Macromol. Symp. **2004**, *215*, 111-126

Synthesis and Structure – Property Relationships for Regular Multigraft Copolymers

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Summary: Multigraft copolymers with polyisoprene backbones and polystyrene branches, having multiple regularly spaced branch points, were synthesized by anionic polymerization high vacuum techniques and controlled chlorosilane linking chemistry. The functionality of the branch points (1, 2 and 4) can be controlled, through the choice of chlorosilane linking agent. The morphologies of the various graft copolymers were investigated by transmission electron microscopy and X-ray scattering. It was concluded that the morphology of these complex architectures is governed by the behavior of the corresponding miktoarm star copolymer associated with each branch point (constituting block copolymer), which follows Milner's theoretical treatment for miktoarm stars. By comparing samples having the same molecular weight backbone and branches but different number of branches it was found that the extent of long range order decreases with increasing number of branch points. The stress-strain properties in tension were investigated for some of these multigraft copolymers. For certain compositions thermoplastic elastomer (TPE) behavior was observed, and in many instances the elongation at break was much higher (2-3X) than that of conventional triblock TPEs.

Keywords: anionic polymerization; graft copolymer; mechanical properties; molecular architecture; morphology

DOI: 10.1002/masy.200451110

Introduction

Graft copolymers are branched block copolymers having a backbone composed of one type of polymer with pendant side chains that are chemically different from the backbone.[1] Graft copolymers are complex materials due to potential variations in: 1. backbone length and polydispersity, 2. branch length and polydispersity, 3. number of branch points per molecule, 4. location of branch points along the backbone, and 5. functionality of the branch points, i.e. the number of branches attached at each branch point. A synthetic approach for producing true model graft copolymers would have all five of these variables under tight control. Unfortunately, the conventional strategies of "grafting from", "grafting onto", and "copolymerization of macromonomers" are usually only effective at controlling the first two parameters, even when living polymerizations are used.

For example, Figure 1 shows a recent example of grafting from chemistry.[2] The backbone is polystyrene (PS) incorporating some 4-methylstyrene as comonomer. Living radical polymerization was used to synthesize this copolymer backbone, so its polydispersity is low. Treatment of the backbone with potassium superbase produced benzylpotassium anionic active sites that are used for the polymerization of 4-methoxystyrene. This method thus controls backbone and branch lengths and polydispersities. On the other hand, the number of branch points per molecule and their placement along the backbone is a statistical process, controlled mostly by the reactivity ratios of styrene and 4-methystyrene. While the branch points would be expected to be trifunctional (two backbone segments and one branch connected to each), creation of effectively tetrafunctional (or higher) branch points could occur due to the presence of two (or more) metallated 4-methystyrene units in close proximity or due to side reactions.

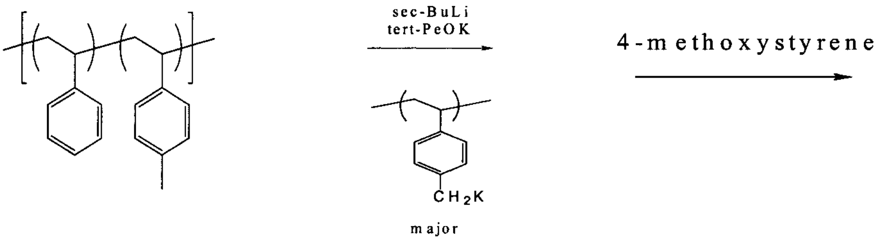

Figure 1. An example of grafting from. A styrene/4-methylstyrene copolymer is metallated with potassium superbase creating anionic sites that can initiate polymerization of 4-methoxystyrene.

A recent example of the grafting onto strategy is shown in Figure 2.[3] A polybutadiene backbone was prepared by living anionic polymerization in a hydrocarbon solvent resulting in a material containing about 7-8 % 1,2- units randomly distributed along a predominantly 1,4- backbone. These pendant vinyl groups react preferentially with chlorosilanes in hydrosilylation reactions to introduce pendant chlorosilane functionality along the backbone (Fig. 2). PS side chains were synthesized anionically, end capped with a few units of butadiene (to reduce steric hindrance), and grafted onto the backbone by reaction with the chlorosilane groups. Like in the example above, this strategy results in narrow polydispersity backbones and side chains, but the number of branches and their placement are statistically controlled. An advantage of the method depicted in Fig. 2 is the capacity to vary branch point functionality through choice of chlorosilane.

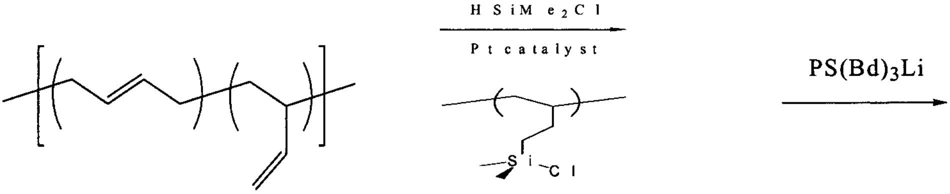

Figure 2. An example of grafting onto. Hydrosilylation chemistry is used to introduce chlorosilane functionality into 1,2-PBD units. Reaction of living polyanions with these chlorosilane units results in graft copolymer formation.

The macromonomer approach has been widely employed for the synthesis of graft copolymers. An example from work by Hawker and co-workers is shown in Figure 3.[4] These workers utilized TEMPO-mediated living radical copolymerization of a polylactide macromonomer with styrene. Thus, narrow polydispersity backbones and branches were achieved but the reactivity ratios dictated branch point placement. It should be noted that even ideal reactivity ratios of 1 for both monomers does not mean that all chains will contain equal numbers of branches or that their spacing along the backbone will be regular.

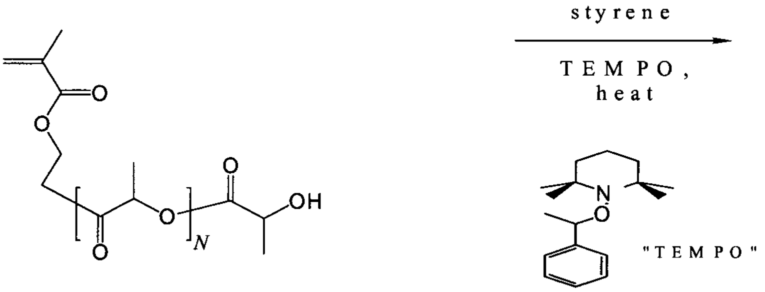

Figure 3. The macromonomer approach. A polylactide macromonomer is copolymerized with styrene in a living radical polymerization to create a graft copolymer.

The obvious strategy for overcoming the problem of control of branch point spacing and extent of branching, as well as for manipulating branch point functionality involves synthesis of segments of the backbone carrying reactive groups at both chain ends, synthesis of branches carrying functionality at one chain end, and controllably linking these segments together. Rempp and co-workers[5] were the first to carry out "polycondensation" of polymers carrying anions at both ends with difunctional electrophiles, such as dibromobutane, to generate a polymer of increased molecular weight. Such a process should obey the kinetics of a step-growth polymerization with polydispersities of about two and the degree of polymerization controlled by the stoichiometry and conversion. Strazielle and Herz[6] reacted triallyloxytriazine (a trifunctional reactant) with dianionic PS (prepared using a dipotassium initiator). Only two of the alylloxy groups reacted with the living dipotassium PS, leaving one allyoxy group at each branch point which was then reacted with living PS made using a monofunctional anionic initiator. This, in principle and after fractionation, should lead to a regular polystyrene comb (branched homopolymer) with uniformity in all five of the molecular parameters outlined above. However, star PS reported in the same paper made using a tetraallyloxy linking agent yielded broader than expected polydispersities, suggesting the presence of side reactions with this chemistry.[6] Recently, a group at Dow Chemical[7] synthesized branched polystyrenes of controlled architecture using the related approach of reacting α,ω-dianionic PS with a mixture of α,α'-dichloro-p-xylene and α,α',α''-trichloromesitylene.

We have recently developed a chlorosilane linking route that is derived from these earlier strategies and applied it to the synthesis of homopolymers and copolymers having multiple, regularly spaced branch points.[8-11] In this paper, we summarize results on the synthesis, molecular characterization, morphology, and tensile properties of copolymers derived from these materials. Described are the "comb", "centipede", and "barbwire" architectures (Figure 4) having polyisoprene (PI) backbones, polystyrene (PS) side chains, and 1, 2, or 4 branches per branch point.

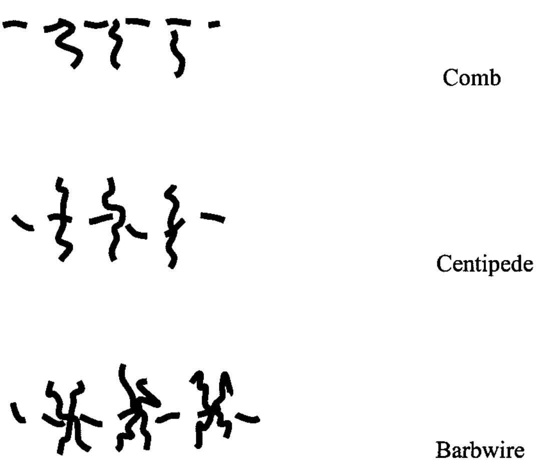

Figure 4. Different multigraft architectures synthesized in this work. In all cases, PI is the backbone and the branches are PS.

Experimental

The synthesis of the copolymers has been previously described in detail.[8,11] Briefly, α,ω-difunctional 1,4-PI is synthesized using a difunctional anionic initiator, (1,3-phenylene)bis(3-methyl-1-phenylpentylidene)dilithium, and reacted with: a. polystyrene carrying a terminal

dichlorosilane functionality to create combs; b. PS chains having centrally located dichlorosilane functionality to create centipedes; and c. PS 4-arm stars having centrally located dichlorosilane functionality to create barbwires. The products obtained were polydisperse due to the presence of materials having different numbers of branch points, as expected for a polycondensation. Fractions with high levels of uniformity in terms of number of branch points were isolated by solvent/nonsolvent fractionation as previously described.[8,11] The products were characterized by size exclusion chromatography (SEC), light scattering, and UV and NMR spectroscopy.
Morphological characterization involved films cast from a non-selective solvent (toluene), followed by annealing at 120° C. Osmium tetraoxide staining of the polydiene phase makes the soft phases appear dark in transmission electron micrographs (TEM). X-ray scattering was used to complement and fortify the TEM results. A complete account of the methods used was previously given.[12] Tensile testing was performed on toluene cast annealed specimens using an Instron tensile tester as previously described.[13] Specimens having a 20 mm gauge length were strained at a crosshead speed of 15 mm/min.

Results and Discussion

The synthesis of the three types of branched architectures is summarized in Figure 5. The synthesis of the appropriate dichlorosilane functionalized species is the key step in the synthesis of the regular multigrafts. In the case of combs, the dichlorosilane end capped PS can be synthesized in quantitative yield. Figure 6 shows overlaid, area-normalized SEC chromatograms of a PS branch before and after end capping with methyltrichlorosilane. The chromatograms exactly coincide showing the absence of coupled product, and the use of >100:1 excess of purified chlorosilane assures complete chain end functionalization. With the use of stoichiometric amounts of the two polymeric reagents, we have been able to synthesize comb structures having up to 90 branch points.[10]

Comb

$$\mathrm{PSLi} + \text{excess } \mathrm{MeSiCl_3} \longrightarrow \mathrm{(PS)(Me)SiCl_2} + \mathrm{LiCl} + \mathrm{MeSiCl_3}\uparrow$$

$$\mathrm{LiPILi} + \mathrm{(PS)(Me)SiCl_2} \longrightarrow \mathrm{PI}\big[\mathrm{(PS)(Me)SiPI}\big]_N + \mathrm{LiCl}$$

Centipede

$$2\,\mathrm{PSLi} + \mathrm{SiCl_4} \longrightarrow \mathrm{(PS)_2SiCl_2} + 2\,\mathrm{LiCl}$$

$$\mathrm{LiPILi} + \mathrm{(PS)_2SiCl_2} \longrightarrow \mathrm{PI}\big[\mathrm{(PS)_2SiPI}\big]_N + \mathrm{LiCl}$$

Barbwire

$$4\,\mathrm{PSLi} + \mathrm{Cl_3Si(CH_2)_6SiCl_3} \longrightarrow \mathrm{Cl(PS)_2Si(CH_2)_6Si(PS)_2Cl} + 4\,\mathrm{LiCl}$$

$$\mathrm{LiPILi} + \mathrm{Cl(PS)_2Si(CH_2)_6Si(PS)_2Cl} \longrightarrow \mathrm{PI}\big[\mathrm{(PS)_2Si(CH_2)_6Si(PS)_2PI}\big]_N + \mathrm{LiCl}$$

Figure 5. Synthesis schemes for the various branched architectures.

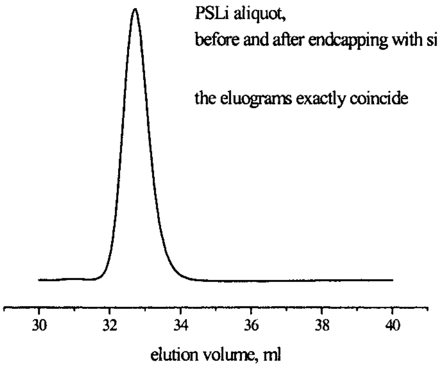

Figure 6. SEC chromatograms after end capping with methyltrichlorosilane and after termination with methanol.

Synthesis of the dichlorosilane functionalized polymer intermediates in the synthesis of centipedes and combs is more difficult, due to the inability to achieve a perfect endpoint in the "vacuum titration" [14] of chlorosilanes with poly(styryllithium). Figure 7 shows SEC chromatograms following a vacuum titration to form $(PS)_2SiCl_2$ during the synthesis of a centipede architecture. Notice that at the endpoint it appears that some $PSSiCl_3$ remains. In our experience, it is difficult to push the yield of the coupled product beyond 95-97 % without detecting the presence of 3-arm star species. The imperfect nature of these titrations limits the ability to synthesize centipedes and barbwires with very large numbers of branch points. To date, we have synthesized centipedes with up to 14 branch points and barbwires with up to 5 branch points.[11,12]

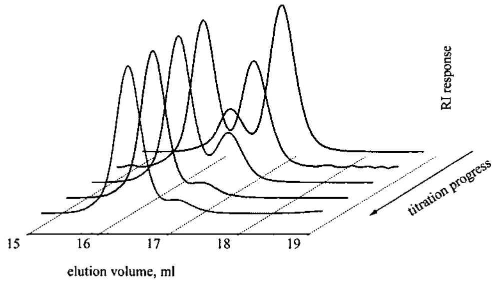

Figure 7. SEC snapshots of the vacuum titration in progress.

The molecular characteristics of the precursors and fractionated products for two barbwire syntheses are given in Table 1. Notice that the polydispersities of the PI backbone segments are 1.13 as opposed to 1.02 to 1.04 for the PS branches. This reflects the slow initiation of isoprene with the difunctional initiator, even in the presence of the polar modifier lithium butoxide. Molecular weights of the repeating units are calculated based on measured molecular weights of the constituents. Functionality of the fractions is calculated by comparing measured molecular weights from light scattering with the unit molecular weight. Three fractions having polydispersities around 1.15 to 1.22 were obtained by fractionating the mother batches of barbwire. Notice that the composition remains almost constant among these fractions while the number of branch points is varied. Thus, these series provide excellent series of model compounds for studying how variations in multigraft architecture and number of branch points affect morphology and mechanical properties.

Table 1. Molecular characteristics of some barbwire copolymers.

Synthetic Experiment			MG6 1			MG6 2		
PS Graft	SEC-MALLS	M_w, kg/mol	8.2			13.0		
	SEC-RI	I, M_w/M_n	1.04			1.02		
PI Spacer	SEC-MALLS	M_w	86.8			63.3		
	SEC-RI	I	1.13			1.13		
Graft Unit			Calculated M_w 120 kg/mol			Calculated M_w 115 kg/mol		
Multigraft Product		fractional cut	1	2	3	1	2	3
	^{1}H NMR	mass% PS	23.5	23.2	23.1	38.3	37.9	38.2
	SEC-UV	mass% PS	24.7	24.5	24.3	39.0	38.9	39.1
	SEC-MALLS	M_w	705	515	411	409	328	287
	SEC-RI	I	1.15	1.16	1.17	1.19	1.22	1.22
	Calculated Number of Branch Points		5.2	3.6	2.7	3.0	2.3	1.9
	Calculated Composition, mass% PS		24.0	22.8	21.6	38.1	36.4	35.2
	Fractionated Final Yield, grams		3.8	4.6	2.8	1.4	2.3	1.8

Milner [15] in 1994 introduced a self-consistent mean field model that predicts the impact of architectural and conformational asymmetry on block copolymer morphology in the strong segregation limit. To a first approximation, the model may be viewed as one that applies to miktoarm stars, star polymers composed of chemically different arms. Milner introduced a parameter, ϵ ($\epsilon \geq 1$), defined as $\epsilon = (n_A/n_B)\,(l_A/l_B)^{1/2}$ where n_A and n_B are the number of chains of each type connected together in the star and l_A and l_B reflect the differences in chain flexibility of the two different chains. In the case of PS/PI block copolymers, the conformational differences are relatively minor, so the architectural term is dominant. Milner's theory predicts how branched architecture, for polymers having a single branch point, will impact the observed morphology as a function of Φ_B, the volume fraction of the B component is varied for polymers having a single branch point.

To be able to apply Milner's theory to more complex architectures such as the polymers of this work, the concept of the "constituting block copolymer" was introduced empirically and shown to be valid for various architectures.[12,16,17] This concept is demonstrated in Fig. 8. For example, regular combs and centipedes may be imagined as made up of A_2B and A_2B_2 miktoarm stars, respectively. In Figure 9, the morphologies observed for four centipede copolymers are plotted on the Milner phase diagram with the values in the boxes representing the PS content in the sample by volume. All but one of the materials exhibited the predicted morphology. The "67" sample is predicted to lie just inside a bicontinuous morphology window based on the Milner model and the constituting block copolymer hypothesis; instead this material is composed of PI cylinders in a PS continuous phase.

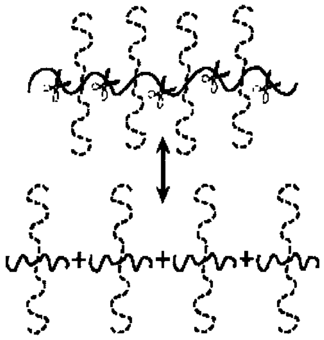

Figure 8. In the multigraft constituting block copolymer concept, the multigraft copolymer is expected to exhibit the same morphology as the simplest constituting miktoarm star copolymer.

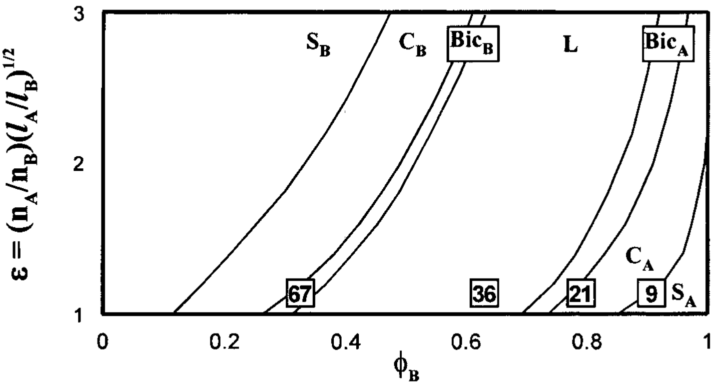

Figure 9. The Milner morphology diagram with the boxes representing four centipede samples having polystyrene volume fractions indicated in the boxes. All but the 67 sample exhibited the morphology predicted by Milner.

Interestingly, when samples made from the same backbone segment and branch but having different numbers of branch points were investigated, they were found to exhibit the same morphology (as expected from the constituting block copolymer hypothesis) but the extent of long range order decreased as the number of branch points was increased (Figure 10).[12] Although every effort was made to anneal these samples to equilibrium morphologies, these differences in long range order could to some extent reflect the increasing hindrances to reorganization imposed by the increasing number of branch points for high molecular weight, highly entangled materials.

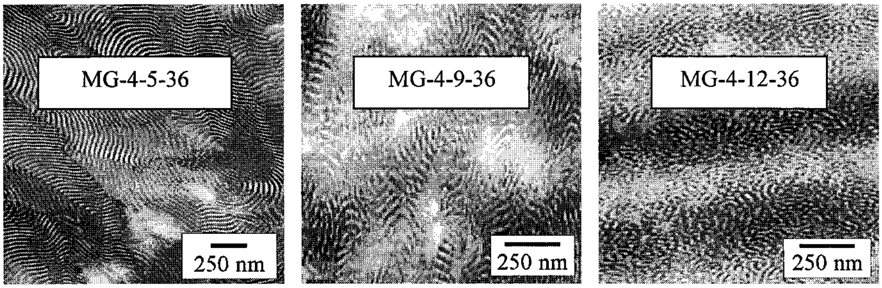

Figure 10. TEM micrographs of three centipede multigrafts having 36 vol% PS and 5, 9, and 12 branch points. Notice the decrease in the extent of long range orientational order on increasing the number of branch points.

The tensile properties of centipede copolymers with various compositions but all with approximately eight branch points are shown in Figure 11. The material having 67 vol % PS is stiff but fails at very low elongation as expected for a material having a PS matrix. The three other materials, exhibiting morphologies of lamellae, PS cylinders, and PS spheres for 37, 22, and 8 % PS, respectively, all exhibit strains at break of >1,000%. A comparison of the tensile properties of two of the centipedes having 22 vol % PS with Styroflex (BASF) and Kraton (Shell) is shown in Figure 12 demonstrating superior mechanical performance of centipedes. The Kraton material used was an SIS triblock of 105,000 in molecular weight and having 21% PS by volume. The Styroflex sample was an SBS material having a statistical SB copolymer as the center block and an overall styrene content of 58 vol % which accounts for its higher stress at break. Clearly, both the stress at break and stress at break of the centipedes increase with increasing number of branch points, and this was confirmed with other specimens.[13] Clearly, the unique architecture of the centipede allows for better stress transfer from the elastomeric backbone to the glassy phases due to the fact that the multiple PS grafts can arrange themselves within multiple PS hard domains.

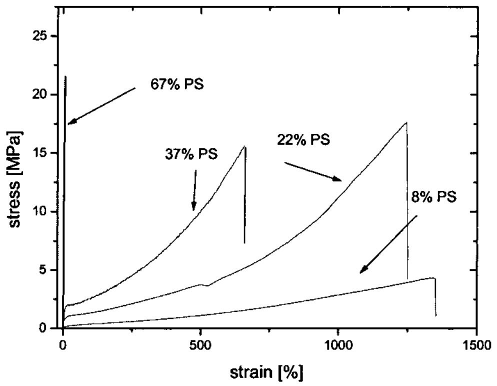

Figure 11. Tensile properties of tetrafunctional multigraft copolymers containing the various volume percents of PS indicated. Strain has been correctly measured using an on-line multisens system.

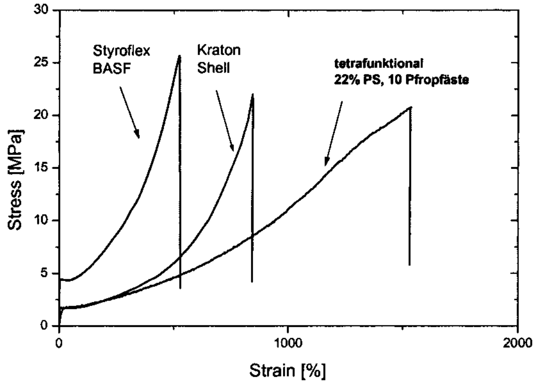

Figure 12. A comparison of the stress-strain properties of two regular centipede graft copolymers with that of two commercial linear triblock TPEs. Strain has been correctly measured using an on-line multisens system.

Finally, it is interesting to examine how an architecturally introduced change in morphology affects the tensile behavior at a constant PS content. In Figure 13, we compare the tensile behavior of centipede and barbwire specimens having essentially the same PS content (21-22 %) and about five branch points. While the elongation at break of the centipede sample, which exhibits a cylindrical morphology, is about same that of the barbwire specimen, the barbwire sample, which exhibits a lamellar morphology, shows twice the tensile strength. Babwires with five branch points are capably of having same tensile strength that of centipedes with about seven to eight branch points.

Clearly the change in morphology from cylindrical to lamellar is due entirely to the change in architecture, and thus this example shows clearly the important impact of block copolymer architecture on their mechanical behavior.

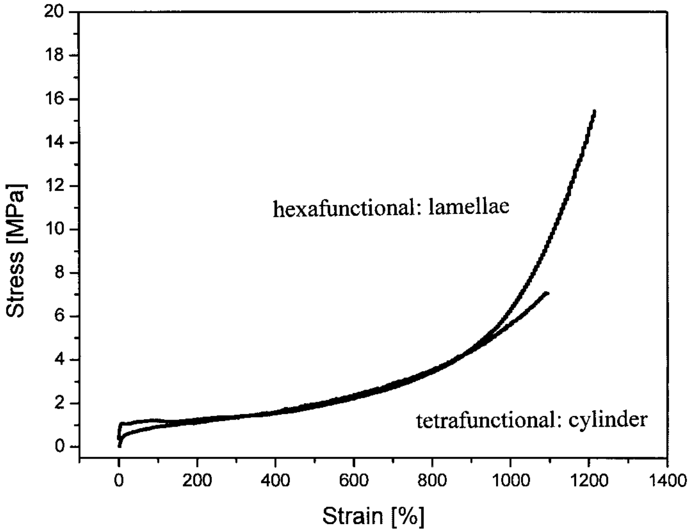

Figure 13. Stress-strain properties of centipede and barbwire specimens having about 24 vol % PS and about 5 branch points. Notice that the shift to a lamellar morphology, which accompanies the change from centipede to barbwire architecture, results in a doubling of the tensile strength of the material.

Conclusions

In summary, well-defined graft copolymers having many precisely positioned branch points of controlled functionality can be synthesized by linking anions (monofunctional branches and difunctional backbone segments) with chlorosilanes. Many branch points may be incorporated into a comb by this strategy but the synthesis of materials with many branch points becomes more difficult for combs and barbwires due to side reactions and steric hindrances to linking. The structure-morphology relationship for multigraft copolymers may be understood by applying Milner's model to the constituting miktoarm star. In multigraft copolymers the observed morphology is independent of the number of branch points but the extent of long range order decreases with increasing number of branch points. Multigraft copolymers show interesting mechanical properties. Strain at break can greatly exceed those of commercial thermoplastic elastomers. Architecturally induced changes in morphology provide a powerful means to manipulate the mechanical properties of graft copolymers.

Acknowledgements

We thank the U. S. Army Research Office for continued support of this research, most recently through DAAGD19-01-1-0544). R. W. acknowledges an Heisenberg-Fellowship from German Science Foundation (DFG). N.H and H.I. acknowledge the financial support of the Greek Ministry of Education (Program: Polymer Science and its Applications) and of the Research Committee of the University of Athens. J.W.M. and K.H. also acknowledges partial support of this research by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U. S. Department of Energy, under contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory managed and operated by UT-Battelle, LLC.

[1] J. W. Mays, S. P. Gido, in: "*McGraw-Hill Yearbook of Science and Technology 2003*", McGraw-Hill, New York 2003, p 163.
[2] B. D. Edgecombe, J. M. J. Frechet, Z. Xu, E. J. Kramer, *Macromolecules*, **1998**, *31*, 1292.
[3] M. Xenidou, N. Hadjichristidis, *Macromolecules*, **1998**, *31*, 5690.
[4] C. J. Hawker, D. Mecerreyes, E. Elce, J. Dao, J. L. Hedrick, I. Barakat, P. Dubois, R. Jerome, W. Volksen, *Macromol. Chem. Phys.*, **1997**, *198*, 155.
[5] G. Finaz, Y. Gallot, J. Parrod,, P. Rempp, *J. Polym. Sci.*,**1962**, *58*, 1363.
[6] C. Strazielle and J. Herz, *Eur. Polym. J.*, **1977** *13*, 223.
[7] J. L. Hahnfield, W. C. Pike, D. E. Kirkpatrick, T. G. Bee, *Polymer Preprints*, **1996**, *37(2)*, 733.
[8] H. Iatrou, J. W. Mays, N. Hadjichristidis, *Macromolecules*, **1998**, *31*, 6697.
[9] K. Hong, D. Uhrig, H. Iatrou, Y. Poulos, N. Hadjichristidis, J. W. Mays, *Polymer Preprints*, **1999**, *40(2)*, 104.
[10] Y. Nakamura, Y. Wan, J. W. Mays, H. Iatrou, N. Hadjichristidis, *Macromolecules*, **2000**, *33*, 8323.
[11] D. Uhrig, J. W. Mays, *Macromolecules*, **2002**, *35*, 7182.
[12] F. L. Beyer, S. P. Gido, C. Buschl, H. Iatrou, D. Uhrig, J. W. Mays, M. Y. Chang, B. A. Garetz, N. P. Balsara, N. Beck Tan, N. Hadjichristidis, *Macromolecules*, **2000**, *33*, 2039.
[13] R. Weidisch, S. P. Gido, D. Uhrig, H. Iatrou, J. Mays, and N. Hadjichristidis, *Macromolecules*, **2001**, *34*, 6333.
[14] H. Iatrou , N. Hadjichristidis, *Macromolecules*, **1992**, *25*, 4649.
[15] S. Milner, *Macromolecules*, **1994**, *27*, 2333.
[16] C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino,J. W. Mays, *Polymer*, **1998**, *39*, 4631.
[17] C. Lee, S. P. Gido, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino, J. W. Mays, *J. Chem. Phys.*, **1997**, *107*, 6460.