Tunable Thermoplastic Elastomer Gels Derived from Controlled-Distribution Triblock Copolymers with Crystallizable Endblocks

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Supplementary Information

The uniaxial tensile tests introduced in **Figure 3a** can be analyzed at low strain levels to extract additional information regarding the shear modulus contributions from physical crosslinks (G_c) and entangled midblocks (G_e). In a previous study,[1] the Slip-Tube Network (STN) model proposed by Rubinstein and Panyukov[2] has been successfully applied to describe the extensional behavior of TPEGs derived from conventional styrenic multiblock copolymers over a broad composition range. The model is written as

$$\sigma = \left(G_c + \frac{G_e}{g(\lambda)} \right)\left(\lambda - \frac{1}{\lambda^2} \right)$$

(1)

Here, σ is the nominal stress, λ is the extension ratio (= L/L_0, where L and L_0 denote the strained and initial specimen lengths), and $g(\lambda)$ is given by an expression of the form $A\lambda + B/\lambda^{1/2} - C$. In the original derivation for spherical micellar crosslinks, values of A, B and C are determined to be 0.74, 0.61 and 0.35, respectively. It must be remembered, however, that the TPEGs visible in **Figure 1** do not consist of spherical micelles, and so we do not expect that these constants are necessarily valid in the present study. Non-linear regression of **Equation 1** (with adjustable A, B and C parameters) to the tensile data provided in **Figure 3a** up to 300% strain ($\lambda = 4.0$, to avoid hyperelastic effects) yields the fits displayed in **Figure S1**. As is evident from this figure, the regressions accurately correspond to all the data with correlation (R) coefficients ranging from 0.999 at low oil levels to 0.984 at the highest oil level that yields meaningful results. Parameter values extracted from these regressions are listed in **Table S1** and reveal relatively modest deviation from the original parameter values (included in **Table S1** for comparison) for TPEGs composed of spherical micelles.
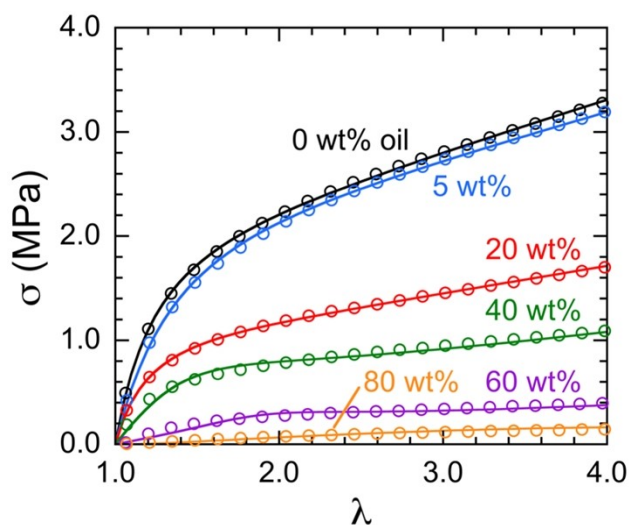
Figure S1. Dependence of nominal stress (σ) on extension (λ) for TPEGs derived from an ESEBE triblock copolymer (see **Scheme 1**) and varying in oil content (labeled and color-coded). The solid lines represent non-linear regressions of **Equation 1** to the data.

Table S1. Parameters extracted from the tensile data for the g(λ) function in the STN model.[2]

Oil fraction (wt%)	A	B	C
0	0.92	−1.36	−1.03
5	1.00	0.09	0.29
20	1.22	−0.41	0.38
40	0.93	2.45	3.13
60	0.60	2.96	3.18
[80	0.00	0.05	−0.60]
Original study	0.74	0.61	0.35

The primary parameters of interest acquired by the STN model are G_c and G_e, which are presented together as functions of oil content in **Figure S2**. In agreement with styrenic TPEGs, G_e dominates at low oil loading levels, whereas G_c slightly surpasses G_e at moderate-to-high oil levels. This general behavior is attributed to the decreasing copolymer population with increasing oil content coupled with a relatively constant bridging fraction, as predicted by simulations.[1] We note,
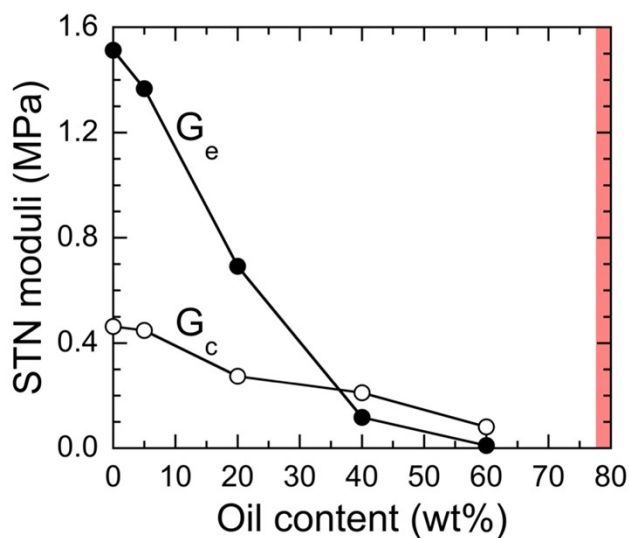
Figure S2. Values of G_c and G_e (labeled) extracted from the STN model of the tensile data in **Figure S1**. The solid lines serve to connect the data, and the red highlight identifies where the model fails due to changes in the copolymer network.

however, that G_c and G_e in **Figure S2** are quite comparable in magnitude at compositions of 40 and 60 wt% MO, suggesting that entanglements are non-negligible even at these oil loading levels. Values of G_c and G_e obtained at 80 wt% MO are not physically meaningful (negative), in which case (*i*) the parameters listed in **Table S1** at this oil level are to be excluded from further consideration (hence the brackets) and (*ii*) the fully elastic network required for the STN model is not intact (i.e., it is highly defective or replaced by flocs, as evidenced in **Figure 1a**).

In addition to these results acquired from the tensile data reported herein, the crosslink density (n) can also be estimated from the rheological data according to

$$G = nkT \qquad (2)$$

where G is the shear modulus, k is the Boltzmann constant and T denotes absolute temperature. The shear modulus is taken here as the complex modulus $G^* = (G'^2 + G''^2)^{1/2}$. As long as $T < T_m$ and the specimen of interest behaves as an elastomer, we can select any temperature for this analysis, but we specifically choose 70 °C to likewise minimize noise in G''. Values of the crosslink density calculated from **Equation 2** are displayed in **Figure S3** and indicate that it remains relatively invariant at ~7 x 10^{25} m^{-3} up to 40 wt% MO and then decreases noticeably to < 3 x 10^{25} m^{-3} at 50 wt% MO, gradually decreasing thereafter to 70 wt% MO. At 80 wt% MO, n plummets
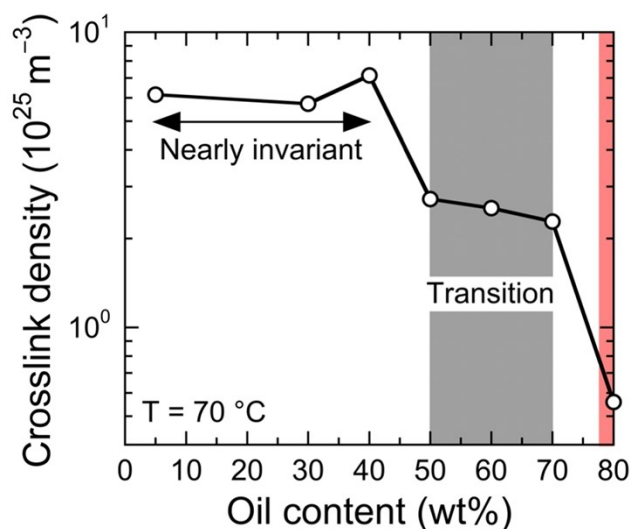
Figure S3. Dependence of the crosslink density on oil level, estimated from dynamic rheological data at 70 °C. The solid line serves to connect the data, and the shaded region identifies a transition threshold over which the morphology of the TPEGs change. The red highlight identifies where the crosslink density drops precipitously due the presence of a defective network or discrete flocs.

to $< 6 \times 10^{24}$ m^{-3}, corroborating that the TPEG at this oil level possesses a significantly lower crosslink density due to the existence of a defective network or flocs (see **Figure 1a**).

References

1. Rubinstein, M.; Panyukov, S. Elasticity of Polymer Networks. *Macromolecules* **2002**, *35*, 6670.

2. Yan, J.; Tuhin, M. O.; Sadler, J. D.; Smith, S. D.; Pasquinelli, M. A.; Spontak, R. J. Network Topology and Stability of Homologous Multiblock Copolymer Physical Gels. *J. Chem. Phys.* **2020**, *153*, 124904.