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Mechanical Properties and Hysteresis Behaviour of Multigraft Copolymers

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Summary: PS-PI multigraft copolymers with tri- tetra- and hexafunctional polystyrene branch points have been studied to investigate the influence of molecular architecture on morphological and tensile properties and to find novel material concepts. It was found that the morphological behaviour of these grafted copolymers can be predicted using theoretical approaches. The number of branch points, however, greatly influences the long-range order of microphase separation. Additionally, two new parameters for adjusting mechanical properties of multigraft copolymers are found in our investigations: 1) functionality of the graft copolymer: tri-, tetra- or hexafunctional and 2) number of branch points per molecule. Tetrafunctional multigraft copolymers show surprising high strain at break values up to 1550 %. With increasing number of branch points strain at break and tensile strength increase, where a linear dependence of mechanical properties on the number of branch points is obvious. Excellent elasticity of tetra and hexafunctional multigraft copolymers at high deformation was proved in hysteresis experiments.

Keywords: elasticity; morphology; multigraft copolymers; self-assembly; tensile properties

Introduction

Molecular architecture of block copolymers plays an important factor in designing thermoplastic elastomers (TPE's) with desired properties. Over the past decade new synthesis techniques have been developed to synthesis graft copolymers having well-defined molecular architectures [1–3], which allow to control the molecular weight of the backbone and the graft arm, the arm polydispersity, the placement and number of branch points and the number of armes grafted to each branch point. The morphological behaviour of graft copolymers with a complex architecture is predicted by the *constituting block copolymer hypothesis*[4–7] and theories for mictoarm stars [8,9] or conformationally asymmetric linear diblocks [10,11]. It has been found that the morphological behavior of regular multigraft copolymers with multiple tri-, tetra- or hexafunctional junction points is generally consistent with the morphologies of their constituting unit [7,12,13]. However, the long-range order that can be achieved is diminished as the number of junction points per molecule increases [12,13]. Preliminary studies of the tensile properties of multigraft copolymers with regularly spaced tetrafunctional junction points have proved significantly larger strain at break and similar tensile strength to commercial TPE's [14]. It is also found that the tensile strength and the strain at break in these

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multigraft materials increased with increasing number of the junction points.

The present study deals with the effect of chain architecture on the tensile and hysteresis behaviour of three series of multigraft copolymers, with trifunctional, tetrafunctional and hexafunctional junction points. All three series have polyisoprene (PI) backbones and polystyrene (PS) branches. The molecular weights of these multigraft copolymers are larger than 250kg/mole, a figure above which the mechanical properties of common triblock thermoplastic elastomers is found to be no longer dependent on molecular weight [15].

Experimental

Sample Preparation

Three series of multigraft copolymers with tri-, tetra- and hexafunctional junction points having a long polyisoprene backbone and polystyrene grafts have been synthesised. Their molecular architecture is shown in Fig. 1. Details of the synthesis and molecular characterization of the PI-PS multigraft copolymers are described by Uhrig and Mays [3]. Each synthesized material was divided into low, middle and high molecular weight fractions by solvent-nonsolvent fractionation. Molecular details of the materials used in this study are summarized in Table 1.

Solution cast films of these multigraft copolymers were prepared from a non-selective solvent (toluene). The solvent was allowed to evaporate slowly over 7–14 days at room temperature. The films were then dried to a constant weight in a vacuum oven at 120 °C for three days. The resulting films were about 0.2 to 0.3 mm thick.

Characterisation of morphology

Morphology studies were performed by transmission electron microscopy (TEM) using a JEOL 100 CX at an accelerating voltage of 100 kV. Ultrathin sections of 40–80 nm were cut at a sample temperature of −110 °C with diamond knives using a Leica Ultracut UCT. These sections were collected on TEM grids and stained in OsO_4 vapor for 4 hours. To verify the structures observed by TEM small-angle X-ray scattering (SAXS) was carried out using Ni-filtered Cu-K_α radiation with a wavelength of 1.54 Å from a rotating anode operated at 40 kV and 200 mA. A Siemens Hi-Star detector located 87.52 cm from the sample was used to record the scattering patterns.The two dimensional scattering patterns were circularly averaged giving the log I vs. q plots.

Tensile Testing

Tensile tests were performed with a ZWICK 1456 universal testing machine according to ISO 527 (specimen type 5A) at a crosshead speed of 15 mm/min. To ensure good measurement statistics, 5 to 10 dog bone shape specimens from each material were prepared by stamping from the annealed films. Multisens mechanical equipment was used to neglect the slippage of the specimens from the clamps and the compliance of the testing machine and thus

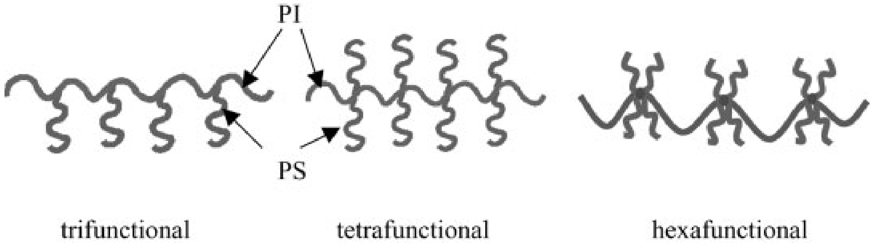

Figure 1.
Molecular architecture of multigraft copolymers.

Table 1.
Molecular characterization and morphology of multigraft copolymers

Sample	Mw [a] ($\times 10^3$g/mol)	junctions/molecule	PS Vol.-% [b]	Morphology	D [c] (nm)
RMG-3-17-3.7	515	3.7	17.2	PS Spheres	40.3
RMG-3-17-2.6	391	2.6	17.5	PS Spheres	42.2
RMG-3-17-2.0	315	2.0	17.8	PS Spheres	41.0
RMG-4-14-5.5	691	5.5	14.2	PS Spheres and Cylinders	28.5
RMG-4-14-3.5	475	3.5	14.2	PS Spheres and Cylinders	28.5
RMG-4-14-2.5	372	2.5	14.0	PS Spheres and Cylinders	31.5
RMG-4-21-10	1170	9.9	22.2	Wormlike	
RMG-4-21-7	830	7.0	22.0	Wormlike cylindrical PS domains	
RMG-4-21-5	600	4.7	21.7	PS Cylinders	
RMG-4-23-6.6	891	6.6	23.3	PS Cylinders	31.5
RMG-4-23-4.4	624	4.4	22.8	PS Cylinders	31.5
RMG-4-23-3.2	472	3.2	22.7	PS Cylinders	33.9
RMG-6-21-5.2	705	5.2	21.8	Microphase separated	34.6
RMG-6-21-3.6	515	3.6	21.6	Lamellae	34.6
RMG-6-21-2.7	411	2.7	21.4	Lamellae	34.6

[a] Weight average molecular weight measured using SEC-MALLS (multi-angle laser light scattering).
[b] PS volume fraction Calculated based on the averaged mass percentage from 1H NMR and SEC-UV analyses.
[c] Domain spacing $D = 2p/q^*$ where q^* is the primary bragg's reflection.

to exactly evaluate the strain of the samples by measuring the elongation in the gauge length only. From this elongation and the applied load during the testing the engineering strain (e) and engineering stress (s) were calculated, respectively.

Hysteresis experiments with varying applied strain were carried out under the same testing conditions.

Results and Discussion

Morphology

The morphology of all studied multigraft copolymers are listed in Table 1. The morphological behaviour of most graft and starblock copolymers differs from that of linear diblock copolymers, which has been studied by Milner [8]. In 1994 he introduced a theoretical model, predicting how the asymmetry of the molecules will impact the observed morphology as a function of the volume fraction of the B-component. In our studies the morphologies formed by the samples studied are in agreement with Milner's model. The TEM and SAXS images of the studied morphologies are shown in our recent study [13]. Tetrafunctional multigraft copolymers show a phase behaviour as known for diblock copolymers [16]. With increasing PS content from 14 to 23 to 41 vol.-% the morphology changes from spheres to cylinders to lamellae, respectively. Increasing the number of branch points at a constant PS content does not change the morphology, but the grain size is decreasing, which could be quantified with SAXS analysis and primarily found by Beyer et al.[12]. Hexafunctional multigraft copolymers with 21 vol.-% PS and low number of branch points show a lamellar morphology. An increasing number of branch points up to 5.2 leads to the formation of a microphase separated wormlike morphology without long-range order. Thus the possibility to develop highly ordered structures becomes kinetically unfavourable as the number of branch points per molecule increases.

Mechanical Behaviour

The characterisation of mechanical behaviour in this study is focused on multigraft copolymers with relatively low PS content of about 14 to 20 vol.-%. The influence of higher PS content on tensile properties will be discussed elsewhere [13]. The stress-strain behaviour of two tetrafunctional multigraft copolymers with about 20 vol.-% PS compared to a Kraton® and a Styroflex® (BASF) copolymer is shown in

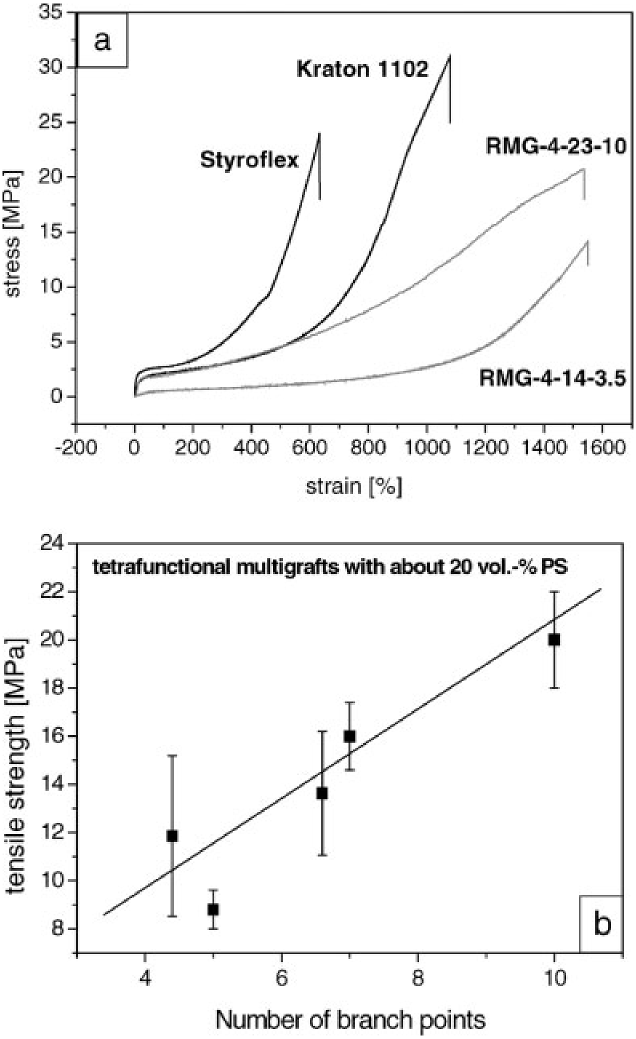

Figure 2.
Mechanical properties of tetrafunctional multigraft copolymers a) Stress strain behaviour compared to commercial TPE's b) Influence of number of branch points on tensile strength.

Fig. 2a. Kraton®, one of the best thermoplastic elastomers (TPE) on the market, is a typical poly(styrene-b-isoprene-b-styrene) triblock copolymer with 27.6 vol.-% PS forming hexagonally packed glassy PS cylinders in a rubbery PI matrix. Styroflex® is a poly(styrene-b-(styrene-co-butadiene)-b-styrene) triblock copolymer with 58 vol.-% PS and with a random SB copolymer as middle block. Samples of these commercial TPE's were prepared and tested using the same procedures as employed with the multigraft materials.

As shown in Fig 2a Kraton® and Styroflex® reveal higher tensile strength but distinct lower strain at break values than tetrafunctional multigraft copolymers. A tetrafunctional multigraft with 22 vol.-% PS and about 10 branch points shows a surprisingly high strain at break of about 1550% far exceeding the values for the commercial TPE's (Styroflex®: 620%; Kraton®: 1050%). The same high strain at break values could be observed for a tetrafunctional copolymer with 14 vol.-% PS and 3.5 branch points. This super-

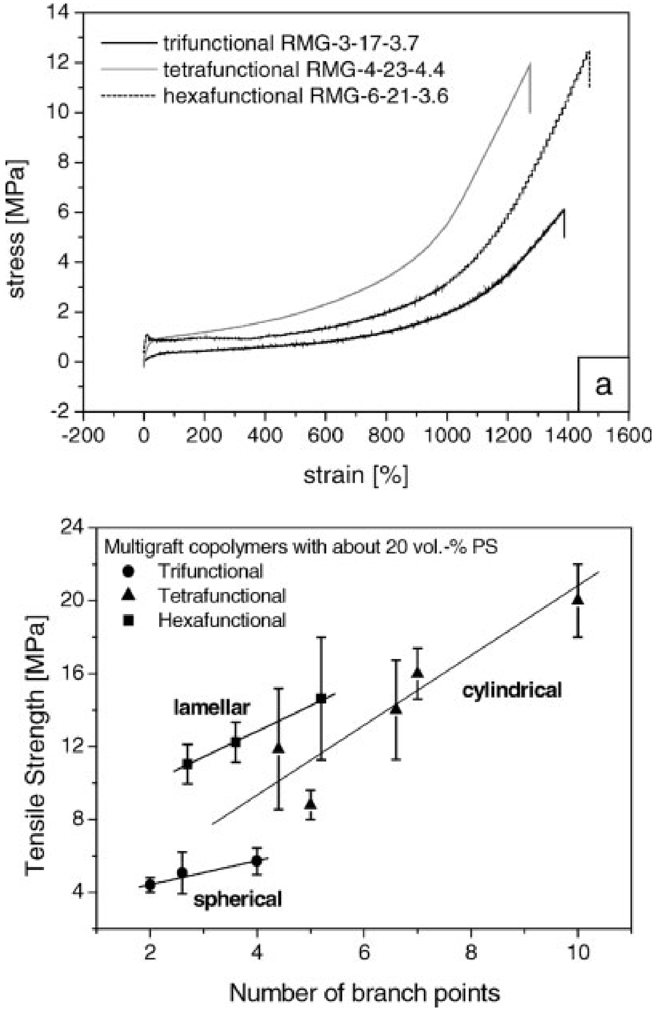

Figure 3.
a) Influence of functionality on stress-strain behaviour and b) Influence of number of branch points on tensile strength for different functionality for multigrafts with a PS content of about 20 vol.-%.

elasticity is caused by their specific molecular architecture, because multiple PS branches are grafted to the long rubbery backbone, which results in a physical crosslinking [14]. Fig. 2b shows the influence of number of branch points on tensile strength for tetrafunctional multigraft copolymers with about 20 vol.-% PS. With increasing number of branch points tensile strength increases nearly linearly within the investigated region. The same behaviour could be observed for the strain at break values [13]. Thus a linear dependence of the mechanical properties on the number of branch points could be found. A large number of branch points leads to enhanced material properties. This exceptional property profile is achieved with a less ordered morphology compared to most commercial TPE's. As already discussed the long-range order of morphology of multigraft copolymers decreases with increasing number of branch points. Thus we could confirm our assumption that a well ordered morphology is not necessary to achieve acceptable properties unlike reported for SBS triblock copolymers [15]. The mechanical properties of multigraft copolymers are influenced by

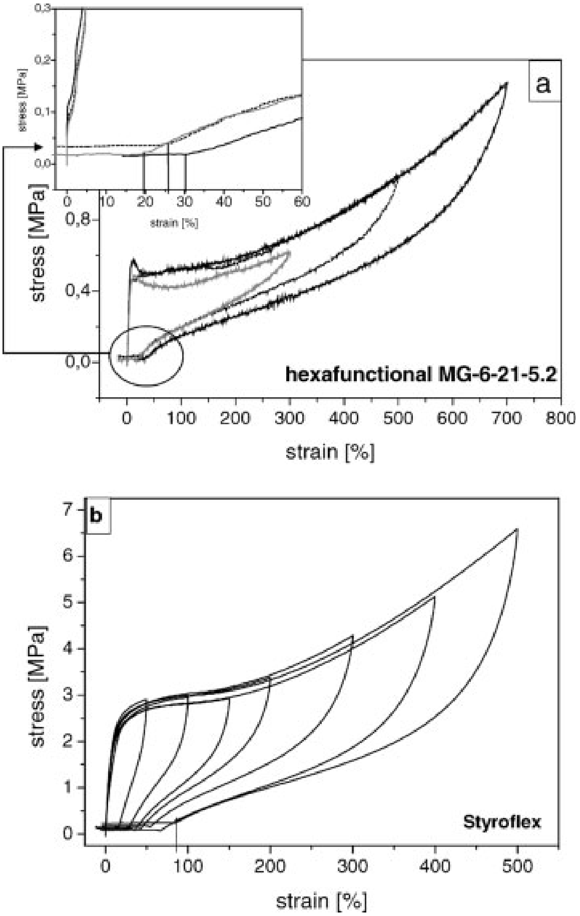

Figure 4.
Hysteresis behaviour (a) of a hexafunctional multigraft copolymer with an inset image showing larger magnification (b) compared to Styroflex®. For each hysteresis a new sample was used.

the number of branch points since an increasing number of branch points is connected with enhanced physical crosslinking and a decreasing grain size. The existence of smaller grain sizes at a large number of branch points per molecule can also be correlated with an improved property profile as earlier shown in the case of weakly segregated block copolymers [17–19].

The influence of functionality on mechanical properties of multigraft copolymers with a PS content of about 20 vol.-% is shown in Fig. 3. While strain at break is less influenced by functionality, tensile strength of the cylinder forming tetrafunctional multigraft is about twice as much compared to the trifunctional material of the same composition but with a spherical morphology (Fig. 3a).

Sumpter et al.[20] have reported on the simulation of chain dynamics in tri- and tetrafunctional multigraft copolymers via Monte Carlo method. The simulation revealed an enhanced density of molecular interactions between the PS nano domains in tetrafunctional materials in contrast to trifunctional materials, suggesting improved mechanical properties. Tetrafunctional multigraft copolymers exhibit a clustered, pseudo-spherical shaped structure with strong interactions between the branches supporting the assumption of enhanced mechanical properties. In contrast trifunctional multigraft copolymers form a comb-like structure that integrates with neighboring molecules which results in a more regular morphology with structures similar to that for triblock copolymers. These results are clearly in agreement with our experiments as shown in Fig. 3a despite different morphologies of trifunctional (spheres) and tetrafunctional (cylinders) multigrafts with 20 vol.-% PS but could also be confirmed for multigrafts with the same morphology [13].

Hexafunctional multigraft materials with lamellar morphology show even higher tensile strength than tetrafunctional multigraft copolymers suggesting new possibilities for design of TPE's with high levels of strain at break. The large tensile strength combined with large strains at break is a surprising result for materials with lamellae morphology. TPE's usually show a rubbery matrix similar to that in tri- and tetrafunctional multigraft copolymers revealing large strains and elasticities. However, a lamellae morphology is usually formed at 35–65 vol.-% PS in SIS triblock copolymers, while for hexafunctional multigrafts lamellae morphology has already been observed to exist at about 20 vol.-% PS, resulting in more distinct yield stress shown in Fig. 3a. These results clearly demonstrate the opportunity of tailoring mechanical properties in a wide range by changing molecular architecture. Fig. 3b shows the combined influence of morphology and number of branch points on tensile strength of multigraft copolymers with about 20 vol.-% PS. Trifunctional multigrafts with spherical structure reveal low tensile strength, which is also not increasing much with increasing number of branch points, which as shown by the low slope. The slope of tensile strength of hexafunctional and tetrafunctional multigrafts is similar, but in the range of low number of branch points hexafunctional multigraft material show larger values.

First hysteresis experiments at 300–900 % deformation have been carried out using multigraft copolymers with about 20 vol.-% PS. In Fig. 4a results of hysteresis tests of a hexafunctional multigraft with 5.2 branch points are shown and were compared with the hysteresis behaviour of commercial Styroflex® (Fig. 4b). While Styroflex® shows a residual strain of 90 % already at an applied strain of 500 % the hexafunctional multigraft reveals only 25 % of residual strain at the same deformation, which can be clearly seen from the mag-

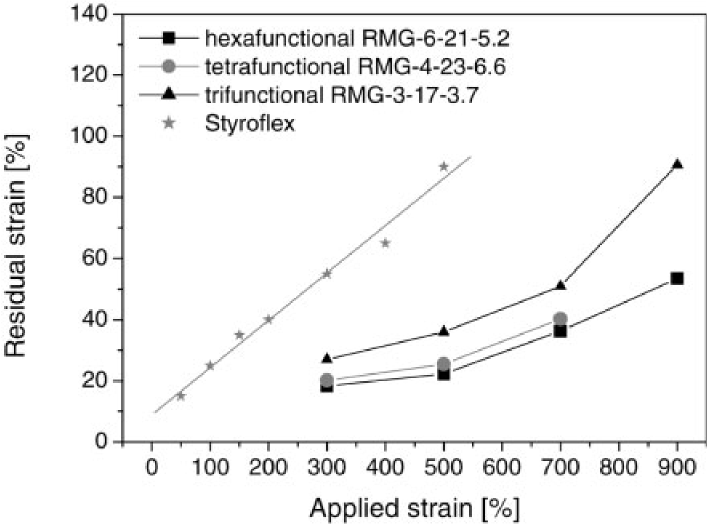

Figure 5.
Residual strain in hysteresis experiments of multigraft copolymers compared to Styroflex®.

nified inset image in Fig. 4a. Multigrafts can be deformed to very high elongations far exceeding strain at break values of commercial TPE's.

In Fig. 5 the residual strain for all three functionalities compared to Styroflex® is plotted vs. applied strain. All multigraft copolymers show exceptional high elasticity. The residual strain is much smaller compared to commercial Styroflex®, especially at higher deformation. Hexafunctional multigraft copolymers show very high elasticity despite their lamellar morphology. Figure 6 shows hysteresis behaviour of a tetrafunctional multigraft copolymer with 14 vol.-% PS and 5.5 branch points. This material can be deformed till 1400 % and reveals a residual strain of only 40 %. The square of the hysteresis loop is relatively small indicating large degree of elasticity of these multigraft copolymers. Based on our experiments we assume new materials behaviour caused by the novel branched architecture of the multigraft copolymers. Relaxation tests and detailed hysteresis measurements are planed in order to explore the details of the materials behaviour compared to common SIS triblock copolymers and also to discuss different material laws, for example the slip-tube model [21].

Conclusions

To characterise the influence of molecular architecture on morphology and mechanical properties multigraft copolymers with tri-, tetra- and hexafunctional branches and with a varying number of branch points were investigated. It could be found that on one hand the functionality of the graft copolymers has a distinct influence on morphology and thus on mechanical properties. An increasing functionality causes a change in morphology according to the Milner-phase-diagram, resulting in a high level of tensile strength for tetrafunctional (cylinder) and hexafunctional (lamellae) multigraft copolymers, which is about the twice of the spherical trifunctional multigrafts. On the other hand an increasing number of branch points per molecule reduces the grain size and long-range order of the morphologies and leads to a linear increase in mechanical properties.

For tetra- and hexafunctional multigraft copolymers high strain at break values far

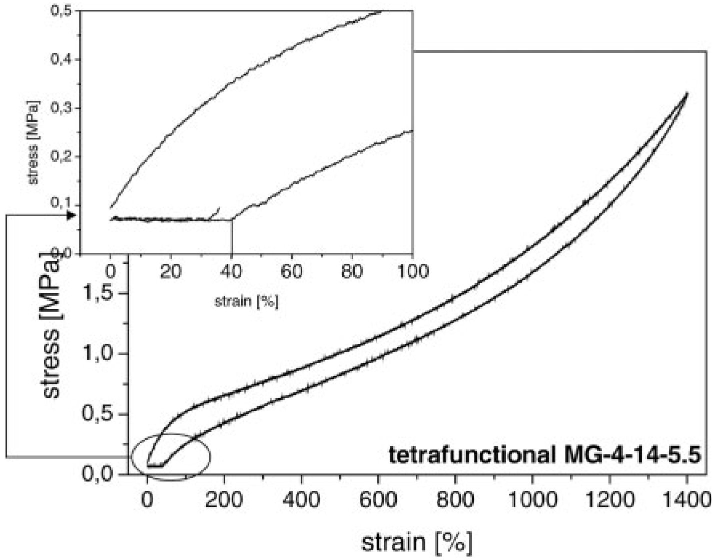

Figure 6.
Hysteresis curve of a tetrafunctional multigraft copolymer with 14 vol.-% PS and 5.5 branch points.

exceeding that of commercial TPE's could be found. Furthermore they show a high elasticity even at very high deformation up to 1400 %. Compared to trifunctional materials tetra- and hexafunctional multigraft copolymers reveal enhanced tensile strength and yield stress. By defined adjustment of molecular architecture novel TPE materials with superelastic properties can be designed, potentially applicable for example in medical technology, automobile industry or for membranes.

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[1] M. Xenidou, N. Hadjichristidis, *Macromolecules* **1998**, *31*, 5690.

[2] H. Iatrou, J. W. Mays, N. Hadjichristidis, *Macromolecules* **1998**, *31*, 6697.

[3] D. Uhrig, J. W. Mays, *Macromolecules* **2002**, *35*, 7182.

[4] S. P. Gido, C. Lee, D. J. Pochan, S. Pispas, J. W. Mays, N. Hadjichristidis, *Macromolecules* **1996**, *29*, 7022.

[5] C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino, J. W. Mays, *Polymer* **1998**, *39*, 4631.

[6] C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino, J. W. Mays, *J. Chem. Phys.* **1997**, *107*, 6460.

[7] M. Xenidou, F. L. Beyer, S. P. Gido, N. Hadjichristidis, N. Beck Tan, *Macromolecules* **1998**, *31*, 7659.

[8] S. T. Milner, *Macromolecules* **1994**, *27*, 2333.

[9] P. D. Olmsted, S. T. Milner, *Macromolecules* **1998**, *31*, 4011.

[10] M. D. Whitmore, J. D. Vavasour, *Acta Polym.* **1995**, *46*, 341.

[11] J. D. Vavasour, M. D. Whitmore, *Macromolecules* **1993**, *26*, 7070.

[12] F. L. Beyer, S. P. Gido, C. Büschl, H. Iatrou, D. Uhrig, J. W. Mays, M. Ying Chang, B. A. Garetz, N. P. Balsara, N. Beck Tan, N. Hadjichristidis, *Macromolecules* **2000**, *33*, 2039.

[13] Y. Zhu, S. P. Gido, U. Staudinger, R. Weidisch, D. Uhrig, J. W. Mays *Macromolecules*, submitted.

[14] R. Weidisch, S. P. Gido, D. Uhrig, H. Iatrou, J. W. Mays, N. Hadjichristidis, *Macromolecules* **2001**, *34*, 6333.

[15] R. P. Quirk, N. R. Legge, in: "*Thermoplastic Elastomers*", N. R. Legge, G. Holden, H. E. Schroeder Eds., Hanser, Munich, 1987, 71ff.

[16] I. W. Hamley, "*The Physics of Block Copolymers*", University Press, Oxford, 1998.

[17] R. Weidisch, M. Stamm, G. H. Michler, H. Fischer, R. Jerome, *Macromolecules* **1999**, *32*, 742.

[18] R. Weidisch, G. H. Michler, M. Arnold, H. Fischer, *J. Mat. Sci.* **2000**, *35*, 1257.

[19] R. Weidisch, G. H. Michler, in: "*Block Copolymers*", F. J. Balta Calleja, Z. Roslaniec, Eds., Marcel Dekker, New York, 2000, p.215ff.

[20] B. G. Sumpter, J. W. Mays, D. W. Noid, S. P. Gido, R. Weidisch, *Polymer News* **2004**, *29*, 302.

[21] A. Roos, C. Creton, *Macromolecules* **2005**, *38*, 7807.