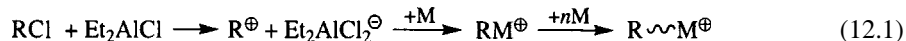


12.1 Introduction

Carbocationic polymerization is relatively a latecomer to the world of thermoplastic elastomers (TPEs). Nonetheless, within a short time this chemistry has enriched the science and technology of TPEs in so many ways that a comprehensive review, such as presented in this volume, would be incomplete without a discussion of TPEs prepared by carbocationic polymerizations. By the time this book is published, just after a decade that the first US Patent disclosing this technology has issued [1], TPEs manufactured by carbocationic polymerization became a commercial reality [2].

This saga commences in the late 1960s, when the demonstrated utility of TPEs prepared by other techniques, mainly styrenic TPEs synthesized by anionic polymerizations, prompted research aimed at the preparation of similar structures/materials by carbocationic processes. An important motivation for these investigations was the desire to replace the unsaturated rubber segments, polybutadiene or polyisoprene used in styrenic TPEs (Kraton[®] Thermoplastic Elastomers, in particular), with the equally inexpensive but saturated (and consequently oxidatively and chemically resistant) polyisobutylene rubber as the elastomeric moiety.

Among the notable early successes toward cationically prepared TPEs were the discovery of the first generation of designed graft copolymers comprising a polyisobutylene backbone carrying polystyrene branches and similar rubbery-glassy sequential polymers (see Section 12.3). These early discoveries were possible because of a sufficient understanding of the initiation step of carbocationic polymerizations induced by active organic chlorides (RCI) in conjunction with certain alkylaluminum coinitiators (Et₂AlCl) (“controlled initiation”):



However, after a flurry of activity by both academic and industrial investigators (see, for example, [3, 4]), research in cationic grafting decelerated, mainly because at this time the other elementary steps (i.e., chain transfer, termination) could not be controlled, and this lack of understanding of the mechanisms frustrated efforts to assemble the needed structures exhibiting superior physical properties and processing advantages.

Materials science of polymers – and the field of TPEs is certainly part of this discipline – is largely applied macromolecular engineering and is predicated upon a detailed understanding of the elementary events of polymerization reactions. In hindsight, it is abundantly evident that the resurgence of carbocationic polymerization research in the 1980s, notably in block copolymers, occurred exactly because of the increased insight into the elementary processes, that is, initiation, propagation, chain transfer, and reversible termination, which in turn led to controlled rates, and products with designed molecular weights and molecular weight distribution.

This chapter concerns three large families of TPEs, of which certain members can be prepared only by carbocationic polymerization techniques: block copolymers, graft copolymers (including bigrafts and graft blocks), and ionomers. All these products arose because of our detailed insight into the mechanism of carbocationic polymerizations: Syntheses of grafts became possible because of understanding controlled initiation, and the synthesis of various blocks because of the discovery of living (more precisely quasiling) carbocationic polymerizations (see Sections 12.2.1 and 12.3.1). PIB-based ionomers exhibiting TPE properties will be discussed in Section 12.4.

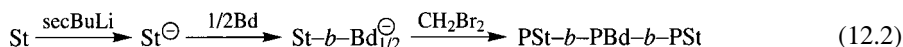
12.2 Block Copolymers

12.2.1 Introduction: Living Carbocationic Polymerization and Sequential Monomer Addition

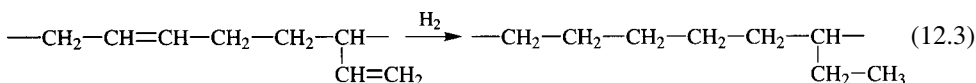
Long before the discovery of living carbocationic polymerizations and that of the introduction of the sequential monomer addition technique for the preparation of triblock TPEs, efforts were made for the synthesis of glassy-rubbery-glassy block copolymers by cationic techniques. Motivation for this research came from the spectacular academic and commercial successes of the rapidly expanding field of styrenic TPEs (notably the Kraton[®] family marketed by Shell) prepared by living anionic polymerizations, and from the realization that similar cationically prepared glassy-rubbery-glassy structures should have better overall properties than the anionically polymerized products.

Thus, Kennedy *et al.* prepared P α MeSt-*b*-PIB-*b*-P α MeSt by initiating bidirectional polymerization of α MeSt, first by using the telechelic *t*Cl-PIB-Cl/Et₂AlCl initiating system [5], and later by the *t*Cl-PIB-Cl/SnCl₄ combination in the presence of the proton trap 2,6-di-*tert*-butylpyridine [6, 7]. While the blocking efficiencies were quite high in both instances, the products were of broad molecular weight distributions, undesirable for good TPE properties. Fodor *et al.* [8] synthesized PSt-*b*-PIB-*b*-PSt by slowly and continuously condensing IB gas to a bifunctional initiating system (*p*-dicumyl chloride/TiCl₄) stirred in a solvent at -90 °C, and after the PIB has reached the desirable molecular weight, added St. In addition to the target triblock, however, side reactions led to PIB-*b*-PSt diblocks which compromised the properties of the TPE. The subsequent discovery of living carbocationic polymerization revolutionized this field and led to well-defined contamination-free PSt-*b*-PIB-*b*-PSt exhibiting excellent TPE properties [1].

The group of anionically prepared TPEs that inspired the early researchers were PSt-*b*-PBd-*b*-PSt and PSt-*b*-PIP-*b*-PSt and the hydrogenated derivative of the former: PSt-*b*-(polyethylene-*co*-1-butene)-*b*-PSt. These commercially available TPEs are preferentially synthesized by first preparing by sequential monomer addition a PSt-*b*-PBd_{1/2}[⊖] Li[⊕] (or PSt-*b*-PI_{1/2}[⊖] Li[⊕]) moiety and subsequently coupling two such fragments by bifunctional coupling agents, such as CH₂Br₂, to give the desired TPE triblock (see Chapter 3):



A major disadvantage of this process is the strict stoichiometric requirement in the coupling step: if the ratio St-*b*-PBd_{1/2}[⊖]/CH₂Br₂ is not exactly 2.0 (a very difficult requirement to meet), the final product will contain PSt-*b*-PBd_{1/2} diblock contaminants that will reduce the ultimate strength properties of the triblock. The resistance to oxidation and ozone of PSt-*b*-PBd-*b*-PSt can be reduced by selectively hydrogenating the rubbery midsegment, which is, in fact, a random copolymer of *cis*- and *trans*-1,4-, and 1,2-Bd repeat units. The rubbery midsegment of hydrogenated PSt-*b*-PBd-*b*-PSt is, formally, a copolymer of ethylene and 1-butene units (PSt-*b*-P(EB)-*b*-PSt):



Corresponding polymers with a PIP midblock can be similarly produced and hydrogenated. Hydrogenation, however, complicates the overall process, increases the cost, and leaves residual double bonds in the products.

Another fundamental shortcoming of these TPEs is their relatively low use temperatures due to the modest T_g (~ 100 °C) of the PSt glassy segments.

The following analysis indicates that cationically prepared PIB-based styrenic TPEs eliminate these process and product deficiencies:

- The use of PIB as the rubbery midsegment eliminates the need for hydrogenation. Hydrogenation of the PBd (or PI) midsegment in Kraton-type TPEs removes the unsaturation present in the original rubbery midsegment, however, gives rise to *tertiary* Hs that are still vulnerable to oxidation. In contrast, PIB is saturated and contains only relatively stable primary and secondary Hs (CH_3 - and $-\text{CH}_2$ -groups). Let the reader be reminded that IB can be polymerized only by cationic means and PIB-based rubbers ($T_g = -73$ °C) are low-cost commodities whose molecular weight can be readily controlled.
- The use of soluble bi-, tri- or multi-functional cationic initiators (X-I-X , I-X_n , where $\text{X} = \text{Cl}$, OH , OMe , epoxides) produces living PIB chains that induce the polymerization of St and leads to linear triblocks and radial blocks; thus the onerous coupling step is eliminated. Indeed many efficient low-cost soluble bi-, tri-, and multifunctional initiators for cationic polymerizations have been described. In contrast, hydrocarbon-soluble bifunctional initiators for anionic polymerization are quite difficult to prepare; hydrocarbon solubility, however, is mandatory because only in this medium can the appropriate PBd (or PI) enchainment be obtained which, on hydrogenation, produces the needed rubbery midsegment (see Eq. 12.3).
- TPEs with relatively high use temperatures can be made by employing St derivatives, such as *p*ClSt, *p*FSt, and Ind, which readily undergo living cationic (but not anionic!) polymerization. The T_g s of these PSt derivatives are much higher than that of PSt (see Table 12.2). Indeed, the T_g s of the glassy segments can be “fine tuned” by randomly copolymerizing cationically responsive St derivatives (see Section 12.2.2.5).

The road toward high-quality styrenic TPEs by cationic routes was opened by three discoveries made in rapid succession: (1) The living carbocationic polymerization of IB yielding high molecular weight narrow molecular weight distribution PIB [9–11]; (2) the living carbocationic polymerization of St and St derivatives [12–15]; and perhaps most importantly, (3) the finding that living PIB di- and trications $^{\oplus}\text{PIB}^{\oplus}$, $^{\oplus}\text{PIB}^{\oplus\oplus}$ in the presence of certain additives readily induce the living polymerization of St and St derivatives [1, 17, 18]. These findings set the stage for the current development of PIB-based styrenic TPEs to be presented in the next section.

Figure 12.1 summarizes the various block architectures exhibiting TPE character readily accessible by carbocationic polymerizations. Structurally, all these constructs comprise a rubbery (soft) inner segment (core) bound to two or more glassy (hard) outer segments (corona). The spatial arrangement of the rubbery/glassy moieties (i.e., linear, star, arborescent), the molecular parameters of the segments (i.e., molecular weight, T_g , relative amounts of rubbery/glassy components, degree of segmental incompatibility), and the micromorphology of the constructs control ultimate TPE properties and processibility. Historically, the first TPEs obtained were linear triblocks and triarm star-blocks [1]. Multiarm star-blocks were developed not much later [19–24]. Star-blocks are attractive alternatives to linear blocks

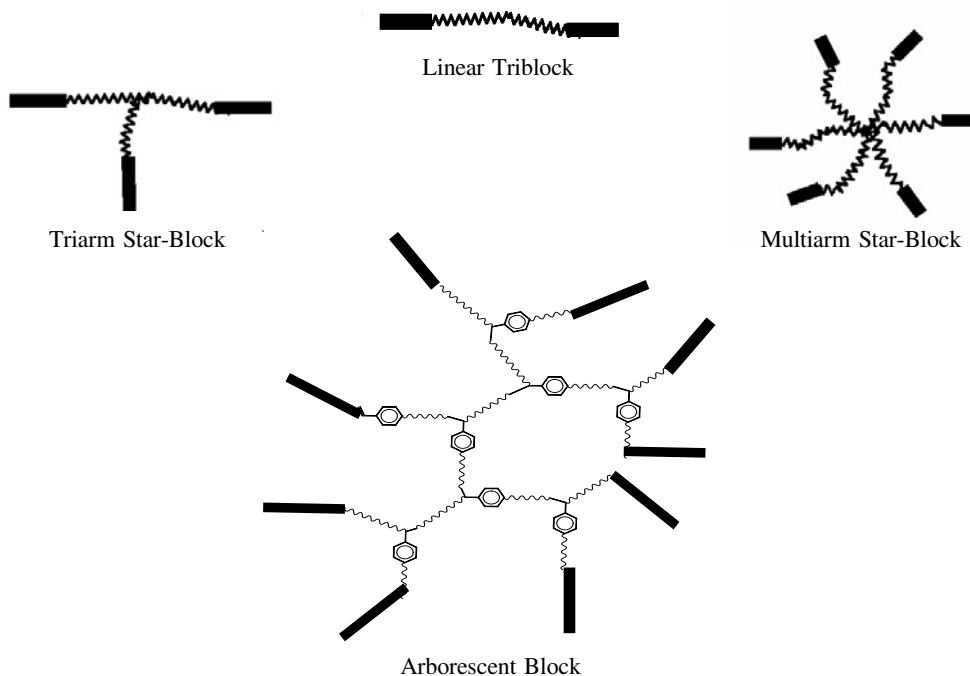


Figure 12.1 Block architectures produced by carbocationic techniques (■ = PSt, ~~~ = PIB)

because of their superior combination of physical and processing properties, including higher moduli combined with lower viscosities at similar molecular weights [25]. Further, multiarm star-blocks have demonstrated superior shear stability to linear blocks [26]. Very recently, arborescent blocks comprising a randomly branched dendritic (tree-like) PIB core carrying multiple PSt outer blocks joined the family of TPEs [27–32].

12.2.2 PIB-Based Linear-, Star-, and Arborescent Blocks

The discovery of living IB polymerization proceeding by well-defined PIB di- and trications and leading to chlorine di- and tri-telechelic PIBs [16, 33] opened the field of block TPEs by carbocationic polymerization. Table 12.1 lists PIB-based block TPEs prepared to date, together with references. The products are organized into two large groups (and appropriate subgroups), i.e., PIB-based TPEs in which the outer glassy block is either a homopolymer or a copolymer. The rationale of this grouping is that the T_g of the glassy blocks can be controlled by the specific monomer employed (e.g., St, *p*MeSt, Ind), or fine-tuned by copolymerizing two monomers yielding a glassy segment (e.g., P(St-*co*-*p*ClSt)) whose T_g falls between those of the homopolymers. The desired T_g can be dialed in by the relative concentration of the two repeat units in the copolymer. Table 12.2 lists the homopolymers and T_g s of the glassy segments.

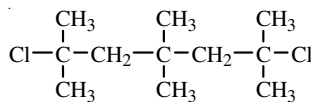
Figure 12.2 shows the bi-, tri- and multifunctional initiators that have been used in the preparation of TPE blocks copolymers by carbocationic polymerization.

Table 12.1 PIB-Based TPE Block Copolymers

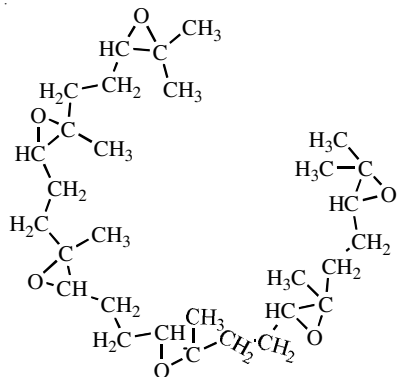
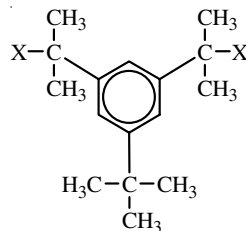
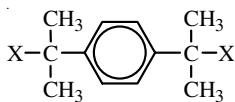
Linear, star, and arborescent blocks with glassy homopolymer blocks	Reference
<i>Linear triblocks</i>	
PSt- <i>b</i> -PIB- <i>b</i> -PSt	[1, 17, 28, 29, 31, 41–58]
P α MeSt- <i>b</i> -PIB- <i>b</i> -P α MeSt	[50, 52, 59, 60, 61]
PpMeSt- <i>b</i> -PIB- <i>b</i> -PpMeSt	[1, 18, 56, 57, 60, 62, 63]
Pp <i>tert</i> BuSt- <i>b</i> -PIB- <i>b</i> -Pp <i>tert</i> BuSt	[1, 18, 56, 64]
PInd- <i>b</i> -PIB- <i>b</i> -PInd	[1, 18, 64, 65]
Pac- <i>b</i> -PIB- <i>b</i> -PAc	[67]
PpClSt- <i>b</i> -PIB- <i>b</i> -PpClSt	[1, 68, 69]
PpFSt- <i>b</i> -PIB- <i>b</i> -PpFSt	[70]
(<i>tr</i> -1,4-PIP)- <i>b</i> -PIB- <i>b</i> -(<i>tr</i> -1,4-PIP)	[71, 72]
cyPIP- <i>b</i> -PIB- <i>b</i> -cyPIP	[71]
<i>Star blocks (tri- and multiarm)</i>	
(PIB- <i>b</i> -PSt) ₃	[1, 17, 38, 48–55]
(PIB- <i>b</i> -P α MeSt) ₃	[60, 61]
(PIB- <i>b</i> -PpMeSt) ₃	[60, 62]
(PIB- <i>b</i> -PInd) ₃	[1, 18]
(PIB- <i>b</i> -PpClSt) ₃	[68, 69]
(PIB- <i>b</i> -PSt) _{<i>n</i>} , <i>n</i> = 5–8	[19–24, 28, 29, 31]
<i>Arborescent blocks</i>	
arb-PIB- <i>b</i> -PSt	[27–32]
<i>Linear blocks with glassy copolymer blocks</i>	
P(<i>pt</i> BuSt- <i>co</i> -Ind)- <i>b</i> -PIB- <i>b</i> -P(<i>pt</i> BuSt- <i>co</i> -Ind)	[11, 18]
P(St- <i>co</i> -pClSt)- <i>b</i> -PIB- <i>b</i> -P(St- <i>co</i> -pClSt)	[1]
PpMeSt- <i>co</i> -Ind)- <i>b</i> -PIB- <i>b</i> -P(pMeSt- <i>co</i> -Ind)	[73]
P(pMeSt- <i>co</i> -pClSt)- <i>b</i> -PIB- <i>b</i> -P(pMeSt- <i>co</i> -pClSt)	[1]
P(Br- <i>p</i> MeSt- <i>co</i> -St)- <i>b</i> -Poly(ethylene- <i>co</i> -butene)- <i>b</i> -P(Br- <i>p</i> MeSt- <i>co</i> -St)	[74]
P(St- <i>b</i> -(PIB- <i>co</i> -pMeSt)- <i>b</i> -St)	[75]

Table 12.2 Glassy Homopolymer Segments Used in Cationically Synthesized TPEs and Their T_g s

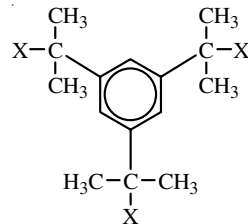
Glassy segment	T_g (°C)
Polystyrene	100
Poly(α -methylstyrene)	173
Poly(<i>p</i> -methylstyrene)	108
Poly(<i>p-tert</i> -butylstyrene)	142
Polyindene	170–220
Polyacenaphthylene	250
Poly(<i>p</i> -fluorostyrene)	109
Poly(<i>p</i> -chlorostyrene)	129
Cyclized poly(<i>tr</i> -1,4-isoprene)	95–190
Poly(methyl methacrylate) (iso/syndio stereo complexes)	102



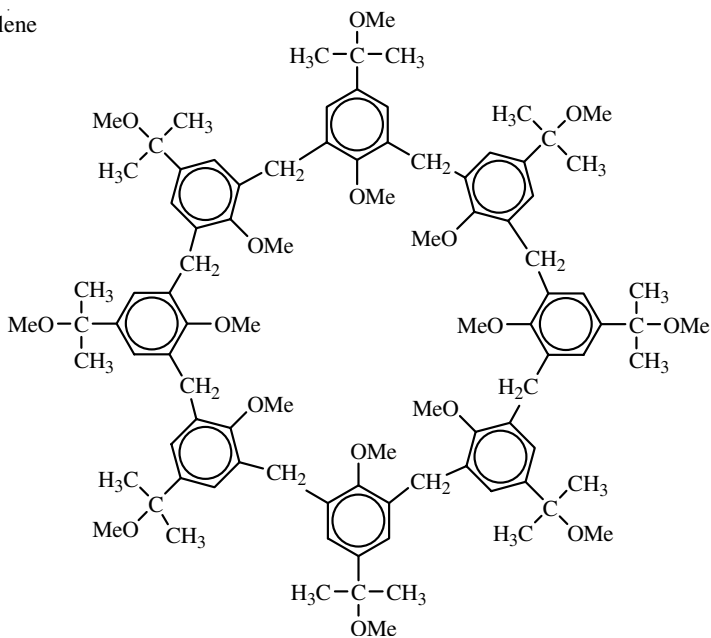
Bifunctional initiators



Hexaepoxy squalene



Trifunctional initiator

5,11,17,23,29,35,41,47-(2-Methoxypropyl)-
49,50,51,52,53,54,55,56-octamethoxycalix-[8]arene**Figure 12.2** Bi-, tri- and multifunctional initiators for the synthesis of linear- and star-blocks (X=Cl, OH, OMe).

12.2.2.1 Glassy Block: Polystyrene

12.2.2.1.1 Linear Blocks: PSt-*b*-PIB-*b*-PSt

PSt-*b*-PIB-*b*-PSt, conceived and developed as the cationic equivalent to anionically prepared PSt-*b*-PBd-*b*-PSt, was the first and still is the best-investigated triblock TPE synthesized by living cationic polymerization using sequential monomer addition. The synthesis, investigated on three continents [1, 17, 36–40, 41–58], invariably involves a bifunctional initiator (see Fig. 12.1), TiCl₄ coinitiator, and the use of a moderately polar solvent mixture at –70 to –90 °C. Fodor and Faust demonstrated that a single solvent, *n*BuCl, could also be used [42], and Shaffer recently developed a polymerization system based on Et₂AlCl coinitiator [56, 57, 75], but the majority of publications uses the original system. Sequential monomer addition is carried out in two steps:

1. The living polymerization of IB to a desirable molecular weight PIB^{\oplus} (say, $M_n \sim 50,000$ g/mol, M_w / M_n 1.1), followed by
2. St addition to the living PIB^{\oplus} charge and growing the triblock to a predetermined length ($M_{n,\text{PSt}} = 5000$ to 25,000 g/mol, M_w / M_n of triblock ≈ 1.1).

To achieve good physical properties, additives such as proton traps and electron pair donors must also be used. Faust and Fodor developed an efficient blocking method, where the living PIB^{\oplus} is capped with 1,1-diphenylethylene before St addition [60]. The details of various synthetic methods have been reviewed [33, 76].

Since PIB and PSt are incompatible, PSt-*b*-PIB-*b*-PSt triblocks exhibit two T_g s and a high degree of microphase separation [17, 28, 29, 31, 36, 41, 46, 48–55, 78, 79].

Several reports concern static and dynamic mechanical properties of PSt-*b*-PIB-*b*-PSt. In general, tensile strengths increase with increasing PSt content and reach a maximum at 17–26 MPa and ~600% elongation. Tensile strength starts to rise at $M_{n,\text{PSt}} \approx 5000$, when the PSt domains start to separate from the continuous PIB matrix. The tensile strengths reach a plateau at ~17 MPa with $M_{n,\text{PSt}} > \sim 15,000$ g/mol [38]. These data were obtained with products prepared in a pilot plant (kg scale) [38] and tested by the use of standard ASTM dumbbells (Figure 12.3.). Testing by the use of microdumbbells gave, as expected, higher values: the maximum tensile strengths reached 20 to 26 MPa and the ultimate elongations 250–1200% [40]. A linear correlation was found between elongations at break and the PIB/PSt molecular weight ratio [38].

Figure 12.4 displays stress-strain plots of various PSt-*b*-PIB-*b*-PSt blocks.

As expected, moduli and tensile strengths increase while elongations decrease with increasing PSt content. At 37–42 wt% PSt yielding occurs. Styrenic block copolymers containing < 40% PSt are elastomeric whereas plastic behavior starts to prevail with > 50% PSt [80]. The high PSt content also increases tension set, which is undesirable for TPEs.

Table 12.3 summarizes and compares mechanical property data obtained with PSt-*b*-PIB-*b*-PSt (20–40 wt% PSt, M_n (block) $\approx 100,000$ g/mol) and PSt-*b*-P(EB)-*b*-PSt (Kraton[®] G1650, 29 wt% PSt, M_n (block) = 107,000 g/mol) [81].

The order-disorder temperature (ODT) of a PSt-*b*-PIB-*b*-PSt with $M_n = 60,000$ g/mol and 30 wt% PSt was found to be 250 °C [82], some 75 °C higher than that reported for PSt-*b*-PBd-*b*-PSt with similar overall glassy/rubbery composition [83]. The higher ODT of PSt-*b*-PIB-*b*-PSt may be due to the larger difference of solubility parameters between PIB and PSt

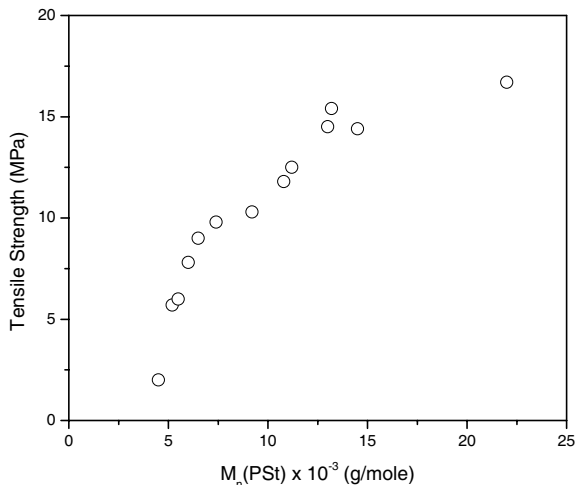


Figure 12.3 Tensile strength of *PSt-b-PIB-b-PSt* as a function of PS M_n

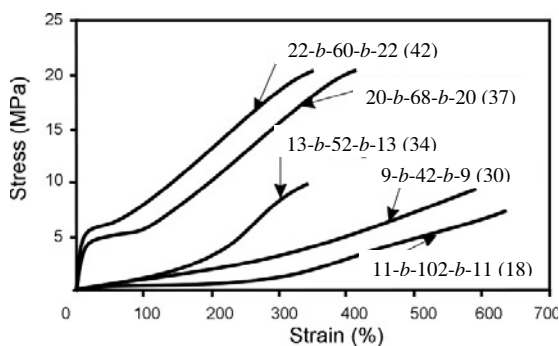


Figure 12.4 Stress-strain plots of various *PSt-b-PIB-b-PSt* blocks (22-*b*-60-*b*-22 (42) stands for a block with M_n (PIB) = 60,000 g/mol, M_n (PS) arms = 22,000 g/mol, 42 wt% PS content; 20-*b*-68-*b*-20 (37); 13-*b*-52-*b*-13 (34); 9-*b*-42-*b*-9 (30) (TS Polymer, Kuraray); 11-*b*-102-*b*-11 (18))

Table 12.3 Comparison of Properties of *PSt-b-PIB-b-PSt* and *PSt-b-P(EB)-b-PSt* (Kraton® G1650)

Physical Property	<i>PSt-b-PIB-b-PSt</i>	<i>PSt-b-P(EB)-b-PSt</i>
Tensile strength (MPa)	6–17	28
300% modulus (MPa)	1–11	4.7
Elongation at break (%)	250–1100	500
Tear strength, die C (kN/m)	10–78	38
Compression set, 70 h, RT	25–45	25
Melt flow, 190 °C, 10 kg (g/10 min)	0.5–88	No flow
Hardness Shore A2	23–87	76
Ozone resistance	Excellent	Excellent
Gehman Low Temperature Stiffening		
T5	–45	–40
T10	–50	–48
Air Permeability · 10 ⁸ (m ² /Pa.s)	11.4	171

than between PBd and PSt ($\delta_{\text{PIB}} = 7.97$, $\delta_{\text{PSt}} = 8.96$, $\delta_{\text{PBd}} = 8.40$ [cal/cm^3] $^{1/2}$ – average of values in [84]). The melt viscosity of PSt-*b*-PIB-*b*-PSt was shown to be lower than that of PSt-*b*-P(EB)-*b*-PSt, and its shear degradation was found to be negligible even at high shear rates [38]. The moldability and flex-fatigue behavior of PSt-*b*-PIB-*b*-PSt were also superior, compared to PSt-*b*-PBd-*b*-PSt and PSt-*b*-P(EB)-*b*-PSt [56]. The thermal stability of PIB-based triblocks is superior to that of PSt-*b*-P(EB)-*b*-PSt (see below). Shore hardness and tear strength of PSt-*b*-PIB-*b*-PSt increased linearly with PSt content. The barrier, electrical and low temperature properties of PSt-*b*-PIB-*b*-PSt were equivalent to those of conventional butyl rubber vulcanizates, and the triblock, like butyl rubber, also showed strain-induced crystallization [36, 38].

The morphology of PSt-*b*-PIB-*b*-PSt (and that of the triarm star (PIB-*b*-PSt) $_3$, as will be discussed later) was investigated by TEM, AFM and SAXS. According to these studies the morphologies of these products were similar to those exhibited by their anionically synthesized counterparts. TEM of PSt-*b*-PIB-*b*-PSt with 20% PSt showed cylindrical (10 nm) or mixed spherical and cylindrical PSt (20–30 nm) domains, while triblocks with < 20% PSt showed

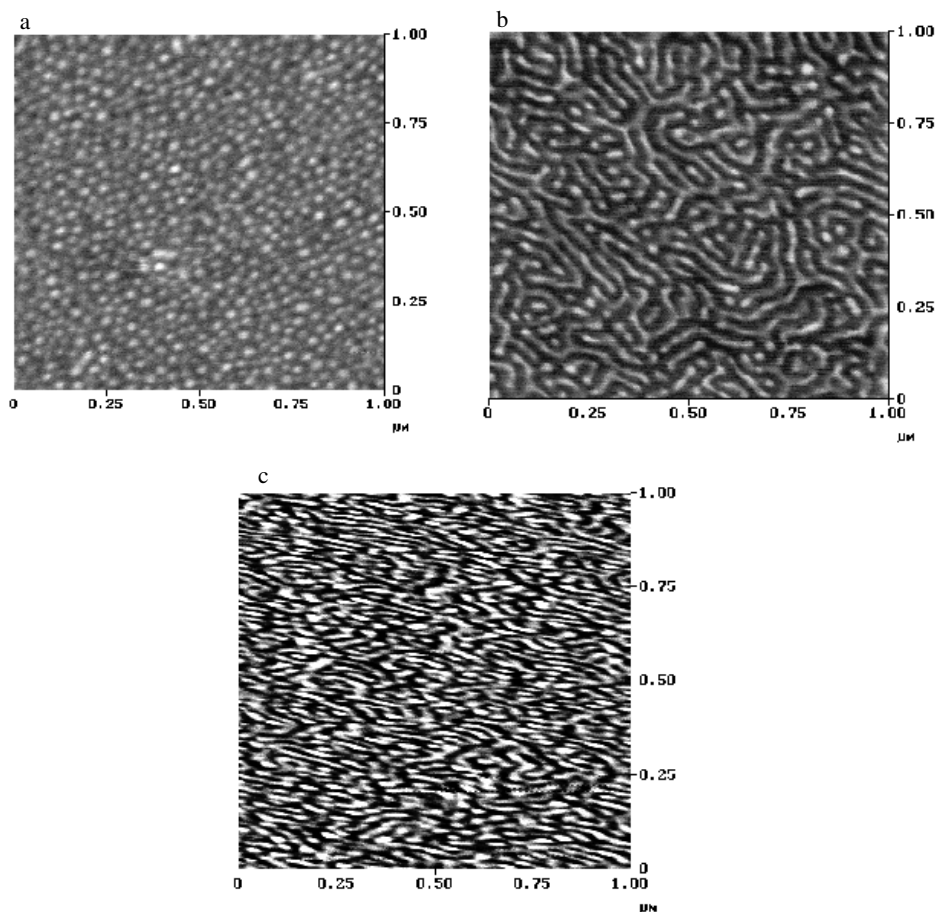


Figure 12.5 Morphology of PSt-*b*-PIB-*b*-PSt block copolymers with varying PSt content. a: 18 wt%; b: 34 wt% and c: 42 wt% (see also Fig. 12.4)

only spherical domains dispersed in a continuous PIB matrix [47, 63, 78]. Linear PSt-*b*-PIB-*b*-PSt triblocks with 40 wt% PSt exhibited a new, bicontinuous gyroid morphology [49]. The PSt morphologies mapped by AFM were found to be very similar to those seen by TEM [28, 29, 58]. Figure 12.5 shows the spherical/cylindrical, cylindrical/lamellar and bicontinuous morphologies exhibited by triblocks containing 20, 30 and 40 wt% PSt, respectively [28, 58, 59]. SAXS of linear PSt-*b*-PIB-*b*-PSt block with M_n (PIB) \approx 50,000 g/mol and 20–34 wt% PSt showed hexagonally packed PSt cylinders within the PIB continuous phase, with cylinder diameters of 14–21 nm. The interdomain distance was around 30–40 nm for all blocks, in line with the similar PIB sequence lengths [46].

Kaneka Inc. recently released characterization data of PSt-*b*-PIB-*b*-PSt produced by this company in semi commercial quantities. According to these data, summarized in Table 12.4 and illustrated in Fig. 12.6 (a-d), the heat aging resistance, weatherability, damping, gas permeability, and compression set of PSt-*b*-PIB-*b*-PSt are clearly superior to that of PSt-*b*-PBd-*b*-PSt.

In summary, PSt-*b*-PIB-*b*-PSt triblock copolymers are novel materials of considerable scientific and industrial interest. They hold promise for a variety of commercial applications including hot melt adhesives, medical, and biomedical applications [85–87], and vibration damping [88]. Thus, the recent commercialization of PSt-*b*-PIB-*b*-PSt by Kaneka Inc. solved the mystery G. Holden posited in his book *Understanding Thermoplastic Elastomers* [89] some three years ago:

“...PSt-*b*-PIB-*b*-PSt can be produced directly from readily available, low-cost monomers. All these facts should make PSt-*b*-PIB-*b*-PSt very competitive with PSt-*b*-P(EB)-*b*-PSt and analogs for many applications. Just why this potential has not been commercially exploited remains somewhat of a mystery.”

Table 12.4 Select Properties of Commercially Available Styrenic Block Polymers

	Methods	Units	SIBS	SEPS	SBS	SEBS
Capillary flow	200 °C, 1216 s ⁻¹	Poise	2500	9100	5100	7100
Hardness	JIS A	–	41	80	70	77
Tensile strength	JIS type 3 dumbbell	MPa	13	42	31	34
Elongation		%	620	480	860	500
Tensile modulus at 100% elongation		MPa	0.8	(3.7)	2.0	2.4
Tear resistance	JIS type B	KN/m	38	46	47	44
Compression set	70 °C, 22 h	%	60	(95)	97	80
tan δ	23 °C, 10 Hz		0.41	0.041	0.101	0.059
O ₂ gas permeability		($\cdot 10^{10}$) cm ³ cm/ (cm ² s cm Hg)	1.1		18.6	9.3
CO ₂ gas permeability			3.9		63.8	20.8
Water vapor permeability	40 °C, 90% RH	g/m ² 24h	0.23		18	2
Damping property rebound	23 °C	%	21	(61)	67	67

SIBS: $M_n = 100,000$ g/mol, St = 31 wt%

SBS: Shell, Kraton D 1102, $M_n = 117,000$ g/mol, St = 30 wt%

SEBS: Shell, KratonG 1650, $M_n = 107,000$ g/mol, St = 29 wt%

SEPS: Kuraray, Septon 4033, $M_n = 104,000$ g/mol, St = 30 wt%

(Compression set, damping property rebound: Septon 2007, $M_n = 87,000$ g/mol, St = 30 wt%)

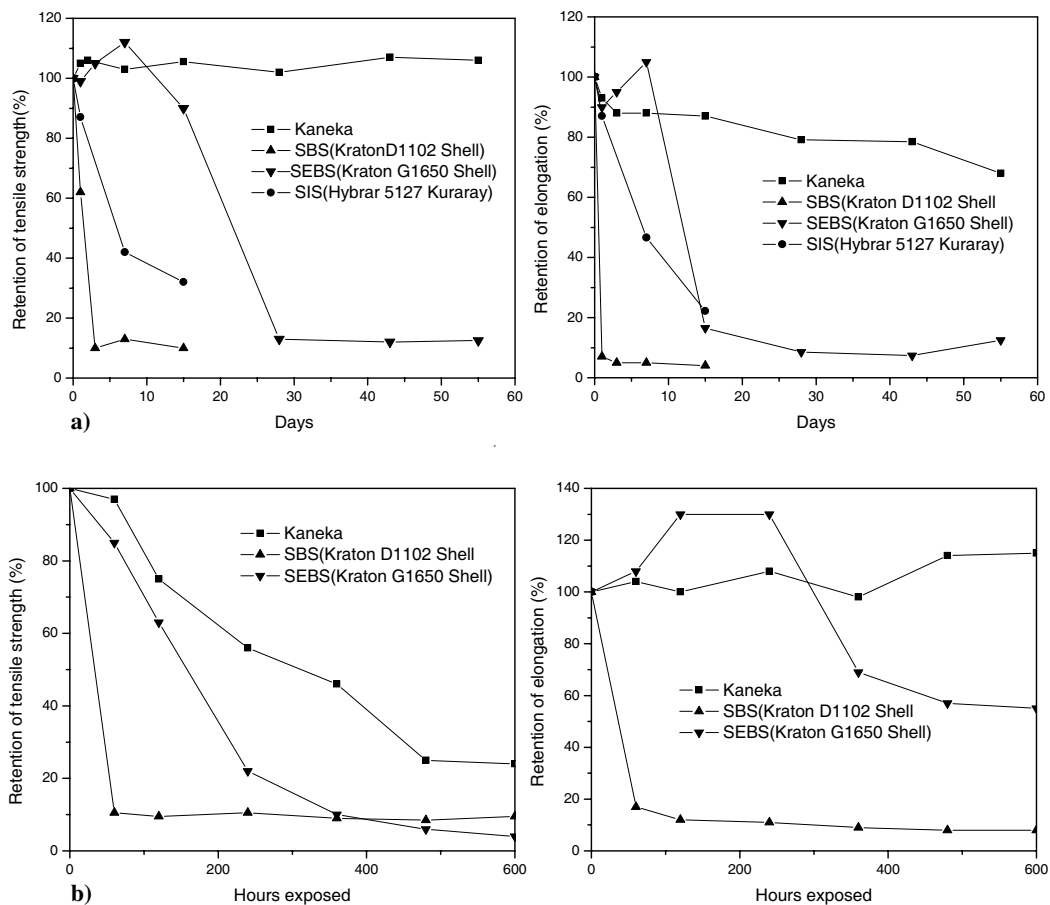


Figure 12.6 Comparison of select properties of $\text{PSt-}b\text{-PIB-}b\text{-PSt}$ with $\text{PSt-}b\text{-PBd-}b\text{-PSt}$, $\text{PSt-}b\text{-P(EB)-}b\text{-PSt}$, $\text{PSt-}b\text{-P(EP)-}b\text{-PSt}$ and crosslinked butyl rubber (SIBS, SBS, SIS and SEPS are abbreviations used by Kaneka for St-IB-St, St-Bd-St, St-I-St, and St-E-P-St, respectively)

a) Heat aging resistance at 150 °C

b) Weatherability by accelerated artificial exposure

(JIS A 1415, Sunshine Weatherometer, 23 ± 2 °C, black panel temperature)

12.2.2.1.2 Tri- and Multiarm Star-Blocks with PST

Figure 12.1 illustrated the structural similarities and differences between linear- and star-block TPEs. Incentives for the exploration of star-blocks comprising a rubbery core surrounded by a glassy corona are due to their ease of synthesis combined with superior mechanical properties and processibility, relative to linear triblocks of similar overall molecular weights and compositions.

In regard to syntheses, PIB-based star-blocks can be prepared at significantly higher temperatures (~ -40 °C) than those needed for the syntheses of triblocks (~ -80 °C). The effect of temperature on these polymerizations has been discussed in depth in [33]. In regard

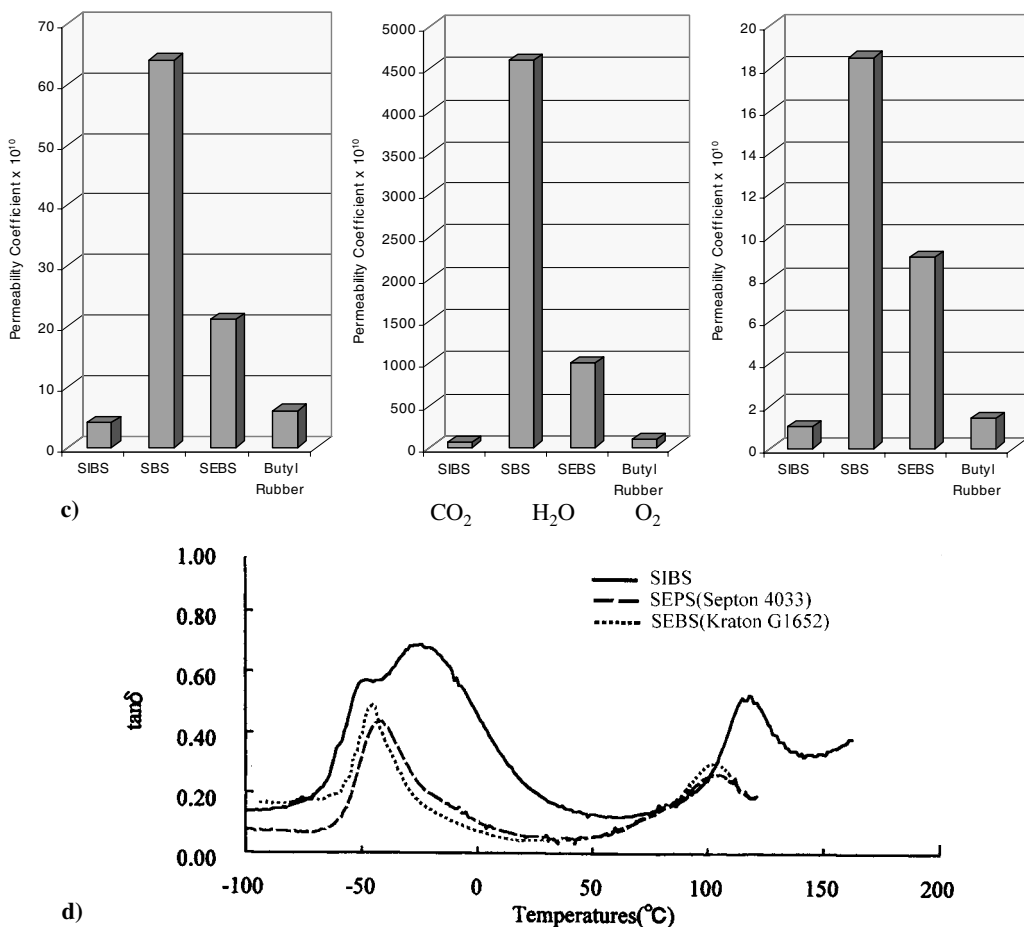


Figure 12.6 c) Gas permeability
d) Damping properties

to properties and processibility, multiarm star-blocks exhibit superior strength and lower modulus, combined with higher melt flow and shear stability [90].

TPE star-blocks comprising a star PIB core connected to PSt outer blocks have been prepared both by “core first” and “arm first” strategies [1, 19–24]. The first tri-arm star-block TPEs were prepared by the core first technique by the use of the tricumyl chloride trifunctional initiator in conjunction with TiCl_4 coinitiator [1, 17, 38]. This initiating system efficiently induced tridirectional living IB polymerization, and after the PIB^\oplus arms have grown to a desired length, St was added. This finding set the stage for further developments in PIB-based star-block TPEs.

Recently, the core first technique was employed for the synthesis of hexa- and octa-arm star-blocks, respectively, by the use of hexaepoxysqualene [24] and calyx [8]arene type of initiators [20–22], both in conjunction with TiCl_4 . The eight-arm star-blocks exhibited excellent TPE properties with up to 26 MPa tensile strength and more than 500% elongation, although they were contaminated by diblocks [21, 22].

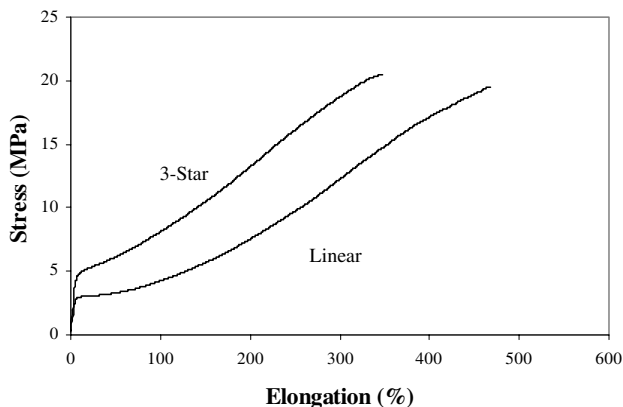


Figure 12.7 Comparison of tensile properties of linear triarm and star-block PIB-PS TPEs. PSt: 40 wt%, M_n (PIB) = 60,000 g/mol – linear, and 90,000 g/mol – three-arm star

Storey *et al.* used the arm first strategy to prepare star-blocks efficiently. The authors started with the living polymerization of St with the cumyl chloride/ $TiCl_4$ combination, followed by the addition of IB to the living PSt[⊕], and completed the synthesis by linking the living PSt-*b*-PIB[⊕] prearms with divinyl benzene [23]. The linking efficiency was ~ 92% after 1 h, and undesirable star-star coupling was negligible.

Figure 12.7 shows stress-strains traces of a linear tri-arm star-block with nearly identical PSt contents (~ 40 wt%) and arm lengths ($M_n = 30,000$ g/mol) [29].

Clearly, the three-arm star-block shows a higher modulus and lower elongation than the linear triblock, however the tensile strengths are almost the same. The higher modulus of the star-block is most likely due to the permanent trifunctional crosslink in the center of the star, which acts as an additional crosslinking point. Remarkably, a linear PSt-*b*-PIB-*b*-PSt with relatively short PSt blocks ($M_n = 5000$ g/mol) showed ~ 8 MPa tensile strength, while a tri-arm star with similarly short PSt blocks exhibited ~ 16 MPa strength [43].

Two decisive advantages of star-blocks over linear triblocks (at similar overall molecular weights and compositions) are superior processibility and shear stability. Improved processibility is due to the lower viscosity of stars over that of the linear analogues. Superior shear stability arises because multi arm stars or star-blocks can sacrifice one or more arms under shear without suffering noticeable deficit in overall properties, i.e., strength or viscosity.

In view of these facts, i.e., ease of synthesis, excellent physical properties, and superior processibility, we project that star-block TPEs will ultimately prevail over their linear counterparts and become the materials of choice in future commercial applications.

12.2.2.1.3 Arborescent Blocks with PSt

Figure 12.1 shows a cartoon of an arborescent block copolymer *arb*-PIB-*b*-PSt. These constructs comprise an arborescent (hyperbranched) rubbery PIB core connected to and surrounded by a glassy corona and therefore are related to multiarm star-blocks. Just as with the other PIB/PSt block copolymers, phase separation in *arb*-PIB-*b*-PSt is dictated by thermodynamics. The fundamental difference between multiarm star-blocks and arborescent

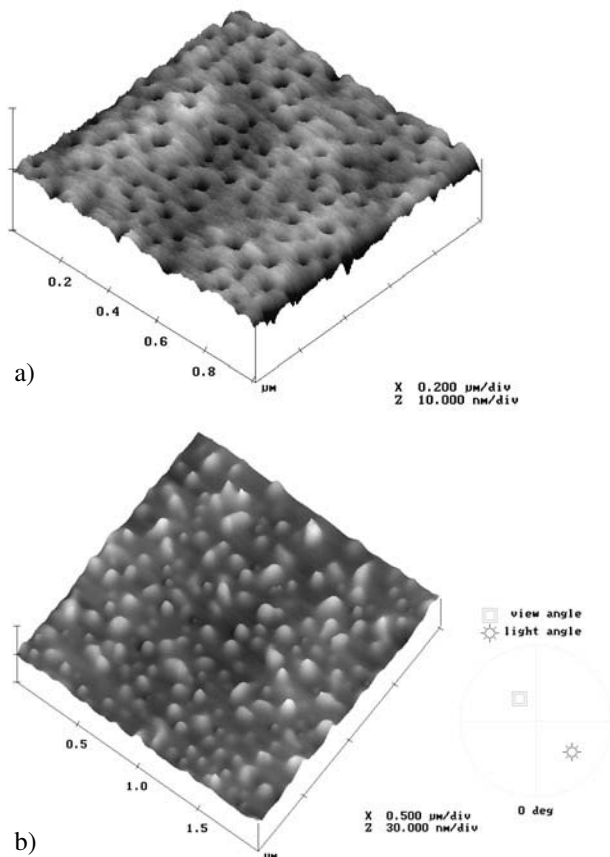


Figure 12.8 AFM images of arborescent PIB-PSt blocks containing 16.4 wt% PSt (a) and 33.8 wt% PSt (b)

blocks is that the (usually) well-defined hub in star-blocks is replaced by an irregular tree-like (arborescent) core in the latter. Arborescent blocks are similar to dendritic polymers, polymers that have recently generated considerable interest due to their unusual structure/property profiles [91–94].

Very high molecular weight *arb*-PIB-*b*-PSts were recently synthesized by copolymerizing in a living system IB and small amounts of an inimer (i.e., a compound combining in one molecule initiating and monomer functions) such as 4-(2-methoxy isopropyl)styrene [95–97]. Arborescent PIBs show some unique mechanical and viscoelastic properties [98–100]. Subsequent research showed that the reactive ends of arborescent PIB[⊕] arms can initiate the polymerization of St and thus *arb*-PIB-*b*-PSt has been obtained by sequential monomer addition in one pot. Surprisingly, in spite of their irregular phase morphology (see Fig. 12.8), these arborescent blocks displayed

TPE characteristics. Figure 12.9 shows representative stress/strain traces. These promising early developments provide incentive for the continued exploration of the synthesis, structure and properties of arborescent stars.

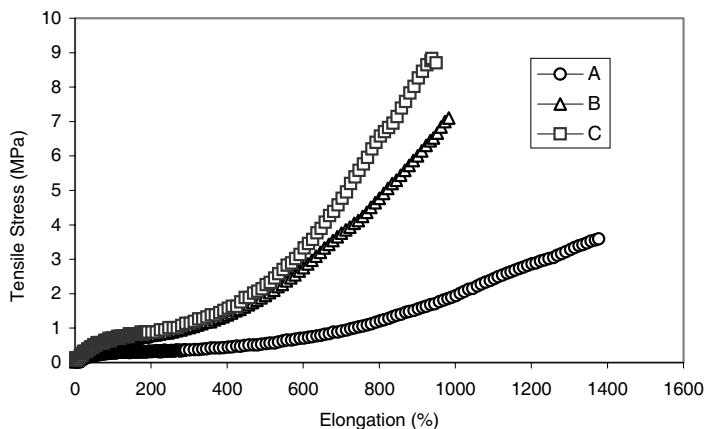


Figure 12.9 Stress/strain profiles of arborescent *arb*-PIB-*b*-PSt blocks
 A: $M_n = 534,200$ g/mol, PDI = 2.3, PSt = 26.8 wt%; B: $M_n = 556,100$ g/mol, PDI = 2.1, PSt = 30.7 wt%; C: $M_n = 550,400$ g/mol, PDI 2.1, PSt = 33.8 wt%

12.2.2.2 Glassy Block: Polystyrene Derivatives

After having presented evidence for the feasibility of syntheses by living cationic polymerizations of various PIB-based block copolymers containing PSt segments and having described the excellent TPE properties such materials exhibit, we now extend our discussion and briefly present advantages PSt *derivatives* offer to TPEs. Specifically, we outline possibilities for designing novel TPEs possessing higher use temperatures ($T_g > 100$ °C); controlling, indeed fine tuning, the T_g of the glassy blocks; decreasing flammability; and producing TPEs with low energy surfaces.

12.2.2.2.1 Linear- and Star-Blocks with P α MeSt

The incentive for the preparation of these blocks was the relatively high T_g of the P α MeSt segment (~ 173 °C) and low cost of the monomers. Also, because of its relatively low ceiling temperature [101] P α MeSt is rather difficult to synthesize by living anionic polymerization. Initial efforts to prepare P α MeSt-*b*-PIB-*b*-P α MeSt TPEs by cationic means were unsuccessful [18] or met with only limited success [59]. Faust reported the first efficient synthesis of PIB-based blocks with P α MeSt hard segments [60, 61]. The living PIB chain ends were end-capped with DPE, the $TiCl_4$ was deactivated by the addition of excess $Ti(OR)_4$, and $SnCl_4$ was used as Lewis acid for the blocking of α MeSt. A series of blocks were prepared, exhibiting excellent TPE properties with up to 25 MPa tensile strength. Samples with 20 wt% P α MeSt showed spherical hard domains (15–20 nm); at 30 wt% P α MeSt content cylindrical, while above 40 wt% lamellar morphology was observed. Similarly to blocks with PSt hard segments, optimum elastomeric properties were obtained in the 20–30 wt% hard phase range; above this value yielding and plastic fracture was observed.

12.2.2.2.2 Linear- and Star-Blocks with PpMeSt

PpMeSt-*b*-PIB-*b*-PpMeSt (T_g of PpMeSt ~ 108 °C) has been synthesized by the same method used for the preparation of the PSt-*b*-PIB-*b*-PSt. However, only a limited amount of information is available in regard to physical-mechanical properties [1, 18, 37, 56, 62]. In

one example, a *PpMeSt-b-PIB-b-PpMeSt* of $M_n = 18,000\text{-}b\text{-}78,000\text{-}b\text{-}18,000$ exhibited 14 MPa tensile strength, 9 MPa 300% modulus, 420% elongation, and 53 Shore A hardness [62]. Improved properties have been achieved by the modified synthetic method of DPE-end capping the di- or trifunctional PIB precursor, and modifying the strength of the TiC_4 coinitiator by the addition of $\text{Ti(IV)isopropoxide}$ [60, 62].

12.2.2.2.3 Linear Blocks with *PptBuSt*

The motivation for the synthesis of this triblock was the relatively high $T_g \sim 142^\circ\text{C}$) of the outer glassy segment and the commercial availability of the monomer. The procedure for the preparation of this TPE was similar to that used for the *PSt-b-PIB-b-PSt* parent [1, 18, 56, 64]. The triblock showed two T_g s ($\text{PIB} = -65^\circ\text{C}$, *PptBuSt* = 144°C), and its tensile properties and hardness were largely determined by the *PptBuSt* content. A representative triblock of $M_n \sim 100,000$ g/mol, with $M_w / M_n = 1.2$ and 40 wt% *PptBuSt*, exhibited 16 MPa tensile stress, 5 MPa 300% modulus, 550% elongation, and 76 Shore A hardness. In another example, *PpMeSt-b-PIB-b-PpMeSt* of $M_n = 17,500\text{-}b\text{-}78,000\text{-}b\text{-}17,500$ exhibited 16 MPa tensile strength, ~ 3 MPa 300% modulus, $\sim 600\%$ elongation, high ODT, and good moldability [56]. The stress-strain behavior of this family of materials was typical of elastomers. Interestingly, *PptBuSt-b-PIB-b-PptBuSt* showed unusually high melt flow indices [1].

12.2.2.2.4 Linear- and Star-Blocks with PInd

Ind, a potentially very inexpensive monomer obtainable from coal tar, is readily converted to PInd ($T_g \sim 220^\circ\text{C}$) by cationic means [3, 4]. The synthesis procedure to prepare *PInd-b-PIB-b-PInd* triblocks [1, 18, 64] was virtually identical to that used with St and St-derivatives, that is, addition of predetermined amounts of Ind to PIB^{\oplus} dications of predetermined molecular weight (see Section 12.2.2.2.1). Representative TPEs showed microphase separation into PIB and PInd domains by T_g (-65°C and 209°C) and electron microscopy, and again the stress-strain behavior was typical of elastomers [1, 65, 66]. A *PInd-b-PIB-b-PInd* of $M_n = 93,500$ g/mol (comprising $M_{n,\text{PIB}} = 54,000$ and $M_{n,\text{Pind}} = 19,600$) exhibited 20 MPa tensile strength, 17 MPa 300% modulus, 400% elongation, 60 Shore A hardness, and 15% tensile set. Owing to its saturated nature, this TPE exhibits good thermostability (95% weight retention up to 346°C in N_2 and 335°C in air). Melt viscosities were similar to that of *Kraton G*[®] [56].

12.2.2.2.5 Linear Blocks with PAC

In view of the very high T_g of PAC ($\sim 250^\circ\text{C}$), efforts have been made for the synthesis of PIB-based TPEs with this St derivative. While the living cationic polymerization of Ac could not be achieved, some circumstantial evidence has been presented for the synthesis of *PAC-b-PIB-b-PAC* carrying very short PAC blocks ($M_n \sim 900$ g/mol) [67]. A triblock contaminated with diblock (perhaps also PIB and PAC) containing 87 wt% PIB and 13 wt% PAC ($M_{n,\text{PIB}} \approx 65,000$) showed 15 MPa tensile strength at $\sim 800\%$ elongation. Because of the low PAC content the polymer was very soft: Shore 2A hardness 37–40 [67].

12.2.2.2.6 Linear and Star-Blocks with *PpClSt* and *PpFSt*

PIB-based TPEs with chlorinated styrenic glassy segments are of interest because of the combination of the relatively high T_g , polarity, and flame resistance of the hard block. In contrast to the living cationic polymerization of *pClSt*, the controlled anionic polymerization

of this monomer is difficult even at $-78\text{ }^{\circ}\text{C}$ owing to chlorine abstraction from the monomer by the lithium counterion [102]. The cationic synthesis, characterization, and some properties of well-characterized linear $PpClSt-b-PIB-b-PpClSt$ and three-arm star($PIB-b-PpClSt$)₃ have been described [68, 69]. Before the synthesis of triblock copolymers by sequential monomer addition, conditions for the living polymerization of $pClSt$ were developed [103]. Subsequently, the blocking of $pClSt$ from living $^{\oplus}PIB^{\oplus}$ and $^{\oplus}PIB^{\oplus\oplus}$ was achieved and the properties of the resulting block TPEs were studied [68, 69]. For example, a linear triblock of $PpClSt-b-PIB-b-PpClSt$ (63/37 wt% overall composition) containing a PIB midsegment of $M_n = 58,200\text{ g/mol}$ ($M_w / M_n = 1.11$), exhibited 21 MPa tensile strength, 15 MPa 300% modulus, 460% elongation, and 70 Shore A hardness. TEM showed cylindrical phase morphology (40–70 nm long, with 25–30 nm diameter). Stress-strain traces of various TPEs of this type were similar to those of typical rubbers.

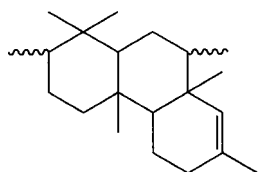
The syntheses of $PpFSt-b-PIB-b-PpFSt$ and star ($PIB-b-PpFSt$)₃ have been accomplished under conditions essentially identical to those used for the preparation of the pCl derivative. A linear block copolymer exhibited the expected TPE character [70]. In view of the presence of a significant quantity of fluorine in this product, we expect these TPEs to exhibit low surface energies.

12.2.2.3 Glassy Block: Cyclized Polyisoprene

A series of TPEs has been prepared in which the glassy outer segments are cyclopolyisoprene ($cyPIP$) [66]. Among the incentives for this effort was the simplicity of the synthesis, the low cost of the monomer, and the possibility for controlling the T_g of the TPE by controlling the length of the PIP blocks and their extent of cyclization. The synthesis of $cyPIP-b-PIB-b-cyPIP$ type TPEs involved three steps in one pot:

1. The living bifunctional polymerization of IB to $^{\oplus}PIB^{\oplus}$,
2. The addition of IP and formation of *tr*-1,4-PIP segments, and
3. The acid-induced cyclization of the latter to glassy $cyPIP$ segments; $T_g = 95\text{ }^{\circ}\text{C}$ to $190\text{ }^{\circ}\text{C}$, depending on the extent of cyclization.

The structure of cationically prepared $cyPIP$ has not been fully elucidated [71, 72]; among the glassy units may be structural elements of three or four fused rings, for example:



(12.4)

Although cyclization reduces the extent of unsaturation in the glassy segment, the product exhibited rather strong UV absorption, characteristic of conjugated double bonds [71, 72].

The tensile strength of extensively cyclized products increases with time. For example, the tensile strength and elongation of a product containing a PIB segment of $M_n = 55\ 000$ and 14.4 mol% $cyPIP$ changed from $\sim 0.5\text{ MPa}$ and $\sim 1250\%$ at 2 days to $\sim 10\text{ MPa}$ and 1100% after 34 days of storage at room temperature [71, 72]. This effect may be caused by progressive phase separation of the rubbery PIB and glassy $cyPIP$ microdomains.

12.2.2.4 Glassy Block: PMMA and PMMA Stereocomplexes

A series of PIB-based TPEs having PMMA glassy segments have been prepared by cationic \rightarrow anionic chain-end transformation. The multistep synthesis proceeded by first preparing a α,ω -ditolyl-PIB, lithiating it, adding 1,1-diphenylethylene (DPE), and initiating the polymerization of MMA by the latter intermediate [104]. A series of PMMA-*b*-PIB-*b*-PMMA with various compositions (molecular weights) have been synthesized, characterized (T_g s at -61 °C and 105 °C), and their physical-mechanical properties investigated [104]. The higher molecular weight products (e.g., those with segmental $M_n \approx 10,000 - 53,000 - 10,000$ g/mol) exhibited good mechanical strength (~ 15 MPa) at 600% elongation [104]. The PMMA segments in these products were essentially syndiotactic PMMA (sPMMA), with T_g somewhat higher than 100 °C. A modified procedure was reported recently where bi-directional living PIB chains were first end-capped with DPE, followed by metalation of the chain ends with K/Na alloy, and replacement of the K^+ with Li^+ . The lithiated chain ends were then used to initiate the anionic polymerization of MMA, yielding PMMA-*b*-PIB-*b*-PMMA triblocks. The triblocks displayed thermoplastic elastomeric behavior with 1.7–8 MPa tensile strength and 150–310% elongation, and phase separation ($T_{g,PIB} = -55$ °C, $T_{g,PMMA} = 94-110$ °C) [105].

Blends of sPMMA and isotactic PMMA (*i*PMMA) yield crystalline stereocomplexes in which the *s*- and *i*PMMA chains are in close contact resulting in a significant rigidification of the blend; the melting point of *i*PMMA-*s*PMMA stereocomplexes is in the 170 °C to 220 °C range (see [106] and references therein). With this in mind, efforts have been made to increase the use temperature of sPMMA-*b*-PIB-*b*-sPMMA by blending this triblock with *i*PMMA, in other words, by preparing PIB-based TPEs in which the outer segments were *i*PMMA-*s*PMMA stereoblock complexes [107].

Stereocomplexation significantly enhanced the mechanical properties, and experimental variables (e.g., segment molecular weight, complexation conditions, annealing, casting conditions, etc.) strongly affected the ultimate properties [107].

The synthesis of PMMA-*b*-PIB-*b*-PMMA by a combination of cationic polymerization (of IB) and group-transfer polymerization (of MMA) has been reported; however, the properties of the products were not investigated [108].

12.2.2.5 Glassy Block: Copolymers. Fine Tuning the T_g by Copolymerization

The T_g of a copolymer produced by the random copolymerization of two monomers falls in between the T_g s of the respective homopolymers. Ideal copolymerization of various substituted styrenic monomers was achieved under semicontinuous carbocationic conditions [109]. It has been demonstrated that *p*MeSt and Ind give close to random copolymers [110] and that the T_g of the copolymers is determined by the relative *p*MeSt/Ind composition. Thus the T_g of such random copolymers can be “fine-tuned” between the T_g s of the *P* α MeSt and PInd (see Table 12.2) [1, 18, 110].

This background knowledge has been used to prepare TPEs with glassy segments of predictable T_g s [1, 73]. Syntheses started by preparing a bifunctional living \oplus PIB \oplus of appropriate molecular weight ($M_n = 50,000$ to $70,000$ g/mol) and narrow dispersity ($M_w / M_n = 1.1$), and adding to this dication mixtures of *p*tBuSt + Ind [43, 51], or *p*MeSt + Ind [73]. The second step was the copolymerization of these styrenic monomers until a preselected