

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Thermoplastic Elastomers Based on Block, Graft, and Star Copolymers

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

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.68586>

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].

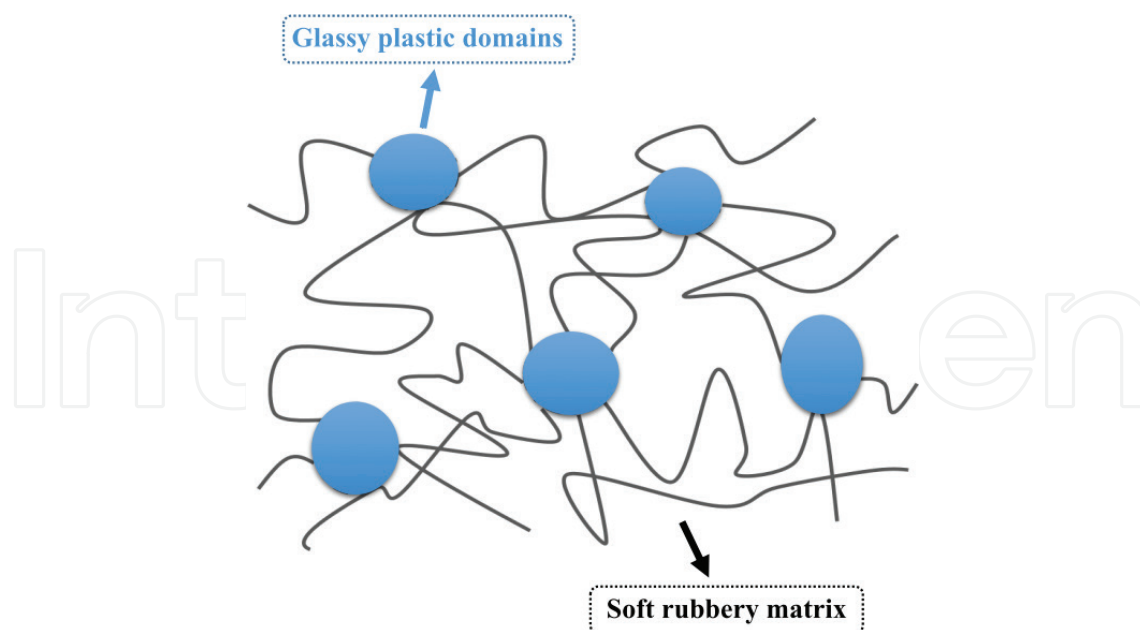


Figure 1. Structure illustration of thermoplastic elastomers.

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 ($T_g \sim -56^\circ\text{C}$). 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-strain 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 α - or para-position: poly(α -methyl styrene) (PMS, $T_g \sim 173^\circ\text{C}$) [20], poly(α -methyl p-methyl styrene) (PMMS, $T_g \sim 183^\circ\text{C}$) [21], poly(tert-butyl styrene) (PtBS, $T_g \sim 130^\circ\text{C}$) [22], and poly(p-adamantyl styrene) (P-AdmS, $T_g \sim 203^\circ\text{C}$) [23, 24].

For the anionic polymerization of α -methyl styrene and its derivative α -methyl p-methyl styrene, the bulky methyl group at the α -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 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 cross-linking, high overall molecular weight is required for polybutadiene/poly(tert-butyl styrene) (PtBS, $T_g \sim 130^\circ\text{C}$) systems [22].

2.1.2. Methacrylate derivatives

Polymers of methacrylate derivatives include syndiotactic poly(methyl methacrylate) (sPMMA, $T_g \sim 120^\circ\text{C}$), poly(ethyl methacrylate) (PEMA, $T_g \sim 90^\circ\text{C}$), poly(tert-butyl methacrylate) (PtBMA, $T_g \sim 116^\circ\text{C}$), poly(isobornyl methacrylate) (PIBMA, $T_g \sim 202^\circ\text{C}$) [25], and poly(1-adamantyl acrylate) (P-AdmA, $T_g \sim 133^\circ\text{C}$) [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

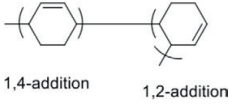
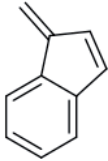
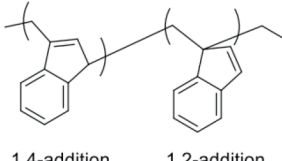
Name	Monomer structure	Polymer structure
1,3-Cyclohexadiene		 1,4-addition 1,2-addition
benzofulvene		 1,4-addition 1,2-addition

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 series 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**.

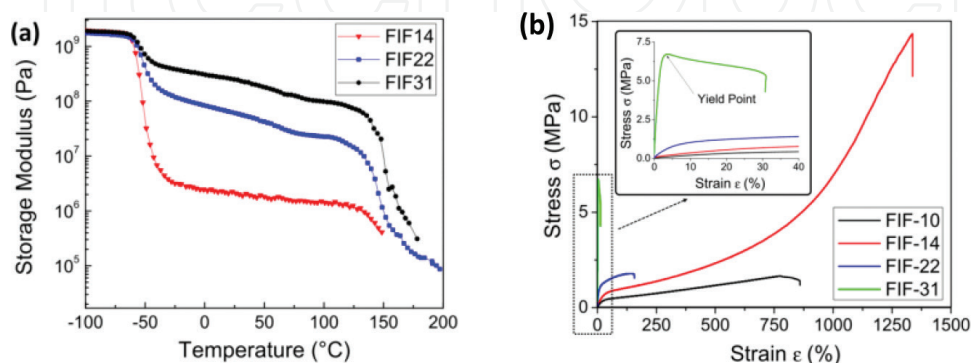
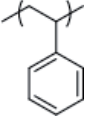
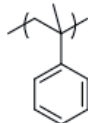
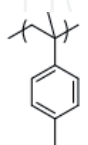
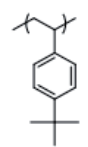
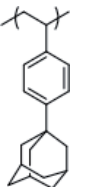
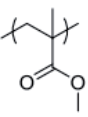
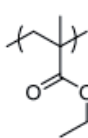
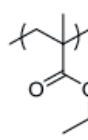
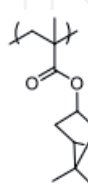
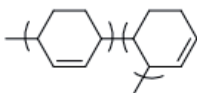
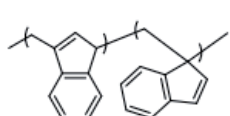


Figure 2. (a) Dynamic mechanical analysis of FIF, (b) tensile test of FIF. (Reprinted with permission from Ref. [40]. Copyright 2016 American Chemical Society).

	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

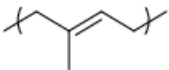
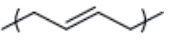
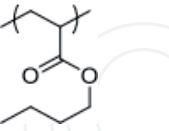
	Name	Structure	T_g
Soft segments	Polyisoprene (PI)		-56°C
	Polybutadiene (PB)		-90°C
	Poly(n-butyl acrylate) (PnBA)		-40°C

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 ($T_g \sim 129^\circ\text{C}$), PID ($T_g \sim 225^\circ\text{C}$), or PACP ($T_g \sim 250^\circ\text{C}$) 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, $T_g \sim 60^\circ\text{C}$) 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 ($T_m \sim 170^\circ\text{C}$). Blends of PLLA and PDLA can form stereocomplex crystals, which further improve chemical resistance with higher melting temperature ($T_m \sim 203^\circ\text{C}$) [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 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 polymenthene (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 polymenthene (HO-PM-OH) was prepared via ring-opening transesterification polymerization (ROTEP). This difunctional PM was used as the initiator for ROTEP of ($\pm$)-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 transesterification [30]. The copolymerization

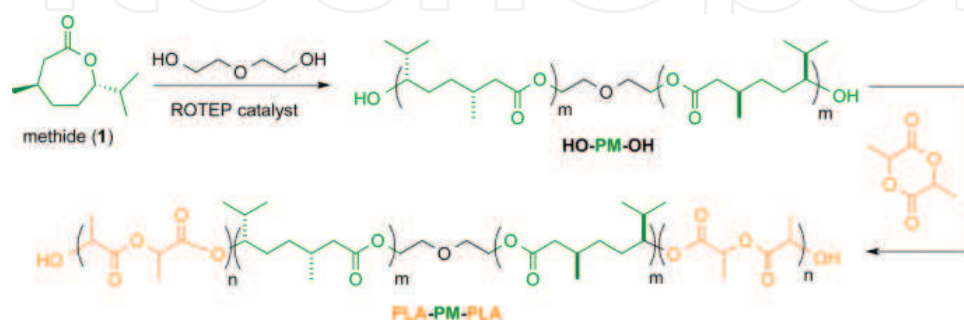


Figure 3. ROTEP to synthesize PLA-PM-PLA. (Reprinted with permission from Ref. [49]. Copyright 2014 American Chemical Society).

of methyl methacrylate with α -methylene- γ -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].

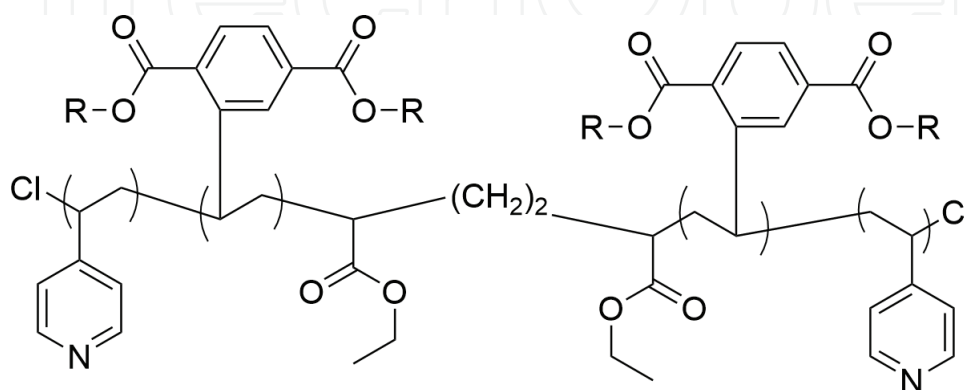


Figure 4. Chemical structure of P4VP-PHCS-P4VP.

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 pre-synthesized 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 “macro-monomer 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

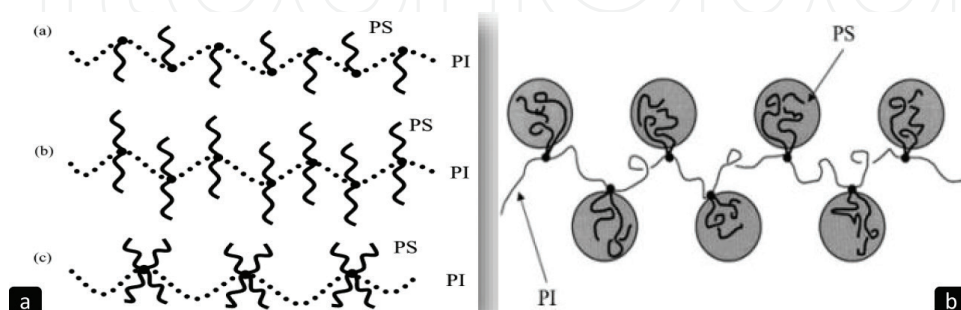


Figure 5. (a) Multigrafted copolymers based on PI backbone and PS branches. (Reprinted with permission from Ref. [75]. Copyright 2002 American Chemical Society.) (b) Chain conformation of multigrafted copolymers in microphase-separated state. (Reprinted with permission from Ref. [78]. Copyright 2001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

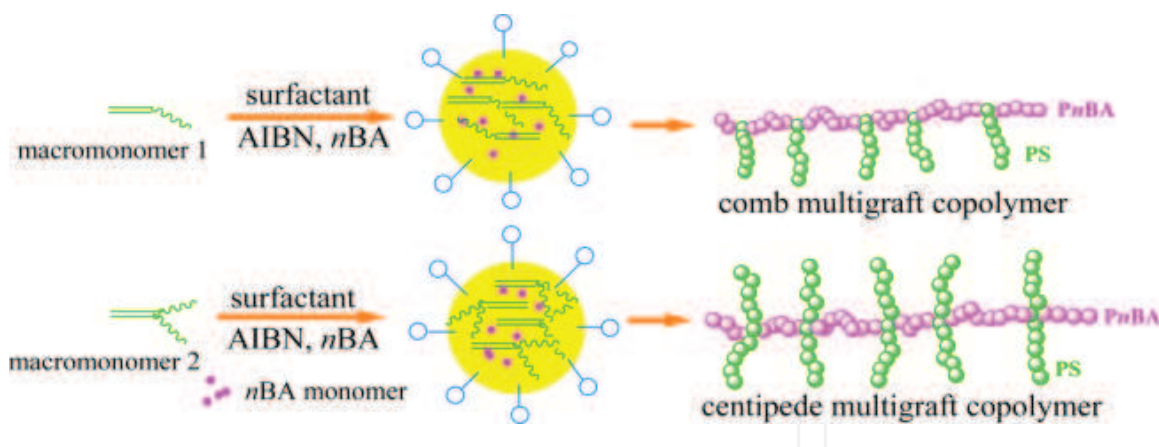


Figure 6. Scheme for emulsion polymerization route to superelastomers. (Reprinted with permission from Ref. [82]. Copyright 2014 American Chemical Society).

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-*b*-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. $(PpCS-PIB)_8$ Eight arms star polymers were prepared through a calixarene core with eight initiation sites [98]. $(PMMA-PIB)_3$ 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

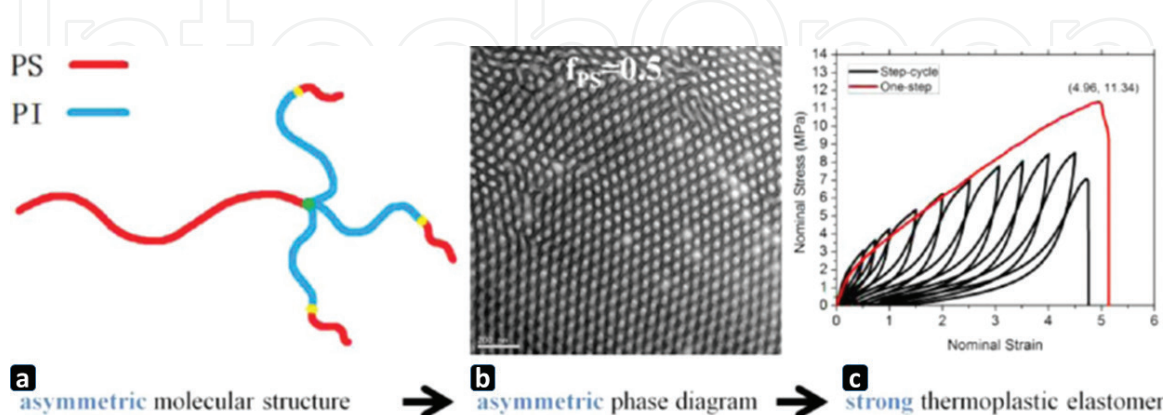


Figure 7. (a) Structure of $S(IS')_3$ miktoarm star copolymer-type TPEs. (b) TEM of $S(IS')_3$ miktoarm star copolymer with 50 vol% PS. (c) Stress-strain curve of $S(IS')_3$. (Reprinted with permission from Ref. [94]. Copyright 2014 American Chemical Society).

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-PnBA)₃ with 36% of PMMA showed 11-MPa ultimate stress with 545% strain at break. (PAN-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.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division. Part of the synthesis and characterization was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Author details

Weiyu Wang^{1*}, Wei Lu², Nam-Goo Kang², Jimmy Mays^{2,3} and Kunlun Hong¹

*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

References

- [1] Bonart R. Thermoplastic elastomers. *Polymer*. 1979;**20**(11):1389-1403. DOI: 10.1016/0032-3861(79)90280-5

- [2] Spontak RJ, Patel NP. Thermoplastic elastomers: Fundamentals and applications. *Current Opinion in Colloid & Interface Science*. 2000;5(5):333-340. DOI: 10.1016/S1359-0294(00)00070-4
- [3] Shanks RA. General purpose elastomers: Structure, chemistry, physics and performance. In: Visakh PM, Thomas S, Chandra AK, Mathew AP, editors. *Advances in Elastomers I*. Berlin Heidelberg: Springer Science & Business Media; 2013. pp. 11-45. DOI: 10.1007/978-3-642-20925-3_2
- [4] Walker BM, Rader CP, editors. *Handbook of Thermoplastic Elastomers*. 2nd ed. New York, NY: Van Nostrand Reinhold; 1988. p. 430. DOI: 10.1002/pol.1989.140270914
- [5] Drobny JG, editor. *Handbook of Thermoplastic Elastomers*. 2nd ed. Elsevier; May 30, 2014. William Andrew; 2014. p. 464. DOI: 10.1016/B978-081551549-4.50002-5
- [6] Bhowmick AK, Stephens H, editors. *Handbook of Elastomers*. 2nd ed. New York, NY: CRC Press; 2000.
- [7] Fakirov S, editor. *Handbook of Condensation Thermoplastic Elastomers*. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA; 2005.
- [8] Legge NR, Holden G, Schroeder HE, editors. *Thermoplastic Elastomers: A Comprehensive Review*. New York, NY: Hanser University Press; 1988. p. 574. DOI: 10.1002/pol.1989.140270710
- [9] Hirao A, Goseki R, Ishizone T. Advances in living anionic polymerization: From functional monomers, polymerization systems, to macromolecular architectures. *Macromolecules*. 2014;47(6):1883-1905. DOI: 10.1021/ma401175m
- [10] Hadjichristidis N, Hirao A, editors. *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*. 1st ed. Japan: Springer; 2015. p. 1082. DOI: 10.1007/978-4-431-54186-8
- [11] Goodwin A, Goodwin KM, Wang W, Yu YG, Lee JS, Mahurin SM, Dai S, Mays JW, Kang NG. Anionic polymerization of oxadiazole-containing 2-vinylpyridine by precisely tuning nucleophilicity and the polyelectrolyte characteristics of the resulting polymers. *Macromolecules*. 2016;49(17):6213-6225. DOI: 10.1021/acs.macromol.6b00875
- [12] Aoshima S, Kanaoka S. A renaissance in living cationic polymerization. *Chemical Reviews*. 2009;109(11):5245-5287. DOI: 10.1021/cr900225g
- [13] Matyjaszewski K, Tsarevsky NV. Macromolecular engineering by atom transfer radical polymerization. *Journal of the American Chemical Society*. 2014;136(18):6513-6533. DOI: 10.1021/ja408069v
- [14] Khosravi E, Szymanska-Buzar T, editors. *Ring Opening Metathesis Polymerisation and Related Chemistry: State of the Art and Visions for the New Century*. 1st ed. The Netherlands: Springer; 2012. p. 488. DOI: 10.1007/978-94-010-0373-5
- [15] Moad G, Rizzardo E, Thang SH. Radical addition-fragmentation chemistry in polymer synthesis. *Polymer*. 2008;49(5):1079-1131. DOI: 10.1016/j.polymer.2007.11.020

- [16] Hawker CJ, Bosman AW, Harth E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chemical Reviews*. 2001;**101**(12):3661-3688. DOI: 10.1021/cr990119u
- [17] Holden G, Milkovich R. Block Polymers of Monovinyl Aromatic Hydrocarbons and Conjugated Dienes [Internet]. August 9, 1966. Available from: <https://www.google.com/patents/US3265765> [Accessed February 12, 2017]
- [18] Handlin DL, Trenor S, Wright K. Applications of thermoplastic elastomers based on styrenic block copolymers. In: Matyjaszewski K, Gnanou Y, Leibler L, editors. *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*. Weinheim, Germany: Wiley-VCH; 2007. pp. 2001-2031. DOI: 10.1002/9783527631421.ch1
- [19] Hsieh H, Quirk RP, editors. *Anionic Polymerization: Principles and Practical Applications*. New York, NY: CRC Press; March 15, 1996. p. 744
- [20] Fetters LJ, Morton M. Synthesis and properties of block polymers. I. Poly- α -methylstyrene-polyisoprene-poly- α -methylstyrene. *Macromolecules*. 1969;**2**(5):453-458. DOI: 10.1021/ma60011a002
- [21] Bolton JM, Hillmyer MA, Hoyer TR. Sustainable thermoplastic elastomers from terpene-derived monomers. *ACS Macro Letters*. 2014;**3**(8):717-720. DOI: 10.1021/mz500339h
- [22] Fetters LJ, Firer EM, Dafaoui M. Synthesis and properties of block copolymers. 4. Poly (p-tert-butylstyrene-diene-p-tert-butylstyrene) and poly (p-tert-butylstyrene-isoprene-styrene). *Macromolecules*. 1977;**10**(6):1200-1207. DOI: 10.1021/ma60060a008
- [23] Kobayashi S, Matsuzawa T, Matsuoka SI, Tajima H, Ishizone T. Living anionic polymerizations of 4-(1-adamantyl) styrene and 3-(4-vinylphenyl)-1,1'-biadamantane. *Macromolecules*. 2006;**39**(18):5979-5986. DOI: 10.1021/ma060977+
- [24] Kobayashi S, Kataoka H, Ishizone T, Kato T, Ono T, Kobukata S, Ogi H. Synthesis and properties of new thermoplastic elastomers containing poly [4-(1-adamantyl) styrene] hard segments. *Macromolecules*. 2008;**41**(14):5502-5508. DOI: 10.1021/ma7028743
- [25] Yu JM, Dubois P, Jérôme R. Poly [alkyl methacrylate-b-butadiene-b-alkyl methacrylate] triblock copolymers: Synthesis, morphology, and mechanical properties at high temperatures. *Macromolecules*. 1996;**29**(26):8362-8370. DOI: 10.1021/ma960886k
- [26] Lu W, Huang C, Hong K, Kang NG, Mays JW. Poly (1-adamantyl acrylate): Living anionic polymerization, block copolymerization, and thermal. *Macromolecules*. 2016;**49**(24): 9406-9414. DOI: 10.1021/acs.macromol.6b01732
- [27] Yu JM, Dubois P, Teyssié P, Jérôme R. Syndiotactic poly (methyl methacrylate)(sPMMA)-polybutadiene (PBD)-sPMMA triblock copolymers: Synthesis, morphology, and mechanical properties. *Macromolecules*. 1996;**29**(19):6090-6099. DOI: 10.1021/ma9603950
- [28] Yu JM, Dubois P, Jérôme R. Synthesis and properties of poly [isobornyl methacrylate (IBMA)-b-butadiene (BD)-b-IBMA] copolymers: New thermoplastic elastomers of a large service temperature range. *Macromolecules*. 1996, Nov 4;**29**(23):7316-7322. DOI: 10.1021/ma960710i

- [29] Varshney SK, Kesani P, Agarwal N, Zhang JX, Rafailovich M. Synthesis of ABA type thermoplastic elastomers based on polyacrylates. *Macromolecule*. 1999;**32**(1):235-237. DOI: 10.1021/ma971428u
- [30] Tong JD, Jérôme R. Synthesis of poly (methyl methacrylate)-b-poly (n-butyl acrylate)-b-poly (methyl methacrylate) triblocks and their potential as thermoplastic elastomers. *Polymer*. 2000;**41**(7):2499-2510. DOI: 10.1016/S0032-3861(99)00412-7
- [31] Natori I. Synthesis of polymers with an alicyclic structure in the main chain. Living anionic polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-tetramethylethylenediamine system. *Macromolecules*. 1997;**30**(12):3696-3697. DOI: 10.1021/ma9712110
- [32] Hong K, Mays JW. 1,3-Cyclohexadiene polymers. 1. Anionic polymerization. *Macromolecules*. 2001;**34**(4):782-786. DOI: 10.1021/ma0015626
- [33] Bornani K, Wang X, Davis JL, Wang X, Wang W, Hinestrosa JP, Mays JW, Kilbey II SM. Impact of chain microstructure on solution and thin film self-assembly of PCHD-based semi-flexible/flexible diblock copolymers. *Soft Matter*. 2015;**11**(32):6509-6519. DOI: 10.1039/C5SM01245G
- [34] Imaizumi K, Ono T, Natori I, Sakurai S, Takeda K. Microphase-separated structure of 1,3-cyclohexadiene/butadiene triblock copolymers and its effect on mechanical and thermal properties. *Journal of Polymer Science Part B: Polymer Physics*. 2001;**39**(1):13-22. DOI: 10.1002/1099-0488(20010101)39:1<13::AID-POLB20>3.0.CO;2-K
- [35] Natori I, Imaizumi K, Yamagishi H, Kazunori M. Hydrocarbon polymers containing six-membered rings in the main chain. Microstructure and properties of poly (1,3-cyclohexadiene). *Journal of Polymer Science Part B: Polymer Physics*. 1998;**36**(10):1657-1668. DOI: 10.1002/(SICI)1099-0488(19980730)36:10<1657::AID-POLB7>3.0.CO;2-M
- [36] Kosaka Y, Kitazawa K, Inomata S, Ishizone T. Living anionic polymerization of benzo-fulvene: Highly reactive fixed transoid 1,3-diene. *ACS Macro Letters*. 2013;**2**(2):164-167. DOI: 10.1021/mz4000078
- [37] Kosaka Y, Goseki R, Kawauchi S, Ishizone T. Living anionic polymerization of benzo-fulvene in hydrocarbon solvent. *Macromolecular Symposia*. 2015;**350**(1):55-66. DOI: 10.1002/masy.201400024
- [38] Kosaka Y, Kawauchi S, Goseki R, Ishizone T. High anionic polymerizability of benzofulvene: New exo-methylene hydrocarbon Monomer. *Macromolecules*. 2015;**48**(13):4421-4430. DOI: 10.1021/acs.macromol.5b00944
- [39] Wang W, Schlegel R, White BT, Williams K, Voyloy D, Steren CA, Goodwin A, Coughlin EB, Gido S, Beiner M, Hong K. High temperature thermoplastic elastomers synthesized by living anionic polymerization in hydrocarbon solvent at room temperature. *Macromolecules*. 2016;**49**(7):2646-2655. DOI: 10.1021/acs.macromol.5b02642
- [40] MatWeb Material Property Data. Kraton® D1112P (SIS) Linear Block Copolymer [Internet]. Available from: <http://www.matweb.com/search/datasheet.aspx?matguid=ec777ddb6a3540ae977fb8f9a53c4d64> [Accessed February 12, 2017], 1996

- [41] Kaszas G, Puskas JE, Kennedy JP, Hager WG. Polyisobutylene-containing block polymers by sequential monomer addition. II. Polystyrene–polyisobutylene–polystyrene triblock polymers: Synthesis, characterization, and physical properties. *Journal of Polymer Science Part A: Polymer Chemistry*. 1991;**29**(3):427-435. DOI: 10.1002/pola.1991.080290316
- [42] Cao X, Faust R. Polyisobutylene-based thermoplastic elastomers. 5. Poly (styrene-*b*-isobutylene-*b*-styrene) triblock copolymers by coupling of living poly (styrene-*b*-isobutylene) diblock copolymers. *Macromolecules*. 1999;**32**(17):5487-5494. DOI: 10.1021/ma990370b
- [43] Kennedy JP, Kurian J. Living carbocationic polymerization of *p*-halostyrenes. III. Syntheses and characterization of novel thermoplastic elastomers of isobutylene and *p*-chlorostyrene. *Journal of Polymer Science Part A: Polymer Chemistry*. 1990;**28**(13):3725-3738. DOI: 10.1002/pola.1990.080281316
- [44] Kennedy JP, Midha S, Tsunogae Y. Polyisobutylene-containing block polymers by sequential monomer addition. VIII: Synthesis, characterization, and physical properties of poly (indene-*b*-isobutylene-*b*-indene) thermoplastic elastomers. *Macromolecules*. 1993;**26**(3):429-435. DOI: 10.1021/ma00055a004
- [45] Fodor Z, Kennedy JP. Polyisobutylene-containing block polymers by sequential monomer addition. *Polymer Bulletin*. 1992;**29**(6):697-704. DOI: 10.1007/BF01041157
- [46] Pan P, Inoue Y. Polymorphism and isomorphism in biodegradable polyesters. *Progress in Polymer Science*. 2009;**34**(7):605-640. DOI: 10.1016/j.progpolymsci.2009.01.003
- [47] Belgacem MN, Gandini A, editors. *Monomers, Polymers and Composites from Renewable Resources*. Elsevier; 2011. p. 560
- [48] Ajellal N, Carpentier JF, Guillaume C, Guillaume SM, Helou M, Poirier V, Sarazin Y, Trifonov A. Metal-catalyzed immortal ring-opening polymerization of lactones, lactides and cyclic carbonates. *Dalton Transactions*. 2010;**39**(69):8363-8376. DOI: 10.1039/C001226B
- [49] Hillmyer MA, Tolman WB. Aliphatic polyester block polymers: Renewable, degradable, and sustainable. *Accounts of Chemical Research*. 2014;**47**(8):2390-2396. DOI: 10.1021/ar500121d
- [50] Hiki S, Miyamoto M, Kimura Y. Synthesis and characterization of hydroxy-terminated [RS]-poly (3-hydroxybutyrate) and its utilization to block copolymerization with L-lactide to obtain a biodegradable thermoplastic elastomer. *Polymer*. 2000;**41**(20):7369-7379. DOI: 10.1016/S0032-3861(00)00086-0
- [51] Wanamaker CL, O'Leary LE, Lynd NA, Hillmyer MA, Tolman WB. Renewable-resource thermoplastic elastomers based on polylactide and polymenthide. *Biomacromolecules*. 2007;**8**(11):3634-3640. DOI: 10.1021/bm700699g
- [52] Wanamaker CL, Bluemle MJ, Pitet LM, O'Leary LE, Tolman WB, Hillmyer MA. Consequences of polylactide stereochemistry on the properties of polylactide-polymenthide-polylactide thermoplastic elastomers. *Biomacromolecules*. 2009;**10**(10):2904-2911. DOI: 10.1021/bm900721p

- [53] Martello MT, Hillmyer MA. Polylactide–poly (6-methyl- ϵ -caprolactone)–polylactide thermoplastic elastomers. *Macromolecules*. 2011;**44**(21):8537-8545. DOI: 10.1021/ma201063t
- [54] Matyjaszewski K, Davis TP, editors. *Handbook of Radical Polymerization*. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA;2003. p. 920. DOI: 10.1002/0471220450
- [55] Fan F, Wang W, Holt AP, Feng H, Uhrig D, Lu X, Hong T, Wang Y, Kang NG, Mays J, Sokolov AP. Effect of molecular weight on the ion transport mechanism in polymerized ionic liquids. *Macromolecules*. 2016;**49**(12):4557-4570. DOI: 10.1021/acs.macromol.6b00714
- [56] Matyjaszewski K, Tsarevsky NV. Nanostructured functional materials prepared by atom transfer radical polymerization. *Nature Chemistry*. 2009;**1**(4):276-288. DOI: 10.1038/nchem.257
- [57] Dong H, Tang W, Matyjaszewski K. Well-defined high-molecular-weight polyacrylonitrile via activators regenerated by electron transfer ATRP. *Macromolecules*. 2007;**40**(9):2974-2977. DOI: 10.1021/ma070424e
- [58] Thomas DB, Sumerlin BS, Lowe AB, McCormick CL. Conditions for facile, controlled RAFT polymerization of acrylamide in water. *Macromolecules*. 2003;**36**(5):1436-1439. DOI: 10.1021/ma025960f
- [59] Keddie DJ. Chemical Society Reviews. A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization. *Chemical Society Reviews*. 2014;**43**(2):496-505. DOI: 10.1039/C3CS60290G
- [60] Matyjaszewski K. Architecturally complex polymers with controlled heterogeneity. *Science*. 2011;**333**(6046):1104-1105. DOI: 10.1126/science.1209660
- [61] Yi Y, Fan X, Wan X, Li L, Zhao N, Chen X, Xu J, Zhou QF. ABA type triblock copolymer based on mesogen-jacketed liquid crystalline polymer: Design, synthesis, and potential as thermoplastic elastomer. *Macromolecules*. 2004;**37**(20):7610-7618. DOI: 10.1021/ma0400463
- [62] Liu X, Zhao RY, Zhao TP, Liu CY, Yang S, Chen EQ. An ABA triblock containing a central soft block of poly [2, 5-di (n-hexogycarbonyl) styrene] and outer hard block of poly (4-vinylpyridine): Synthesis, phase behavior and mechanical enhancement. *RSC Advances*. 2014;**4**(35):18431-18441. DOI: 10.1039/C4RA01652A
- [63] Braunecker WA, Matyjaszewski K. Controlled/living radical polymerization: Features, developments, and perspectives. *Progress in Polymer Science*. 2007;**32**(1):93-146. DOI: 10.1016/j.progpolymsci.2006.11.002
- [64] Butté A, Storti G, Morbidelli M. Miniemulsion living free radical polymerization by RAFT. *Macromolecules*. 2001;**34**(17):5885-5896. DOI: 10.1021/ma002130y
- [65] Delaittre G, Charleux B. Kinetics of in-situ formation of poly (acrylic acid)-b-polystyrene amphiphilic block copolymers via nitroxide-mediated controlled free-radical emulsion polymerization. Discussion on the effect of compartmentalization on the polymerization rate. *Macromolecules*. 2008;**41**(7):2361-2367. DOI: 10.1021/ma702498u

- [66] Luo Y, Wang X, Zhu Y, Li BG, Zhu S. Polystyrene-block-poly (n-butyl acrylate)-block-polystyrene triblock copolymer thermoplastic elastomer synthesized via RAFT emulsion polymerization. *Macromolecules*. 2010;**43**(18):7472-7481. DOI: 10.1021/ma101348k
- [67] Zhan X, He R, Zhang Q, Chen F. Microstructure and mechanical properties of amphiphilic tetrablock copolymer elastomers via RAFT miniemulsion polymerization: Influence of poly [styrene-alt-(maleic anhydride)] segments. *RSC Advances*. 2014;**4**(93):51201-51207. DOI: 10.1039/C4RA06185C
- [68] Wang S, Vajjala Kesava S, Gomez ED, Robertson ML. Sustainable thermoplastic elastomers derived from fatty acids. *Macromolecules*. 2013;**46**(18):7202-7212. DOI: 10.1021/ma4011846
- [69] Hayashi M, Matsushima S, Noro A, Matsushita Y. Mechanical property enhancement of ABA block copolymer-based elastomers by incorporating transient cross-links into soft middle block. *Macromolecules*. 2015;**48**(2):421-431. DOI: 10.1021/ma502239w
- [70] Feng C, Li Y, Yang D, Hu J, Zhang X, Huang X. Well-defined graft copolymers: from controlled synthesis to multipurpose applications. *Chemical Society Reviews*. 2011;**40**(3):1282-1295. DOI: 10.1039/B921358A
- [71] Uhrig D, Mays J. Synthesis of well-defined multigraft copolymers. *Polymer Chemistry*. 2011;**2**(1):69-76. DOI: 10.1039/C0PY00185F
- [72] Ito S, Goseki R, Ishizone T, Hirao A. Synthesis of well-controlled graft polymers by living anionic polymerization towards exact graft polymers. *Polymer Chemistry*. 2014;**5**(19):5523-5534. DOI: 10.1039/C4PY00584H
- [73] Uhrig D, Schlegel R, Weidisch R, Mays J. Multigraft copolymer superelastomers: Synthesis morphology, and properties. *European Polymer Journal*. 2011;**47**(4):560-568. DOI: 10.1016/j.eurpolymj.2010.10.030
- [74] Iatrou H, Mays JW, Hadjichristidis N. Regular comb polystyrenes and graft polyisoprene/polystyrene copolymers with double branches ("centipedes"). Quality of (1,3-phenylene) bis (3-methyl-1-phenylpentylidene) dilithium initiator in the presence of polar additives. *Macromolecules*. 1998;**31**(19):6697-6701. DOI: 10.1021/ma980738p
- [75] Uhrig D, Mays JW. Synthesis of combs, centipedes, and barbwires: Poly (isoprene-graft-styrene) regular multigraft copolymers with trifunctional, tetrafunctional, and hexafunctional branch points. *Macromolecules*. 2002;**35**(19):7182-7190. DOI: 10.1021/ma0204271
- [76] Beyer FL, Gido SP, Büschl C, Iatrou H, Uhrig D, Mays JW, Chang MY, Garetz BA, Balsara NP, Tan NB, Hadjichristidis N. Graft copolymers with regularly spaced, tetrafunctional branch points: Morphology and grain structure. *Macromolecules*. 2000;**33**(6):2039-2048. DOI: 10.1021/ma991141s
- [77] Duan Y, Thunga M, Schlegel R, Schneider K, Rettler E, Weidisch R, Siesler HW, Stamm M, Mays JW, Hadjichristidis N. Morphology and deformation mechanisms and tensile properties of tetrafunctional multigraft copolymers. *Macromolecules*. 2009;**42**(12):4155-4164. DOI: 10.1021/ma900414h

- [78] Weidisch R, Gido SP, Uhrig D, Iatrou H, Mays J, Hadjichristidis N. Tetrafunctional multi-graft copolymers as novel thermoplastic elastomers. *Macromolecules*. 2001;**34**(18):6333-6337. DOI: 10.1021/ma001966y
- [79] Staudinger U, Weidisch R, Zhu Y, Gido S, Uhrig D, Mays J, Iatrou H, Hadjichristidis N, Wiley Online Library. Mechanical properties and hysteresis behaviour of multigraft copolymers. *Macromolecular Symposia*. 2006;**233**(1):42-50. DOI: 10.1002/masy.200690027
- [80] Schlegel R, Wilkin D, Duan Y, Weidisch R, Heinrich G, Uhrig D, Mays JW, Iatrou H, Hadjichristidis NS. Stress softening of multigraft copolymers. *Polymer*. 2009;**50**(26): 6297-6304. DOI: 10.1016/j.polymer.2009.10.026
- [81] Goodwin A, Wang W, Kang NG, Wang Y, Hong K, Mays J. All-acrylic multigraft copolymers: Effect of side chain molecular weight and volume fraction on mechanical behavior. *Industrial & Engineering Chemistry Research*. 2015;**54**(39):9566-9576. DOI: 10.1021/acs.iecr.5b02560
- [82] Wang W, Wang W, Lu X, Bobade S, Chen J, Kang NG, Zhang Q, Mays J. Synthesis and characterization of comb and centipede multigraft copolymers PnBA-g-PS with high molecular weight using miniemulsion polymerization. *Macromolecules*. 2014;**47**(21): 7284-7295. DOI: 10.1021/ma501866t
- [83] Wang W, Wang W, Li H, Lu X, Chen J, Kang NG, Zhang Q, Mays J. Synthesis and characterization of graft copolymers poly (isoprene-g-styrene) of high molecular weight by a combination of anionic polymerization and emulsion polymerization. *Industrial & Engineering Chemistry Research*. 2015;**54**(4):1292-1300. DOI: 10.1021/ie504457e
- [84] Li H, Wang W, Li C, Tan J, Yin D, Zhang H, Zhang B, Yin C, Zhang Q. Synthesis and characterization of brush-like multigraft copolymers PnBA-g-PMMA by a combination of emulsion AGET ATRP and emulsion polymerization. *Journal of Colloid and Interface Science*. 2015;**453**:226-236. DOI: 10.1016/j.jcis.2015.04.051
- [85] Li H, Wang W, Tan J, Li C, Zhang Q. Synthesis and characterization of graft copolymers PnBA-g-PS by miniemulsion polymerization. *RSC Advances*. 2015;**5**(56):45459-45466. DOI: 10.1039/C5RA06502J
- [86] Hadjichristidis N. Synthesis of miktoarm star (μ -star) polymers. *Journal of Polymer Science Part A: Polymer Chemistry*. 1999;**37**(7):857-871. DOI: 10.1002/(SICI)1099-0518(19990401)37:7<857::AID-POLA1>3.0.CO;2-P
- [87] Khanna K, Varshney S, Kakkar A. Miktoarm star polymers: Advances in synthesis, self-assembly, and applications. *Polymer Chemistry*. 2010;**1**(8):1171-1185. DOI: 10.1039/C0PY00082E
- [88] Bi LK, Fetters LJ. Synthesis and properties of block copolymers. 3. Polystyrene-polydiene star block copolymers. *Macromolecules*. 1976;**9**(5):732-742. DOI: 10.1021/ma60053a010
- [89] Bi LK, Fetters LJ. Domain morphology of star block copolymers of polystyrene and polyisoprene. *Macromolecules*. 1975;**8**(1):90-92. DOI: 10.1021/ma60043a026

- [90] Lai C, Russel WB, Register RA, Marchand GR, Adamson DH. Phase behavior of styrene–isoprene diblock derivatives with varying conformational asymmetry. *Macromolecules*. 2000;**33**(9):3461–3466. DOI: 10.1021/ma991156q
- [91] Milner ST. Chain architecture and asymmetry in copolymer microphases. *Macromolecules*. 1994;**27**(8):2333–2335. DOI: 10.1021/ma00086a057
- [92] Vavasour JD, Whitmore MD. Self-consistent field theory of block copolymers with conformational asymmetry. *Macromolecules*. 1993;**26**(25):7070–7075. DOI: 10.1021/ma00077a054
- [93] Lynd NA, Oyerokun FT, O'Donoghue DL, Handlin Jr DL, Fredrickson GH. Design of soft and strong thermoplastic elastomers based on nonlinear block copolymer architectures using self-consistent-field theory. *Macromolecules*. 2010;**43**(7):3479–3486. DOI: 10.1021/ma902517v
- [94] Shi W, Lynd NA, Montarnal D, Luo Y, Fredrickson GH, Kramer EJ, Ntaras C, Avgeropoulos A, Hexemer A. Toward strong thermoplastic elastomers with asymmetric miktoarm block copolymer architectures. *Macromolecules*. 2014;**47**(6):2037–2043. DOI: 10.1021/ma402566g
- [95] Shi W, Hamilton AL, Delaney KT, Fredrickson GH, Kramer EJ, Ntaras C, Avgeropoulos A, Lynd NA, Demassieux Q, Creton C. Aperiodic “bricks and mortar” mesophase: A new equilibrium state of soft matter and application as a stiff thermoplastic elastomer. *Macromolecules*. 2015;**48**(15):5378–5384. DOI: 10.1021/acs.macromol.5b01210
- [96] Shi W, Hamilton AL, Delaney KT, Fredrickson GH, Kramer EJ, Ntaras C, Avgeropoulos A, Lynd NA. Creating extremely asymmetric lamellar structures via fluctuation-assisted unbinding of miktoarm star block copolymer alloys. *Journal of the American Chemical Society*. 2015;**137**(19):6160–6163. DOI: 10.1021/jacs.5b02881
- [97] Matmour R, Gnanou Y. Synthesis of complex polymeric architectures using multilithiated carbanionic initiators—Comparison with other approaches. *Progress in Polymer Science*. 2013;**38**(1):30–62. DOI: 10.1016/j.progpolymsci.2012.08.003
- [98] Jacob S, Kennedy JP. Synthesis and characterization of novel octa-arm star-block thermoplastic elastomers consisting of poly (p-chlorostyrene-b-isobutylene) arms radiating from a calix [8] arene core. *Polymer Bulletin*. 1998;**41**(2):167–174. DOI: 10.1007/s002890050348
- [99] Keszler B, Fenyvesi GY, Kennedy JP. Novel star-block polymers: Three polyisobutylene-b-poly (methyl methacrylate) arms radiating from an aromatic core. *Journal of Polymer Science Part A: Polymer Chemistry*. 2000;**38**(4):706–714. DOI: 10.1002/(SICI)1099-0518(20000215)38:4<706::AID-POLA5>3.0.CO;2-D
- [100] Shim JS, Asthana S, Omura N, Kennedy JP. Novel thermoplastic elastomers. I. Synthesis and characterization of star-block copolymers of PSt-b-PIB arms emanating from cyclosiloxane cores. *Journal of Polymer Science Part A: Polymer Chemistry*. 1998;**36**(17):2997–3012. DOI: 10.1002/(SICI)1099-0518(199812)36:17<2997::AID-POLA1>3.0.CO;2-1

- [101] Shim JS, Kennedy JP. Novel thermoplastic elastomers. II. Properties of star-block copolymers of PSt-b-PIB arms emanating from cyclosiloxane cores. *Journal of Polymer Science Part A: Polymer Chemistry*. 1999;**37**(6):815-824. DOI: 10.1002/(SICI)1099-0518(19990315)37:6<815::AID-POLA17>3.0.CO;2-5
- [102] Shim JS, Kennedy JP. Novel thermoplastic elastomers. III. Synthesis, characterization, and properties of star-block copolymers of poly (indene-b-isobutylene) arms emanating from cyclosiloxane cores. *Journal of Polymer Science Part A: Polymer Chemistry*. 2000;**38**(2):279-290. DOI: 10.1002/(SICI)1099-0518(20000115)38:2<279::AID-POLA2>3.0.CO;2-8
- [103] Imaeda T, Hashimoto T, Irie S, Urushisaki M, Sakaguchi T. Synthesis of ABA-triblock and star-diblock copolymers with poly (2-adamantyl vinyl ether) and poly (n-butyl vinyl ether) segments: New thermoplastic elastomers composed solely of poly (vinyl ether) backbones. *Journal of Polymer Science Part A: Polymer Chemistry*. 2013;**51**(8):1796-1807. DOI: 10.1002/pola.26561
- [104] Dufour B, Koynov K, Pakula T, Matyjaszewski K. PBA-PMMA 3-arm star block copolymer thermoplastic elastomers. *Macromolecular Chemistry and Physics*. 2008; **209**(16):1686-1693. DOI: 10.1002/macp.200800151
- [105] Dufour B, Tang C, Koynov K, Zhang Y, Pakula T, Matyjaszewski K. Polar three-arm star block copolymer thermoplastic elastomers based on polyacrylonitrile. *Macromolecules*. 2008;**41**(7):2451-2458. DOI: 10.1021/ma702561b
- [106] Pakula T, Koynov K, Boerner H, Huang J, Lee HI, Pietrasik J, Sumerlin B, Matyjaszewski K. Effect of chain topology on the self-organization and the mechanical properties of poly (n-butyl acrylate)-b-polystyrene block copolymers. *Polymer*. 2011;**52**(12):2576-2583. DOI: 10.1016/j.polymer.2011.04.021
- [107] Juhari A, Mosnáček J, Yoon JA, Nese A, Koynov K, Kowalewski T, Matyjaszewski K. Star-like poly (n-butyl acrylate)-b-poly (α -methylene- γ -butyrolactone) block copolymers for high temperature thermoplastic elastomers applications. *Polymer*. 2010;**51**(21):4806-4813. DOI: 10.1016/j.polymer.2010.08.017

IntechOpen

