Multigraft Copolymer Superelastomers: Synthesis Morphology, and Properties

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Abstract

The synthesis of well-defined multigraft copolymers having a polydiene backbone with polystyrene side chains is briefly reviewed, with particular focus on controlling branch point spacing and branch point functionality. Use of living anionic polymerization and chlorosilane linking chemistry has led to the synthesis of series of materials having regularly spaced
trifunctional (comb), tetrafunctional (centipede), and hexafunctional (barbwire) branch points. The morphologies of these materials were characterized by transmission electron microscopy and small-angle X-ray scattering, and it was found that the morphologies were controlled by the local architectural asymmetry associated with each branch point. Mechanical properties studies revealed that such multigraft copolymers represent a new class of thermoplastic elastomers (TPEs) with superior elongation at break and low residual strains as compared to conventional TPEs.

Introduction

Thermoplastic elastomers (TPEs) represent an important segment of the worldwide elastomer market due to their combination of mechanical properties comparable to vulcanized rubbers and straightforward processing similar to that of thermoplastics [1]. TPEs are also of interest because of their capacity to self-assemble to form ordered phase separated structures having nanoscale dimensions, with morphologies and properties tunable by controlling the volume fractions of hard and soft segments [2]. Two of the most important commercial classes of TPEs commercially, as well as the most studied class of TPEs in terms of their fundamental properties, are SIS and SBS triblock copolymers. Here S represents glassy polystyrene (PS) end-blocks and I and B represent rubbery polyisoprene (PI) and polybutadiene (PBD) mid-blocks, respectively. For these materials the morphology formed, and thus the mechanical properties, are directly linked to the volume fractions of the two components.

The use of branching to improve the properties of styrene/diene TPEs has been explored since the 1970s. Fetters and coworkers synthesized star block copolymers, star polymers where each
arm is a block copolymer, having PS outer blocks and PI inner blocks and reported improved tensile strength relative to linear triblocks of comparable composition and segment molecular weights [3]. Commercial star-block copolymers based on S/I and S/B compositions have been commercialized by companies such as Phillips, BASF, etc. Graft copolymers are another class of branched block copolymers having a backbone composed of one type of polymer with pendant side chains that are chemically different from the backbone [4]. The concept of using multigraft copolymers as TPEs is interesting, because if the backbone is chosen as the soft segment with hard segments as the side chains there will be multiple tether points connecting the rubbery backbone to reinforcing rigid domain. This would appear to offer potential to create elastomers exhibiting improved mechanical properties.

**Synthesis of Multigraft Copolymer TPEs**

The first work on synthesis of multigraft copolymers by metallation of a polydiene backbone (a “grafting from strategy”) dates back to the late 1960s [5-7]. These works were plagued by serious degradation of the polydiene backbones. The first systematic study of graft copolymers having polydiene backbones with PS grafts as TPEs was work of Falk and coworkers [8]. These workers employed milder metallation conditions in order to minimize polymer degradation. They concluded that the elastomeric properties of their PBD-g-PS multigraft copolymers were similar to that of corresponding SBS triblock copolymers and offer the advantage of higher melt flow [8].

Hadjichristidis and Roovers [9] synthesized PI-g-PS multigraft copolymers (see Figure 1) by following the synthetic approach of Falk et al. but improved the level of control during the
synthesis by employing high vacuum line techniques [10,11] in a vessel equipped with an optical cell.

**FIGURE 1**

Even under these optimized conditions, some homopolystyrene is present and must be removed by fractionation. Isolation of the PS is in fact useful in characterizing the molecular architecture of the resulting copolymers. The branch points are randomly spaced along the PI backbone and the branch points are trifunctional (one side chain per branching site).

Cameron and Qureshi employed a “grafting to” approach to make PI-g-PS multigraft copolymers having randomly placed trifunctional branch points [12]. This involved the use of hydrosilation chemistry to introduce chlorosilane functionality onto 1,2- units of PBD, followed by reaction with poly(styryllithium) (Figure 2). The grafting to approach offers the advantage of being able to characterize both the backbone and side chains prior to the grafting reaction, and the reaction of the PS anions with chlorosilane groups is known to be free of side reactions.

**FIGURE 2**

Xenidou and Hadjichristidis subsequently extended this strategy to make PBD-g-PS multigrafts carrying two PS grafts per randomly placed branch point (i.e. tetrafunctional branch points) by employing dichloromethylsilane in the hydrosilylation step [13].
In situ synthesis and polymerization of macromonomers has been shown to be an effective strategy for synthesis of comb and graft polymers [14]. This same macromonomer approach using copolymerization of PS-based macromonomers with diene monomers in the presence of randomizers has been used to make multigraft copolymers having polydiene backbones with randomly placed tetrafunctional and pentafunctional multigrafts [15,16]. The synthesis of PBD-g-PS “doubly tailed” multigrafts is shown in Figure 3.

Beginning in 1990, Mays and Hadjichristidis initiated systematic programs on synthesis of PI-g-PS (and to a lesser extent PBD-g-PS) graft copolymers, starting with species having a single branch point, which could be located in the middle of the PI backbone or moved off-center to a desired location along the PI backbone, and then to more complex structures including regular doubly grafted structures such as π and H shaped graft copolymers [17]. Their syntheses involved the use of well-established chlorosilane linking chemistry [18] to connect together individual segments of the graft copolymer that bear anions at one chain end or at both ends, as demonstrated in Figure 4 for the synthesis of π shaped graft copolymers.

This work allowed precise control over the number of branch points and branch point spacing, as well as backbone and side chain lengths.
The application of this chemistry to synthesize multigraft copolymers having regularly spaced branch points and control of the number of branches per branch point was first demonstrated by Hadjichristidis and Mays [19] and extended by Uhrig and Mays [20]. As shown in Figure 5, the strategy exploits a step growth reaction between two polymeric macromonomers: one being a PS bearing two reactive chlorosilane groups and the other being a PI having reactive anions at both ends of the chain.

These materials, having trifunctional, tetrafunctional, and hexafunctional branch points are called, respectively, “comb”, “centipede”, and “barbwire” architectures [19,20] and are illustrated in Figure 6.

While both the PI backbone segments and the PS branches of these materials have very narrow polydispersity indices (PDI) since they are made by living anionic polymerization, due to the step-growth polymerization mechanism that is used to build the multigraft structures the final products have PDIs of 2 or slightly higher. However, this polydispersity reflects primarily the presence of structures having different numbers of branch points and by solvent/nonsolvent fractionation several specimens having narrow PDI and different average numbers of branches
may be isolated [19,20]. Such specimens are ideal for studying the influence of branching architecture and degree of branching on properties of multigraft copolymers.

**Morphology of Multigraft Copolymers**

Milner developed a self-consistent mean field model that predicts the influence of architectural and conformational asymmetry on block copolymer morphology in the strong segregation limit [21]. Milner introduced an asymmetry parameter $\varepsilon$, defined as $\varepsilon = (n_A/n_B) \left(l_A/l_B\right)^{1/2}$ where $n_A$ and $n_B$ are the numbers of chemically different chains connected together in the star and $l_A$ and $l_B$ reflect differences in conformational flexibility of the two polymeric species. This theory predicts to a good approximation the morphology of miktoarm stars of various architectures as a function of $\Phi_B$, the volume fraction of the B component.

In order to apply Milner’s theory to graft copolymer architectures having more than one branch point the “constituting miktoarm star” concept, illustrated in Figure 7, may be used [22].

**FIGURE 7**

The idea is basically that it is the local symmetry or asymmetry in the multigraft that controls morphology. For example, a centipede multigraft copolymer may be considered as a number of $A_2B_2$ miktoarm stars that are linked together. In Figure 8, morphologies observed for four centipede copolymers are plotted on Milner’s miktoarm star phase diagram; the values in the boxes are the PS volume fractions.
All but the “67” sample exhibit the morphology predicted by Milner. This specimen is expected, based on the Milner model, to exhibit a bicontinuous morphology but instead forms a cylindrical morphology. When specimens made from the same backbone and side chain segments but having different numbers of branch points were investigated it was found that they exhibit the same morphologies, as expected, but the extent of long range order decreased as the number of branch points was increased [22]. This is seen in Figure 9 where “MG” represents multigraft, the “4’ indicates tetrafunctional branch points or centipede architecture, “5”, “9”, and “12” represent the number of branch points, and “36” represents the volume percent PS in the materials.

Mechanical Properties of Multigraft Copolymers
Multigraft copolymers show high strains at break and, in comparison to commercial materials like Kraton (20 % PS) and Styroflex (58 % PS), they retain adequate tensile strengths. This was demonstrated by Weidisch and coworkers by mechanical testing of regularly spaced tetrafunctional multigraft copolymers exhibiting unorientated morphologies [23]. 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 high tensile strength is attributed to a sufficient molecular
weight of the PS grafts. In hysteresis tests multigraft copolymers show low residual strains when stretched previously to elongations above 1000% (Figure 10). Model fits according to the non-affine tube model and an energy-based softening model were performed in other works [27]. In particular for multigraft copolymers with spherical morphologies, low softening characteristics, low residual strains and large extensibilities were found, and evidence could be given by the softening parameter b and the average number of statistical segments between two successively trapped entanglements (Figure 11).

FIGURE 10

FIGURE 11

Functionality and number of branch points have a strong effect on tensile strength. It was found that $\sigma_B$ increases approximately linearly with either parameter within the investigated region (Figure 12). It is possible to correlate the increase in number of branch points with decrease in grain size and long range order, finer distribution of the PS microdomains, and resultant augmentation of mechanical properties. For TPEs in general, the PS domains act as ‘chemical’, yet resolvable crosslinks, similar to crosslinked rubber.

FIGURE 12

In contrast to SBS triblocks and trifunctional graft copolymers, multigrafts with tetrafunctional branch points provide improved stress transfer between the polymer matrix and the PS domains. This was demonstrated additionally by computer simulations of the molecular interactions.
between PS grafts in the nanodomains [25]. The studies on hysteresis behavior revealed that physical crosslinking strongly influences hysteresis characteristics at high deformations. Evidence was given further by the dynamic flocculation model, which assumes successive breakdown and re-agglomeration of filler clusters [26]. From the fit parameters of the model it was suggested that the deformation mechanism of multigraft copolymers is comparable to that of filled elastomers [26]. The stress softening was shown to be in correlation to the number of branch points and it can be reduced by improved distribution of the PS domains. Results from relaxation tests and application of rubber elasticity model to stress strain data revealed that i) the PS domains of high continuity result in lower stress relaxation, and ii) a highly ramified PS domain structure lowers the physical cross-link modulus during the first hysteresis cycle (Figure 13). The latter was attributed to a preferred break down of PS-PS domain bridges due to local stress concentrations [28]. In these works the PS-domains of the multigrafts were considered as filler particles assuming a spherical shape, and it is relevant to consider their true shape especially during the deformation process.

FIGURE 13

Detailed information on microstructural damage and deformation mechanisms were obtained by synchrotron small-angle X-ray scattering (SAXS) and in-situ deformation Fourier transform infrared spectroscopy (FTIR) characterization [29]. It was suggested that on the molecular level, PS domains can be termed double functionalized (the number of PI chains connected to one PS-domain is for graft copolymers usually twice as compared to triblock copolymers) and this may dramatically improve the stress transformation between the two phases [29]. Further, by in-situ
deformation FTIR molecular orientation was found to be similar for PI and PS, suggesting a large interface between PI and PS – phase and therefore to mainly soft physical cross-links, represented by the PS domains.

Conclusions
Well-defined graft copolymers having multiple regularly spaced branch points of controlled functionality may be synthesized by anionic polymerization and chlorosilane linking chemistry. The structure-morphology relationships for these materials may be understood by applying Milner’s model to the miktoarm star that constitutes the repeating unit of the multigraft copolymer. Multigraft copolymers exhibit superelastomeric properties: strain at break can far exceed that of conventional triblock copolymer TPEs with low residual strains. This behavior is attributed to improved stress transfer between the phases and multiple tethering of the elastomeric backbone to the glassy domains.

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Figure Captions

Figure 1. Synthesis of graft copolymer by metallation of polyisoprene.

Figure 2. Hydrosilylation of polybutadiene.

Figure 3. Synthesis of polybutadiene graft copolymer by in situ macromonomer preparation.

Figure 4. Synthesis of poly(isoprene-graft-styrene) "π" copolymer by modular strategy.

Figure 5. Synthesis of poly(isoprene-graft-styrene) multigraft copolymers by modular strategy.

Figure 6. Multigraft copolymer architectures: (a) trifunctional branch points, "comb"; (b) tetrafunctional branch points, "centipede"; (c) hexafunctional branch points, "barbwire".

Figure 7. A multigraft is understood by its "constituting block copolymer" repeat unit.

Figure 8. Mapping of experimentally observed centipede morphological behavior onto Milner's theoretical predictive diagram.

Figure 9. TEM micrographs of centipedes with 36% polystyrene content.

Figure 10. Hysteresis curve of a tetrafunctional multigraft copolymer with 14 vol-% PS and 5.5 branch points.

Figure 11. Hysteresis data with model fits according to the non-affine tube model and the softening model for a tetrafunctional multigraft copolymer with 15 vol-% PS and 5.3 branch points (coarsely fractionated, second hysteresis cycle) [24,27].

Figure 12. Influence of the number of branch points on tensile strength, $s_B$ [24,28].

Figure 13. Influence of the number of branch points on stress relaxation, $R^s$. 
FIGURE 2

[Chemical structure diagram showing the reaction of SiCl(HSiMe₂Cl) with a Pt catalyst to produce a modified product.]
FIGURE 3

\[
\text{sec-BuLi} + \text{styrene} \xrightarrow{\text{benzene}} \text{end-cap with a few units of butadiene} \xrightarrow{\text{PS(Bd)Li}}
\]

\[
2 \text{PS(Bd)Li} + \text{titration} \xrightarrow{\text{benzene}} \text{PS(Bd)Li} + 2 \text{LiCl}
\]

\[
\text{butadiene} + \text{sec-BuLi} \xrightarrow{\text{benzene}} \text{PB-graft-PS multigraft polymer}
\]
FIGURE 4

\[
\begin{align*}
\text{PI}Li + \text{excess CH}_3\text{SiCl}_3 & \xrightarrow{\text{benzene}} \quad (\text{PI})\text{Si}(\text{CH}_3)\text{Cl}_2 + \text{LiCl} + \text{CH}_3\text{SiCl}_3 \\
\quad \text{II} \\
\text{I} + \text{PSLi} & \xrightarrow{\text{slow add'n}} \quad (\text{PI})(\text{PS})\text{Si}(\text{CH}_3)\text{Cl} + \text{LiCl} \\
\quad \text{II} \\
\text{LiDLi} + \text{isoprene} & \xrightarrow{\text{sec-BuOLi}} \quad \text{LiPILi} \\
\quad \text{III} \\
2 \text{II} + \text{III} & \xrightarrow{\text{THF}} \quad (\text{PI})(\text{PS})(\text{CH}_3)\text{Si}(\text{PI})\text{Si}(\text{CH}_3)(\text{PI})(\text{PS}) + 2 \text{LiCl} \\
\text{PI-graft-PS} \\
\end{align*}
\]
Comb

\[
\text{PSLi + excess MeSiCl}_3 \rightarrow (\text{PS})(\text{Me})\text{SiCl}_2 + \text{LiCl} + \text{MeSiCl}_3
\]

\[
\text{LiPILi + (PS)(Me)SiCl}_2 \rightarrow \text{Pl}[\text{(PS)(Me)SiPI}_n + \text{LiCl}
\]

Centipede

\[
2 \text{PSLi + SiCl}_4 \rightarrow (\text{PS})_2\text{SiCl}_2 + 2 \text{LiCl}
\]

\[
\text{LiPILi + (PS)_2SiCl}_2 \rightarrow \text{Pl}[\text{(PS)_2SiPI}_n + \text{LiCl}
\]

Barbwire

\[
4 \text{PSLi + Cl}_3\text{Si(CH}_2)_6\text{SiCl}_3 \rightarrow \text{Cl(PS)}_2\text{Si(CH}_2)_6\text{Si(PS)}_2\text{Cl} + 4 \text{LiCl}
\]

\[
\text{LiPILi + Cl(PS)}_2\text{Si(CH}_2)_6\text{Si(PS)}_2\text{Cl} \rightarrow \text{Pl}[\text{(PS)}_2\text{Si(CH}_2)_6\text{Si(PS)}_2\text{PI}_n + \text{LiCl}
\]
FIGURE 8

\[ \varepsilon = \left( \frac{n_A}{n_B} \right) \left( \frac{l_A}{l_B} \right)^{1/2} \]

\[ \phi_B \]

Points labeled: S_B, C_B, Bic_B, L, C_A, Bic_A, 67, 36, 21, 9, S_A.
FIGURE 10
MG 4-15 – 5.3cf

\( G_c = 0.084 \text{ N/mm}^2 \)
\( G_e = 0.086 \text{ N/mm}^2 \)
\( \frac{n_e}{T_e} = 171 \)
\( b = 0.086 (\text{Nm})^{-1/2} \)