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Chapter 5

# Thermoplastic Elastomers Based on Block, Graft, and Star Copolymers

Weiyu Wang, Wei Lu, Nam-Goo Kang,
Jimmy Mays and Kunlun Hong

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**Abstract**

In this book chapter, we focus on recent advances in thermoplastic elastomers based on synthetic polymers from the aspects of polymer architectures such as linear block, graft, and star copolymers. The first section is an introduction that covers a brief history and classification of thermoplastic elastomers (TPEs). The second section summarizes ABA triblock copolymers synthesized by various methods for TPE applications. The third section reviews TPEs based on graft copolymers, and the fourth section reviews TPEs based on star copolymers. The differences between TPE research in academia and industry are addressed in the last section as a perspective, with a view toward the generation of new, advanced, commercially viable TPEs.

**Keywords:** thermoplastic elastomers, living/controlled polymerization, polymer architecture, functional polymers, mechanical properties

## 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] (**Figure 1**). Such materials have the elasticity of a 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 time, which makes TPEs one of the most commonly used polymeric materials in many fields [5].

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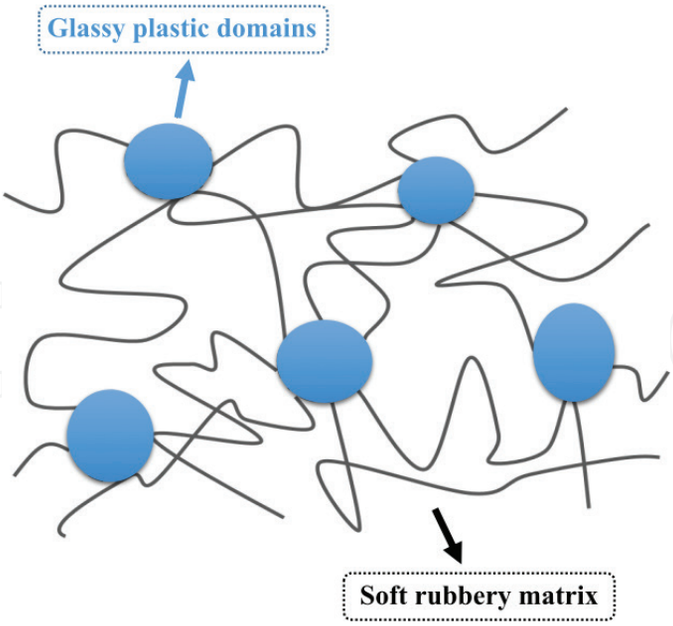



**Figure 1.** Structure illustration of thermoplastic elastomers.

Commercially available TPEs, based on chemical composition and morphology, can be categorized into eight different groups: (1) styrenic block copolymers (SBCs), (2) polymer blends by dynamic vulcanization (TPVs), (3) polyolefin-based thermoplastic elastomers (TPOs), (4) halogen-containing polyolefins, (5) thermoplastic polyurethane elastomers (TPUs), (6) polyamide-based thermoplastic elastomers (COPA), (7) polyether ester elastomers (COPE), and (8) ionomeric thermoplastic elastomers. These have been extensively reviewed in many handbooks [5–8].

Starting from the 1990s, many 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 [9–11]/cationic polymerization [12], atomic transfer radical polymerization (ATRP) [13], ring-opening metathesis polymerization (ROMP) [14], reversible addition-fragmentation chain-transfer polymerization (RAFT) [15], nitroxide-mediated radical polymerization (NMRP) [16], and so on. Many of these new polymers have great potential to be used as thermoplastic elastomers.

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) graft polymers, and (3) star-branched polymers.

## 2. ABA triblock copolymer-type TPEs

### 2.1. Polymers synthesized by anionic polymerization

The most common ABA triblock copolymer-type TPEs are polystyrene-b-polyisoprene-b-polystyrene (SIS) and polystyrene-b-polybutadiene-b-polystyrene (SBS) triblock copolymers,

designed and synthesized by Milkovich and Holden from Shell Development Company in 1965 [17]. With proper composition, PI forms a continuous rubber matrix, which is physically cross-linked by rigid component PS due to the thermodynamic incompatibility between these two components. 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 ($T_g$ ~ −56°C). As the temperature increases but remains lower than the $T_g$ of PS (95°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°C, the polymer enters the melt-flow zone and behaves as a viscous liquid.

As many applications benefit from low-cost SBCs or styrenic-based TPEs (S-TPEs), high-temperature applications and other advanced consumptions of S-TPEs, such as in tire rubber, are largely limited by the relatively 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 [18, 19]. These efforts mainly explored anionic polymerization of polymers with higher glass transition temperatures. Such polymers include the following:

### *2.1.1. Styrene derivatives*

Styrene derivative polymers include polystyrene with functionalities at $\alpha$- or para-position: poly($\alpha$-methyl styrene) (PMS, $T_g$ ~173°C) [20], poly($\alpha$-methyl p-methyl styrene) (PMMS, $T_g$ ~183°C) [21], poly(tert-butyl styrene) (PtBS, $T_g$ ~130°C) [22], and poly(p-adamantyl styrene) (P-AdmS, $T_g$ ~203°C) [23, 24].

For the anionic polymerization of $\alpha$-methyl styrene and its derivative $\alpha$-methyl p-methyl styrene, the bulky methyl group at the $\alpha$-position results in a low monomer ceiling temperature. In order to achieve quantitative yield, polymerization of these monomers requires low polymerization temperature (−78°C) in polar solvent (THF), which is not desirable in large-scale industry application [19]. High $T_g$ polystyrene derivatives with bulky pendent 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 cross-linking, high overall molecular weight is required for polybutadiene/poly(tert-butyl styrene) (PtBS, $T_g$ ~130°C) systems [22].

### *2.1.2. Methacrylate derivatives*

Polymers of methacrylate derivatives include syndiotactic poly(methyl methacrylate) (sPMMA, $T_g$ ~120°C), poly(ethyl methacrylate) (PEMA, $T_g$ ~90°C), poly(tert-butyl methacrylate) (PtBMA, $T_g$ ~116°C), poly(isobornyl methacrylate) (PIBMA, $T_g$ ~202°C) [25], and poly(1-adamantyl acrylate) (P-AdmA, $T_g$ ~133°C) [26].

Since the glass transition temperature of poly(alkyl methacrylate) depends both on tacticity and on the size of alkyl substituents [25–28], 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 [28]. 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 increases the $T_g$.

In a typical synthesis of all acrylic TPEs such as PMMA-poly(n-butyl acrylate)-PMMA triblock copolymers, PMMA-poly(tert-butyl acrylate)-PMMA precursor was first synthesized by sequential anionic polymerization of MMA, tert-butyl acrylate, and MMA in THF at −78°C. By transalcoholysis with n-butanol of the precursor, PMMA-poly(n-butyl acrylate)-PMMA triblock copolymer was prepared with PMMA as the rigid domain and poly(n-butyl acrylate) (PnBA) as the rubbery matrix [29, 30].

The polymerization of the abovementioned monomers requires low polymerization temperature in a polar solvent. However, anionic polymerization on an industry scale is generally carried out in hydrocarbon solvent at mild temperature [18]. Thus, a high $T_g$ polymer system that can be synthesized in hydrocarbon solvent at mild temperature is ideal for large-scale application. To follow this endeavor, the anionic polymerization of a third group of monomers was explored:

### *2.1.3. Rigid-conjugated diene monomers*

Polymer prepared by rigid-conjugated diene monomers includes poly(1,3-cyclohexadiene) (PCHD) and polybenzofulvene (PBF) (**Table 1**). 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-butyllithium/tetramethyl-ethylenediamine (TMEDA), n-butyllithium/1,2-dimethoxyethane (DME), or sec-butyllithium/1,4-diazabicyclo[2.2.2]-octane (DABCO) [31–33]. Resulting poly(1,3-cyclohexadiene) (PCHD) has 55, 75, and 90% of 1,4-addition, respectively. $T_g$s of these polymers decreased from 155 to 110°C as the percentage of

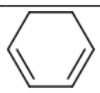
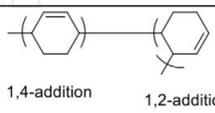
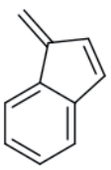
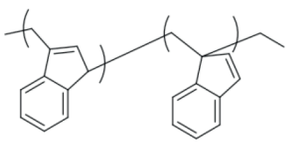
| Name | Monomer structure | Polymer structure |
|---|---|---|
| 1,3-Cyclohexadiene |  |   |
| benzofulvene |  |   |

**Table** 1. Monomer and polymer structure of 1,3-cyclohexadiene (CHD) and benzofulvene (BF).

1,2-microstructure decreased. PCHD-PB-PCHD triblock copolymer with 30 wt% of PCHD exhibited 10.2 MPa ultimate stress with a relatively low strain at break of 290% [34]. 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%, indicating a stronger physical cross-linking. The end block PCHD of this triblock copolymer can completely hydrogenated into polycyclohexylene, a polyolefin with $T_g$ above 231°C [35]. The completely hydrogenated triblock copolymers displayed 10.0-MPa tensile stress at 600% strain without breaking.

Benzofulvene (BF), the polymer from which was first synthesized by Ishizone, is another interesting conjugated diene monomer that undergoes living anionic polymerization in both THF and benzene [36–39]. The resulting PBF has a $T_g$ of 160°C when polymerizing in THF, and 145°C in benzene. The relatively high $T_g$ and the ability to synthesize PBF-PI diblock copolymer in hydrocarbon solvent at room temperature make benzofulvene an ideal candidate to prepare high-temperature thermoplastic elastomer.

By using a difunctional lithium anionic initiator, we synthesized a serious of PBF-PI-PBF triblock copolymer (FIF) via sequential living anionic polymerization with 14, 22, and 31 vol% of PBF [39]. In dynamic mechanical analysis (**Figure 2a**), all samples showed two $T_g$s, respectively, at −56°C for PI, and 145°C for PBF. For FIF with 14 vol% of PBF, the polymer displayed 1390% strain at break with 14.3 MPa ultimate stress (**Figure 2b**). These mechanical properties are competitive with Kraton D1112P [40], a widely used commercial SIS triblock copolymer-type thermoplastic elastomer.

Another interesting feature of BF is that by using different additive or solvent during the polymerization, the microstructure of the resulting polymer can be tuned from 24% (benzene as the solvent), 41% (THF as the solvent), to 98% (1,2-dimethoxyethane as the additive and benzene as the solvent). The $T_g$ of PBF with these three polymers is increased linearly from 152, 162, to 199°C as the percentage of 1,2-addition increases. Such properties open new opportunities to prepare TPEs with tunable upper service temperature. The chemical structures and $T_g$s of the abovementioned rigid and soft components have been summarized in **Table 2**.

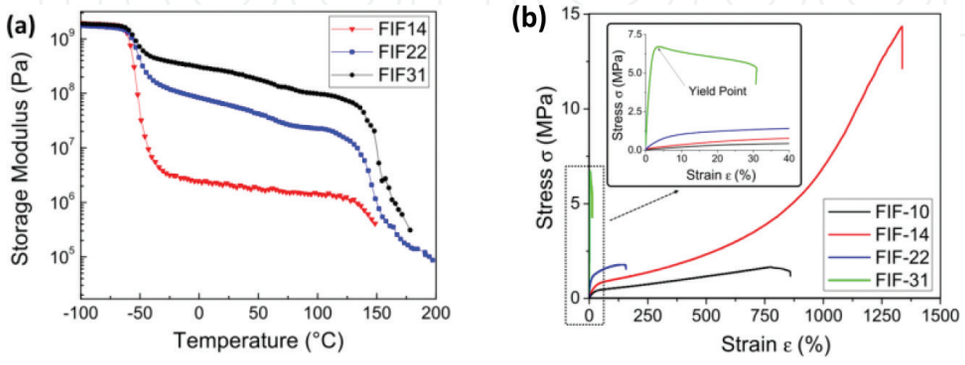
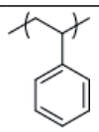
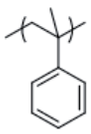
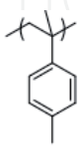
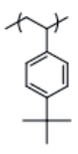
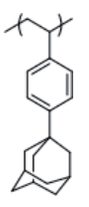
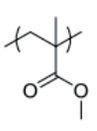
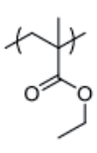
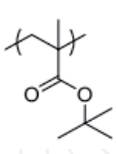
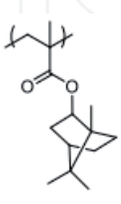
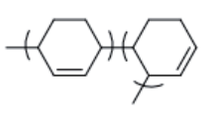
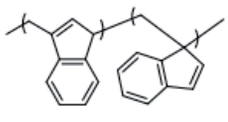



**Figure 2.** (a) Dynamic mechanical analysis of FIF, (b) tensile test of FIF. (Reprinted with permission from Ref. [40]. Copyright 2016 American Chemical Society).

| | Name | Structure | $T_g$ |
|---|---|---|---|
| Styrene derivatives | Polystyrene (PS) |  | 95°C |
| | Poly(α-methyl styrene) (PMS) |  | 173°C |
| | Poly(α-methyl p-methyl styrene) (PMMS) |  | 183°C |
| | Poly(tert-butyl styrene) (PtBS) |  | 130°C |
| | Poly(p-adamantyl styrene) (P-AdmS) |  | 203°C |
| Methacrylate derivatives | Poly(methyl methacrylate) (sPMMA) |  | 120°C |
| | Poly(ethyl methacrylate) (PEMA) |  | 90°C |
| | Poly(tert-butyl methacrylate) (PtBMA) |  | 116°C |
| | Poly(isobornyl methacrylate) (PIBMA) |  | 202°C |
| Rigid conjugated polydienes | Poly(1,3-cyclohexadiene) (PCHD) |  | 140–150°C |
| | Polybenzofulvene (PBF) |  | 140–195°C |

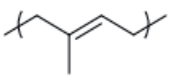
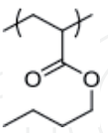
| | Name | Structure | $T_g$ |
|---|---|---|---|
| Soft segments | Polyisoprene (PI) |  | −56°C |
| | Polybutadiene (PB) |  | −90°C |
| | Poly(n-butyl acrylate) (PnBA) |  | −40°C |

**Table** 2. Hard and soft segments of ABA-type TPEs synthesized by anionic polymerization.

### 2.2. Block copolymers synthesized by cationic polymerization

Since PI or PB was mainly used as the elastic domains for TPEs synthesized by living anionic polymerization, poor resistance to UV/oxidation can become another issue for PI or PB containing TPEs. A renaissance in living cationic polymerization [12] advanced many research toward TPEs with better UV/oxidation stability and higher UST by employing isobutylene as the elastic block. Many cationically 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 [41, 42].

Another feature that distinguishes cationic polymerization from anionic polymerization is the ability to control the polymerization of high $T_g$ monomers such as p-chlorostyrene (pCS) [43], indene (ID) [44], and acenaphthylene (ACP) [44, 45]. Triblock copolymers using PpCS ($T_g$ ~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 PpCS is a polar polymer with weather and flame resistance. Indene is potentially a very cost-effective monomer for high-temperature applications.

### 2.3. Block copolymers synthesized by ring-opening transesterification polymerization

Poly(lactide) (PLA, $T_g$ ~60°C) is an amorphous biodegradable polymer synthesized by ring-opening transesterification polymerization (ROTEP) from racemic D,L-lactide, whereas isotactic poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline polymers ($T_m$ ~170°C). Blends of PLLA and PDLA can form stereocomplex crystals, which further improve chemical resistance with higher melting temperature ($T_m$ ~203°C) [46]. 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), and ε-decalactone (DL) potentially could be produced from sustainable resources [47]. These monomers undergo ring-opening transesterification polymerization (ROTEP), yielding biodegradable elastic polymers [48, 49].

Since ROTEP generated polymers with hydroxyl functionality on both ends, the resulting polymers could be directly used as a macroinitiators to polymerize 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% [50]. Using polymenthide (PM) as elastic block, the strain at break was largely improved to 960% compared to PHA system. With diethylene glycol as a difunctional initiator and $ZnEt_2$ as the catalyst, α, ω-functionalized polymenthide (HO-PM-OH) was prepared via ring-opening transesterification polymerization (ROTEP). This difunctional PM was used as the initiator for ROTEP of (±)-lactide to yield PLA-PM-PLA triblock copolymers used as TPEs (**Figure 3**). Sample PLLA-PM-PLLA (13-33-13) displayed a strain at break of 765% with ultimate tensile strength of 19.5 MPa [51, 52]. 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 [53].

### 2.4. Block copolymers prepared by controlled radical polymerization

Starting from the late 1990s, tremendous progress has been achieved in the field of controlled radical polymerization such as atomic transfer radical polymerization (ATRP) [13, 54], reversible addition-fragmentation chain-transfer polymerization (RAFT) [15, 55], and nitroxide-mediated radical polymerization (NMRP) [16]. These techniques open up various opportunities to prepare functionalized polymers with predictable molecular weight, narrow molecular-weight distribution, and complicated macromolecular architectures [56]. Controlled polymerization was achieved for many monomers such as acrylonitrile [57], acrylamide [58], and vinyl amide [59], 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 [60]. However, ABA-type block copolymers synthesized by ATRP have received limited success for TPE applications mainly due to two reasons: (1) relatively broad distribution of the hard block reduces the strength of phase separation and (2) unavoidable diblock copolymer mixture in triblock copolymers acts as plasticizer diminishing the phase boundary [25, 30]. 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 transalcoholysis [30]. The copolymerization

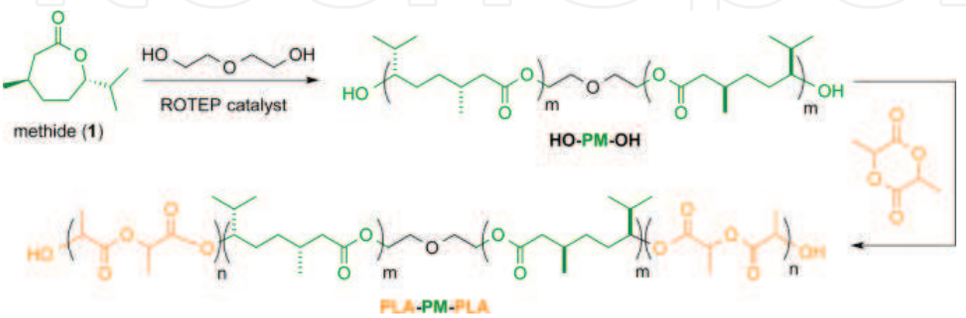



**Figure 3.** ROTEP to synthesize PLA-PM-PLA. (Reprinted with permission from Ref. [49]. Copyright 2014 American Chemical Society).

of methyl methacrylate with $\alpha$-methylene-$\gamma$-butyrolactone as glassy block was necessary to improve the tensile properties of triblock copolymers with poly(n-butyl acrylate) as elastic block [58]. However, the ultimate stress was still lower than 3.2 MPa with strain at break of 650%.

Poly[2, 5-bis[(n-hexogycarbonyl)]styrene] (PMPCS) is a mesogen-jacketed liquid crystalline polymer with a $T_g$ 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 [61]. Poly2,5-bis[(n-hexogycarbonyl)]styrene (PHCS) is an amorphous polymer with a $T_g$ of about −10°C due to long-chain alkyl substitution at the 2- and 5- positions of styrene (**Figure 4**). Poly(4-vinylpyridine) (P4VP) is a high $T_g$ polymer that can complex with $Zn^{2+}$. Tuning stress-strain properties, glass transition temperature and morphology of TPEs based on P4VP-PHCS-P4VP was achieved by adding different amounts of $Zn(ClO_4)_2$ [62].

In order to minimize undesired chain transfer and termination reactions, controlled radical polymerization needs to maintain a very low radical concentration. This increases the reaction time compared to conventional free radical and ionic polymerization [63]. Radical segregation effect introduced by (mini)emulsion polymerization in heterogeneous system, on the other hand, reduced the reaction time and suppressed radical termination [64, 65]. Combining emulsion polymerization with RAFT, PS-PnBA-PS triblock copolymers with different molecular weight and composition were prepared in shorter reaction time [66]. By varying weight percentage of PS from 20.2 to 71.5%, the ultimate tensile strength was in the range from 3.0 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 [67], ultimate stress increased whereas strain at break decreased as the percentage of PSM increased. Another TPE based on PS and poly(lauryl acrylate) was prepared by a solution RAFT polymerization process [68]. 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 cross-linked the elastic domain through hydrogen-bonding association [69].

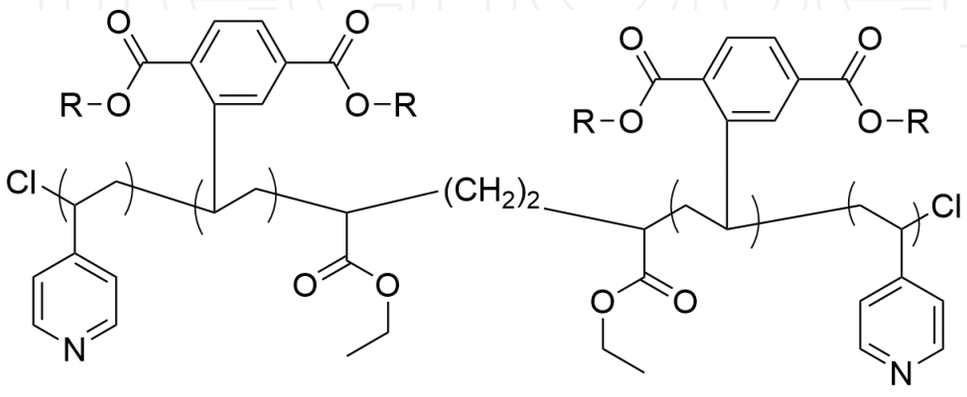



**Figure 4.** Chemical structure of P4VP-PHCS-P4VP.

## 3. Graft copolymer-type TPEs

As an important class of commercial polymeric materials, graft copolymers are composed of a polymer backbone with polymer side chains attached to it. Graft polymers can be prepared by three strategies: (1) "Grafting onto," where both polymer backbone and side chain are presynthesized and then through the end functionalities on side chain and in-chain functionality on backbone, side chains are grafted onto the 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 [70–73].

By using anionic polymerization followed by polycondensation, Mays and coworkers prepared a series of graft copolymers with regular spaced trifunctional, tetrafunctional, and hexafunctional junction points where PI was the backbone and PS was the side chain [74, 75]. Structure-property relationship of these graft copolymers was elucidated by characterizing morphology [76, 77] and mechanical properties [78–80] of grafted polymers with different compositions (14–23 vol% of PS) and architectures (trifunctional, tetrafunctional, and hexafunctional 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 cross-links (**Figure 5**). Both tetra- and hexafunctional multigraft polymers displayed higher elasticity than commercial TPEs like Kraton or Styroflex. Polymers with more functionalities at one junction point had higher tensile stress and modulus.

Inspired by this work, the same group prepared graft all-acrylic TPEs based on PMMA side chain and PnBA backbone [81]. 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 were found in PnBA-g-PMMA graft polymers due to high entanglement molecular weight of PnBA and phase blending

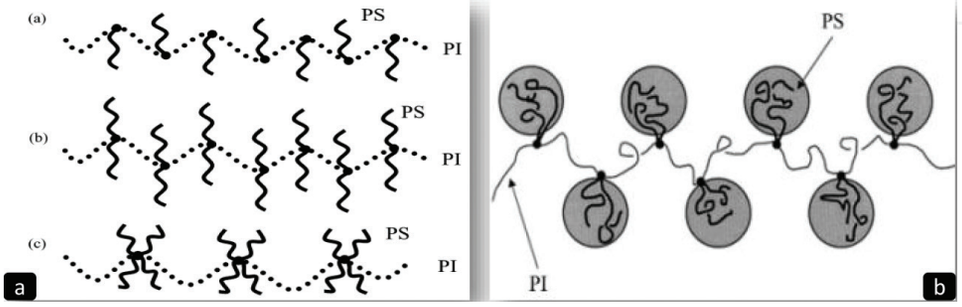



**Figure 5.** (a) Multigrafted copolymers based on PI backbone and PS branches. (Reprinted with permission from Ref. [75]. Copyright 2002 American Chemical Society.) (b) Chain conformation of multigrafted copolymers in microphase-separated state. (Reprinted with permission from Ref. [78]. Copyright 2001 American Chemical Society).

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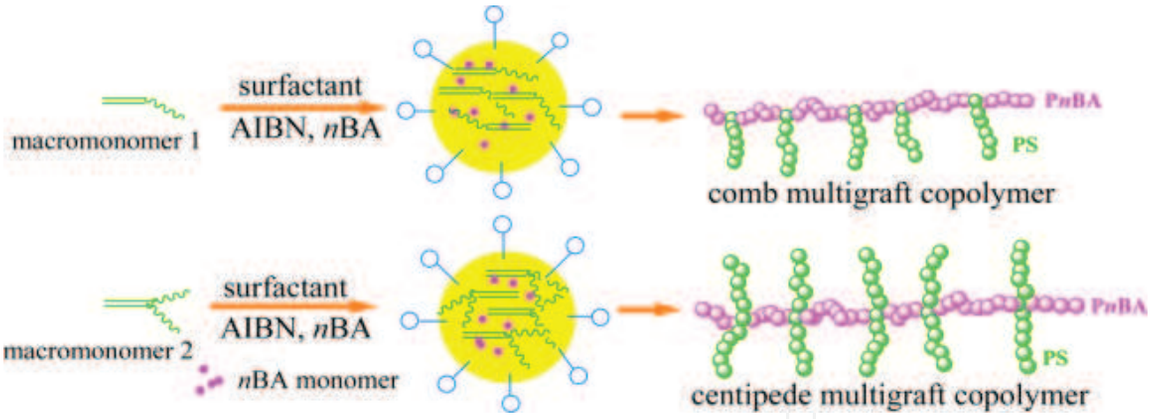



**Figure 6.** Scheme for emulsion polymerization route to superelastomers. (Reprinted with permission from Ref. [82]. Copyright 2014 American Chemical Society).

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, and PI or PnBA as the backbone [82–85]. In a typical procedure (**Figure 6**), a hydroxyl end-functionalized PS (PS-OH) was first prepared by living anionic polymerization. Through esterification reaction, the end group of PS-OH was converted into a polymerizable styrene group as the PS macromonomer for emulsion polymerization.

## 4. Star-branched copolymer-type TPEs

Star-branched polymers are polymers with more than two arms radiating from the same core. If these arms have different chemical compositions or molecular weights, 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 multifunctional initiator [86, 87].

When more than two PS-b-PI diblock copolymers are connected at the same core through the end of PI end blocks, such $(PS\text{-}b\text{-}PI)_x$ star-branched polymers displayed mechanical properties similar to SIS linear triblock TPEs. By using an arm-first divinylbenzene-linking strategy, Bi and Fetters [88] prepared polystyrene-polydiene star block copolymers with number of arms up to 29. They found that these star copolymers had superior tensile properties compared to linear triblock copolymers of similar composition. The enhancement of tensile strength saturated when the number of arms larger than six. Morphological analysis indicated multi-arm star polymers had smaller PS domain size as compared with linear polymers with the same molecular weight [89]. Thus, star polymers had more condensed physical cross-links per unit volume, which were attributed to their higher tensile strength. Another reason for better tensile strength was that the core in star polymers acted as permanent cross-links due to covalent

chemical linkage. Besides better tensile stress of star polymers, the intrinsic viscosity of star polymers was lower than their linear analogs.

Confirmed by both experiments [90] and theory [91], the morphological dependence of block copolymers could be decoupled from chemical composition by varying chain architecture. Progress in self-consistent field theory (SCFT) [92] facilitated the ability to design TPEs based on nonlinear architectures such as miktoarm star polymer with superior mechanical properties [93]. For SIS triblock copolymer, over 36 vol% of PS component leads to lamellar morphology which is unfavorable for TPE applications [94]. For $A(BA')_4$ miktoarm star polymer with one A block and four BA' blocks emanating from the same core, Fredrickson [93, 94] predicted a stable morphology, of cylindrical A phase hexagonally dispersed in B matrix with a volume fraction of A polymer up to 70%. As shown in **Figure 7a**, asymmetric miktoarm star polymer $S(IS')_3$ contains one long PS chain and three PS'-PI chains connecting at the same core. For $S(IS')_3$ with 50 vol% of PS, a stable cylindrical morphology was observed (**Figure 7b**) where lamellar morphology was typically observed for an SIS triblock copolymer with the same composition [94]. The high volume fraction of PS enabled these 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 (**Figure 7c**). 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 [95]. Using similar miktoarm star polymer by blending with PS, a lamellar morphology with up to 97 wt% of PS was observed by Shi [96].

For the "core-first" strategy: developing multifunctional anionic initiators received limited success mainly because of the poor solubility of such initiators in hydrocarbon solvents [97]. However, multifunctional initiators for cationic polymerization are possible. $(PpCS\text{-}PIB)_8$ Eight arms star polymers were prepared through a calixarene core with eight initiation sites [98]. $(PMMA\text{-}PIB)_3$ Three arms star polymers were prepared by a trifunctional cationic initiator followed by ATRP of MMA [99]. For the "arm-first" strategy: at the end of living cationic polymerization, vinyl functionality was introduced by reacting the living cation of with allyltrimethylsilane. The vinyl end functionality further reacted with Si-H on cyclosiloxane by

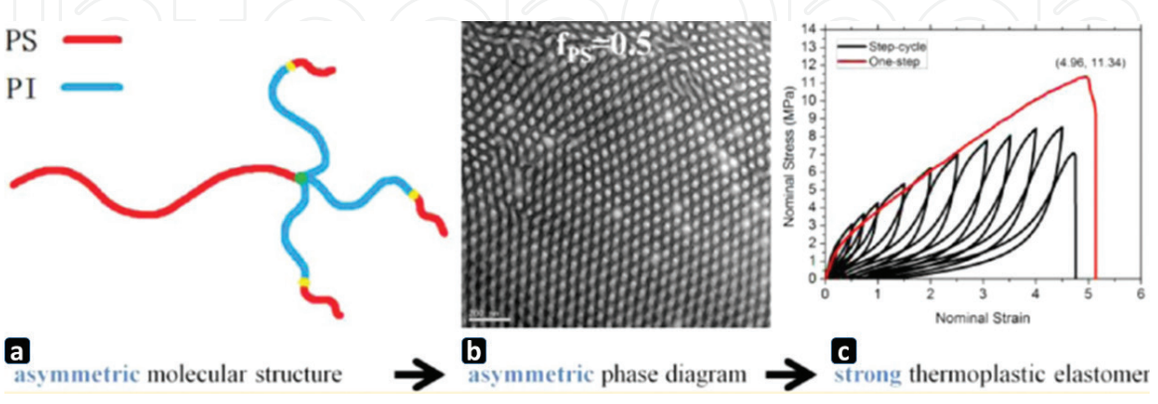



**Figure 7.** (a) Structure of $S(IS')_3$ miktoarm star copolymer-type TPEs. (b) TEM of $S(IS')_3$ miktoarm star copolymer with 50 vol% PS. (c) Stress-strain curve of $S(IS')_3$. (Reprinted with permission from Ref. [94]. Copyright 2014 American Chemical Society).

Pt-catalyzed hydrosilylation and produced star polymers with different number of arms based on different numbers of Si-H on cyclosiloxane [100–102]. 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 [103].

By using trifunctional ATRP initiator for "core-first" strategy, three arms star polymers with PMMA [104], polyacrylonitrile (PAN) [105], and PS [106] as glassy segment, PnBA as elastic segment were prepared for TPE properties evaluation. As an all-acrylic TPE, three arms star $(PMMA\text{-}PnBA)_3$ with 36% of PMMA showed 11-MPa ultimate stress with 545% strain at break. $(PAN\text{-}PnBA)_3$ Star polymers displayed ultimate tensile stress from 6.3 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 belows 250°C . As the temperature further raised up to 280°C, the PAN domain started to cross-link chemically, and the storage modulus of these materials dropped when the 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 [107]. The highest ultimate tensile stress achieved was 7.8 MPa. Strain at break was lower than 140%.

## 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 twenty-first century, progress made in different polymerization techniques has advanced to new types of TPEs with various chemical compositions and macromolecular architectures. However, each polymerization technique has both merits and weaknesses.

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 limits large-scale production of (methyl) acrylate-based TPEs by anionic polymerization.

Ring-opening transesterification polymerization produced biodegradable polymers from sustainable resources. However, most metal-catalyzed ROTEPs 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-$(PS)_n$ ($n$ = 1–3) 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 with highly tunable mechanical properties 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 point in the same macromonomer.

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## Author details

Weiyu Wang[1]*, Wei Lu[2], Nam-Goo Kang[2], Jimmy Mays[2,3] and Kunlun Hong[1]

*Address all correspondence to: wangw1@ornl.gov

1 Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

2 Department of Chemistry, University of Tennessee, Knoxville, Tennessee, USA

3 Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

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