

Cationic Polymerization Astronomy. Synthesis of Polymer Stars by Cationic Means

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I. Introduction

This brief Account on carbocationic polymerization astronomy [astronomy is defined by Webster as the study of stars] concerns a survey of stars made by cationic techniques, their microstructures, and some thoughts on their properties. Star polymers are linear chains (arms) covalently attached to a core.¹ They are beautiful, interesting, and useful molecules challenging both the researcher and the technologist. Current strong interest in stars arose not long ago when it was rationalized that such molecules offer substantial processing advantages over their linear counterparts, i.e., they combine high molecular weights with low viscosities.

The preferred route to well-defined stars is by various living polymerization techniques^{2–4} which can lead to well-defined products both in terms of composition and microarchitecture, i.e., desired molecular weights, narrow molecular weight distributions, useful end groups. The synthesis of stars was first accomplished by living anionic polymerization^{2,3,5,6} with commercial consequences soon following, i.e., motor oil additives made of hydrogenated polyisoprene arms radiating from a cross-linked polydivinylbenzene (PDVB) core.⁷ These developments soon engendered other synthetic methodologies, i.e., stars by group transfer polymerization,⁸ and cationic techniques.^{9–14} The first star prepared by cationic chemistry, albeit only

with three arms, consisted of three polyisobutylene (PIB) arms radiating from a phenyl ring core.⁹ From this point on, developments rapidly accelerated, and today, a few short years later, it became worthwhile to survey the panorama of stars made by cationic techniques.

II. Synthesis

Figure 1 and Table 1 summarize the field: Figure 1 was constructed to provide a general outline of the synthetic options for cationically prepared stars, whereas Table 1 is a summary of specific systems subdivided according to the headings used in Table 1. The information is organized by increasing synthetic complexity.

II.1. Core-First or Arm-Growing Method. The simplest most straightforward method to stars is by the core-first (or arm-growing) method in which a multifunctional initiator induces the living polymerization of a monomer. The number of arms is controlled by the number of functions of the initiator and the molecular weight of the arm is controlled by $[M]/[I]$, where M = monomer and I = initiator, and the brackets are molar concentrations. If initiation is reasonably rapid relative to propagation and each potential initiating site is active, well-defined stars with narrow molecular weight distribution are obtained. In regard to microstructure, both the arms and the core can be well-defined. Indeed the very first cationic star polymers, albeit with only three or four arms, were made by a core first method. These stars were made by the use of 1,3,5-tri- $C(CH_3)_2Cl$ -substituted aromatic rings which in the presence of $TiCl_4$ induced the polymerization of isobutylene (see Table 1).^{9,20}

The great advantage of this method is that the arm ends remain living, and they can be nurtured to grow to any desirable lengths (molecular weights) or to start the polymerization of a second monomer, a process which leads to star-block copolymers. In this manner the core-first method was used to prepare star-blocks having arms of a rubbery block next to the core (inner core) and a glassy block at the outer rim of the corona (outer core); these materials are thermoplastic elastomers with desirable processing characteristics (see later).^{39–42,57,58,64–66} Otherwise, because of the living character of the arm termini, the cationic arm ends can be functionalized which opens avenues for the preparation of telechelic stars.^{37,38} This method has also been used to prepare three-, four-, and six-arm stars with poly(alkyl vinyl ether)^{21–25,26}, polytetrahydrofuran,^{27,28} polyoxazoline,^{29–32} and polystyrene^{33,34} arms (see Table 1). Star formation by the core-first route is much less diffusion controlled than in multifunctional arm-linking (see below) where steric hindrance is often limiting.

Recent interesting examples for the synthesis of well-defined eight-arm stars concern the use of calix[8]arene derivatives as initiators in conjunction with $BCl_3/TiCl_4$ mixtures, for the living polymerization of isobutylene,^{35–38} and for the block polymerization of isobutylene and styrene^{39,40} or isobutylene and *p*-chlorostyrene.^{41,42} The

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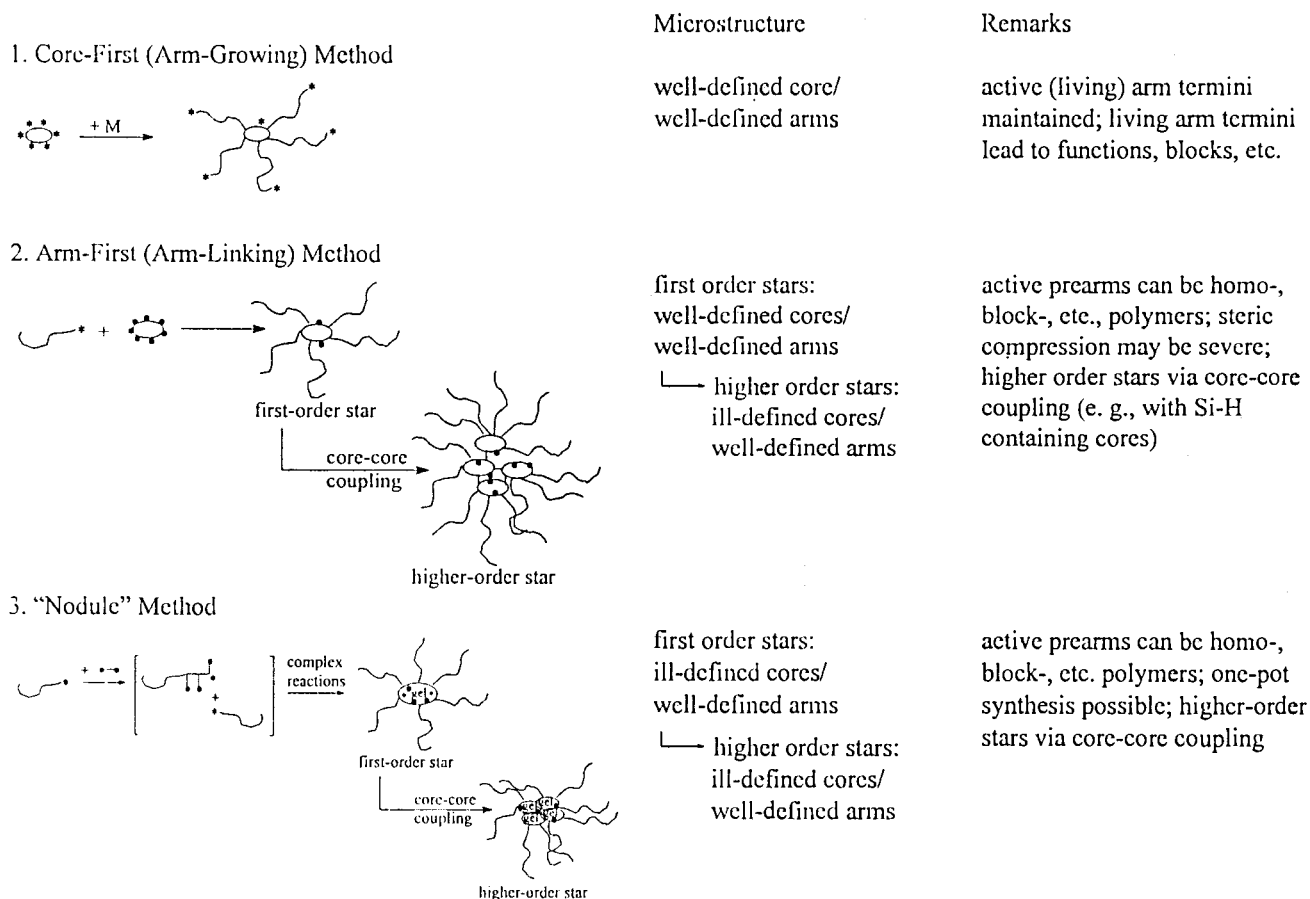


FIGURE 1. Outline of synthetic strategies for stars (M = monomer, * = living site, ● = reactive function).

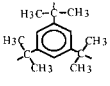
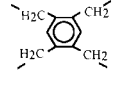
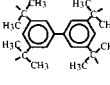
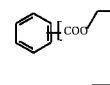
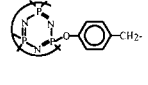
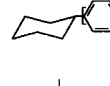
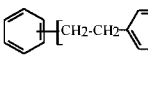
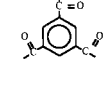
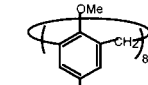
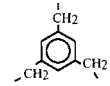
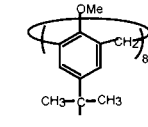
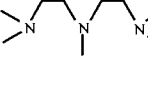
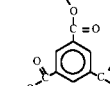
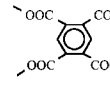
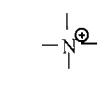
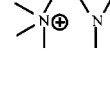
relative concentrations of BCl_3 and TiCl_4 are critical for the synthesis of well-defined ($M_w/M_n = 1.1$) eight-arm stars. These studies were extended to the preparation of allyl-ended stars^{37,38} useful for the downstream synthesis of telechelic stars; the allyl functionalization at the arm termini was quantitative by the use of allyltrimethylsilane.³⁷

II.2. Arm-First or Arm-Linking Method. The second somewhat more demanding route to stars, particularly well-defined stars, is by the arm-first (or arm-linking) method. By this route one first prepares reactive prearms (i.e., chains which will give rise to the arms) which are subsequently linked by a multifunctional linking agent to the final structure. The prearms can be living homopolymers,^{43–49,51} block copolymers,⁵⁰ etc., which upon linking will yield the corresponding stars. For example the linking of allyl-terminated PSt-*b*-PIB- blocks with D_6H lead to star-blocks with advantageous thermoplastic properties (see later). The number of star arms is controlled by the number of functional groups of the linking agent. Steric congestion at the linking site may be severe, particularly when the number of arm attachment points are above four or five which restricts the use of this method to stars with only a few arms. For example, a series of stars with polytetrahydrofuran arms have been assembled by quenching living THF polymerization by NH_3 ⁴⁷ (or amines) which in this case functions as a tetrafunctional linking agent (see Table 1). Multifunctional sodiomalonates,⁴³ silyl vinyl ethers,^{13,44} and cyclic

siloxanes containing Si-H groups^{48–51} have also been used as linking agents.

II.3. The "Nodule" Method. Finally the "nodule" method (so termed in deference to Rempp⁶ who first used this technique to make stars and called the cross-linked cores nodules) is complex conceptually but very simple experimentally. While the two other methods discussed above are easy to conceptualize but require at least two demanding synthesis steps, the nodule method is difficult to visualize but very easy to practice, and it usually requires only one step (one-pot process). The mechanism of the nodule method embraces a series of convoluted steps and defies rigorous analysis. Rempp's publication in which this method was first described⁶ was a purely intuitive *tour de force*, and only subsequent characterization research substantiated this seminal proposition. Many years later, after this methodology was adapted for the synthesis of stars by carbocationic systems, Kennedy et al.^{10,11,52–54} provided the first mechanistic interpretation of the nodule method. Briefly, the synthesis starts by producing living prearms to which a quantity of bifunctional monomer (the linking agent) is added; a diblock copolymer is formed the second block of which contains numerous unreacted functions (i.e., the second function of the linking agent), plus the living site. After a variety of ill-defined random simultaneous and consecutive reactions, a microgel core, the "nodule", is formed which carries the arms. The nodule is teeming with reactive functions and living sites. These complex and random

Table 1. Structural Elements of Stars Prepared by Cationic Methods^a

Core	Arms	Number of Arms	Ref.	Core	Arms	Number of Arms	Ref.
1. Core-First (Arm Growing) Method							
	PIB	3	4, 15-19		PTHF	4	28
	PIB	4	20	$\text{CH}_3\text{-CH}_2\text{-[C(CH}_2\text{-O-CO-)]}_3$	POX	3	29,30
$\text{Me-C[CH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{-CH(CH}_3\text{)]}_3$	PIBVE	3	21-25	$\text{.H}_2\text{C-C(CH}_2\text{)=CH}_2$	POX	4	31
	PIBVE	4	21		POX	4	32
	PIBVE	4	25, 26		PSt	6	33, 34
	PTHF	3	27		PIB	8	35-38
	PTHF	3	28		PSt- <i>b</i> -PIB- PpClSt- <i>b</i> -PIB-	8 8 8	39, 40 41, 42
2. Arm-First (Arm-Linking) Method							
$\text{CH}_3\text{-C[CH}_2\text{-O-C}_6\text{H}_4\text{-CO-CH}_2\text{]}_3$	PIBVE	3	13, 43, 44		PTBA	5	14
$\text{C[CH}_2\text{-O-C}_6\text{H}_4\text{-CO-CH}_2\text{]}_4$	PIBVE	4	13, 43, 44	D_5^{H}	PIB	5	48
	PTHF	3	45, 46	D_6^{H}	PIB	5	48
	PTBA	4	14	$\text{T}_8^{\text{D}^{\text{H}}}$	PIB	8	49
	PTHF	4	47	D_6^{H}	PSt- <i>b</i> -PIB-	6	50
	PTHF	7	47				
2a. Arm-First Followed by Core-Core Coupling							
D_6^{H}	PIB	20-24	51	D_6^{H}	PSt- <i>b</i> -PIB-	6-24	50
3. "Nodule" Method							
PDVB	PIB	8-100	10,11, 52-56	PDVB	PIBVE- <i>b</i> - PHOVE-	8-16	60-62
PDVB	PSt- <i>b</i> -PIB-	40-50	57-59	PDVB	P(<i>p</i> -OMe)St	7-50	63
PDVE	PIBVE	3-60	12				

^a Abbreviations used for arms: PDVB = polydivinylbenzene, PDVE = polydivinyl ether, PIB = polyisobutylene, PSt = polystyrene, IBVE = isobutyl vinyl ether, HOVE = hydroxyethyl vinyl ether, THF = tetrahydrofuran, POX = polyoxazoline, TBA = *tert*-butyl aziridine, D_n^{H} , where $n = 4, 5, 6,$ or 8 are, respectively, tetra-, penta-, hexa-, or octamethylcyclorosiloxane, $\text{T}_8^{\text{D}^{\text{H}}}$ = octa(dimethylsiloxy)octasilsesquioxane.

reactions extend way beyond the core-building stage and, simultaneously with core formation, coupling between the individual cores also starts to proceed (core-core coupling). Core-core coupling leads to higher-order stars (i.e., stars with a complex aggregate of covalently linked cores) and is indicated by multimodal GPC traces arising after many hours of synthesis. The appearance of complex GPC traces after long reaction times, particularly sharp peaks at low elution counts (high molecular weights), indicates the presence of high molecular weight higher-order stars formed by core-core coupling. If the arms are long, steric congestion prevents core-core coupling and uniform stars ($M_w/M_n < 1.3$) with a relatively low number of arms (~ 8) are formed.⁵³ While the number of star arms obtained by the nodule method is a complex function of reaction variables, it is not too difficult to prepare stars with very high (> 50) number of arms in this manner.^{11,52,53} The linking of living glassy-*b*-rubbery diblocks by the nodule method has also produced thermoplastic elastomers.⁵⁷⁻⁵⁹

In the case of stars with PIB arms and PDVB cores, the radial nature of the stars was demonstrated by core destruction analysis, i.e., by determining the molecular weight of the star, selectively destroying the aromatic core, and determining the molecular weight of the surviving aliphatic arms.¹¹ Thus, stars produced by the nodule method have well-defined arms and ill-defined cores.

III. Properties

III.1. Stars with Homopolymer Arms (Homo-Stars).

Justification for sustained interest in stars is mainly due to their rheological and processing properties. Specifically, the various viscosities, e.g., bulk, intrinsic, solution viscosities, of stars having relatively short arms are substantially lower than those of their linear counterparts of the same molecular weight.^{2,3,67} The linear viscoelastic properties of stars have been studied by many investigators^{2,67-72} who reported that these properties primarily depend on the arm molecular weight. Therefore, the processing of stars demands much less energy than those of equivalent linear chains. The viscosity of stars depends mainly on the arm molecular weight and much less on the number of arms or the molecular weight of the star.⁵⁴ The fact that the arms radiate from a relatively small common core increases the segment density distribution and reduces the coil dimensions relative to those of linear chains of the same molecular weight.⁷³⁻⁷⁶ Stars due to their branched structure have higher segment densities and consequently smaller polymer coil dimensions than linear polymers of the same molecular weight.⁷³⁻⁷⁶ Hence, the hydrodynamic volume of stars are much lower than those of linear chains of the same molecular weight.

Many groups have studied, by modeling and mathematical techniques, the effect of the number of arms, f , on various branching properties including the branching coefficient, g (the branching coefficient is the ratio of the radius of gyration of branched and linear polymers of the same molecular weight).⁷⁷⁻⁸⁵ The agreement between

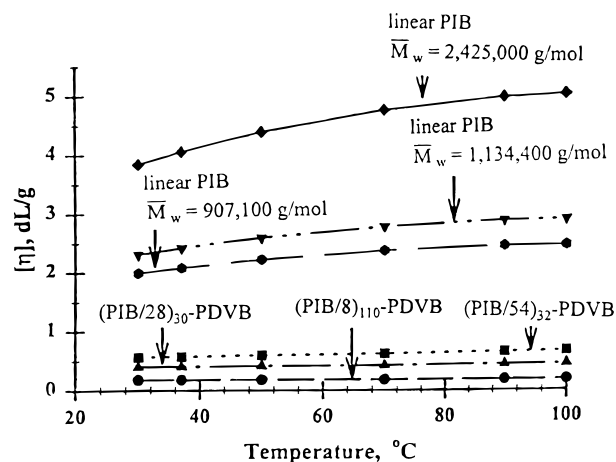


FIGURE 2. Variation of intrinsic viscosity as a function of temperature for various PIB-based stars and corresponding linear polymers. PDVB = polydivinylbenzene. The numbers after the slash mark are molecular weights $\times 1000$.

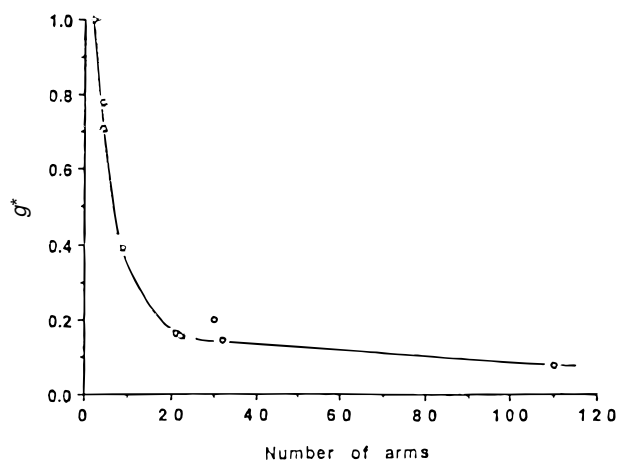


FIGURE 3. Plot of g^* values versus the number of arms.

experimental results was satisfactory for stars with $f > 8$ whereas at higher arm numbers Daoud and Cotton's scaling model provided good guidance.

Of the stars made by cationic techniques those with PIB arms have been studied in respect to solution and mechanical properties. Figure 2 shows the various products investigated and their intrinsic viscosities as a function of temperature.⁵⁴ The intrinsic viscosities of PIB-based stars are much lower than those of linear PIB chains of similar molecular weight. Figure 3 depicts the variation of g^* (i.e., $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$) as a function of the number of arms of PIB stars.⁵¹ The dependence of g^* on temperature shows an inverse relationship because $[\eta]_{\text{linear}}$ is more sensitive to temperature than $[\eta]_{\text{star}}$ (see Figure 2). The observed radius of gyration R_g of a PIB star with PIB arms and PDVB core suggested that the star in a good solvent (THF) assumes the shape of a rigid sphere rather than a random coil.⁵⁴ The slope of the $\log R_g$ vs M_w plot was 0.33 which also indicates a spherical conformation.⁸⁶

Stars of PIB arms radiating from a cyclosiloxane core exhibit outstanding chemical and thermal resistance.⁵¹ While siloxanes are very acid sensitive, 50% H_2SO_4 had practically no effect on these stars even after 3 weeks at 70 °C; in contrast, in xylene solution, the cores underwent

Table 2. Tensile and Dynamic Melt Viscosity Properties of Select PIB-Based Thermoplastic Elastomers

TPE structure	synth. meth.	<i>f</i>	glassy outer-core (wt %)	tensile (MPa)	elong. (%)	complex viscosity (η^* , poise)		ref
						$\omega = 1$	$\omega = 100$	
Triblocks ("two-arm star")								
(PSt/8- <i>b</i> -PIB/59) ₂	C-F	2	18	10.3	670	5.4×10^4	1.2×10^3	57, 58
(PSt/11- <i>b</i> -PIB/40) ₂	C-F	2	20	20.7	590	7.1×10^4	4.3×10^3	50, 90
Star-Blocks ^a								
(PSt/6- <i>b</i> -PIB/30) ₅₀ -PDVB	N	50		15.2	610			57, 58
(PSt/12- <i>b</i> -PIB/35) ₄₅ -PDVB	N	45		24.3	450	7.8×10^3	1.5×10^2	57, 58
(PSt/7- <i>b</i> -PIB/34) ₈ -C8	C-F	8	17	17.6	810			39, 40
(PSt/14- <i>b</i> -PIB/46) ₈ -C8	C-F	8	20	24.0	625	6.7×10^3	1.1×10^2	39, 40
(PSt/15- <i>b</i> -PIB/34) ₈ -C8	C-F	8	32	25.6	550			39, 40
(P <i>p</i> ClSt/11- <i>b</i> -PIB/38) ₈ -C8	C-F	8	22	21.9	650			41, 42
(P <i>p</i> ClSt/16- <i>b</i> -PIB/39) ₈ -C8	C-F	8	29	26.9	425			41, 42
(PSt/9- <i>b</i> -PIB/30) ₅ -D ₆	A-F	5	27	18.1	520	5.6×10^3	1.0×10^2	90
(PSt/12- <i>b</i> -PIB/33) ₁₆ -(D ₆) ₈ ^b	A-F	16	27	23.8	520			90

^a Cores: PDVB = polydivinylbenzene, C8 = calix[8]arene, D₆ = hexamethylcyclhexasiloxane; the numbers after the slash mark are molecular weights $\times 1000$. ^b Core-core coupled of ~ 8 D₆ cores.

rapid hydrolysis. Evidently in the absence of solvent, the acid-resistant tightly coiled PIB corona protects the vulnerable cyclosiloxane cores whereas in solution the corona swells and the core becomes exposed to the acid so that rapid degradation can ensue.⁵¹ Similar experiments were also carried out with the strong base *t*-BuOK.⁵¹ The thermal stability of PIB stars were essentially identical to that of linear PIB (5% decomposition at ~ 260 °C).⁵¹

The viscosity of stars is mainly a function of arm molecular weight which has important consequences in respect to their application as rheology control agents. Linear polymers, if their molecular weights are higher than their entanglement molecular weight M_e , degrade under shear with a corresponding viscosity decline. In contrast, star polymers of the same molecular weight have less entanglements so they may lose a few arms under shear; however, such a loss of a few arms has little effect on the viscosity.^{7,87} Thus, a star with 20–25 arms can lose 5–10 arms without appreciable viscosity deficit. In branched polymers, shear degradation preferentially occurs at the branch point and produces little change in the viscosity of the solution.⁸⁸ Indeed, stars were found to be superior to linear polymers as rheology control agents in lubricating oils (viscosity index improvers).⁷ The viscosity index of multiarm PIB stars was in the technologically desirable range and decreased the pour point of base oils.⁵⁴ On the basis of these studies, PIB-based stars may be of use as lubricating oil additives for automotive application.

III.2. Stars with Block Copolymer Arms (Star-Blocks).

Star-blocks with rubbery-*b*-glassy arms, specifically with a rubbery inner-core and glassy outer-core, are thermoplastic elastomers (TPEs), on account of their radial shape, exhibit much lower viscosities than conventional triblock TPEs (the latter can be viewed as "two-arm stars"). Table 2 summarizes some recent star-blocks with PIB inner-cores and styrenic outer-cores, together with microstructures, synthesis methods, arms numbers, and select mechanical and processing properties. Significantly, although these star-blocks were unpurified and contained 10–20% diblock contaminants, they exhibit excellent TPE characteristics. In view of the extraordinary sensitivity of the mechanical properties of linear TPEs to even small (<5%) amounts of diblocks contamination, the excellent

mechanical properties of star-blocks, containing a relatively high quantity of diblocks, is truly remarkable. The relative insensitivity toward diblock impurities is due to the high degree of interconnectedness of the glassy domains in the star-blocks. And because of this the strengths of the (contaminated) star-blocks are superior to those of the (pure) triblocks (see Table 2). Also, the molecular weight (or wt %) of polystyrene in the star-block is much lower than in the triblock for equivalent strength (see for example, entries 1 and 3 in Table 2). The products in Table 2 exhibit outstanding thermal and oxidative stabilities.^{40,89}

The dynamic melt viscosities of these star-blocks have been studied in comparison with triblocks having similar PSt contents. The plots showed characteristics of thermoplastic elastomers, i.e., absence of Newtonian behavior, even in the low-frequency region. The complex viscosities of the star-blocks were a few orders of magnitude lower than that of linear triblock with similar PSt content (see Table 2).^{39,40,57,58} Evidently, the star-blocks show better flow properties. It is known that the melt viscosities of TPEs depend mainly on the relative PSt contents and PSt block lengths.^{91,92} Leblanc⁹³ observed that the activation energy for flow for poly(styrene-*b*-butadiene) stars was lower than that of similar linear triblocks with comparable PSt content, and it was hypothesized that aggregates of stars flow.

IV. Conclusions and Glimpse into the Future

Cationic polymerization astronomy is a young energetically growing discipline, equally challenging the scientist and technologist. It has brought forward a series of fundamentally new materials with a combination of desirable ultimate properties. The main justification for contemporary interest in stars derives from their advantageous viscosity properties. They combine high molecular weight with low viscosities. We have organized a large amount of disparate information in terms of synthesis principles which lead to a three-tier hierarchy (see Figure 1 and Table 1 with specifics). Scientific developments will most likely move toward the design and synthesis by living polymerization of novel microstructures expected to lead

to new stars with a combination of useful new properties. The versatility of demonstrated preparative methodologies already in place (i.e., the synthesis of homopolymer and diblock copolymer arms) point toward possible new developments in additives for lubricating oils and easily processible thermoplastic elastomers. Yet-unexploited innovations on the horizon include telechelic stars, i.e., stars with $-OH$, $-NH_2$, etc., termini, for applications in adhesives and coatings.

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