Flow instabilities · softener · wall slip · entropic segregation · rheo-dielectric properties · flocculation · carbon black · carbon nanotubes (CNT)

The impact of softeners (DEHP, DBP) on the rheological response of HNBR melts is discussed in the frame of compatibility and wall slip effects based on entropic segregation. The influence of filler flocculation (carbon black, CNT) on oscillatory and steady shear flow properties is described and analyzed by dielectric spectroscopy measured online in a plate-plate rheometer.

Einfluss von Weichmachern und Füllstoffen auf die rheologischen und dielektrischen Eigenschaften von Elastomerschmelzen

Fließinstabilitäten · Weichmacher · Wandgleiten · entropische Entmischung · rheo-dielektrische Eigenschaften · Flockulation · Ruß · Kohlenstoffnanoröhrchen

Der Einfluss von Weichmachern (DEHP, DBP) auf die rheologischen Eigenschaften von HNBR-Schmelzen wird im Rahmen von Verträglichkeit und entropisch-bedingten Wandgleiteffekten diskutiert. Der Effekt der Füllerflockulation (Ruß, CNT) auf die schwing- und scherrheologischen Eigenschaften wird beschrieben und mittels online dielektischer Spektroskopie im Platte-Platte Rheometer analysiert.

Figures and tables:
By a kind approval of the authors.

Authors

**Patrick Stratmann,
Markus Möwes,
Manfred Klüppel, Hannover**

Corresponding Author:
Prof. Dr. Manfred Klüppel,
Deutsches Institut für Kautschuktechnologie e.V.
Eupener Straße 33,
30519 Hannover,
E-Mail: Manfred.klueppel@
DIKautschuk.de

Impact of Softener and Filler on the Rheological and Dielectric Response of Elastomer Melts

Introduction

Starting in the early 1960th, in the last decades much insight has been obtained regarding the role of entropy in the rheological properties of rubber melts with special focus on flow instabilities [1-7]. In particular, investigations about the interaction of rubber and softener and the effect on rheological data have been obtained in former studies [5-7]. In addition, magneto-rheological studies have been performed in view of affecting rheological properties by external magnetic fields [8,9]. A deeper understanding of filler networking in rubber melts at elevated temperatures has been obtained based on combined rheological and dielectric analysis [10,11]. This confirms our basic concepts and fundamental theoretical investigations of rubber reinforcement by nano-structured filler particles [12-14]. In particular, it has been demonstrated that nanoscopic gaps are present between adjacent filler particles that are filled with bound polymer chains. Due to confinement effects resulting from the attractive filler surface, these polymer chains are strongly immobilized, forming glassy-like polymer bridges, which transmit the stress in the filler network. Upon deformation of cross-linked rubbers [12-14] and melts [11], these bridges break down delivering a strong non-linear response of the systems.

In the present paper we will address different rheological phenomena of elastomer melts regarding the effects of softeners and fillers, whereby also dielectric investigations under shear flow are considered. In particular, we will focus on wall slip effects due to entropy driven shear induced decomposition in concentrated polymer solutions which often appears during rubber processing. The effect of polymer-softener compatibility on the apparent flow curves of rubber melts is considered, which is important for choosing a suitable softener for tailor made processing properties. Finally, the role of filler shape in the flow behavior of filled rubber melts is addressed by applying combined rheological and dielectric investigations

Experimental methods

Steady shear rheological investigations have been performed with a high pressure capillary viscosimeter (Göttfert 6000) with radial capillaries of different geometries. The pressure drop was measured directly along the capillaries at five pressure holes. In addition, a tuned up special rotational rheometer (Physica MCR 501 S, Anton Paar) has been applied with plate-plate geometry for the combined evaluation of rheological and dielectric properties of filled rubber melts under steady and oscillating shearing. The dielectric analysis was performed with a dielectric broadband spectrometer (Novocontrol BDS 80) in the frequency range 10^{-1} to 10^{7} Hz.

Results and discussion

Entropy Driven Wall Slip Effects

If a solvent or softener is added to a polymer melt, a low viscose film may be formed close to the wall during capillary flow. The reason for this film is a segregation of the softener due to entropic forces acting on the stretched polymer chains perpendicular to the flow direction. Since the polymers are not stretched in the middle of the capillary, the chains tend to diffuse to the capillary center where the entropy gains its maximum. This results in a drift of the softener to the wall implying that the viscosity is significantly lower at the wall. This scenario is depicted schematically in Figure **1**, where the coil stretching is characterized by the ratio of coil diameters λ:

Accordingly, the polymers are strongly stretched close to the wall but are not stretched in the middle of the capillary, where the entropy gains its maximum. This results in an entropic force F_{entr} acting on the polymers implying a drift of the polymer to the center and the softener to the wall. For that reason the viscosity is significantly lower close to the wall. In a simplified model one can treat this viscosity gradient as an apparent, low viscose layer close to the wall.

In Figure **2** the apparent flow curves for a hydrated Nitrile-Butadiene Rubber (HN-
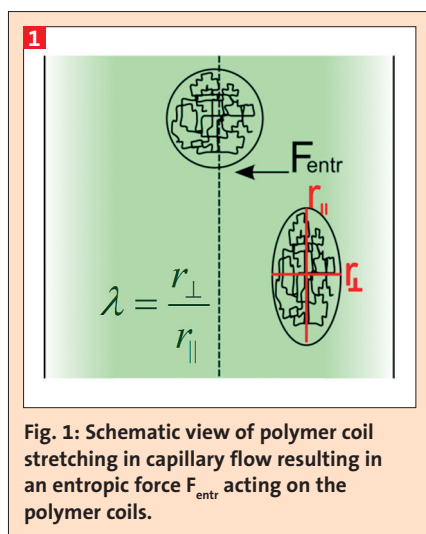
Fig. 1: Schematic view of polymer coil stretching in capillary flow resulting in an entropic force F_{entr} acting on the polymer coils.

Fig. 2: Apparent flow curves of HNBR with 20 vol% DEHP for three capillary radii R = 1.5, 2 and 3 mm. The two insets demonstrate that the radial dependence of the apparent shear rate vs. $1/R^2$ gives a linear plot while the classical $1/R$-plot is not linear. The master curve is obtained from an extrapolation of the upper $1/R^2$-plot to ∞

BR) with 39 wgt.% Acryl-Nitrile (ACN) with 20 vol% of the softener Di-(2-ethylhexyl)-phthalat (DEHP, often used trivial name DOP), measured at 100 °C with three different capillary radii R = 1.5, 2 and 3 mm, are shown. The radial dependence is demonstrated by the $1/R^2$-plot in the upper inset while the classical $1/R$-plot delivers no straight line. The observed dependence $\dot{\gamma}_{app} \sim 1/R^2$ can be related to slip flow on a low viscose film with a slip velocity $v_{slip} \sim 1/R$, which is equal to the scaling behavior of the inverse shear stress. Contrary, if there would be a mechanical slip with constant slip velocity v_{slip} caused by plug flow one would assume that the apparent shear rate varies as $\dot{\gamma}_{app} \sim 1/R$ (compare e.g. [15]).

A qualitative explanation for the $1/R^2$-dependence is shear-induced segregation, which leads to a lower viscose film at the die wall, whereby the thickness of film depends on the curvature of the capillary. The reason for the formation of the film is the inhomogeneous state of stress of polymer molecules in the capillary streaming field delivering entropic forces acting on the polymer chains which is shown schematically in Fig. 1 [6,7]. The polymers close to the middle of the capillary are less stretched than the ones near the capillary wall due to the smaller shear stress, which increases linear with the capillary radius. The resulting inhomogeneous configuration of deformation of the polymers leads to an entropy gradient along the capillary radius, which forces the polymers to move to the center of the capillary. Due to the induced entropic pressure gradient, the low molecular weight softener moves to the wall and will segregate from the polymer if the compatibility is not sufficient.
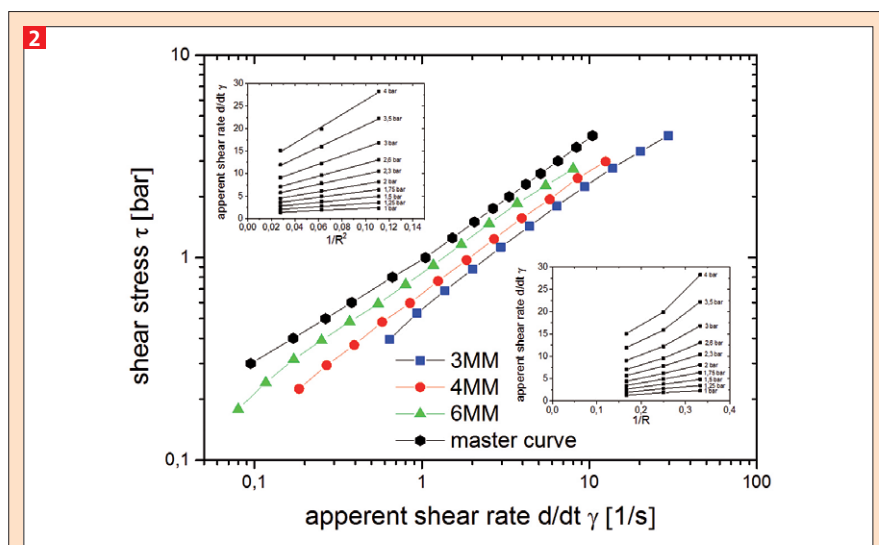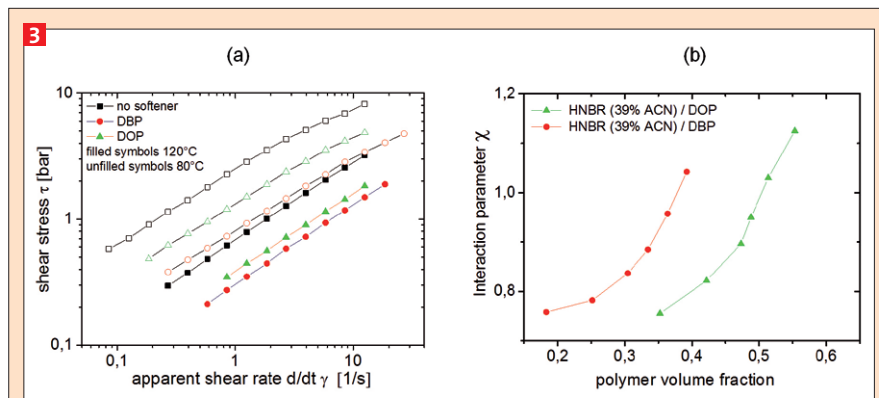
Effect of polymer-softener compatibility on the apparent flow curves

The effect of polymer-softener compatibility on the apparent flow curves of rubber melts has been investigated at various temperatures for a saturated HNBR (39% ACN) with 20 vol.% Di-(2-ethylhexyl)-phthalat (DEHP) and Di-n-butylphthalat (DBP), respectively. The compatibility of both systems has been characterized by the Flory-Huggins interaction parameter obtained from equilibrium swelling data of variously cross-linked rubber samples. This procedure requires the network chain density which was obtained by fitting uniaxial stress-strain data with the extended non-affine tube model [12]. This model considers cross-link and entanglement contributions via topological constraint

of the network strands in dense polymer networks. The fits are in very good agreement with experimental data [16]. Based on these investigations, the Flory-Huggins interaction parameter was obtained by using the Flory-Rehner equation [17].

The results regarding polymer-softener compatibility are shown in Figure 3 (b). It is found that the low molecular DBP swells the HNBR networks more than the DEHP, i.e. the polymer volume fraction is lower. However, the interaction parameter is higher for the DBP indicating that it is less compatible with HNBR. As a result, the apparent flow curves of the HNBR melt with 20 vol.% DBP are located below that with 20 vol.% DEHP for both temperatures as shown in Figure 3 (a). This can be traced back mainly to the lower inter-
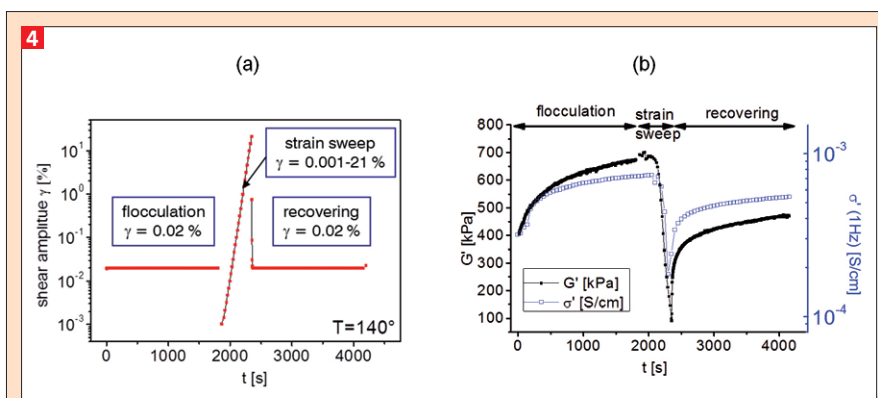

Fig. 3: Apparent flow curves at 120 °C and 80 °C for d=4 mm of a HNBR-melt as well as with 20 vol.% softener, DBP and DEHP (trivial DOP), respectively (a) and Flory-Huggins interaction parameters for both systems at various polymer concentrations, as indicated (b).

4

Fig: 4: Time dependence of the storage modulus G' and conductivity σ' at 1 Hz of EPDM-melts with 22 vol.% carbon black N339 (b) measured during oscillatory shearing at 140 °C for variously switched amplitudes as depicted by the strain history (a).
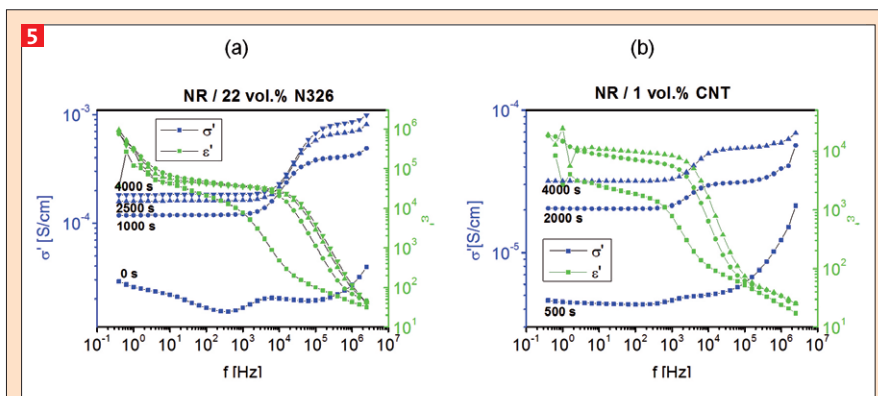
5

Fig: 5: Dielectric spectra of NR-melts with 22 vol.% carbon black N326 (a) and 1 vol.% CNT (b), measured during oscillatory harmonic shearing at 120 °C for small amplitudes at different times, as indicated.

nal friction of the less compatible DBP, but also the lower molecular weight of this softener type will reduce the viscosity. The observed dependence of the viscosity on compatibility between polymer and softener agrees with previous findings where non-hydrated, unsaturated NBR has been investigated with four different softeners [5-7].

Impact of filler shape on the rheo-dielectric properties of filled polymer melts
By applying combined rheological and dielectric investigations, the flow behavior of rubber melts filled with differently shaped carbon fillers, carbon black (N326, N339) and multi-wall carbon nanotubes (CNT, Nanocyl NC7000), has been investigated in a plate-plate rheometer at elevated temperatures for various flocculation times and shear rates. Initially, the samples were strained harmonically $\gamma = \gamma_0 \sin \omega t$ at a frequency $\omega = 1Hz$ and the mechanical and dielectric response has been monitored simultaneously. As an example, characteristic

results for an EPDM-melt with 22 vol.% carbon black are shown in Figure **4**.

Starting with a small strain amplitudes of γ_0 =0.02 % for 1800 seconds, flocculation of the filler particles takes place. Thereby, a successive increase of the small strain modulus G' and the dc-conductivity, i.e. real part of the conductivity σ' at 1 Hz, to an apparent plateau value is observed indicating that the filler particles move closer together [10-14]. Then a strain sweep up to 21 % is performed, leading to a drastic drop of the modulus and conductivity due to strain-induced breakdown of the filler network. Afterwards, the strain amplitude is again switched to γ_0 = 0.02 for 1800 seconds, whereby recovery of the filler network occurs and an increase of G' and σ' is again observed.

Figure **5** shows the dielectric spectra of natural rubber (NR) samples during the first flocculation phase more closely. For both samples filled with carbon black and CNT, respectively, the frequency dependent real part of the con-

ductivity σ' and permittivity ε' is shown for various flocculation times, as indicated. Obviously, with increasing flocculation time a successive increase of both quantities is observed correlating with the data in Fig. 4 (b). We point out that both fillers deliver similar conductivity and permittivity spectra though the concentration of CNT is much lower. This is a typical shape effect of the filler since the CNTs have a length of about 1 µm, allowing for an effective transport of charge carriers over longer distances compared to carbon black with a typical particle size of about 100 nm. For both filler types the permittivity ε' shows very high values between 10^3 and 10^5, which can be related to the percolation structure of the filler networks with a huge number of gaps and dead ends [10-14]. These are acting as micro-capacities which all sum up to form the macroscopically observed high polarization ability of the samples. At small frequencies additional boundary polarization effects appear due to the contact resistance with the electrodes also denoted electrode polarization. At high frequencies a relaxation transition appears when the diffusion time of the charge carriers is exceeded. The relaxation time τ scales with the inter-particle resistance and the traveling distance of the charge carriers between the dead ends. The latter is of the order of the correlation length of the percolation network. The observed increase of the relaxation frequency with increasing time for both filler types gives again a strong indication that the filler particles move closer together and the inter-particle resistance decreases during the flocculation process. This agrees with previous investigations [10-14].

In a further experiment, a steady shear has been applied after a previous flocculation phase, whereby the shear rate was increased successively. The obtained dielectric spectra of the samples with two types of electrically conducting fillers are depicted in Figure **6**.

From the data in Fig. 6 it becomes obvious that the samples filled with carbon black and CNTs, show a generally different dielectric response upon steady shearing. On the one side, for the NR-melt filled with carbon black the dc-conductivity plateau decreases significantly with increasing shear rate, which can be related to a shear induced fracture of filler clusters. The permittivity ε' decreases slightly with increasing shear

rate but remains at very high values between 10^4 and 10^5. As described above, the strong polarization of the samples results from the large number of gaps and dead ends of the carbon black network. These act as microscopic capacitances which are charged and discharged by the free electrons moving in the alternating electrical field. At moderate frequencies, they can diffuse between the dead ends. At high frequencies, if the charging-discharging time becomes smaller than the characteristic diffusion time, a relaxation transition appears and the permittivity drops significantly. The observed relaxation time τ typically lies between 10^{-4} and 10^{-5} s. It decreases slightly with increasing shear rate because the fracture of filler clusters decreases the traveling distance of the charge carriers between the dead ends, i.e. the cluster size (correlation length of the filler network) becomes smaller.

On the other side, the NR-melt filled with CNTs shows a different trend: The permittivity ε' as well as the dc-conductivity plateau both increase by almost one order of magnitude and the relaxation time decreases significantly with increasing shear rate. This indicates that a shear-induced flocculation takes place, i.e. the CNTs orientate in flow direction and move closer together due to pronounced attractive excluded volume interactions [17]. This compares to a nematic ordering of the CNTs as found e.g. for rod like liquid crystals. According to the larger interface and smaller distance in the aligned (ordered) state, the capacitance as well as the conductivity perpendicular to the flow direction both increase. In addition, the relaxation time increases with increasing orientation because the charge carriers can cross the gaps between neighboring CNTs more easily implying that the inter-particle resistance decreases. The behavior of the relaxation time during flocculation in the first phase (Fig. 5) and steady shearing in the second phase (Fig. 6) for the NR-melt filled with 1 vol.% CNTs is depicted in Figure 7. The reason for the observed drop of τ is the same in both experimental phases. In both cases, flocculation and steady shearing, the contact between CNTs becomes more intimate and the inter-particle resistance decreases implying that the traveling time of the charge carriers between dead ends of the CNT clusters decreases.
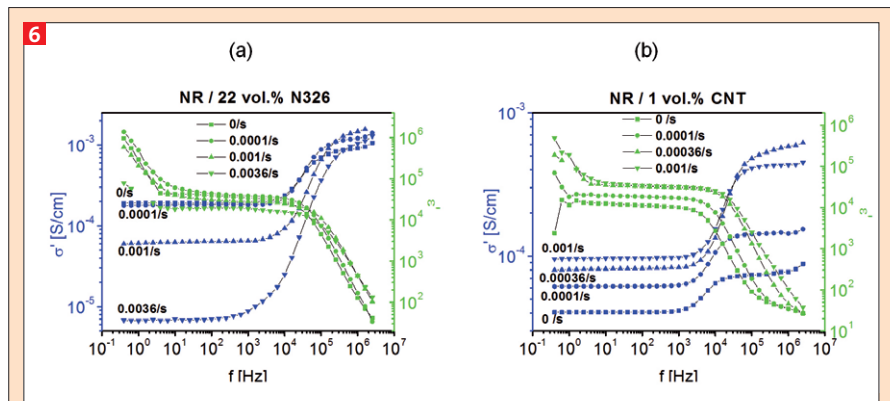

Fig: 6: Dielectric spectra of NR-melts with 22 vol.% carbon black (a) and 1 vol.% CNT (b), measured perpendicular to the flow direction during steady shearing at 120 °C for different shear rates $\dot{\gamma}$, as indicated.
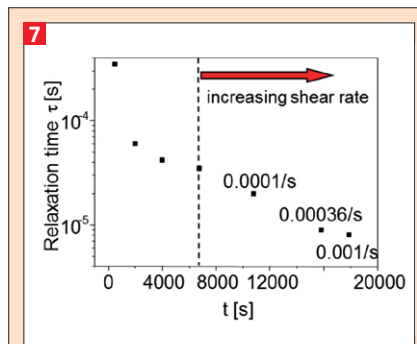

Fig. 7: Relaxation time τ of the NR-melt filled with 1 vol.% CNT vs. flocculation time (first phase) and shear rate (second phase), respectively. The decreasing characteristic of τ indicates that the traveling time of the charge carriers between dead ends of the filler clusters decreases in both cases.

Literature
[1] W. F. Busse, J. Polym. Sci. **5**, 1261, (1967).
[2] J. L. den Otter, Rheol. Acta **10**, 200, (1971).
[3] J. K. Lund, H. A. Pohl, Canadian J. Chem. Eng., 231, (1965).
[4] W. Gleisle, Rheol. Acta **21**, 484, (1982).
[5] R. Badura, M. Klüppel, R. H. Schuster; „Interaction of Rubber and Softener and the Effect on Rheological Data", J. Appl. Polym. Sci., Appl. Polym. Symp. **50**, 95, (1992).
[6] M. Klüppel, R. Badura, R. H. Schuster, „Thermodynamik und Rheologie weichgemachter Nitrilkautschuke", Kautschuk Gummi Kunstst. **45**, 614, (1992).
[7] M. M. Möwes, M. Klüppel, „Flow instabilities in concentrated polymer solutions and melts", Kautschuk Gummi Kunstst. **64**/4, 29 (2011).
[8] C. W. Karl, J. McIntyre, T. Alshuth, M. Klüppel, „Magneto-rheological elastomers with switchable mechanical properties", Kautschuk Gummi Kunstst. **66**/1-2, 46, (2013).
[9] S. Aloui, M. Klüppel, "Magneto-Rheological Response of Elastomer Composites with Hybrid-Magnetic Fillers", Smart Mater. Struct. **24** , 025016 (11pp) (2015).
[10] F. Fleck, M. M. Möwes, M. Klüppel, "Effect of Ionic Liquids on Mechanical and Rheo-Dielectric Properties of Carbon Black filled Elastomers", Proceedings: IRC-Rubber Con, Manchester, UK, 14. – 15. Mai (2014).
[11] M. M. Möwes, M. Klüppel, U. Giese, „Monitoring of carbon black networking in rubber melts under oscillatory shear by dielectric spectroscopy", Proceedings: 9th Fall Rubber Colloquium, 273, Hannover, 3. - 5. Nov. (2010).
[12] T. A. Vilgis, G. Heinrich, M. Klüppel, „Reinforcement of Polymer Nano-Composites", Cambridge University Press, Cambridge, New York, ISBN 978-0-521-87480-9, 2009
[13] M. Klüppel, "The role of disorder in filler reinforcement of elastomers on various length scales", Adv. Polym. Sci. **164**, 1 (2003).
[14] J. G. Meier, M. Klüppel, „Carbon Black Networking in Elastomers Monitored by Dynamic-Mechanical and Dielectric Spectroscopy", Macromol. Mater. Eng. **293**, 12, (2008).
[15] S. Brockhaus, V. Schöppner, B. Klie, U. Giese, „Grundlegende Studie und alternative Methoden zur Bewertung des Wandgleitens bei hochviskosen Kautschukmischungen", Kautschuk, Gummi, Kunstst. **67,** 11/12, 45, (2014).
[16] I. H. Syed, P. Stratmann, G. Hempel, M. Klüppel, K. Saalwächter, Macromolecules, submitted.
[17] M. Rubinstein, R. Colby, "Polymer Physics", Oxford University Press Inc., New York, 2003.