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Tetrafunctional Multigraft Copolymers as Novel Thermoplastic Elastomers

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ABSTRACT: Tensile properties and morphology of tetrafunctional multigraft copolymers are investigated dependent on PS volume fraction and number of branch points. It is found that tetrafunctional multigraft copolymers with 22 vol % PS and seven branch points show a surprising high strain at break of about 2100%, about double that of commercial thermoplastic elastomers (TPE's) such as Kraton. With increasing number of branch points, strain at break and tensile strength increases, and strain at break is about 2300% for a sample with 10 branch points. Investigation of morphology using transmission electron microscopy indicates that a sample with 22 vol % PS has a wormlike microphase-separated structure with much lower long range order than other TPE's s such as Kraton. The multigraft copolymers of this study have two PS arms at each branch point. This, together with a large number of branch points per molecule, allows the elastic PI backbone to couple into a large number of reinforcing PS domains, resulting in huge elasticity, combined with a high tensile strength. Two parameters for adjusting mechanical properties of multigraft copolymers are found in our investigations: (1) functionality of the graft copolymer, tri- or tetrafunctional, and (2) number of branch points per molecule.

Introduction

Thermoplastic elastomers (TPE's) represent an important class of materials that are widely used for different technical applications. For example, poly(styrene-*b*-butadiene-*b*-styrene), SBS, triblock copolymers combine the mechanical performance of vulcanized rubbers with the straightforward processing of thermoplastics due to the thermal reversibility of cross-links generated by the microphase separation of PS domains.[1] There are four types of TPE materials with commercial importance, each consisting of a hard block (crystalline or glassy) coupled to a rubbery soft block: polystyrene/elastomer, polyurethane/elastomer, polyester/elastomer, and polyamide/elastomer. TPE's are also interesting because of the possibility of tailoring tensile properties by varying the ratio of hard/soft fractions. In SBS triblock copolymers control of the microphase-separated morphology of PS domains dispersed in a continuous rubbery poly(butadiene) (PBD) matrix, through varying the component volume fractions, allows to control of mechanical properties.[1,2]

It has been demonstrated by Kennedy and Delvaux[3] that graft copolymer molecular architecture can enhance TPE properties. However, there have been no detailed studies on the influence of morphology and molecular architecture of multigraft copolymers on mechanical properties. This paper reports on the mechanical properties of PS−PI multigraft copolymers with tetrafunctional branch architecture. The materials are comprised of PI backbones with two PS branches grafted at each of several tetrafunctional branch points per molecule. We find that such materials may be capable of providing an improved property profile, depending on the desired properties, as compared to commercial TPE's such as SBS triblock copolymers or other architectures. Recently, synthetic techniques have allowed the synthesis of multigraft copolymers with well-defined architectures.[4,10] Using these techniques, it is possible to control backbone molecular weight, arm molecular weight, and number and placement of branch points along the backbone. These architecturally controlled multigraft copolymers have been shown to form well-ordered microphase-separated morphologies which depend on both composition and molecular architecture.[5−8] Tetrafunctional multigraft copolymers comprised of a PI backbone and two PS branches at each regularly space branch site were used in this study, and their molecular characteristics are described in Table 1. It was also shown that the relevant value of χN for controlling microphase separation is calculated on a per junction point basis.[8] This places the multigraft copolymers investigated in this study in the strong segregation limit. Recently, it was shown[9] that an increasing number of branch points in multigraft copolymers is correlated to a decreasing grain size.

Experimental Section

The synthesis of tetrafunctional multigraft copolymers was described by Iatrou, Mays, and Hadjichristidis.[10] Chlorosilane coupling agents are used to link together living PS and PI chains which have been synthesized anionically. The final structure is precisely controlled with regard to the molecular weights of the PS graft blocks and the molecular weights of the PI connectors between each grafting point. However, the end-linking chemistry is similar kinetically to a condensation polymerization (step growth) and thus produces a distribution of total molecular weights; i.e., there is a distribution in the total PI backbone length and the number of PS grafts. Our

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Table 1. Characterization Data of Multigraft Copolymers: Molecular Weights of PI Connector, PS Arms, Total Molecular Weight, Polydispersity (PDI), Number of Branch Points, and Volume Fraction of PS

sample	vol % PS[a]	PI connector M_n (SEC, g/mol)	PS arm M_n (SEC, g/mol)	total M_n (SEC-MALLS, g/mol)	total M_w (LALLS, g/mol)	PDI (SEC)	no. of branch points[b]
MG-4-8-9	8.3	100 600	6 500	994 000	1 020 000	1.22	8.3
MG-4-7-21	22.0	82 800	13 400	798 000	830 000	1.23	7.0
MG-4-8-36	37.1	60 300	23 900	983 000	950 000	1.32	8.2
MG-4-8-67	66.9	26 100	29 100	827 000	800 000	1.26	8.8
MG-4-5-21	21.7	82 800	13 400	565 000	600 000	1.29	4.7
MG-4-10-21	22.2	82 800	13 400	1 094 000	1 170 000	1.26	9.9
Styroflex[c]	58.0			133 700		1.20	
Kraton[d]	20.5			104 800		1.15	

[a] Calculated using $\rho_{PI} = 0.91$ g/cm^3 and $\rho_{PS} = 1.05$ g/cm^3 based on ^{1}H NMR. [b] Number of branch points calculated as (total M_n − PI connector M_n)/(constituting block copolymer M_n). [c] Provided by BASF as commercial material under trade name Styroflex (S−SB−S triblock copolymer), characterization in ref 19. [d] Provided by BASF as commercial TPE (SIS triblock copolymer) from Shell-AG under the trade name Kraton.

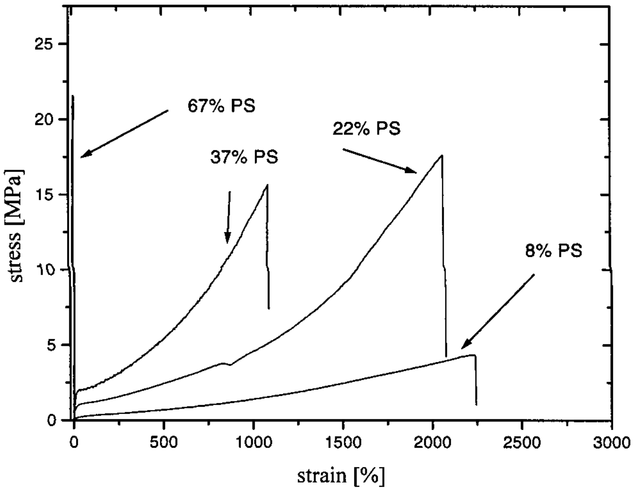

Figure 1. Stress−strain curves for multigraft copolymers (samples MG-4-8-9, MG-4-7-21, MG-4-8-36, and MG-4-8-67), depending on volume fraction of PS at a cross head speed of 15 mm/min.

previous work has demonstrated that near-monodisperse samples of graft copolymer with a precise number of grafts can be obtained from the overall reaction product by fractionation. The molecular characterization of the multigraft copolymers used in this study was described in detail previously.[9] This characterization work utilized size exclusion chromatography (SEC), membrane osmometry, low-angle laser laser light scattering (LALLS), and ^{1}H NMR.

To prepare samples for both tensile testing and morphological characterization, multigraft copolymers were dissolved as a 5 wt % solution in toluene, a nonselective solvent for both PS and PI. The solvent was allowed to evaporate slowly over 5−7 days at room temperature, yielding films about 0.3 mm thick. These films were dried to constant weight in a vacuum oven at 120 °C for 3 days in order to promote equilibrium structures. After annealing, dogbone samples for tensile testing were stamped from the films with a standard die having a 20 mm gauge length. After annealing the samples for 3 days, the tensile properties were constant, and further annealing did not change properties.

Tensile tests were performed using a universal testing machine Instron 1123 with 100 N load cell at a cross head speed of 15 mm/min. Stress−strain data for the samples utilized engineering stresses based on the measured initial cross-sectional dimensions of the specimens. For each sample and strain rate at least 10 samples were investigated. Thin sections, approximately 50 nm thick, for TEM study were prepared by ultramicrotoming the same annealed sample films using a Leica EM-FCS microtome, equipped with a cyogenic sample chamber operated at −110 °C. The isoprene blocks were stained with OsO_4. Electron microscopic observations were performed with a JEOL 1000CX transmission electron microscope (TEM) operated at 100 kV.

Results and Discussion

Multigraft copolymers with 8%, 22%, 37%, and 67% PS and 7−9 branch points, each with a different microphase-separated morphology, were investigated. Figure 1 shows stress−strain curves at a cross head speed of 15 mm/min. The morphology was unoriented, and therefore a dependence of mechanical properties on direction of extension of the specimens was not observed. Obviously, materials between 8% and 37% PS exhibit the behavior of a TPE as indicated by the large increase of stress at higher strains. While samples with 8% PS and eight branch points show a small tensile strength, multigraft copolymers with 22% PS and seven branch points reveal both a high tensile strength and high strain at break. With increasing PS content, the strain at break decreases dramatically without a corresponding increase in strength. As shown in Figure 1, the strain drops from 2100% for samples with 22% PS to 1150% for 37% PS. This strong decrease in strain at break is accompanied by the change in morphology from cylindrical to lamellar morphology.[9] At high PS contents the material becomes brittle. For instance, at 67% PS the strain at break is only about 2%, and yielding does not occur. Multigraft copolymers with 67% PS have a hexagonal structure consisting of PI cylinders in a continuous PS matrix.[9,20] Previous workers have shown[11−13] that a cavitation mechanism occurs in diblock copolymers with rubbery cylinders causing a yielding combined with a high toughness. In contrast, TEM (not shown) of our 67% PS sample reveals that cavitation does not occur in the rubbery PI cylinders; rather, the material fails through brittle fracture of the PS matrix.[20]

Clearly the most intriguing TPE properties with both high tensile strength and strain at break can be observed at 22% PS where a cylindrical morphology is expected. Morphology of this sample is shown in Figure 2 where small wormlike cylindrical PS domains in a PI matrix which lack long-range order are visible. Recently, it was shown via observation of the form factor in small-angle X-ray scattering (SAXS) and TEM [9] that these multigraft copolymers with 22% PS form wormlike cylindrical domains. This is clearly in contrast to common SBS triblock copolymers, where an ordered hexagonal morphology is observed. We repeated the previously published morphological characterization of this material with the samples prepared for mechanical testing and obtained the same results. With increasing number of branch points the morphologies of the 22%

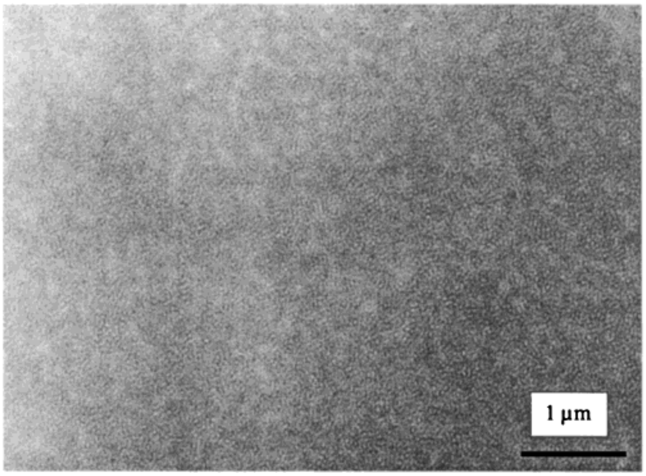

Figure 2. TEM micrograph for sample MG-4-7-21 with wormlike cylindrical PS domains.

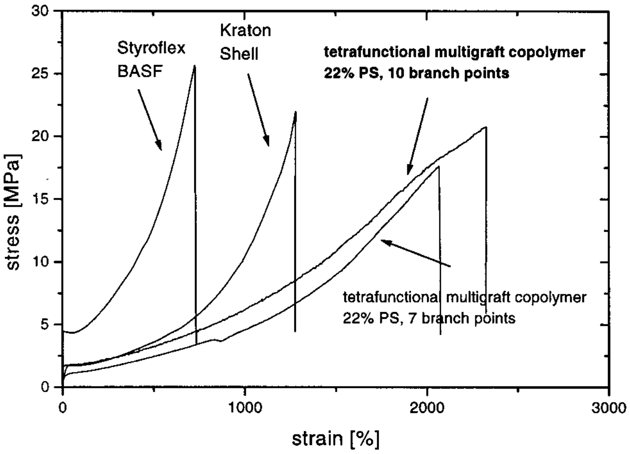

Figure 3. Mechanical properties of multigraft copolymers (MG-4-7-21 and MG-4-10-21) compared to commercial TPE's Kraton (20% PS) and Styroflex (58% PS, discussed in ref 19), revealing the exceptional large strain at break of tetrafunctional multigraft copolymers.

PS samples show a decrease in long-range order.[9] Since sample MG-4-7-21 has about seven branch points, a quite low extent of long-range order exists.

Figure 3 shows a comparison between two multigraft copolymers (MG-4-7-21 and MG-4-10-21) and two commercial TPE's, a Shell Kraton and a BASF Styroflex. Kraton, one of the best commercial TPE's on the market, is a typical poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymer with a hexagonal cylinder morphology. Styroflex is a SBS triblock copolymer with a styrene-*co*-butadiene copolymer as the middle block provided by BASF. It shows a higher yield stress and tensile strength than the Kraton or the tetrafunctional multigrafts but a lower strain at break. Samples of these two commercial TPE's were prepared and tested using the same procedures as employed with the multigraft materials. Obviously, the tetrafunctional multigraft copolymers show much higher strains at break than observed for the commercial TPE's. For a multigraft copolymer with 22% PS and 10 branch points the strain at break is almost twice that observed for Kraton with 20% PS. The combination of a huge strain at break and an acceptable tensile strength of about 21 MPa indicates the exceptional property profile of tetrafunctional multigraft copolymers. The tensile strength of multigraft copolymers with 22% PS is only slightly lower than that of the commercial TPE Kraton. The reason for the higher tensile strength of Styroflex is the increased PS content of 58%. Furthermore, first hysteresis experiments at about 500% deformation have proved the high elasticity of these multigraft copolymers as compared to that of Kraton. After relaxing for 10 min after straining up to 500% almost no residual deformation was observed. Even after a deformation of about 1500% the residual deformation after relaxing for 10 min was less than 100%. It is demonstrated that the multigraft copolymers with 10 branch points show even a higher tensile strength and strain at break than materials with seven branch points, indicating an influence of number of branch points on mechanical properties. Since morphology of samples with 10 branch points is in principle similar to that with seven branch points (the long-range order decreases with increasing number of branch points as discussed in ref 9), the reason for improved properties for sample MG-4-10-21 seems to be the increased number of branch points.

Mechanical properties of common TPE's such as SBS triblock copolymers arise from the midblock conformation, due to the triblock architecture, leading to bridges between the PS blocks. The requirements for this behavior are strongly segregated components with narrow interfaces and a sufficiently high molecular weight of the PS blocks. The lower limit of polystyrene block size is set by the incompatibility requirements, and the upper limit of molecular weights is set by viscosity considerations, which affect both processability and efficency of phase separation in the melt. This means that the styrene–diene ratio (morphology) controls the modulus of the TPE, with the polystyrene domains acting as *filler*. Because of these conditions, the molecular weight of the PS blocks is generally in the range of 10 000–15 000 g/mol while the polydiene molecular weight varies from 50 000 to 70 000 g/mol.[14] Thus, molecular architecture and morphology of SBS triblock copolymers leads to a *physical cross-linking* which is generally reported as the reason for their excellent elastomeric properties. It was shown by Quirk and Legge[14] that mechanical properties of TPE's only show a molecular weight dependence below 100 kg/mol which is attributed to the limit of phase separation. At higher molecular weights (M_n > 100 kg/mol) it does not influence mechanical properties. The multigraft copolymers used in this study have molecular weights far exceeding 100 kg/mol; thus, mechanical properties are independent of molecular weight.

In contrast to triblock copolymers, graft copolymers have a backbone with chemically different branches, and their morphology and properties can be tailored by changing molecular architecture.[15] To achieve acceptable mechanical properties with graft copolymers, it is necessary to use a rubbery backbone with glassy branches at two or more branch points and a fairly high molecular weight of rubbery backbone and glassy branches.[15] It was reported by Kennedy et al.[3,15] that graft copolymers with trifunctional branch points randomly distributed along the backbone can lead to TPE's with improved properties. In contrast, the tetrafunctional multigraft copolymers used in our study consist of two glassy branches per grafting point. In the case of sample MG-4-10-21 this means that an average of 10 branch points exist, and each of these branch points has two styrene branches. This provides enhanced stress transfer between the rubbery matrix and polystyrene

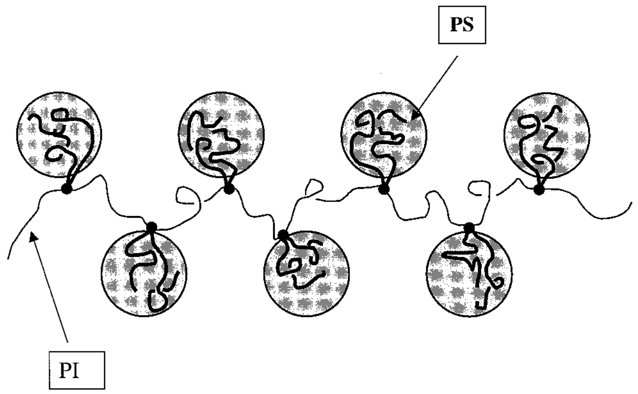

Figure 4. Schematic representation of tetrafunctional multigraft copolymers with PS domains in a PI matrix.

domains as compared to triblock copolymers and trifunctional graft copolymers. This is schematically illustrated in Figure 4 where a rubbery PI backbone has multiple branch points connected with two PS chains. In the microphase-separated morphology, the junction points must reside at the interface between the PS cylindrical domains and the PI matrix. We hypothesize that the enhanced mechanical properties of the multigraft materials arise from improved coupling of each highly elastic PI backbone to the reinforcing PS domains. This results from having two PS arms at each branch point and a relatively large number of branch points per molecule. Note that in such a microphase-separated morphology the two PS blocks which share a common junction point must both reside in the same PS domain.

It is shown in Figure 3 that tetrafunctional multigraft copolymers sustain an exceptional level of strain far exceeding that of commercial TPE's. It is interesting that this exceptional property profile can be achieved with a less ordered morphology. For SBS triblock copolymers it was reported[1,2,14] that a well-ordered morphology is one requirement that must be met in order to get acceptable TPE's. In the case of multigraft copolymers, however, a large number of branch points are necessary rather than a well-ordered morphology. Existence of smaller grain sizes can also be correlated with an improved property profile as recently shown in the case of weakly segregated block copolymers.[16−18] Multigraft copolymers with fewer than five branch points reveal a quite low strain at break. First test experiments have shown that samples with five branch points show only a strain at break of about 1500% and a tensile strength of 7 MPa,[20] indicating that strain at break as well as the ultimate tensile strength increases with increasing number of branch points. This means that the branch points connected to the PS domains provide a high strength combined with a smaller grain size. The enhanced number of physical cross-links in tetrafunctional multigraft copolymers leads to a *"physical multi-cross-linking"*, causing a huge strain at break and elasticity.

Conclusions

In this study, for the first time the tensile properties of tetrafunctional multigraft copolymers are investigated depending on composition and number of branch points. While samples with 67% PS show a strain at break of only about 2%, much smaller than rubber toughened polymers, materials with 22% PS show an exceptional combination of high strength and huge strain at break. The strain at break of these materials exceed 2000%, about twice of the commercial TPE's. While the rubbery PI backbone provide a huge elasticity, the PS branches reinforce the coupling (physical cross-linking) between rubbery backbone and PS domains. In contrast to trifunctional multigraft copolymers, tetrafunctional multigraft copolymers have two PS arms at each branch point which together with a large number of branch points results in a huge elasticity of the PI backbone combined with a high tensile strength. With increasing number of branch points the strain at break increases, which indicates that an increasing number of PS branches reinforce the coupling between the backbone and PS domains, resulting in an increase of elasticity of the material. The new concept of using tetrafunctional multigraft copolymers as TPE's not only reveals a new type of TPE's with an exceptional property profile but also demonstrates how the molecule architecture influences the properties of microphase-separated graft copolymers. There are two new parameters for adjusting mechanical properties of multigraft copolymers found in our investigations: (1) functionality of the graft copolymer, tri- or tetrafunctional, and (2) number of branch points correlated to a change of grain size. By using these parameters in addition to that already reported by Kennedy et al.,[15] it may be possible to develop novel TPE's with an exceptional property profile based on tetrafunctional multigraft copolymers.

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