the thermal stability of the three diblock copolymers in the melt was analysed. The thermal stability of the block copolymers at a temperature of  $180^\circ\text{C}$  is shown in Figure 2. The dependence of the dynamic moduli as a function of time differs for the three diblock copolymers and depicts three different scenarios. Figure 2(a) shows that the storage modulus  $G'$  of the diblock copolymer  $S_{86}I_{14}^{47}$  with a spherical morphology increases, while the loss modulus  $G''$  decreases with time. The time-dependence of the dynamic moduli can be explained by an increase of ordering of the lattice structure of the spherical morphology (increase of long-range order). This effect takes place on a large time scale, since the measurement temperature of  $180^\circ\text{C}$  is just slightly below the order-disorder transition temperature ( $T_{\text{ODT}} \approx 184^\circ\text{C}$  for  $S_{86}I_{14}^{47}$ ) and therefore the thermodynamic driving force is weak. The dynamic moduli of the diblock copolymer with a cylindrical morphology do not change much with time (Fig. 2(b)). An increase of storage modulus for the diblock copolymer with a lamellar morphology is shown in Fig. 2(c). In this case, the interface becomes “sharper” with time which leads to an increase of storage modulus.



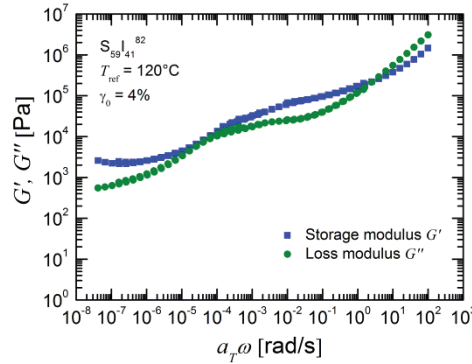
**FIGURE 2.** Storage modulus  $G'$  and loss modulus  $G''$  as a function of time  $t$  at a temperature of  $180^\circ\text{C}$  for the diblock copolymers of this study. The angular frequency  $\omega$  was 0.1 rad/s and the shear amplitude was 4%.

Our linear viscoelastic shear oscillations reveal that at low frequencies, the diblock copolymers show a non-terminal behaviour. This effect is demonstrated for the diblock copolymer with a lamellar morphology in Fig. 3. Although diblock copolymers are two-component systems with styrene and isoprene units, the application of the time-temperature superposition principle yields satisfactory mastercurves. In the case of polystyrene-*block*-polyisoprene copolymers, the response of the diblock copolymer to a deformation is strongly influenced by the polystyrene phase which has a higher glass transition temperature than polyisoprene. Consequently, at high frequencies the contribution of the polystyrene phase is much larger than the contribution of the polyisoprene phase. At low frequencies, the rheological response of the diblock copolymer is determined by the microphase-separated morphology.

The analysis of creep experiments is based on the time-dependent creep compliance  $J(t)$  and the recovered compliance  $J_r(t')$ . These two quantities are defined by

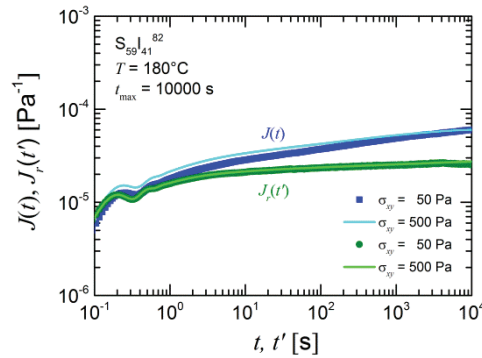
$$J(t) = \frac{\gamma(t)}{\sigma_0}, \quad J_r(t') = \frac{\gamma_{\max} - \gamma(t')}{\sigma_0} \quad (1)$$

where  $\sigma_0$  denotes the creep stress in the first interval,  $\gamma(t)$  the shear strain of the sample and  $\gamma_{\max}$  the shear strain at time  $t = t_{\max}$ . The recovery time is defined by  $t' = t - t_{\max}$ .



**FIGURE 3.** Storage modulus  $G'$  and loss modulus  $G''$  as a function of angular frequency  $\omega$  for the diblock copolymer with a lamellar morphology ( $S_{59}I_{41}^{82}$ ). The reference temperature was 120°C.

The results of the creep recovery experiments of the block copolymer with a lamellar morphology ( $S_{59}I_{41}^{82}$ ) are presented in Figure 4. In contrast to homopolymers, the creep curves of the diblock copolymers do not depict the slope 1 in a double-logarithmic scale. This result is in agreement with the linear viscoelastic shear oscillations showing a non-terminal behaviour at low frequencies which corresponds to the creep behaviour at large times. Furthermore, the recovered creep compliance almost attains values which do not differ much from the values of the creep compliance. This effect implies that the diblock copolymers are characterised by a pronounced elasticity. This result is also demonstrated by the so-called creep-ringing effect at low creep and recovery times in Fig. 4 (oscillating values of compliance in the interval from 0.1 to 1 s), see also Ref. [9].



**FIGURE 4.** Creep compliance  $J(t)$  and recovered compliance  $J_r(t')$  as a function of time  $t$  and recovery time  $t'$ , respectively, for the diblock copolymer with a lamellar morphology ( $S_{59}I_{41}^{82}$ ) at a temperature of 180°C. The creep stress  $\sigma_0$  was 50 Pa and 500 Pa, respectively, and the creep time  $t_{\max} = 10000$  s.

## CONCLUSIONS

Our rheological experiments reveal that the molecular structure strongly influences the viscous and elastic properties of melts of diblock copolymers. The molecular weight of the diblock copolymers plays a key role for the formation of microphases and the dynamical properties in the melt state. The time sweeps show that morphological ordering processes take place in the melt. Linear viscoelastic shear oscillations reveal that below the order-disorder transition temperature a non-terminal behaviour exists for the diblock copolymers. In creep-recovery experiments at low stresses, diblock copolymers do not display a Newtonian flow regime with slope 1 at large times. On the contrary, viscous flow is strongly suppressed at low creep stresses. Diblock copolymer melts in the microphase-separated state are characterized by a pronounced elastic behaviour.

## ACKNOWLEDGMENTS

The authors are thankful to Ivonne Ternes for rheological experiments, Silvio Neumann for thermal analysis and nuclear magnetic resonance investigations and Maren Brinkmann for gel permeation chromatography measurements. The experimental support of Dr. Vasyi Garamus at P12 is gratefully acknowledged. The authors also gratefully acknowledge financial support from the German Research Foundation (DFG) via SFB 986 "M3," projects A2 and Z2.

## REFERENCES

1. F.S. Bates, G.H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525-557 (1990).
2. R.G. Larson, K.I. Winey, S.S. Patel, H. Watanabe, R. Bruinsma, *Rheol. Acta* **32**, 245-253 (1993).
3. C.D. Han, D.M. Baek, J.K. Kim, T. Ogawa, N. Sakamoto, T. Hashimoto, *Macromol.* **28**, 5043-5062 (1995).
4. K.A. Koppi, M. Tirell, F.S. Bates, K. Almdal, R.H. Colby, *J. Phys. II France* **2**, 1941-1959 (1992).
5. J.M. Sebastian, C. Lai, W.W. Graessley, R.A. Register, *Macromol.* **35**, 2700-2706 (2002).
6. J.M. Sebastian, C. Lai, W.W. Graessley, R.A. Register, *Macromol.* **35**, 2707-2713 (2002).
7. J. LaMonte Adams, D.J. Quiram, W.W. Graessley, R.A. Register, G.R. Marchand, *Macromol.* **29**, 2929-2938 (1996).
8. H. Münstedt, N. Katsikis, J. Kaschta, *Macromol.* **41**, 9777-9783 (2008).
9. C. Baravian, D. Quemada, *Rheol. Acta* **37**, 223-233 (1998).