Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Hydrogen bonding and thermoplastic elastomers – A nice couple with temperature-adjustable mechanical properties

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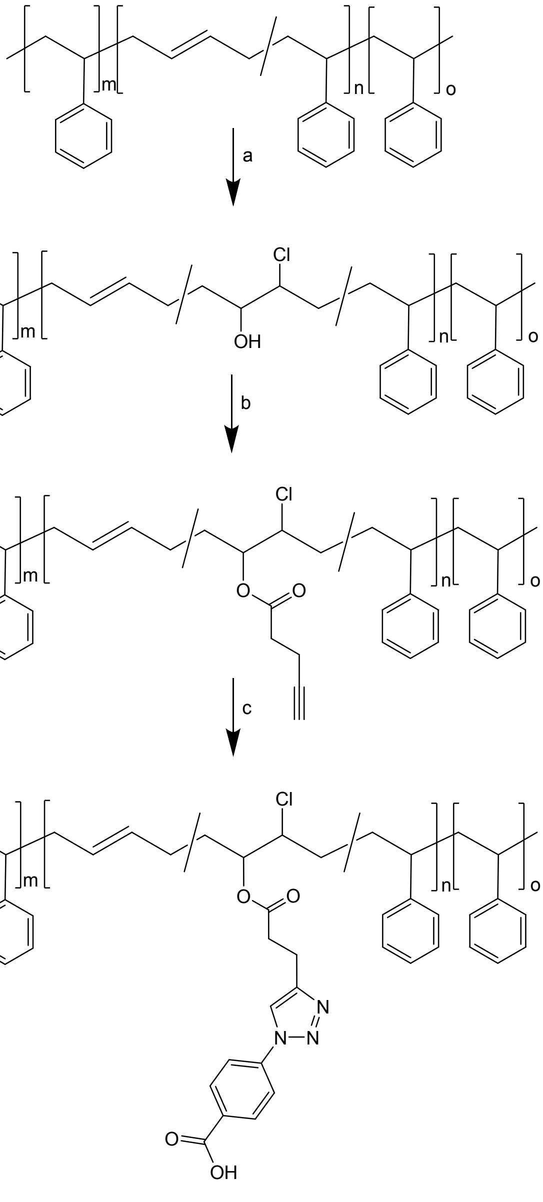
1. Modification

1.1 Experimental

Exemplarily, the modification route for S-S/B-S-4 is given. The modification was performed as reported earlier[17]. In Scheme 1 is the modification route shown.



Scheme 1: Modification of the butadiene units using three-step pathway. a) 1. *meta*-Chloroperbenzoic acid, THF, RT, overnight; 2. Hydrochloric acid, THF, RT, 4 h. b) 4-Pentynoic acid, DCC, DMAP, DCM, RT, overnight. c) 4-Azidobenzoic acid, copper bromide, PMDTA, THF, RT, overnight.

1.1.1 Epoxidation and Hydrolysis

The epoxidation and ring-opening reaction was performed according to the literature[36]. In a typical experiment 10.01 g (0.1 mol of C=C) of Styroflex 2G66 was weighed into a threenecked round-bottom flask equipped with a dropping funnel. It was dissolved in 200 mL anhydrous THF in an inert atmosphere at room temperature. A solution of 1.52 g (8.79 mmol, 0.09 eq with respect to C=C) of mCPBA in 50 mL THF was added to the polymer solution dropwise and stirred overnight at room temperature. The resulting epoxide was turned into the targeted hydroxide via a ring-opening reaction by dropwise addition of 1.06 g (0.01 mol, 1.2 eq with respect to mCPBA) HCl in 20 mL THF over 30 minutes at room temperature. The reaction solution was stirred for another 3.5 hours to complete the ring-opening reaction. The purification of the polymer was performed by three cycles of precipitation into 1500 mL methanol and redissolving the separated polymer in 180 mL THF. The purified polymer was dried under vacuum at 25°C overnight and was obtained as a colorless solid (9.00 g, 78% conversion, 85% yield), S-S/B-S-OH.

1.1.2 Esterification

9.00 g (5.80 mmol of –OH) of S-S/B-S-OH, 0.80 g (8.15mmol, 1.4 eq) 4-pentynoic acid and 100 mg (0.82 mmol, 0.14 eq) DMAP were dissolved in 170 mL anhydrous DCM. To this solution a solution of 1.71 g (8.29 mmol, 1.4 eq) DCC in 20 mL anhydrous DCM was added at room temperature dropwise. The reaction mixture was stirred overnight at room temperature. The purification of the polymer was performed by three cycles of precipitation into 1500 mL methanol and redissolving the separated polymer in 180 mL DCM. The purified polymer was dried under vacuum at 25°C overnight and the product was obtained as a colorless solid (7.46 g, 94% conversion, 83% yield), S-S/B-S-C≡C.

1.1.3 CuAAC

6.50 g (3.94 mmol of alkyne groups) of the alkyne-modified polymer and 0.90 g (5.52 mmol, 1.4 eq) 4-azidobenzoic acid were dissolved in 100 mL anhydrous THF and degassed by three freeze-thawing cycles. After degassing, 0.06 g (0.42 mmol, 0.1 eq) copper(I)bromide and 90 µL (0.43 mmol, 0.1 eq) PMDTA were added to the solution. The reaction mixture was stirred overnight at room temperature. An additional amount of 50 mL THF was given to the reaction solution and it was stirred with about 3 g of Amberlite MB-6113 to remove all remaining copper from the system. Afterwards, the mixture was filtered and purified by aluminium oxide flash chromatography.

The solution was concentrated *in vacuo* and the purification of the polymer was performed by three cycles of precipitation into 1000 mL methanol and redissolving the separated polymer in 100 mL THF. The purified polymer was dried under vacuum at 25°C overnight and the product was obtained as a colorless solid (5.27 g, 83% conversion, 87% yield), S-S/B-S-4.

1.2 ^{1}H NMR

In Figure 1 is shown from bottom to top the extracted polymer samples over the modification steps. At the bottom is shown the unmodified S-S/B-S, the second spectra shows S-S/B-S-OH, the third S-S/B-S-C≡C and the top is shown the carboxylic acid modified S-S/B-S-4.

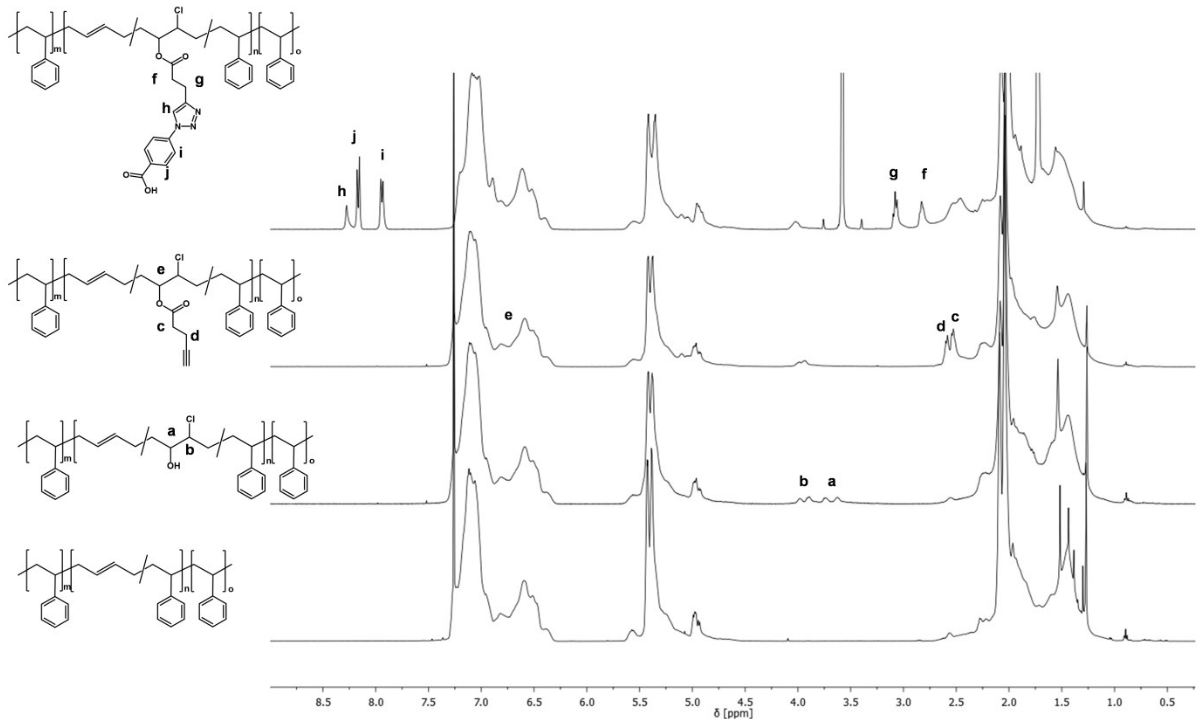


Figure 1: ^{1}H NMR spectra of every modification step is shown from the bottom to the top.

2. Dynamic mechanical analysis

2.1 Calculation of the closed fraction

For the calculation of the closed fraction, the model developed by Leibler *et al.*[54] was applied. The determination of the plateau modulus G_1 (complexed species) can be performed as follows (equation 1):

$$G_1 \cong cRT\left[\frac{p}{N_s}+\frac{1}{N_e}\right]. \qquad (1)$$

The plateau modulus of the free species and therefore the unfunctionalized S-S/B-S (G_2) can be determined using equation 2.

$$G_2 \cong cRT\left[\frac{1}{N_e}\right] \qquad (2)$$

Subtracting equation 1 from equation 2 leads to an expression for the closed fraction of hydrogen bonding motifs p (equation 3).

$$p \cong \frac{N_s(G_1 - G_2)}{cRT} \tag{3}$$

In equation 3, c is the number concentration of monomers, R the ideal gas constant and T the temperature at measurement ($T = 313$ K). N_s is the number of monomers between hydrogen bonds and finally N_e is defined as the number of monomers entangled in a strand (equation 1 and 2). The calculation of the number concentration is shown in equation 4. The density ρ of Styroflex is used and the molecular weight of one monomer is calculated to be 77.5 g/mol taking the different fractions of styrene and butadiene into account.

$$c = \frac{\rho}{M} = \frac{998\,kg\ \cdot mol}{0.0775\,kg\ \cdot m^3} = 12877\frac{mol}{m^3} \tag{4}$$

N_e is given by equation 5 whereby M_e is the entanglement molecular weight.

$$N_e = \frac{M_e}{M} = \frac{4000\,g \cdot mol}{77.5\,g \cdot mol} = 52 \tag{5}$$

N_s depends on the degree of modification and can be calculated according to equation 6. N is the total number of monomers per chain (N = 1728) and S is the number of hydrogen bonding motifs per chain.

$$N_s = \frac{N}{(S+1)} \tag{6}$$

The plateau modulus of the free species and therefore the pristine S-S/B-S (G_2) can be determined using equation 2 which is independent from the degree of modification and therefor valid for all samples. However, from the comparison of the calculated value and the measured value it turns out that the calculated value of $G_2^{calc} = 6.49 \cdot 10^5$ Pa is in good agreement to the measured value of $G_2^{found} = 6.40 \cdot 10^5$ Pa. In Table 1 the calculated values of the parameters defined above and the plateau moduli used in these calculations are shown.

Table 1: Calculated parameters of *S*, N_s and *p* as well as measured G values are shown.

Sample code	Degree of Modification [%]	*S*	N_s	G [Pa]	*p*
S-S/B-S	-	-	1728	$6.40 \cdot 10^5$	-
S-S/B-S-4	4	69.1	24.6	$1.46 \cdot 10^5$	0.60
S-S/B-S-7	7	121	14.2	$1.57 \cdot 10^5$	0.39
S-S/B-S-15	15	259	6.64	$1.86 \cdot 10^5$	0.24

In Figure 2 the measured values for G' are depicted (same as in Figure 6, at 40°C). In horizontal lines the obtained values of the plateau modulus G_1 are marked for each sample. As discussed in the paper, the minimum of the tan δ value depicts the value of the plateau modulus and therefore the corresponding tan δ functions are shown at the bottom of the figure. The determination of G_1 from the measured data is essential to calculate p afterwards.

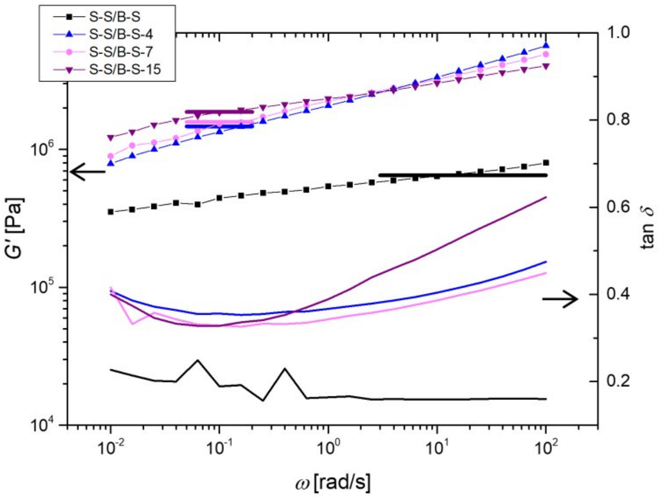


Figure 2: G' values of each sample are shown (T = 40°C, same as Figure 6 in the paper) as well as the corresponding tan δ functions at the bottom of the figure. Horizontal lines mark the area where the tan δ functions have their minimum and the value of G_1 for each sample was obtained to calculate *p*.

2.2 Master curve of S-S/B-S

The master curve of S-S/B-S is shown in Figure 3. Four measurements were conducted at T = 120°C, T = 140°C, T = 160°C and T = 180°C. The terminal flow region can be observed at small frequencies. The slope of G' is 1 and the slope of G'' is 2 in this region. The behavior of the polymer in this region is dominanted by viscous behavior due to reptation of the polymer chains while at higher frequencies the elastic behavior is dominating. At high frequencies the beginning of the rubbery plateau can be observed. Calculating the M_e from the master curve leads to value of M_e = 4000 g/mol (see equation 1) if we assume G^0_N = 570 [kPa].

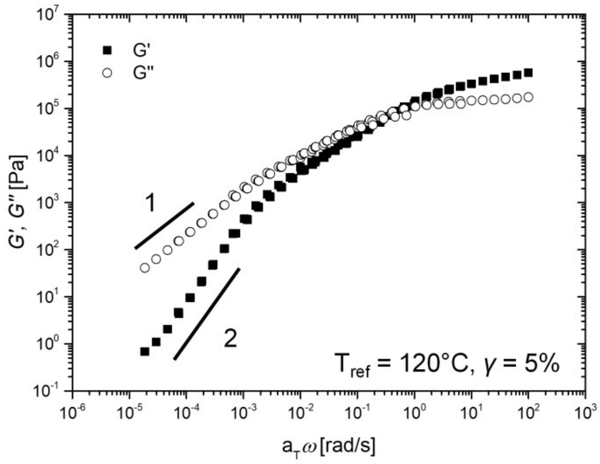


Figure 3: Master curve of S-S/B-S at T_{ref} = 120°C and γ = 5%.

2.3 Master curve of S/B

The master curve of S/B is shown in Figure 4. Four measurements were conducted at T = 140°C, T = 120°C, T = 100°C and T = 80°C. The terminal flow region cannot be observed at small frequencies. Possibly, the temperatures applied were not high enough. Anyway, the crossing point of G' and G'' can be observed which indicates a totally different behavior at low and high frequencies. The behavior of the polymer in the region of small frequencies is dominanted by viscous behavior while at higher frequencies it is more elastic dominated. At high frequencies the beginning of the rubbery plateau can be observed as well. Calculating the M_e from the master curve leads to value of M_e = 4000 g/mol as well (see equation 1) if we assume G^0_N = 570 [kPa].

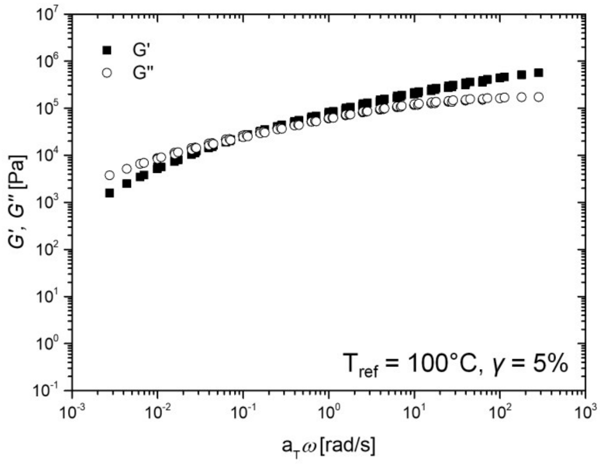


Figure 4: Master curve of S/B at T_{ref} = 100°C and γ = 5%.

3. SAXS

To determine the approximate size of one of the polar domains inside the unipolar matrix, the linker molecule was drawn in the software *Jmol* (Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/), all bond length and angles were corrected and the size of the domain was measured. In Figure 5 the resulting sketch is shown. Due to the fact that there are only two positions at which rotational movement inside the linker chain can occur, these approximations are reasonable.

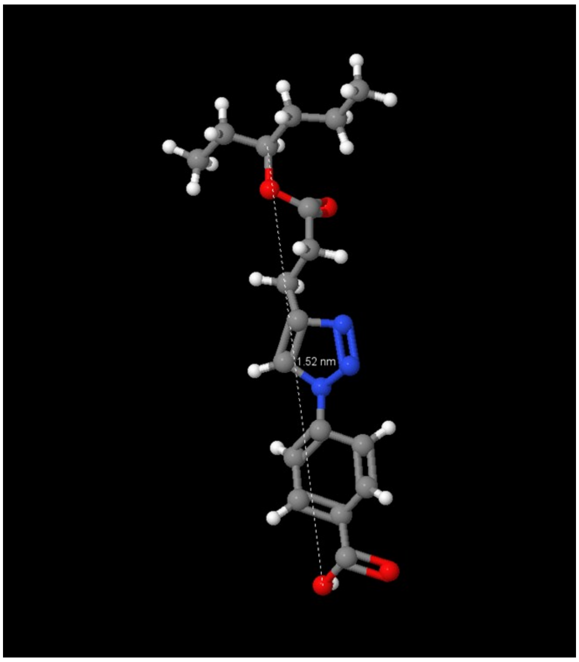


Figure 5: Schematically sketch of the side group linker molecule and its measured length.