Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are the predominant form of styrene-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). The work described in this dissertation is aimed toward developing thermoplastic elastomers with a higher UST and lower cost.

In order to develop TPEs with a higher UST, we employed benzofulvene, an anionically polymerizable monomer, for the synthesis of new TPEs. This approach led to the development of novel TPEs with improved performance compared to traditional TPEs. The mechanical properties of these new TPEs were also studied, and the results showed significant improvements over conventional TPEs.

14. ABSTRACT
Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are the predominant form of styrene-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). The work described in this dissertation is aimed toward developing thermoplastic elastomers with a higher UST and lower cost.

15. SUBJECT TERMS
anionic polymerization, thermoplastic elastomer, phase behavior
Novel Thermoplastic Elastomers based on Benzofulvene: Synthesis and Mechanical Properties

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Additionally, we report the effects of partial and complete hydrogenation on the thermal stability, mechanical and morphological properties of high temperature thermoplastic elastomers comprised of polybenzofulvene-polyisoprene-polybenzofulvene (FIF) triblock copolymers. After hydrogenation of polyisoprene and unsaturated carbon bonds in the five member ring of PBF, ultimate tensile stress was reduced to 11.2 MPa with strain at break of 750%. The upper service temperature also decreased to 125 °C. The fully hydrogenated triblock copolymer demonstrated an ultimate stress of 14 MPa at 744 % strain. The glass transition temperature (Tg) of fully hydrogenated PBF was 130 °C. Thermal stability was greatly improved by both partial and complete hydrogenation.

Lastly, we developed a cost efficient method to prepare high molecular weight “comb-shaped” graft copolymers, poly(isoprene-g-styrene), with polyisoprene as the backbone and polystyrene as side chains. The grafted polymers were synthesized via free radical emulsion polymerization by copolymerization of isoprene with a polystyrene macromonomer synthesized using anionic polymerization. A small amount of toluene was used in order to successfully disperse the macromonomer. Both a redox and thermal initiation system were used in the emulsion polymerization. The multigraft copolymers obtained were very high in molecular weight (5-12 x105 g/mol), and up to 10 branches per chain, on average, could be incorporated. A material incorporating 29 wt% polystyrene exhibits a disordered microphase separated morphology and elastomeric properties. These materials show promise as new, highly tunable, and potentially low cost thermoplastic elastomers.
Novel Thermoplastic Elastomers based on Benzofulvene: Synthesis and Mechanical Properties

A Dissertation Presented for the Doctor of Philosophy Degree The University of Tennessee, Knoxville

Weiyu Wang
December 2015
Acknowledgements

First of all, I gratefully thank my advisor Dr. Jimmy W. Mays for his mentorship which is beyond support, encouragement and guidance throughout my doctoral study throughout pass four and half years. His spirit of collaboration, wisdom of interpersonal skills and passion of career pursuits, constructively influenced my mind-set within and outside graduate school.

I would like to thank my doctoral committee members: Dr. Michael Best for his valuable time and advising, Dr. Michael Kilbey and Dr. Alexei Sokolov for bringing me on board on fascinating fundamental research projects and expanding my knowledge about polymeric materials. I enjoyed and would like to continue our collaboration in my future career.

I sincerely thank Dr. Nam-Goo Kang, Dr. Kunlun Hong (ORNL), Dr. Sang-Woog Ryu (Chungbuk National University, Korea), Dr. Suxiang Deng (GM, China) and Dr. David Uhrig (ORNL) for coaching me with essential experiment techniques when I started in UTK.

Working in Mays’ group provided me with various opportunities to interact with world leading polymer scientists and engineers including: Dr. Mario Beiner and Dr. Ralf Schlegel from Fraunhofer institute in German (mechanical properties). Dr. Samuel Gido and Katherine Williams from the University of Massachusetts (TEM and SAXS). Dr. Frank Bates and Yiming Zeng from the University of Minnesota (Parr reactor hydrogenation). Dr. Shi-Qing Wang and Jianning Liu from the University of Akron (rheology).
Additionally, I would also like to thank Dr. Herbert Chao (Total Valley), Dr. Zhiyi Bao (Zeon Chemical), Dr. Naixiong Jin (Eastman) and Ilir Koliqi (Tosoh Bioscience LLC.) for their career advices.

I am also very fortunate to work with professors, post-docs and fellow graduate students in the University of Tennessee and Oak Ridge National Lab including: Dr. Mark Dadmum, Dr. Adam Imel, Dr. Jihua Chen (ORNL) and Halie Martin for TEM. Dr. Yangyang Wang (ORNL), Dr. Shiwang Chen, Dr. Fei Fan, Adam Holt for rheology and dielectric spectroscopy. Dr. Jesse Davis and Kamlesh R. Bornani for light scattering. Dr. Dimitry Voyloy for AFM. Dr. Carlos Steren for NMR. Dr. Chunhui Bao for ATRP and RAFT. Also current and ex-group members in Mays’ group including: Dr. Shahinur Rahman, Dr. Kostas Mischronis, Dr. Beomgoo Kang, Tom Malmgren, Dr. Xiaojun Wang, Dr. Justin Roop, Dr. Vikram Srivastava, Dr. Sachin Bobade, Andrew Goodwin, Christopher Hurley, Wei Lu, Xinyi Lu, Hongbo Feng, Benjamin Ripy, Huiqun Wang and Tyler White. It has been a great pleasure to work with all of them. The presence of all these people during my doctoral study are vital for my growth and success. I sincerely appreciate every one of them.

Finally, I would like to thank my father Jimin Wang and my mother Yun Wang for their patience, sacrifice and selfless love which makes today possible. To my grandfather who passed away shortly after I came to Knoxville in 2011, may he rest in peace.

Weiyu Wang
Abstract

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Chapter 1: Recent Advances in Thermoplastic Elastomers based on Synthetic Polymers
1.1 Introduction:

Thermoplastic elastomers (TPEs) are biphasic synthetic polymer materials consisting of a continuous soft rubbery matrix physically cross linked by glassy plastic domains.\(^1\)\(^2\) Such materials have the elasticity of conventional rubber but are suitable for high throughput plastic processing techniques such as injection molding and melt extrusion without requiring a curing process.\(^3\)\(^4\) This feature allows TPEs to be manufactured on a large scale using short production times, which makes TPEs one of the most commonly used polymeric materials in many fields.\(^5\)

Based on chemical composition and morphology, commercially available TPEs can be categorized into six different groups:\(^3\) (1) thermoplastic polyurethanes (TPUs), (2) styrenic thermoplastic elastomers (S-TPEs), (3) rubbery-polyolefin blends (TPOs), (4) thermoplastic vulcanizates (TPVs), (5) copolyesters thermoplastic elastomers (TPC-ET) and (6) thermoplastic polyamides (TPA). These have been extensively reviewed in many handbooks.\(^4\)\(^-\)\(^7\)

As a brief historical introduction of thermoplastic elastomers, polyurethanes fibers started to emerge in the plastic/rubber market in the early 1950s with the discovery and development of basic diisocyanate addition.\(^8\) In 1952, Snyder first patented multiblock linear copolyester fibers with stress and strain characteristics competitive with nature rubber. From the current point of view, these materials would be considered as multiblock TPUs.\(^9\) Many other polyurethane based thermoplastic gum elastomers were introduced by Bayer, Dupont and Goodyear in late 1950s.\(^10\)
Polyurethane based TPEs showing high abrasion resistance with excellent elasticity and tensile strength were commercialized by B.F Goodrich in 1960s.\textsuperscript{11}

A significant event in the development of TPEs was in 1965, when Milkovich and Holden from Shell Development Company synthesized and characterized ABA triblock copolymers based on polystyrene as the hard segment (A block) and polyisoprene as the rubbery matrix (B block) by living anionic polymerization.\textsuperscript{12} The termination free (living) anionic polymerization technique allowed styrenic TPEs to be prepared with predicted molecular weight, narrow molecular weight distribution and quantitative yield with negligible impurities in a short production cycle.\textsuperscript{13} The stress-strain and elongation recovery of styrenic TPEs displayed similar behavior to conventional vulcanized rubber without filler reinforcement or crosslinking.\textsuperscript{14} This new type of TPE with lower cost and well-defined structure, along with living anionic polymerization,\textsuperscript{15,16} stimulated numerous research activities in polymer thermodynamics,\textsuperscript{17} self-consistent field theory\textsuperscript{18} and polymer solution properties\textsuperscript{19} for the interest of both academic research and industrial applications.

Shell Chemical quickly realized the potential of processing styrenic TPEs (later given the trade name Kraton\textsuperscript{6}) with injection molding and melt extrusion. After almost 50 years, styrenic block copolymers (SBCs) have developed into one of the major products in the field of plastic/elastomer industry, and they are used in many fields such as paving, roofing, footwear, coatings, adhesives, sealants, medical tubing and some other advanced systems.\textsuperscript{20} The global consumption of styrenic block copolymers,
meanwhile, was predicted to increase from 1.8 million tons (5.5 billion US dollars) in 2013 to 2.5 million tons (8.4 billion US dollars) in 2020 with an annual growth rate of 4.5% (Figure 1.1).\textsuperscript{21}

\textbf{Figure 1.1}: a) Applications of SBCs. b) Global Market of SBCs. \textsuperscript{21}

Many other types of TPEs were introduced from the 1960s to 1980s. Hercules Inc. in 1966 patented the first thermoplastic polyolefin blends (TPO) based on mixtures of elastic poly(ethylene-co-propylene) (PEP) with over 50% of crystalline polypropylene (PP).\textsuperscript{22} In late 1970s, Monsanto Company started to focus on a dynamic vulcanization process to chemically crosslink blends of PEP-diene and PP, which was commercialized with trade name of Santoprene\textsuperscript{®} (TPV).\textsuperscript{23} Copolyester thermoplastic elastomers (TPC-ET) named Hytrel\textsuperscript{®}, commercialized by DuPont in 1972, combined good mechanical properties with chemical and heat resistance.\textsuperscript{5} Dow Chemical Company developed Estamid\textsuperscript{®} in 1982, a segmented polyamide based thermoplastic elastomer (TPA) with low density, superior mechanical properties at low temperature (-40°C) and service temperature above 200°C.\textsuperscript{8}
Starting from the 1990s, many companies strategized their TPE research focus on specific market applications by adding new monomers, functionalities and using sustainable resources to improve properties of existing TPEs systems. In scientific research communities, fascinating polymers with various functionalities, well-defined structures and advanced macromolecular architectures were prepared thanks to developments in living/controlled polymerization techniques such as living anionic\textsuperscript{16,24}/cationic polymerization,\textsuperscript{25} atomic transfer radical polymerization (ATRP),\textsuperscript{26} ring opening metathesis polymerization (ROMP),\textsuperscript{27} reversible addition-fragmentation chain transfer polymerization (RAFT),\textsuperscript{28} nitroxide mediated radical polymerization (NMRP)\textsuperscript{29} and so on. However, a large gap still exists between reactions on a laboratory scale and synthesis at the scale of pilot plants. Along with innovations in synthetic polymer chemistry, this chapter summarizes recent advances in thermoplastic elastomers based on synthetic polymers from the aspect of polymer architectures including: (1) ABA type triblock polymers, (2) grafted polymers and (3) star branched polymers. Service temperature, tensile properties of stress and strain at break will be summarized for different composition and architectures. The difference between TPE research in academia and industry will be addressed as the perspective.

1.2 ABA triblock copolymer type TPEs:

1.2.1 Polymers prepared by anionic polymerization:

The most common ABA triblock copolymers type TPEs are polystyrene-b-polyisoprene-b-polystyrene (SIS) and polystyrene-b-polybutadiene-b-polystyrene
(SBS) triblock copolymers. Three things need to be taken into consideration when designing the composition of SIS type triblock copolymers for TPEs applications: (1) Under the designed composition, PI needs to form a continuous rubbery matrix to provide enough elasticity. (2) Overall molecular weight needs to be high enough to drive micro-phase separation for efficient stress reinforcement. (3) Molecular weight should also not be too high considering that high viscosity may cause difficulty in processing and achieving ordered phase separation in the melt.30

In a typical SIS TPE, the molecular weight ($M_n$) of PS is generally targeted at 10 to 15 kg/mol whereas the $M_n$ of PI is targeted at 50 to 70 kg/mol.31 Due to the thermodynamic incompatibility between PS and PI, the minor component PS will micro-phase separate from PI, forming either spherical (less than 20 vol% PS) or cylindrical (20 vol% to 35 vol% of PS) glassy domains, which act as physical crosslinks and reinforce the entangled PI rubbery matrix (Figure 1.2). In a dynamic mechanical analysis of SIS with temperature ramp/frequency sweep, SIS behaves like a glassy plastic with a high storage modulus ($G'$) when the temperature is below the glass transition temperature of PI ($T_g \approx -56^\circ C$). As the temperature increases but remains lower than the $T_g$ of PS ($95^\circ C$), the polyisoprene chains start to move and $G'$ reaches the rubbery plateau value. This temperature range is considered as the service temperature range where such polymers act as elastomer with typical stress-stain behavior. When the temperature is above $95^\circ C$, the polymer enters the melt flow zone and behaves as a viscous liquid. Most TPEs are processed by melt extrusion or injection
molding with processing temperature higher than $T_g$ or melting temperature ($T_m$) where elastic and glassy domains are miscible and the system is in one phase.

As many applications benefit from low cost S-TPEs, high temperature applications and other advanced consumptions of S-TPEs, such as in tire rubber, are largely limited by the relative low glass transition temperature of PS. When the service conditions approach 95 °C, softening of PS domains dramatically reduces the tensile stress of S-TPEs. One major research interest in the field of anionic polymerization is to increase the upper service temperature of S-TPEs without changing the polymerization procedure, which has already existed in pilot plants for almost 50 years.\textsuperscript{14}

\textbf{Figure 1.2:} Schematic of SIS TPEs.

Many strategies and alternative monomers have been explored by using anionic polymerization in order to improve the upper service temperature (UST) of TPEs. The first strategy was to use \textit{styrene derivatives} with functionalities at $\alpha$- or \textit{para}- position such as poly($\alpha$-methyl styrene) ($T_g \sim 173$ °C),\textsuperscript{32} poly($\alpha$-methyl \textit{p}-methyl styrene) ($T_g$
~183 °C), poly(tert-butyl styrene) (PtBS, $T_g \sim 130$ °C) and poly(p-adamantyl styrene) (P-AdmS, $T_g \sim 203$ °C). In order to achieve quantitative yield, anionic polymerization of α-methyl styrene generally requires low polymerization temperature (-78 °C) in polar solvent (THF) due to the low monomer ceiling temperature caused by the bulky methyl group at the α position. High $T_g$ polystyrene derivatives with bulky pendant groups such as tert-butyl or adamantyl, at the para position will cause phase blending with polydienes due to the lipophilic nature of the tert-butyl or adamantyl group. In order to increase the strength of phase separation and generate effective physical crosslinking, high overall molecular weight is required for polybutadiene/poly(tert-butyl styrene) (PtBS, $T_g \sim 130$ °C) systems. Another approach to increase stress was through catalytic hydrogenation of polydienes into polyolefin, which was used in designing TPEs based on polyisoprene and poly(p-adamantyl styrene). Catalytic hydrogenation to fully saturate PS, forming poly(vinylcyclohexane) (PVCH, $T_g \sim 147$ °C), produced TPEs with higher UST and better thermal stabilities. Mechanical properties and service temperatures of all the above mentioned TPEs are summarized in Table 1.1, no 1-5.
Table 1.1: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in hydrogenation solvent

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment ((T_{g_h} , ^\circ C))</th>
<th>Soft Segment ((T_{g_s} , ^\circ C))</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
</tbody>
</table>
| 1   |  \(\begin{array}{c} \text{phenyl} \\
|     | \quad \text{(95 °C)} \\
|     | \text{(-64 °C)} \\
|     | \quad \text{benzene} \\
|     | \quad \text{(173 °C)} \\
|     | \end{array}\) | 25.5MPa                           | 1200%                | 33%   | Anionic PLZ (THF, -78 °C) | 32   |
|     |                                   |                                   | 44.6MPa              | 1100%             | 33%  |                                    |      |
| 2   |  \(\begin{array}{c} \text{phenyl} \\
|     | \quad \text{(182 °C)} \\
|     | \text{(-39 °C)} \\
|     | \quad \text{benzene} \\
|     | \quad \text{(50 °C)} \\
|     | \end{array}\) | 0.5 to 10.8 MPa                  | 525% to 1340%       | 50%  | Anionic PLZ (THF, -78 °C)        | 33   |
|     |                                   |                                   |                      |                   |      | Coupling Reaction               |      |
| 3   |  \(\begin{array}{c} \text{phenyl} \\
|     | \quad \text{(130 °C)} \\
|     | \text{(-90 °C)} \\
|     | \quad \text{benzene} \\
|     | \quad \text{(r.t.)} \\
|     | \end{array}\) | 24.6 MPa                          | 1080%               | 50%  | Anionic PLZ (benzene, r.t.)      | 34   |
| 4   |  \(\begin{array}{c} \text{phenyl} \\
|     | \quad \text{(180 °C)} \\
|     | \text{(-60 °C)} \\
|     | \end{array}\) | 22.3 MPa                          | 590%                | 45%  | Anionic PLZ (CHₓ, 40 °C)         | 35   |
|     |                                   |                                   |                      |                   |      | Catalytic Hydrogenation         |      |
| 5   |  \(\begin{array}{c} \text{cyclohexyl} \\
|     | \quad \text{(147 °C)} \\
|     | \quad \text{(-60 °C)} \\
|     | \end{array}\) | 28 MPa                            | 652%                | 39.5%| Anionic PLZ (CHₓ, 40 °C)         | 38   |
|     |                                   |                                   |                      |                   |      | Catalytic Hydrogenation         |      |
A second anionic polymerization strategy to improve UST was to use methyl methacrylate and its derivatives as the hard segment with polybutadienes (PB) or poly(n-butyl acrylate) (PnBA) as the soft segment.

Since the glass transition temperature of poly(alkyl methacrylate) depends both on tacticity and size of alkyl substituents, incorporating methacrylate derivatives with different tacticities as the hard segment in ABA type triblock copolymers could tune the service condition over a large temperature range. When using polydienes as the elastic matrix, methacrylate derivatives were initiated in THF at -78 °C through a difunctional polydiene anion, which was synthesized in a hydrocarbon solvent since anionic polymerization of butadiene or isoprene in polar solvents forms less cis-1,4 microstructure, and thus dramatically increased the T_g. Methyl methacrylate polymerized by this method contains 75 to 79 % of syndiotactic repeating units and has a glass transition temperature higher than 120 °C (Table 1.2, no. 6).

Other methacrylate derivatives, such as poly(ethyl methacrylate) (PEMA, T_g ~ 90°C), poly(tert-butyl methacrylate) (PtBMA, T_g~116 °C) and poly(isobornyl methacrylate) (PIBMA, T_g~202 °C), also could be anionic polymerized by similar methods. Resulting triblock copolymers with polybutadiene as the rubbery matrix displayed high ultimate stress at break and strain at break over 500 %. Notice that when PIBMA was used as the rigid block, triblock copolymers exhibited 600 % strain at break with ultimate tensile stress of 2.2 MPa even when the temperature was 150 °C. Tuning UST from 130 °C to 149 °C was possible by randomly copolymerizing
Table 1.2: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in polar solvent

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment ($T_g, °C$)</th>
<th>Soft Segment ($T_g, °C$)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td><img src="image1" alt="Hard Segment" /></td>
<td><img src="image2" alt="Soft Segment" /></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td></td>
<td>(120 °C)</td>
<td>(-62 °C)</td>
<td>34.0 MPa</td>
<td>890%</td>
<td>36%</td>
</tr>
<tr>
<td>7</td>
<td><img src="image3" alt="Hard Segment" /></td>
<td><img src="image4" alt="Soft Segment" /></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td></td>
<td>(90 °C)</td>
<td>(-60 °C)</td>
<td>18.7 MPa</td>
<td>1120%</td>
<td>35%</td>
</tr>
<tr>
<td></td>
<td>(116 °C)</td>
<td>(-60 °C)</td>
<td>24.4 MPa</td>
<td>1080%</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td>(132 °C)</td>
<td></td>
<td>32.0 MPa</td>
<td>835%</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td>(160 °C)</td>
<td></td>
<td>35.0 MPa</td>
<td>650%</td>
<td>42%</td>
</tr>
<tr>
<td>8</td>
<td><img src="image5" alt="Hard Segment" /></td>
<td><img src="image6" alt="Soft Segment" /></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td></td>
<td>(130 - 149 °C)</td>
<td>(-58 °C)</td>
<td>24.0 MPa</td>
<td>1000%</td>
<td>34%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27.0 MPa</td>
<td>1000%</td>
<td>31%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>30.0 MPa</td>
<td>1100%</td>
<td>24%</td>
</tr>
<tr>
<td>9</td>
<td><img src="image7" alt="Hard Segment" /></td>
<td><img src="image8" alt="Soft Segment" /></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td></td>
<td>(118 °C)</td>
<td>(-60 °C)</td>
<td>32.0 MPa</td>
<td>900%</td>
<td>13%</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>25%</td>
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<td>25%</td>
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</table>

Note: The chemical structures are not transcribed into a readable format here.
IBMA with MMA with different feed ratios.\textsuperscript{44} UST of styrenic TPEs were enhanced by incorporating MMA as the minor component (13 wt\%) in linear PMMA-PS-PB-PS-PMMA pentablock terpolymers TPEs (32 MPa ultimate stress, 900 \% strain at break)\textsuperscript{45,46} (\textbf{Table 1.2}, no. 7-9).

The above mentioned TPEs systems contained polybutadiene as the elastic block. In all acrylic TPEs where poly(alkyl acrylate) was used as the soft block, TPEs have better UV and oxidation resistance due to the lack of unsaturation.\textsuperscript{47-55} A typical all acrylic TPE, PMMA-PnBA-PMMA triblock copolymers, was prepared by transalcoholysis of PMMA-poly(tert-butyl acrylate)-PMMA precursor which was synthesized by sequential anionic polymerization of MMA, tert-butyl acrylate and MMA in THF at -78 °C.\textsuperscript{47,48} By keeping the molecular weight of PnBA at 100 kg/mol and varying the weight percentage of PMMA from 9.1 \% to 50 \%, the ultimate tensile strength was increased from 1.8 MPa to 16.1 MPa where the elongation at break decreased from 1016 \% to 228 \%.\textsuperscript{48} (\textbf{Table 1.3}, no. 10) Difunctional atom transfer radical polymerization (ATRP) initiator was employed to prepare PMMA-PnBA-PMMA triblock copolymers without transalcoholysis.\textsuperscript{49} Tong compared mechanical properties of two different PMMA-PnBA-PMMA triblock copolymers synthesized by anionic polymerization and ATRP with similar molecular weight and composition. The sample prepared by anionic polymerization showed much higher initial stress, modulus with ultimate stress of 8.6 MPa and strain at break of 700 \%. The sample prepared by
Table 1.3: Mechanical properties of ABA triblock copolymer type TPEs – all acrylic polymers

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_g, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
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<tr>
<td>10</td>
<td>(126 °C)</td>
<td>(-40 °C)</td>
<td>1.8 MPa</td>
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<td></td>
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<td>14.7 MPa</td>
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<td>16.1 MPa</td>
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<td></td>
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<td>1016%</td>
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<td>610%</td>
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<td>228%</td>
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<td>9.1%</td>
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<td>28.6%</td>
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<td>50.0%</td>
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<td></td>
<td></td>
<td></td>
<td>Anionic PLZ (THF, -78 °C)</td>
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<td></td>
<td></td>
<td></td>
<td>Transalcoholysis (PTSA, 150 °C)</td>
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<tr>
<td>11</td>
<td>(107 °C)</td>
<td>(-40 °C)</td>
<td>8.6MPa</td>
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<td></td>
<td></td>
<td></td>
<td>700%</td>
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<td>24.2%</td>
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<td></td>
<td></td>
<td></td>
<td>Anionic PLZ (THF, -78 °C)</td>
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<td></td>
<td></td>
<td></td>
<td>Transalcoholysis (PTSA, 150 °C)</td>
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<tr>
<td>12</td>
<td>(117 °C)</td>
<td>(-35 °C)</td>
<td>7.1MPa</td>
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<td>480%</td>
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<td>22.2%</td>
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<td></td>
<td></td>
<td></td>
<td>Anionic PLZ (THF, -78 °C)</td>
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<td></td>
<td></td>
<td></td>
<td>Transalcoholysis (PTSA, 150 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-21 °C)</td>
<td></td>
<td>15.2MPa</td>
<td></td>
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<td></td>
<td></td>
<td>680%</td>
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<td></td>
<td>21.1%</td>
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<tr>
<td></td>
<td>(-35 °C)</td>
<td></td>
<td>16.4MPa</td>
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<td></td>
<td>390%</td>
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<td></td>
<td>22.8%</td>
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<td>Anionic PLZ (THF, -78 °C)</td>
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<td>Transalcoholysis (PTSA, 150 °C)</td>
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<tr>
<td></td>
<td>(-50 °C)</td>
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</table>
ATRP, however, broke at 400 % of strain with ultimate stress of 4.1 MPa\(^5\) (Table 1.3, no. 11). The reason will be discussed later in section 1.2.4.

The mechanical properties of all acrylic TPEs are generally inferior to styrenic TPEs due to phase blending and high entanglement molecular weight (\(M_e\)) of poly(alkyl acrylate) (\(M_e\) for PB is 1,700 g/mol whereas \(M_e\) for PnBA is 28,000 g/mol).\(^5\) Longer alkyl substitution enhanced the strength of phase separation with PMMA but also increased the \(M_e\) and decreased strain at break. The glass transition temperature decreased as the length of alkyl substitution increased.\(^5\) By using different alcohols during transalcoholysis, all acrylic TPEs with poly(ethyl acrylate), poly(n-propyl acrylate) and poly(iso-octyl acrylate) as the elastic middle block were synthesized.\(^5\) With similar composition (22 wt% of PMMA) and overall molecular weight, all acrylic TPEs with poly(iso-octyl acrylate) as the middle block showed the highest ultimate stress (16.2 MPa) but lowest strain at break (390 %) compared to TPEs with other middle blocks.\(^5\) (Table 1.3, no. 12)

A third anionic polymerization strategy to improve UST is to use rigid conjugated diene monomers such as 1,3-cyclohexadiene (CHD) as the glassy block. One feature of anionic polymerization of conjugated dienes is that the microstructure of the resulting polymer varies with different initiation systems. 1,3-cyclohexadiene demonstrated controlled anionic polymerization behavior with three different initiation systems: n-BuLi/tetramethylethylenediamine (TMEDA), n-BuLi/1,2-dimethoxyethane (DME), or sec-BuLi/1,4-diazabicyclo[2.2.2]-octane (DABCO).\(^5\) Resulting poly(1,3-
cyclohexadiene) (PCHD) has 55%, 75% and 90% of 1,4-addition respectively. $T_g$ of these polymers decreased from 155°C to 110°C as the percentage of 1,2-microstructure was decreased. PCHD-PB-PCHD\textsuperscript{58} triblock copolymer with 30 wt% of PCHD exhibited 10.2 MPa ultimate stress with a relatively low strain at break of 290%. This might be due to side reactions during anionic polymerization of CHD. By partial hydrogenation of PB without saturated PCHD, ultimate stress increased to 14.0 MPa with better strain at break of 570%, which indicated a stronger physical crosslinking. The end block PCHD of this triblock copolymer was completely hydrogenated into polycyclohexane, a polyolefin with $T_g$ above 231°C.\textsuperscript{59} The completely hydrogenated triblock copolymers displayed 10.0 MPa tensile stress at 600% strain without breaking. (Table 1.4, no. 13)

1.2.2 Polymers prepared by cationic polymerization:

The late 1960s witnessed the rapid development of styrenic thermoplastic elastomers from research in laboratories to commercial products. S-TPEs suffered from two major disadvantages: (1) The upper service temperature limited many advanced applications of S-TPEs. (2) Polydiene middle block’s lack of tolerance to strong UV and oxidation. Hydrogenation to saturate polydienes improves the resistance of S-TPEs to UV. However, tertiary protons introduced after hydrogenation lacked stability to strong oxidation reagents.\textsuperscript{64}

A renaissance in living cationic polymerization\textsuperscript{25} advanced many research towards TPEs with better UV/oxidation stability and higher UST. Many cationically-
### Table 1.4: Mechanical properties of ABA triblock copolymer type TPEs based on hydrogenated polymers

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment ($T_g$, °C)</th>
<th>Soft Segment ($T_g$, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td>10.2 MPa</td>
<td>290%</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-60 °C)</td>
<td>14.0 MPa</td>
<td>570%</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(140 °C)</td>
<td>10.8 MPa&gt;</td>
<td>600%&gt;</td>
<td>30%</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td>14.3 MPa</td>
<td>1390%</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-56 °C)</td>
<td>11.2 MPa</td>
<td>750%</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-48 °C)</td>
<td>16.8 MPa&gt;</td>
<td>510%&gt;</td>
<td>20%</td>
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<tr>
<td></td>
<td></td>
<td>(125 °C)</td>
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</tbody>
</table>
synthesized TPEs used polyisobutylene (PIB) as the elastic middle block due to its softness and chemical resistance. Triblock copolymer PS-PIB-PS prepared by sequential living cationic polymerization through a difunctional initiator displayed an ultimate tensile stress of 26 MPa, which was competitive with commercial Kraton SIS TPEs.\textsuperscript{65,66} The molecular weight of PIB should be targeted between 40,000 to 160,000 g/mol in order to promote tensile properties. Phase separation was observed between PS and PIB when the Mn of PS was above 5000 g/mol. Other triblock copolymers with PIB as the elastic middle block and glassy end block of polystyrene derivatives, such as poly(\(\alpha\)-methyl styrene),\textsuperscript{67,68,69,70} poly(\(p\)-methyl styrene)\textsuperscript{71} and poly(tert-butyl styrene),\textsuperscript{69} were also synthesized by living cationic polymerization. PMMA-PIB-PMMA triblock copolymer was prepared by a cationic/anionic mechanism switching process.\textsuperscript{72} All these triblock copolymers demonstrated similar stress-strain behavior compared to TPEs developed by anionic polymerization with polydienes as the rubbery matrix. (Table 1.5, no. 15-18)

One feature that distinguishes cationic polymerization from anionic polymerization is the ability to control the polymerization of high T\(g\) monomers such as \(p\)-chlorostyrene (\(p\)CS),\textsuperscript{71} indene (ID)\textsuperscript{69,73} and acenaphthylene (ACP).\textsuperscript{74} Triblock copolymers using \(Pp\)CS (T\(g\), 129 °C), PID (T\(g\), 225°C) or PACP (T\(g\), 250°C) as the hard segment and PIB as the soft segment were successfully prepared by cationic polymerization and showed stress-strain behavior similar to typical TPEs. Notice that
**Table 1.5:** Mechanical properties of ABA triblock copolymer type TPEs synthesized by cationic polymerization

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment ($T_g$, °C)</th>
<th>Soft Segment ($T_g$, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>15</td>
<td>(89 °C)</td>
<td>(-61 °C)</td>
<td>26MPa</td>
<td>760%</td>
<td>25.1%</td>
</tr>
<tr>
<td>16</td>
<td>(180°C)</td>
<td>(-61 °C)</td>
<td>24.5MPa</td>
<td>370%</td>
<td>44.7%</td>
</tr>
<tr>
<td>17</td>
<td>(110 °C)</td>
<td>(-62 °C)</td>
<td>15.1MPa</td>
<td>560%</td>
<td>32%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(130 °C)</td>
<td>18.1MPa</td>
<td>400%</td>
<td>50%</td>
</tr>
<tr>
<td>18</td>
<td>(108 °C)</td>
<td>(-60 °C)</td>
<td>14.5MPa</td>
<td>650%</td>
<td>34%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anionic PLZ (CH$_x$, 40 °C)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(123 °C)</td>
<td>(-61 °C)</td>
<td>21MPa</td>
<td>460%</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10MPa</td>
<td>1200%</td>
<td>30%</td>
</tr>
<tr>
<td>20</td>
<td>(225 °C)</td>
<td>(-62 °C)</td>
<td>15.7MPa</td>
<td>600%</td>
<td>20.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.5MPa</td>
<td>400%</td>
<td>40%</td>
</tr>
<tr>
<td>21</td>
<td>(250 °C)</td>
<td>(-61 °C)</td>
<td>14.7MPa</td>
<td>793%</td>
<td>13%</td>
</tr>
</tbody>
</table>
PpCS is a polar polymer with weather and flame resistance. Indene is potentially a very cost effective monomer for high temperature applications. (Table 1.5, no. 19-21)

Alkyl vinyl ethers are another unique group of monomers polymerized by living cationic polymerization. Hydrolysis of cationically synthesized poly(tert-butyl vinyl ether) (PtBVE) produced well defined poly(vinyl alcohol) (PVA).75 As a widely used water soluble polymer in coating and textiles, semicrystalline PVA has a Tg of 80 °C and Tm of 208 °C which makes it a candidate for TPEs with oil resistance. PVA-PIB-PVA triblock copolymer could be prepared by direct hydrolysis of PtBVE-PIB-PtBVE. However, mechanical properties were not measured since the resulting polymers had very limited solubility and were largely degraded by thermal processing. Cyclohexyl vinyl ether (CHVE) could be statistically copolymerized with tert-butyl vinyl ether by living cationic polymerization initiated from difunctional polyisobutylene living cation. Hydrolysis of the resulting triblock copolymers yielded P(CHVE-stat-VA)-PIB-P(CHVE-stat-VA)76 containing statistical copolymer of PCHVE and PVA as the rigid phase. With 22 wt% of P(CHVE-stat-VA), polymers broke at 830 % strain with ultimate stress of 11.5 MPa. (Table 1.6, no. 22-23)

Similar to poly(alkyl acrylate), the Tg of poly(alkyl vinyl ether) could also be tuned with alkyl substituents of different lengths.77 With poly(n-butyl vinyl ether) (PnBVE, Tg, ~ -55 °C) as the elastic block, ABA-type triblock copolymer with (PTCVE, Tg ~ 77 °C ),77 poly(tricyclodecyl vinyl ether)78 and poly(2-adamantyl vinyl ether) (PADVE, Tg ~ 155 °C) as glassy blocks were synthesized by living cationic
### Table 1.6: Mechanical properties of ABA triblock copolymer type TPEs – all vinyl ether polymers

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_g, ^\circ C)</th>
<th>Soft Segment (T_g, ^\circ C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 22  | ![Hard Segment](image1) \((88 \, ^\circ C)\) | ![Soft Segment](image2) \((-61 \, ^\circ C)\) | 15.11 MPa  
9.16 MPa | 800%  
1300% | 31%  
22% | Cationic PLZ  
(CH\(_3\)Cl/MCH\(_x\), -80 °C) | 75 |
| 23  | ![Hard Segment](image3) \((-61 \, ^\circ C)\) | ![Soft Segment](image4) \((-61 \, ^\circ C)\) | 24.5 MPa  
11.5 MPa | 370%  
830% | 44.7%  
22% | Cationic PLZ  
(CH\(_3\)Cl/MCH\(_x\), -80 °C)  
Hydrolysis | 76 |
| 24  | ![Hard Segment](image5) \((68 \, ^\circ C)\) | ![Soft Segment](image6) \((70 \, ^\circ C)\) | 1.35 MPa  
0.74 MPa | 116%  
92% | 30.7%  
27.6% | Cationic PLZ  
(Toluene, 0 °C) | 77 |
| 25  | ![Hard Segment](image7) \((77 \, ^\circ C)\) | ![Soft Segment](image8) \((-52 \, ^\circ C)\) | 2.4 MPa | 90% | 24.4% | Cationic PLZ  
(Toluene, 0 °C) | 78 |
| 26  | ![Hard Segment](image9) \((155 \, ^\circ C)\) | ![Soft Segment](image10) \((-52 \, ^\circ C)\) | 5.55 MPa  
1.52 MPa | 245%  
355% | 30%  
17.2% | Cationic PLZ  
(Toluene, 0 °C) | 79 |
polymerization.\textsuperscript{79} Despite the similarity of monomer structures, microphase separation was observed by transmission electron microscopy (TEM). All of these vinyl ether TPEs showed relatively low strain at break (<355 %) and ultimate stress (<5.55 MPa), possibly because of high entanglement molecular weight of PnBVE. All vinyl ether triblock copolymers with poly(6-acetoxyhexyl vinyl ether) and poly (2-(2-methoxyethoxy)ethyl vinyl ether) as elastic blocks showed excellent CO\textsubscript{2} separation ability with modest mechanical properties (\textbf{Figure 1.3}).\textsuperscript{77} (\textbf{Table 1.6}, no. 24-26)

\subsection*{1.2.3 Polymers prepared by metal catalyzed ring opening polymerization:
}

Poly(lactide) (PLA, T\textsubscript{g} ~60\textdegree C) is an amorphous biodegradable polymer synthesized by metal catalyzed ring opening polymerization (ROP) from racemic D,L-lactide whereas isotactic poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline polymers (T\textsubscript{m} ~170 \textdegree C). Blends of PLLA and PDLA can form stereocomplex crystals which further improves chemical resistance with higher melting temperature (T\textsubscript{m} ~203 \textdegree C).\textsuperscript{80}

In the early research stage about incorporating PLA as the end block for ABA triblock copolymers for TPE applications, difunctional hydroxyl terminated PI,\textsuperscript{81} PIB,\textsuperscript{82} polydimethylsiloxane (PDMS)\textsuperscript{83} and poly(ethylene-co-propylene)\textsuperscript{84} were used as the initiators. These elastic middle block were prepared by either living anionic or cationic polymerization followed by termination with hydroxyl functionality. TPEs based on these systems received limited success with relative low stress and strain at break (\textbf{Table 1.7}, no. 27-30).
Figure 1.3: CO₂ separation plots for poly(6-acetoxyhexyl vinyl ether) and poly (2-(2-methoxymethoxy)ethyl vinyl ether) based triblock copolymers together with commodity polymers [polystyrene, natural rubber, and poly(vinyl chloride)] for comparison.⁷
**Table 1.7:** Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with PLA as the glassy segment.

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T,g, °C)</th>
<th>Soft Segment (T,g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods Ref.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td></td>
<td></td>
<td>3.1 MPa 200% 18 vol%</td>
<td>Anionic PLZ (Toluene, 25 °C)</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.2 MPa 650% 28 vol%</td>
<td>Metal Catalyzed ROP (Toluene, 125 °C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.1 MPa 450% 40 vol%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td>N/A N/A N/A</td>
<td>Cationic PLZ (CH3Cl/MCHx, -80 °C) ROP (THF)</td>
<td>82</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td>N/A N/A N/A</td>
<td>Metal Catalyzed ROP (Toluene, 125 °C)</td>
<td>83</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td>2.98 MPa 215% 45%</td>
<td>Anionic PLZ Catlytic Hydrogenation</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Metal Catalyzed ROP (Toluene, 125 °C)</td>
<td></td>
</tr>
</tbody>
</table>
Preparing polymers from renewable resource materials instead of from petroleum resources has been a lasting goal of chemists for many decades. Monomers including 3-hydroxybutyrate (HA), menthide (MD), 6-methyl-ε-caprolactone (MCL), ε-caprolactone (CL), β-methyl-δ-valerolactone (MCL), ε-decalactone (DL) potentially could be produced from sustainable resources. These monomers undergo metal catalyzed ring opening polymerization (ROP), yielding biodegradable elastic polymers. Since ROP generated polymers with hydroxyl functionality on both ends, the resulting polymers could be directly used as a macroinitiators for lactide, producing various types of biodegradable ABA triblock copolymer TPEs. When poly(3-hydroxybutyrate) (PHA) was used as elastic block, TPEs had strain at break lower than 200%. Using polymenthide (PM) as elastic block, the strain at break could be largely improved to 960% compared to PHA system but ultimate stress was decreased to 1.7 MPa even with 40 vol% of PLA. This low tensile stress might be due to the overall molecular weight not being high enough for strong phase separation. With 30 vol% of poly(6-methyl-ε-caprolactone) (PMCL) as the elastic block, 1880% strain at break was achieved with 10.2 MPa ultimate stress (Table 1.8, no. 31-33).

Very recently, Xiong developed an economically viable strategy to prepare β-methyl-δ-valerolactone (MCL) through an artificial biosynthetic approach (Figure 1.4). Ring opening polymerization of MCL generated elastic amorphous aliphatic polyester with T_g of -52 °C. Excellent tensile properties were obtained by utilizing PMCL as the elastic block with PLA as the hard segment. With 32 vol% of PLA, PLA-
Table 1.8: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with sustainable recourse

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_g, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>31</td>
<td>(50 ~ 80 °C)</td>
<td>(-2 °C)</td>
<td>10MPa</td>
<td>200%</td>
<td>44%</td>
</tr>
<tr>
<td>32</td>
<td>(44 °C)</td>
<td>(-26 °C)</td>
<td>1.7MPa</td>
<td>960%</td>
<td>40.7%</td>
</tr>
<tr>
<td>33</td>
<td>(45 °C)</td>
<td>(-43 °C)</td>
<td>10.2MPa</td>
<td>1880%</td>
<td>30%</td>
</tr>
<tr>
<td>34</td>
<td>(45 °C)</td>
<td>(-52 °C)</td>
<td>25MPa</td>
<td>1725%</td>
<td>32vol %</td>
</tr>
<tr>
<td>35</td>
<td>(T_m, 152 °C)</td>
<td>(-30°C)</td>
<td>17MPa</td>
<td>2800%</td>
<td>20%</td>
</tr>
<tr>
<td>36</td>
<td>(45 °C)</td>
<td>(-63 °C)</td>
<td>9.9MPa</td>
<td>2100%</td>
<td>17vol %</td>
</tr>
<tr>
<td>37</td>
<td>(170 ~190 °C)</td>
<td>(-21 °C)</td>
<td>4.1MPa</td>
<td>1600%&gt;</td>
<td>6vol%</td>
</tr>
</tbody>
</table>
Figure 1.4: (a) Total biosynthetic pathway for the production of MVL. (b) A semisynthetic route to produce MVL from mevalonate. (c) Conversion of MVL to an elastomeric triblock polymer that can be repeatedly stretched to 18 times its original length without breaking.92
PMCL-PLA triblock copolymer displayed 1725 % strain at break with ultimate stress of 25 MPa, which is competitive with commercial Kraton polymer based on petroleum resources (Table 1.8, no. 34).

As a low T_g semicrystalline polymer, poly(ε-caprolactone) (PCL, T_g ~ -60 °C, T_m ~ 60 °C) is a biodegradable material with great potential for medical applications. Copolymerizing ε-caprolactone with ε-decalactone or lactide created amorphous elastic polymers suitable for TPE applications. Statistical copolymer constructed from ε-caprolactone and D-lactide had a T_g of -30 °C. With 20 wt% of isotactic poly(L-lactide) (PLLA) as the glassy block, triblock copolymers showed exceptionally high strain at break of 2800 % and decent ultimate stress of 17 MPa. By varying volume fraction of the hard segment PLA from 17 % to 32 %, TPEs based on random copolymer of ε-caprolactone / ε-decalactone as soft segment demonstrated tunable ultimate stress from 9.9 MPa to 18 MPa with strain at break from 1200 % to 2100 % (Table 1.8, no. 35-36).

Incorporating biodegradable PLA (T_g ~ 60°C) enabled TPEs for many biomedical applications. However, high temperature applications are largely limited due to the low T_g of PLA. Poly(α-methylene-γ-butyrolactone) (PMBL) is a rigid thermoplastic with a T_g of about 195 °C. The renewable monomer MBL was derived from tulipalin A and subjected to radical polymerization. After converting di-hydroxyl terminated poly(menthide) into difunctional atomic transfer radical polymerization initiator, PMBL-PM-PMBL triblock type TPEs for high temperature
application were prepared. Ultimate tensile stress ranging from 3.9 MPa to 13 MPa and
strain at break ranging from 730 % to 1800 % were achieved based on different volume
fractions of PMBL (Table 1.8, no. 37).

1.2.4 Polymers prepared by controlled radical polymerization techniques:

Starting from the late 1990s, tremendous progress has been achieved in the field
of controlled radical polymerization such as atomic transfer radical polymerization
(ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT) and
nitrosoxide mediated radical polymerization (NMRP). These techniques open up
various opportunities to prepare functionalized polymers with predictable molecular
weight, narrow molecular weight distribution and complicated macromolecular
architectures. Controlled polymerization was achieved for many monomers such as
acrylonitrile, acrylamide and vinyl amide, which cannot be controllably
polymerized by anionic or cationic mechanisms.

Many block, star, grafted and brush polymers with different functionalities have
been prepared by ATRP. However, ABA type block copolymers synthesized by
ATRP have received limited success for TPE applications mainly due to two reasons:
(1) broad distribution of hard block reduces the strength of phase separation, (2)
unavoidable diblock copolymer mixture in triblock copolymers acted as plasticizer
diminishing the phase boundary. Significantly lower tensile stress and strain were
observed for PMMA-PnBA-PMMA triblock copolymers prepared by ATRP compared
with triblock copolymers prepared by anionic polymerization followed by
tansalcoholysis. The copolymerization of methyl methacrylate with α-methylene-γ-butyrolactone as glassy block was necessary to improve tensile properties of triblock copolymers with poly(n-butyl acrylate) as elastic block. However, the ultimate stress was still lower than 3.2 MPa with strain at break of 650% (Table 1.9, no. 38).

Poly[2,5-bis[(n-hexogycarbonyl)]styrene] (PMPCS) is a mesogen-jacked liquid crystalline polymer with a Tg of about 120 °C. As a new type of rod-coil-rod TPE based on PMPCS and PnBA, tensile tests showed 1050 % strain at break with 3.2 MPa ultimate stress. Different from PMPCS, poly2,5-bis[(n-hexogycarbonyl)]styrene (PHCS) is an amorphous polymer with a Tg of about -10 °C due to long chain alkyl substitution at the 2- and 5- positions of styrene. Poly(4-vinylpyridine) (P4VP) is a high Tg polymer that can complex with Zn2+ (Figure 1.5). Tuning stress-strain properties, glass transition temperature and morphology of TPEs based on P4VP-PHCS-P4VP was achieved by adding different amounts of Zn(ClO4)2 (Table 1.9, no. 39-40).

Figure 1.5: Illustration of a Zn2+/VHV hybrid via metal-ligand complexation.
Table 1.9: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ATRP

<table>
<thead>
<tr>
<th>No</th>
<th>Hard Segment (T_g, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>(195 °C)</td>
<td>(-50 °C)</td>
<td>0.5MPa 310% 13.8%</td>
<td>ATRP (DMF, 65°C)</td>
<td>104</td>
</tr>
<tr>
<td>39</td>
<td>(119 °C)</td>
<td>(-45 °C)</td>
<td>3.2MPa 1050% 37.58%</td>
<td>ATRP (Chlorobenzene, 65°C)</td>
<td>105</td>
</tr>
<tr>
<td>40</td>
<td>(60 °C)</td>
<td>(-10 °C)</td>
<td>6.6MPa 400% 17%</td>
<td>ATRP (Chlorobenzene, 65°C)</td>
<td>106</td>
</tr>
</tbody>
</table>
In order to minimize undesired chain transfer and termination reactions, controlled radical polymerization needs to maintain a very low radical concentration. This increases reaction time compared to conventional free radical and ionic polymerization.\textsuperscript{107} Radical segregation effect introduced by (mini)emulsion polymerization in heterogeneous system, on the other hand, reduced the reaction time and suppressed radical termination.\textsuperscript{108,109} Combining emulsion polymerization with RAFT, PS-PnBA-PS triblock copolymers with different molecular weight and composition were prepared in shorter reaction time.\textsuperscript{110} By varying weight percentage of PS from 20.2 % to 71.5 %, ultimate tensile strength was in the range from 3.0 MPa to 12.5 MPa and strain at break was in the range from 90 % to 1300 %. It was also found that by using a poly[styrene-alt-(maleic anhydride)] (PSM) as a macro-chain transfer agent in emulsion polymerization for PS-PnBA-PS\textsuperscript{111}, ultimate stress increased whereas strain at break decreased as the percentage of PSM increased. Another TPEs based on PS and poly(lauryl acrylate) were prepared by a solution of RAFT polymerization process.\textsuperscript{112} Ultimate stress was lower than 1 MPa and strain at break was lower than 280 %. An interesting ABA triblock copolymer was prepared by RAFT polymerization based on P4VP as a hard segment and random copolymer of PnBA and poly(acrylamide) (PAM) as the elastic block. The PAM moiety in the middle block crosslinked the elastic domain through hydrogen bonding association.\textsuperscript{113} (\textbf{Table 1.10}, no. 41-43).
Table 1.10: Mechanical properties of ABA triblock copolymer type TPEs synthesized by RAFT polymerization

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_g, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>41</td>
<td></td>
<td></td>
<td>3.2MPa</td>
<td>1300%</td>
<td>20.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.0MPa</td>
<td>620%</td>
<td>36.1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.3MPa</td>
<td>520%</td>
<td>46.1%</td>
</tr>
<tr>
<td>42</td>
<td></td>
<td></td>
<td>3.2MPa</td>
<td>1050%</td>
<td>37.58%</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td>6.6MPa</td>
<td>400%</td>
<td>17%</td>
</tr>
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<td></td>
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</tbody>
</table>
1.2.5 Polymers prepared by metathesis polymerization techniques:

Polyolefins represent almost two-thirds of global consumption of plastic and elastomer products. Ethylene and propylene are the two main feedstocks for polyolefins due to their low cost and availability. Linear polyethylene (PE), as well as isotactic and syndiotactic polypropylene (i-PP and s-PP) are semicrystalline polymers and could be employed as the hard segment for TPE applications. Atactic polypropylene (a-PP) and poly(ethylene-co-propylene) (PEP) are amorphous soft polymers and suitable for TPE’s elastic segment.114

In 1959, Natta already proposed a possible TPE structure based on i-PP as the hard segment and a-PP as the soft segment.115 After almost half a century, in 2006, two different groups reported two kinds of TPEs based on ethylene and/or propylene monomers synthesized by living coordination polymerization (LCP). Sita116 used a specifically designed zirconium/borate complex for programmable stereomodulated living Ziegler-Natta polymerization. Simply by adjusting the zirconium/borate ratio and disrupting propylene feeding during the polymerization, diblock, triblock and tetrablock copolymers of a-PP and i-PP were prepared with 40 wt% of i-PP.

Coates117 prepared a nickel catalyst that produced i-PP at -60°C and a-PP at 0°C. Simply by changing the reaction temperature, i-PP-b-a-PP-b-i-PP triblock and i-PP-b-a-PP-b-i-PP-b-a-PP-b-i-PP pentablock copolymers were prepared. Triblock copolymer showed 1800 % strain at break with 40 MPa ultimate stress in tensile test, whereas pentablock copolymers showed 2250 % strain at break with ultimate stress of
240 MPa. The same group used titanium catalysts to prepare s-PP-b-PEP-b-s-PP triblock copolymers. The resulting triblock copolymer exhibited 80 MPa ultimate stress with 500 % strain at break. Very recently, Sita\textsuperscript{118} reported another triblock TPEs based on poly(1,3-methylenecyclohexane) (PMCH) and a-PP. Triblock copolymers of PMCH-b-a-PP-b-PMCH were prepared by LCP with hafnium catalysts (Figure 1.6). Interestingly, the rigid block PMCH was prepared by ring closing of 1,6-heptadiene, and the resulting polymer PMCH was micro-phase separated with a-PP (Table 1.11, no. 44-46).

Figure 1.6: Triblock TPEs based on PMCH and a-PP.\textsuperscript{118}
Table 1.11: Mechanical properties of ABA triblock copolymer type TPEs synthesized by coordination polymerization

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_m, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>44</td>
<td>(T_m, 130 °C)</td>
<td>(-45 °C)</td>
<td>18.5MPa</td>
<td>1227%</td>
<td>40%</td>
</tr>
<tr>
<td>45</td>
<td>(T_m, 130 °C)</td>
<td>(-44 °C)</td>
<td>40MPa</td>
<td>1800%</td>
<td>24%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-57 °C)</td>
<td>240MPa</td>
<td>2250%</td>
<td>24%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80MPa</td>
<td>500%</td>
<td>24%</td>
</tr>
<tr>
<td>46</td>
<td>(60 °C)</td>
<td>(-10 °C)</td>
<td>8.9MPa</td>
<td>2773%</td>
<td>9vol%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.4MPa</td>
<td>2631%</td>
<td>17vol%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.3MPa</td>
<td>1390%</td>
<td>23vol%</td>
</tr>
</tbody>
</table>
1.3 Star branched polymers for TPEs:

Star branched polymers are polymers with more than two arms radiating from the same core. If these arms have different chemical composition or molecular weight, the star polymer is named miktoarm (mixed-arm) star polymer. Generally, star polymers are prepared by two methods: (1) “Arm-first” where polymer arms are synthesized first and coupled onto a core decorated with appropriate reaction sites. (2) “Core first”, where polymer arms are grown from a multi-functional initiator.119,120

When more than two PS-b-PI diblock copolymers are connected at the same core through the end of PI end blocks, with proper composition, such (PS-b-PI)_x star branched polymers displayed mechanical properties similar to SIS linear triblock TPEs. By using an arm-first divinylbenzene linking strategy, Fetters121 prepared polystyrene-polydiene star block copolymers with number of arms up to 29. They found these star polymers had superior tensile properties compared to linear triblock copolymers of similar composition. The enhancement of tensile strength saturated when the number of arms was more than six. Morphological analysis indicated for the same molecular weight, multi-arm star polymers had smaller PS domains size as compared with linear polymers122. Thus, star polymers had more condensed physical crosslinks per unit volume, which attributed to their higher tensile strength. Another reason for better tensile strength was that the core in star polymers acted as permanent crosslinks due to covalent chemical linkage. Besides better tensile stress of star polymers, the intrinsic viscosity of star polymers were lower than their linear analogues. PS/PI and PS/PB
diblock star copolymer TPEs are now commercially available under the trade name Kraton® (Table 1.12, no. 47).

Confirmed by both experiments123 and theory124, the morphological dependence of block copolymers could be decoupled from chemical composition by varying chain architecture. Progress in self-consistent field theory (SCFT)125 facilitated the ability to design TPEs based on nonlinear architectures such as miktoarm star polymers with superior mechanical properties.126 For SIS triblock copolymer, over 36 vol% of PS component leads to lamellar morphology which is unfavorable for TPE applications (Figure 1.7).127 For A(BA`)4 miktoarm star polymer with one A block and 4 BA` block emanating from the same core, Fredrickson126 predicted a stable morphology, of cylindrical A phase hexagonally dispersed in B matrix with volume fraction of A polymer up to 70%. As for experiments, miktoarm star polymer S(IS`)3 with 50 vol% of PS achieved stable cylindrical morphology.128 High volume fraction of PS enabled this new types of TPE with a higher modulus, strength toughness and recoverable elasticity. While SIS’ with 50 vol% of PS yield at low elongation indicated its thermoplastic nature (Table 1.12, no. 48). By blending with PS homopolymers, a new stiff TPE (modulus was 99.2 MPa) with aperiodic “bricks and mortar” mesophase morphology was achieved with up to 82 wt% of PS.129 Using similar miktoarm star polymer by blending with PS, Lynd created lamellar morphology with up to 97 wt% of PS.130
Table 1.12: Mechanical properties of star-branched polymer type TPEs synthesized by anionic polymerization

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T_g, °C)</th>
<th>Soft Segment (T_g, °C)</th>
<th>Mechanical Properties</th>
<th>Architecture</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td>33.8MPa</td>
<td>1110%</td>
<td>29%</td>
<td>SIS Linear</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>37.3MPa</td>
<td>1110%</td>
<td>29%</td>
<td>(SI)_1 Star</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39.2MPa</td>
<td>1030%</td>
<td>32%</td>
<td>(SI)_2 Star</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39.7MPa</td>
<td>1100%</td>
<td>33%</td>
<td>(SI)_22 Star</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
<td>12.6MPa</td>
<td>742%</td>
<td>40vol%</td>
<td>S(IS')_3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.3MPa</td>
<td>496%</td>
<td>50vol%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.96MPa</td>
<td>294%</td>
<td>70vol%</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.7: S(IS’)_3 miktoarm star copolymer type TPEs.\textsuperscript{128}

For the “core-first” strategy: developing multifunctional anionic initiators received limited success mainly because of the poor solubility of such initiators in hydrocarbon solvents.\textsuperscript{131} However multifunctional initiators for cationic polymerization are possible. (P_{pCS-PIB})\textsubscript{8} eight arms star polymers were prepared through a calix[8]arene core with eight initiation sites.\textsuperscript{132} (PMMA-PIB)\textsubscript{3} three arms star polymers were prepared by a trifunctional cationic initiator followed by ATRP of MMA.\textsuperscript{133} For the “arm-first” strategy: at the end of living cationic polymerization, vinyl functionality was introduced by reacting the living cation of PS-PIB\textsuperscript{+} and PID-PIB\textsuperscript{+} with allyltrimethylsilane. The vinyl end functionality further reacted with Si-H on cyclosiloxane by Pt catalyzed hydrosilylation and produced star polymers of (PS-PIB)\textsubscript{n} and (PID-PIB)\textsubscript{n} based on different numbers of Si-H on cyclosiloxane.\textsuperscript{134,135,136} Similar to arm first divinylbenzene linking strategy for anionic polymerization, 1,4-cyclohexane dimethanol divinyl ether was applied as the linking agent for arm first cationic polymerization to prepare star polymers with poly(2-admantyl vinyl ether) as
hard segment and poly(n-butyl vinyl ether) as elastic segment.\textsuperscript{79} (Table 1.13, no. 49-53).

By using tri-functional ATRP initiator for “core first” strategy, three arms star polymers with PMMA,\textsuperscript{137} polyacrylonitrile (PAN),\textsuperscript{138} and PS\textsuperscript{139} as glassy segment, PnBA as elastic segment were prepared for TPE properties evaluation. As an all acrylic TPE, three arm star (PMMA-PnBA)\textsubscript{3} with 36 % of PMMA showed 11 MPa ultimate stress with 545 % strain at break. (PAN-PnBA)\textsubscript{3} star polymers displayed ultimate tensile stress from 6.3 MPa to 12.7 MPa as the strain at break in the range from 382 % to 700 %. Phase separation between PAN and PnBA was retained when the temperature was below 250 °C. As temperature was further raised up to 280 °C, the PAN domain started to crosslink chemically, and the storage modulus of these materials dropped when temperature was close to 300 °C. With multifunctional ATRP initiator of 10 and 20 initiation sites, 10 arms and 20 arms PMBL/PnBA star polymers were prepared for high temperature TPE applications.\textsuperscript{140} The highest ultimate tensile stress achieved was 7.8 MPa. Strain at break was lower than 140 % (Table 1.14, no. 54-57).

1.4 Grafted polymers for TPEs:

As an important class of commercial polymeric materials, graft copolymers are composed of a polymer backbone with polymer side chains attached to it. Grafted polymers can be prepared by three strategies: (1) “Grafting onto”, where both polymer backbone and side chain are pre-synthesized and then through the end functionalities on side chain and in-chain functionality on backbone, side chains are grafted onto the
<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment ($T_g$, °C)</th>
<th>Soft Segment ($T_g$, °C)</th>
<th>Mechanical Properties</th>
<th>Architecture</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>(95 °C)</td>
<td>(-64 °C)</td>
<td>18.1 MPa 540% 23%</td>
<td>(PS-PIB)$_5$ Star</td>
<td>Cationic PLZ</td>
<td>134,135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.2 MPa 550% 23%</td>
<td>(PS-PIB)$_6$ Star</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21.1 MPa 560% 23%</td>
<td>(PS-PIB)$_{21}$ Star</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>(194 °C)</td>
<td>(-62 °C)</td>
<td>12.7 MPa 545% 23%</td>
<td>(PID-PIB)$_5$ Star</td>
<td>Cationic PLZ</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.8 MPa 550% 23%</td>
<td>(PID-PIB)$_{21}$ Star</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>(127 °C)</td>
<td>(-62 °C)</td>
<td>22-27 MPa 400-650% 23-31%</td>
<td>(PpCS-PIB)$_8$ Star</td>
<td>Cationic PLZ</td>
<td>132</td>
</tr>
<tr>
<td>52</td>
<td>(113 °C)</td>
<td>(-62 °C)</td>
<td>22.5 MPa 125% 31.7%</td>
<td>(PMMA-PIB)$_3$ Star</td>
<td>Cationic PLZ ATRP</td>
<td>133</td>
</tr>
<tr>
<td>53</td>
<td>(165 °C)</td>
<td>(-47 °C)</td>
<td>6.9 MPa 330% 21.1%</td>
<td>(PADVE-PnBVE)$_6$ Star</td>
<td>Cationic PLZ</td>
<td>79</td>
</tr>
</tbody>
</table>
Table 1.14: Mechanical properties of star-branched polymer type TPEs synthesized by ATRP

<table>
<thead>
<tr>
<th>No.</th>
<th>Hard Segment (T&lt;sub&gt;g&lt;/sub&gt;, °C)</th>
<th>Soft Segment (T&lt;sub&gt;g&lt;/sub&gt;, °C)</th>
<th>Mechanical Properties</th>
<th>Architecture</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>11MPa 545% 36%</td>
<td>(PMMA-PnBA)&lt;sub&gt;3&lt;/sub&gt; Star</td>
<td>ATRP</td>
<td>137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>6.8MPa 700% 11%</td>
<td>(PAN-PnBA)&lt;sub&gt;3&lt;/sub&gt; Star</td>
<td>ATRP</td>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>2.35MPa 700% 20.5%</td>
<td>(PS-PnBA)&lt;sub&gt;3&lt;/sub&gt; Star</td>
<td>ATRP</td>
<td>139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>7.8MPa 140% 24.2%</td>
<td>(PMBL-PnBA)&lt;sub&gt;10&lt;/sub&gt; Star</td>
<td>ATRP</td>
<td>140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
polymer backbones. (2) “Grafting from”, where multifunctional polymer backbones serve as the macroinitiator and initiated the polymerization of side chain monomers to graft from the backbone. (3) “Grafted through” or “macromonomer” approaches”, where polymer side chains having a polymerizable end group are synthesized, and those macromonomers are subsequently polymerized to form the backbone creating graft polymer.141,142,143,144

By using anionic polymerization followed by polycondensation, Mays and co-workers prepared a series of grafted polymers with regular spaced trifunctional, tetrafunctional and hexafunctonal junction points where PI was the backbone and PS was the side chain.145,146 Structure-property relationship of these grafted polymers were elucidated by characterizing morphology147,148 and mechanical properties149,150,151 of grafted polymers with different compositions (14 to 23 vol% of PS) and architectures (trifunctional, tetrafunctional and hexafunctonal junction points). From their research, multigraft polymers with tetrafunctional junction points showed 1550 % strain at break which is 500% higher than that for the commercial product Kraton 1102. This superelasticity is a consequence of having the PI backbone anchored by multiple PS physical crosslinks (Figure 1.8). Both tetra- and hexafunctonal multigraft polymers displayed higher elasticity than commercial TPE’s like Kraton or Styroflex. Polymers with more functionalities at one junction point had higher tensile stress and modulus (Table 1.15, no. 58).
Table 1.15: Mechanical properties of grafted polymer type TPEs synthesized by anionic polymerization

<table>
<thead>
<tr>
<th>No.</th>
<th>Side Chain $(T_{g_s}, °C)$</th>
<th>Backbone $(T_{g_b}, °C)$</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>58</td>
<td></td>
<td></td>
<td>6.39MPa</td>
<td>1386%</td>
<td>17vol %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.15MPa</td>
<td>1550%</td>
<td>14vol %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.63MPa</td>
<td>1373%</td>
<td>21vol %</td>
</tr>
<tr>
<td>59</td>
<td></td>
<td></td>
<td>0.05MPa</td>
<td>&gt;500%</td>
<td>26%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.55MPa</td>
<td>450%</td>
<td>22%</td>
</tr>
</tbody>
</table>

*MG-n-m-x, n is the number of functionality of then junction point, m is the weight percentage of hard segment, x is the average number of junction points.
Inspired by this work, the same group prepared graft all acrylic TPEs based on PMMA side chain and PnBA backbone. The PMMA macromonomers were synthesized by living anionic polymerization and copolymerized with nBA by RAFT polymerization. Similar to other linear and star all acrylic TPEs, low modulus and stress was found in PnBA-g-PMMA graft polymers due to high $M_e$ of PnBA and phase blending between PMMA and PnBA. Zhang and Mays further extended the versatilities of graft polymer architecture by a cost efficient process combining (mini)emulsion polymerization with anionic polymerization or ATRP to prepare trifunctional and tetrafunctional grafted copolymers with PS or PMMA as side chain, PI or PnBA as the backbone. However, mechanical properties of these materials from tensile test were not presented (Table 1.15, no. 59).

Polyhedral oligomeric silsesquioxanes (POSS) are silicon containing organic-inorganic materials. Hybrid materials with silicone combines thermal/oxidative resistance from inorganic materials and processability of organic materials. Copolymerizing ethylene and propylene with ethyl-POSS-norbornene by coordination
polymerization produced random terpolymers of ethylene-propylene-silsesquioxane.\textsuperscript{159} High stress (>10 MPa) was observed for these silica containing TPEs. Similar research conducted by Bazan\textsuperscript{160}, which copolymerized ethylene with 5-norbornene-2-bromo-2-methylpropanoate (NBMP) which yielded a PE backbone with randomly distributed 2-bromo-2-methylpropanoate as ATRP initiator. Further grafting n-Butyl acrylate by ATRP produced PE-g-PnBA TPEs with 15 MPa ultimate stress and 490 % strain at break. The same group further prepared PE-b-(PE-co-PNBMP)-b-PE, a triblock copolymer with PE at both end and macroinitiator in the middle block.\textsuperscript{161} Graft polymers showed ultimate tensile stress of 27 MPa with 1310 % strain at break (Table \textbf{1.16}, no. 60-62).

Traditionally there are two types of macromolecular architectures that form a continuous rubbery matrix and suitable for TPEs: (1) linear and star polymers with glassy end (out) block and elastic middle (inner) block (architecture I); (2) graft polymers with elastic backbone and rigid side chain (architecture II). Tang and Wang\textsuperscript{162} proposed a reversed graft architecture with elastic side chain grafted on rigid backbone (architecture III, Figure \textbf{1.9}). Notice that in architecture III, the backbone does not necessarily need to be a glassy polymers. Rigid polymers and inorganic materials such as cellulose,\textsuperscript{162,163,164,165} carbon nanotubes\textsuperscript{166,167} and even iron magnetic particles\textsuperscript{168} could be used as backbone.

In order to validate the effectiveness of architecture III, ATRP-initiator-functionalized rigid cellulose was prepared with different number of initiation sites.\textsuperscript{162}
Table 1.16: Mechanical properties of grafted polymer type TPEs synthesized by ring opening metathesis polymerization

<table>
<thead>
<tr>
<th>No</th>
<th>Side Chain</th>
<th>Backbone</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt / %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.2MPa</td>
<td>723%</td>
<td>21%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.4MPa</td>
<td>448%</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.3MPa</td>
<td>450%</td>
<td>36%</td>
</tr>
<tr>
<td>61</td>
<td></td>
<td></td>
<td>15MPa</td>
<td>490%</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3MPa</td>
<td>780%</td>
<td>28%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9MPa</td>
<td>1170%</td>
<td>29%</td>
</tr>
<tr>
<td>62</td>
<td></td>
<td></td>
<td>20MPa</td>
<td>2000%</td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
MMA and nBA was randomly copolymerized on the cellulose backbone in DMF at 70 °C. Compared with linear, star and grafted all acrylic TPEs, architecture III type all acrylic TPEs displayed higher ultimate stress (11.1 MPa) with modest strain at break (550 %). Another reason for high stress was attributed to the hydrogen bonding between the carbonyl group on acrylic side chains and hydroxyl groups on cellulose. Microphase separation was observed between all acrylic side chain and cellulose backbone. Sustainable TPEs with monomers derived from rosin and fatty acids were prepared by the same strategy.164

Grafting polyisoprene onto the backbone of cellulose was achieved by Wang,163 and the resulting materials could mimic mechanical properties of human skin (Figure 1.10).165 Different from cellulose-g-(PnBA-co-PMMA), for which only one Tg corresponding to (PnBA-co-PMMA) was reported, two distinguishable Tg/s were observed through dynamic mechanical analysis in cellulose-g-Pl. (Table 1.17, no. 63-
Figure 1.10: Design concept and synthesis of nanostructured elastomers mimicking the mechanical properties of human skin. (a) ATRP macroinitiator, (b) Cross-linked brush polymers were synthesized and self-assembled into two-phase morphology. (c) Two phase morphology of CBPs can be reconfigured into that close to the skin microstructure model.163
<table>
<thead>
<tr>
<th>No</th>
<th>Side Chain</th>
<th>Backbone</th>
<th>Mechanical Properties</th>
<th>Synthetic Methods</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress / MPa</td>
<td>Strain / %</td>
<td>wt %</td>
</tr>
<tr>
<td>63</td>
<td></td>
<td></td>
<td>2.3MPa</td>
<td>1000%</td>
<td>39.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.6MPa</td>
<td>660%</td>
<td>47.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.1MPa</td>
<td>550%</td>
<td>54.8%</td>
</tr>
<tr>
<td>64</td>
<td></td>
<td></td>
<td>0.25MPa</td>
<td>1000%</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.0MPa</td>
<td>500%</td>
<td>30%</td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td>9.7MPa</td>
<td>160%</td>
<td>4.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>32MPa</td>
<td>60%</td>
<td>20.6%</td>
</tr>
<tr>
<td>66</td>
<td>Carbon Nanotube</td>
<td></td>
<td>2.4MPa</td>
<td>951%</td>
<td>0%</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>7.8MPa</td>
<td>520%</td>
<td>1.7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.9MPa</td>
<td>293%</td>
<td>3.8%</td>
</tr>
<tr>
<td>67</td>
<td>Fe3O4 Nano particle</td>
<td></td>
<td>3.5MPa</td>
<td>921%</td>
<td>1.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.0MPa</td>
<td>641%</td>
<td>2.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.6MPa</td>
<td>458%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>
By replacing cellulose with functionalized carbon nanotubes (CNT) and Fe3O4 nanoparticles (NPs), TPEs with type III architecture were successfully prepared. When carbon nanotubes were used as the rigid segment, 1.7 % of CNT loading increased the ultimate tensile stress from 2.4 MPa to 7.8 MPa. Strain at break was reduced from 951 % to 520 %. TPEs with Fe3O4 showed recyclability under magnetic field. (Table 1.17, no. 66-67)

1.5 Perspective:

The past 60 years has witnessed rapid development of thermoplastic elastomers from discoveries in the laboratory to widely applied commodities involved in everyone’s daily life. Starting from the 21 century, progress made in different polymerization techniques has advanced new types of TPEs with various chemical compositions and macromolecular architectures. However, each polymerization technique has both merits and weakness.

Kraton styrenic thermoplastic elastomers are the most commercially successful polymeric materials synthesized by living anionic polymerization. The disadvantage of S-TPEs is obvious: low service temperature and poor UV/oxidation resistance. All acrylic TPEs show better chemical resistance, however, the mechanical properties of these materials are much lower than those of S-TPEs.

Cationic polymerization was used to prepare PIB based TPEs showing higher service temperature with better chemical resistance. The problem for cationic polymerization is the low polymerization temperature, which is not favorable for
industrial applications. Low polymerization temperature also limited large scale production of (methyl) acrylate based TPEs by anionic polymerization.

Metal catalyzed ring opening polymerization produced biodegradable polymers from sustainable resources. However, most metal catalyzed ROP need toxic tin as the catalyst. Atomic transfer radical polymerization needs to reduce the radical concentration in order to control the polymerization. Polymers prepared by ATRP generally contain residual metal catalyst. Terminating the reaction at low conversion is necessary for block polymers preparation by ATRP.

Well defined PI-g-(PS)_n (n=1,2,3) showed great mechanical properties competitive with Kraton products. However, these anionically prepared polymers required laborious synthetic procedures. As one of the most favorable polymerization techniques in industry, emulsion polymerization offers many benefits: polymers with high weight average molecular could be prepared quickly in water as the reaction medium. Particles of polymers could be directly applied for coating and painting without purification. Recent research using macromonomer approaches to synthesize PI-g-PS by a combination of anionic polymerization and emulsion polymerization opens up opportunities to prepare thermoplastic elastomers by a cost efficient strategy. However, the PS macromonomer was prepared by anionic polymerization. Living anionic polymerization required oxygen and moisture free environment in order to retain the reactivity of chain end anion. Thrilling opportunities are waiting if PS
macromonomer could be prepared by all emulsion process with more than one branch points in the same macromonomer.

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Chapter 2: Scope of the Dissertation
2.1 Research Motivation:

After Milkovich and Holden first patented SIS triblock copolymer type TPEs in 1965, for almost 50 years, one of the major research goals in the field of anionic polymerization for industrial application has been to produce high temperature thermoplastic elastomers that meet the following requirements:

1). The polymer needs to be synthesized in hydrocarbon solvent at mild temperature, since most of the anionic polymerization capability in industry is designed for synthesis of PS-PI-PS triblock copolymer type thermoplastic elastomers under inert atmosphere in cyclohexane at around 60 °C. TPEs based on methyl methacrylate derivatives showed higher upper service temperature; however, polymerization in THF at -78 °C would not be a favorable choice for large-scale production. Another reason to avoid using THF as the solvent is that polymerizing isoprene or butadiene in THF increases the presence of the 1,2-microstructure, which compromises the elasticity.

2). For high temperature applications, the upper service temperature of the thermoplastic elastomers needs to be higher than 100 °C. One potential application of high temperature TPEs is to replace or reduce the amount of carbon black in tire compounding as a rigid filler. Since polymer weigh less than carbon black, reducing the amount of carbon black in tire would produce tires with lower weight, thus better fuel economy. However, this application received limited success with SIS TPEs due to the low glass transition temperature of PS.
3). Building blocks in the triblock copolymers need to microphase separate in order to form an efficient physical crosslink structure that enhances the tensile properties. Thus, exploring new building blocks with above mentioned requirements to prepare thermoplastic elastomers with high upper service temperature is of great interest in the anionic polymerization community.

Benzofulvene is a rigid conjugated diene monomer recently discovered to undergo living anionic polymerization in both the hydrocarbon solvent benzene at room temperature and the polar solvent THF at -78°C and produce polymers with T_g above 145°C.4,5 (Figure 2.1) This high temperature polymer with living anionic polymerization ability in hydrocarbon solvent at room temperature triggered our attention to incorporate PBF as a rigid block for TPE applications, since most of the reactors for anionic polymerization in pilot plants are designed for mild temperature polymerization in hydrocarbon solvents. Thus, the first motivation in this dissertation is to evaluate the possibility of preparing ABA triblock copolymers with polybenzofulvene as the glassy end blocks and polyisoprene as the elastic middle block for high temperature thermoplastic elastomer applications.

Well-defined multi-grafted copolymers PI-g-(PS)_n (n=1,2,3) with polystyrene as the glassy side chain and polyisoprene as the elastic backbone, indeed, showed great mechanical properties competitive with or greater than Kraton products. Considering the fact that preparing these materials required complicated titration anionic polymerization techniques and time consuming solvent/non-solvent fractionation,6,7 the
second motivation is to *develop a cost effective strategy to prepare graft copolymers for thermoplastic elastic application.*

**Figure 2.1:** Anionic polymerization of benzofulvene

2.2 Outline:

As *Chapter 1* summarized recent advances in the field of thermoplastic elastomers by using synthetic polymers, *Chapter 2* is the introduces of the scope of the dissertation, and the rest of this thesis is arranged as follows:

*Chapter 3* gives the overview of most experimental techniques with high vacuum lines used in this dissertation.

*Chapter 4* describes the work of developing high temperature thermoplastic elastomers based on polybenzofulvene as the hard segment.

*Chapter 5* describes further investigations into the effects of partial and complete hydrogenation on the properties of polybenzofulvene based TPEs.

*Chapter 6* describes an economically viable method to prepare thermoplastic elastomers combining anionic polymerization and emulsion polymerization.

*Chapter 7* concludes this thesis and provides future perspectives.
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