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14. ABSTRACT A novel hydrocarbon-soluble trifunctional organolithium initiator, with no polar-additive requirements, has been synthesized for anionic polymerization. The complete synthesis of the unsaturated tri-Diphenylethylene compound 4,4,4-(ethane-1,1,1-triyl)tris(((3-(1-phenylvinyl)benzyl)oxy)benzene) is described and the efficiency of the final product has been evaluated using ¹ H NMR and NALDI-TOF MS. Activation of initiator was performed in-situ using stoichiometric amounts of sec-BuLi. Three arm Polystyrene and Polyisoprene stars with narrow molecular weight distribution were obtained over a low, narrow molecular weight. The 'living' nature of the					
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Report Title

Final Report: Synthesis of Novel Hydrocarbon Soluble Multifunctional Anionic Initiators: Tools for Synthesis of Novel Dendrimer and Molecular Brush Polymer Architectures. Research Area:7.4

ABSTRACT

A novel hydrocarbon-soluble trifunctional organolithium initiator, with no polar-additive requirements, has been synthesized for anionic polymerization. The complete synthesis of the unsaturated tri-Diphenylethylene compound 4,4,4-(ethane-1,1,1-triyl)tris(((3-(1-phenylvinyl)benzyl)oxy)benzene) is described and the efficiency of the final product has been evaluated using ¹H NMR and NALDI-TOF MS. Activation of initiator was performed in-situ using stoichiometric amounts of sec-BuLi. Three arm Polystyrene and Polyisoprene stars with narrow molecular weight distribution were obtained even at low, per branch, molecular weight. The 'living' nature of the polymerization was confirmed by the sequential polymerization of styrene, and isoprene. The branching parameter g' values of the final branched polymers were measured and are in good agreement with g' values of three arm stars from the literature.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
01/26/2015 4.00	Tianzi Huang, Xiaojun Wang, Thomas Malmgren, Kunlun Hong, Jimmy W. Mays. Thermal Stability of Fluorinated Polydienes Synthesized by Addition of Difluorocarbene, Macromolecular Chemistry and Physics, (01 2012): 0. doi: 10.1002/macp.201100548
01/26/2015 5.00	Xiaojun Wang, Thomas Malmgren, Tianzi Huang, Jimmy W. Mays. Enhancing stability of poly(1,3-cyclohexadiene)-based materials by bromination and dehydrobromination, European Polymer Journal, (3 2012): 0. doi: 10.1016/j.eurpolymj.2012.01.003
TOTAL:	2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Optimization of Macromolecular Architecture in Styrene/Diene Block Copolymer Thermoplastic Elastomers”, Jimmy Mays, invited presentation at Fraunhofer-Institut für Werkstoffmechanik, Halle, Germany, July 11, 2013.

“Optimization of Macromolecular Architecture in Styrene/Diene Block Copolymer Thermoplastic Elastomers”, J. W. Mays and Samuel P. Gido, invited lecture at Case Western Reserve University, March 8, 2013.

“Optimization of Macromolecular Architecture in Styrene/Diene Block Copolymer Thermoplastic Elastomers”, J. W. Mays, S. Gido, R. Weidisch, invited lecture at the DYNACOP Final Conference on Dynamics of Architecturally Complex Polymers: Current and Future Trends, Leeds, England, December 12-14, 2012.

“Polymer Synthesis at and Beyond the Limits of Characterization: Limitations of SEC”, J. W. Mays, invited Keynote Speaker, NIST Workshop on Macromolecular Separations-By-Design, Gaithersburg, MD, October 10 – 11, 2012.

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

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(d) ManuscriptsReceivedPaper

01/26/2015	6.00	. Synthesis of Trifunctional Organolithium Initiator and Anionic Polymerization in Hydrocarbon Solvents in the Absence of Polar Additives , ()
03/10/2012	1.00	Akinbode I. Isaacs Sodeye, Tianzi Huang, Samuel P. Gido, Jimmy W. Mays. Polymer Electrolyte Membranes from Fluorinated Polyisoprene-block-Sulfonated Polystyrene: Membrane Structure and Transport Properties, Polymer (10 2010)
03/10/2012	2.00	Akinbode I. Isaacs Sodeye, Tianzi Huang, Samuel P. Gido, Jimmy W. Mays. POLYMER ELECTROLYTE MEMBRANES FROM FLUORINATED POLYISOPRENE-BLOCK-SULFONATED POLYSTYRENE: STRUCTURAL EVOLUTION WITH HYDRATION AND HEATING, Polymer (05 2011)
03/10/2012	3.00	Akinbode I. Isaacs Sodeye, Tianzi Huang, Samuel P. Gido, Jimmy W. Mays. POLYMER ELECTROLYTE MEMBRANES FROM FLUORINATED POLYISOPRENE-BLOCK-SULFONATED POLYSTYRENE: MICRODOMAIN ORIENTATION BY EXTERNAL FIELD, Polymer (09 2011)

TOTAL: 4**Number of Manuscripts:**

BooksReceivedBook**TOTAL:**

Received

Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2010 Founding Fellow, ACS Division of Polymer Chemistry.

2010 Gold Medal of the Greek Polymer Society.

2011 Herman Mark Senior Scholar Award, ACS Division of Polymer Chemistry.

2011 Outstanding Alumni Award, University of Akron.

2011 Fellow, American Chemical Society.

2012 Fellow, ACS Division of Polymeric Materials Science and Engineering.

2012 Fellow, American Association for the Advancement of Science.

2013 Bill & Melinda Gates Foundation Grand Challenges Explorations Award.

2014 Fellow, Royal Society of Chemistry.

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Chris Hurley	0.75	
FTE Equivalent:	0.75	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Jimmy Mays	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

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Names of Personnel receiving masters degrees

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Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

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Sub Contractors (DD882)

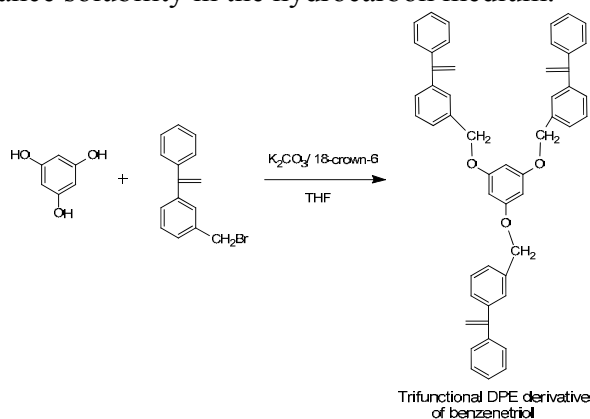
Inventions (DD882)

Scientific Progress

Technology Transfer

Final Project Report, Synthesis of Novel Hydrocarbon Soluble Multifunctional Anionic Initiators, PI Jimmy Mays

In this project, we have carried out what we proposed as a high risk, high payoff effort to finally synthesize efficient trifunctional and multifunctional anionic initiators that can be used in hydrocarbon media to efficiently polymerize dienes via living polymerization to high 1,4-polydienes. Our strategy has been to use alkyllithium reagents derived from multiply functionalized 1,1-diphenylethylenes (DPEs) bearing bulky substituents and separated through ether or ethylene oxide linkages. Such a strategy should minimize aggregation and improve solubility in hydrocarbon solvents. Our new multifunctional anionic initiators also limit resonance delocalization of anions with a methylene ether or ethylene oxide bridge at the meta-position of every DPE unit in the core molecule (**Scheme 1**). This imparts flexibility around the spacer and avoids extensive aggregation. Moreover, we are investigating using a long alkyllithium, such as undecyllithium for adduct formation with the diphenylethylene domains of the precursor initiator to enhance solubility in the hydrocarbon medium.



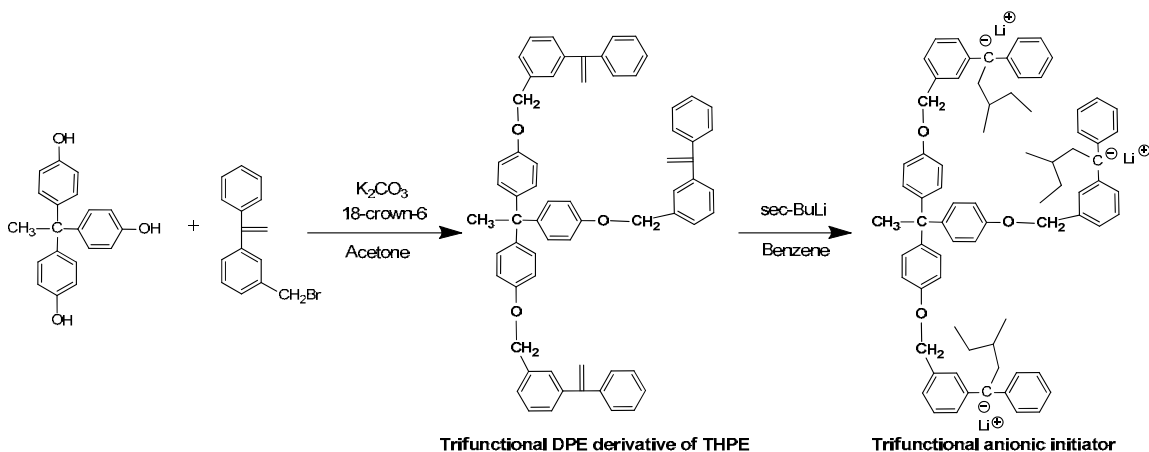
Scheme 1: Synthesis of tris-(diphenylethylene)methylether derivative of benzenetriol

Failure of the synthesis of trifunctional carbanionic initiator using benzenetriol as precursor:

We first attempted to make trifunctional diphenylethylene derivative using benzenetriol as precursor. Accordingly, 1-(*m*-bromomethylphenyl)-1-phenylethylene (BrMDPE) was synthesized using *m*-methylbenzophenone via the Wittig reaction. The obtained BrMDPE (~60 % yield) was thoroughly characterized using ^1H and ^{13}C NMR. The Williamson etherification of BrMDPE with benzenetriol was performed in acetone under reflux in the presence of K_2CO_3 and 18-crown-6. Unfortunately, the rigid, planar, benzenetriol core moiety did not undergo etherification efficiently (**Scheme 1**). Limited solubility of benzenetriol during the alkylation reaction was attributed to poor selectivity and product yield. *We obtained incomplete reaction and multiple alkylated products, and it was difficult to separate the products using column chromatography. After much work this approach was abandoned.*

Successful synthesis of trifunctional carbanion using tris(4-hydroxyphenyl)ethane as precursor:

We thus switched to another more flexible and highly soluble core moiety, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) for the alkylation reaction with BrMDPE (**Scheme 2**). The etherification proceeded smoothly with this compound in the presence of K_2CO_3 and 18-crown-6 in acetone at refluxing conditions for 10 h. The reaction product contained mono-, di- and tri-substituted THPE with MDPE. Using column chromatography, the individual compounds were isolated and the targeted product, 1,1,1-tris(4-methoxyphenyl-1-phenylethylene)ethane (TMPPEE), was characterized by 1H NMR (**Figure 1**).



Scheme 2: Synthesis of 1,1,1-tris(4-methoxyphenyl-1-phenylethylene)ethane (TMPPEE) and its *sec*-BuLi adduct formation.

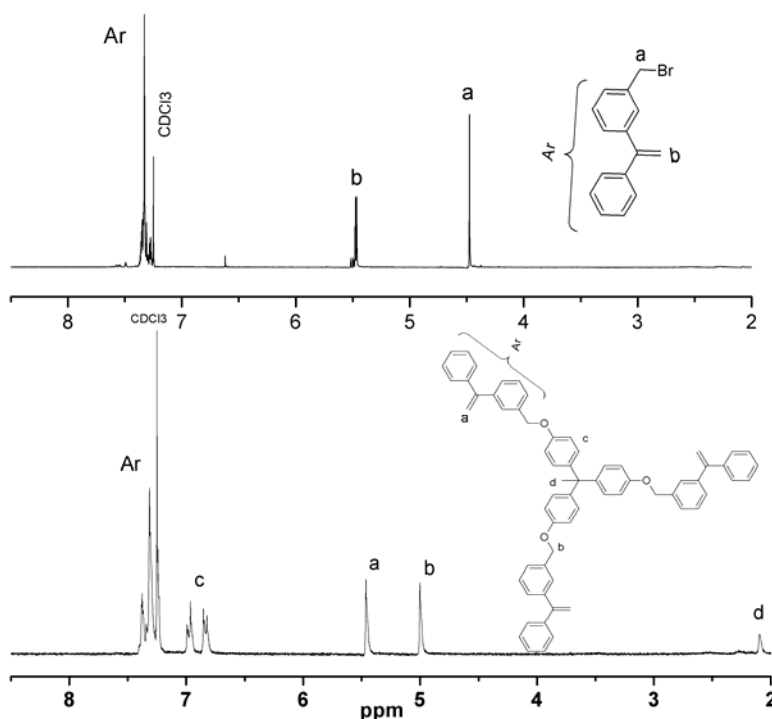


Figure 1: 1H NMR of 1,1,1-tris(4-methoxyphenyl-1-phenylethylene)ethane (TMPPEE)

The DPEs of the TMPPEE were reacted with an equimolar amount of sec-BuLi in benzene at room temperature. Upon addition of sec-BuLi, the pale-yellow color of the TMPPEE solution in benzene changed immediately to reddish-orange indicating formation of the three carbanions (**Figure 2**). Interestingly, the solution remained stable under stirring conditions, but on standing for an hour without stirring at room temperature a gel-like precipitate settled partially, which disperses nicely into solution with stirring. It appears that the tri-carbanion-containing TMPPEE initiator is in equilibrium with aggregated species in benzene. Unlike other reported multifunctional carbanionic initiators, however, this initiator produces a homogeneous suspension in benzene, which is stable at room temperature. We have repeated the synthesis of this initiator on a larger scale and are able to achieve 87 % yield in a simple 2-step reaction. Thus, this initiator could be readily synthesized by others so that it could become widely used in anionic polymerization, even industrially.



Figure 2: Solution of trifunctional TMPPEE-BuLi adduct in benzene.

Evidence for aggregation in the polymerization of styrene and isoprene in benzene at low initiator concentrations ($C < 2 \times 10^{-3}$ M):

The polymerization of styrene was carried out using this initiator in benzene at room temperature. Here we emphasize that it is critical, in our opinion, to use high vacuum techniques and butyllithium purged, all glass sealed reactors in the initial work with such an initiator to insure that there are no terminating impurities present that could deactivate some anions and lead to a mixture of linear (2-arm) and 3-arm star products. We employed specialized techniques that we have previously described in detail. Thus any difficulties observed in our work can be attributed to problems with the initiator rather than experimental conditions (impurities).

Upon addition of styrene to the active TMPPEE initiator, the color of the solution changed from orange to deep yellow. However, at the end of the polymerization, it was noticed that the color of the reaction mixture did not immediately disappear in regions of the reaction mixture upon addition of methanol. The observation that the color of reaction mixture disappeared slowly in the presence of methanol confirms that a portion of trifunctional initiator is highly stabilized via aggregation. The PDI of several polystyrenes made thus far using this initiator are in the range of 1.2 to 1.25 (**Figure 3**). Note that a rather sharp distribution is obtained with tailing at low molecular weights. Very high molecular weights may also be achieved (**Figure 3**). This would be considered a narrow PDI for most controlled/living polymerizations and the initiator even at this stage could be considered a success, however we are convinced that because of the aggregation initiation is not efficient, leading to tailing at low molecular weight, and the aggregation also creates heterogeneity in the polymerization medium. Furthermore, the recovered polystyrene from the reaction exhibited somewhat higher molecular weight, taking into account the effects of branching, than theoretically calculated based on the feed ratio of monomer to initiator. This suggests that some of the anions that exist in aggregated form did not contribute to initiation and thus the product is almost certainly a mixture of linear polymer and 3-arm star.

The polymerization of isoprene using the trifunctional organolithium TMPPEE initiator at low concentration was performed using high vacuum technique according to standard

protocol. The polymerization was performed in a custom glass reactor containing ampoules of *sec*-butyllithium (0.36 mmol), the unsaturated TMPPEE (0.113 mmol), isoprene (4.85 g, 71.2 mmol), methanol (~ 1 mL) and a purge flask with a solution of *n*-butyllithium in benzene. The main reactor for polymerization was washed with the purge solution to remove impurities from the glassware. The *n*-butyllithium was subsequently removed by repeated distillation of benzene from the purge flask. The initiator precursor TMPPEE and *sec*-BuLi were sequentially added to the reactor containing 300 mL of benzene by fracturing the break-seals which resulted in the immediate development of a yellow color, transitioning to orange and finally to red within five minutes. After 14 hours the solution was observed to be opaque orange in color with visible aggregates in solution. The isoprene added to the solution by fracturing the break-seal and the color converted to a pale yellow. The polymerization was terminated by degassed methanol after 24 hours. The resulting polymer was of higher than expected molecular weight and broad molecular weight distribution.

It must be emphasized that this aggregation behavior of the trifunctional initiator in hydrocarbon solvents is in no way surprising but was anticipated based upon our extensive prior experience with similar dilithium initiators. In our prior work with a “double DPE initiator”, addition of lithium *sec*-butoxide in varying ratios caused PDIs to be reduced from 1.2 (no butoxide) to 1.03 when the butoxide to initiator anion ratio was 14. Also, in the absence of butoxide gelation was seen in the reactor and the color of the anions failed to disappear completely upon addition of methanol, in agreement with earlier work by Tung. Addition of appropriate amounts of lithium *sec*-butoxide eliminated these problems and a highly efficient and useful difunctional initiator was obtained and subsequently used to generate a host of well-defined controlled architecture polymers and copolymers.

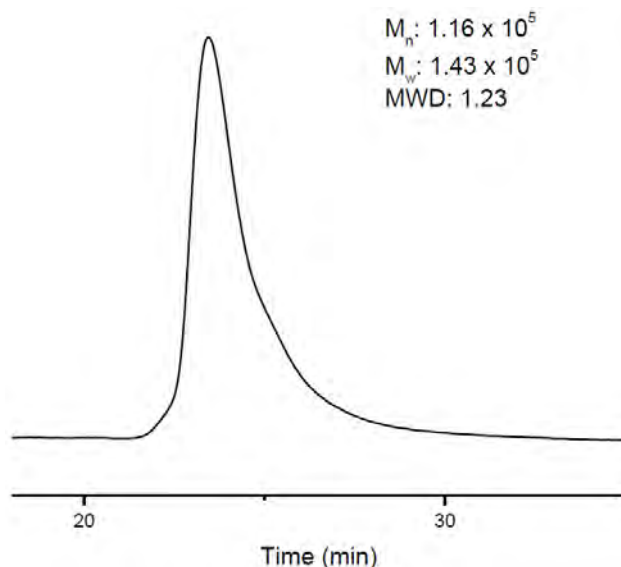


Figure 3. SEC of PS made with the trifunctional initiator of Scheme 2 (note tailing at low MW).

Synthesis of Near-Monodisperse PS and PI Stars at High Initiator Concentrations ($C > 2 \times 10^{-3}$ M)

Before exploring the use of polar additives, we decided to investigate the effect of initiator concentration on the polydispersity of the star polymers synthesized using the new initiator. Our motivation here is the fact that aggregation of organolithium compounds is concentration dependent and in our system there is a complex competition between intramolecular aggregation and intermolecular aggregation which should be shifted upon changing concentration.

Polymerizations of styrene and isoprene were carried out in all glass, custom-made, evacuated, *n*-BuLi-washed and benzene-rinsed reactors. The reagents were added *via* break-seals, for characterization purposes aliquots were removed by heat-sealing at constrictions. Styrene and isoprene were polymerized in benzene using trilitium initiator of TMPPEE in the absence of any polar additive. Deliberate termination was completed using degassed methanol. Polymerization was performed in a custom made glass reactor equipped with ampoules containing *sec*-BuLi (1.08 mmol), TMPPEE (0.345 mmol in 10 mL of benzene), styrene (10 g, 96 mmol), and methanol (2 mL). Initially, the ampoules with TMPPEE and *sec*-BuLi were introduced by smashing the break-seals in the reactor containing 130 mL of purified benzene and left to react overnight at room temperature. The solution after couple of minutes obtained a pale yellow color that within minutes (~30 min) turned into orange and finally accumulated a clear red-orange color (next day). Then, styrene was added in the reactor the color fade from red-orange to orange-yellow and left to polymerize for 20 hours before the polymerization was terminated by the degassed methanol.

The three-arm PS and PI stars exhibit very narrow molecular weight distributions ($M_w/M_n \leq 1.06$) in all cases, with very high initiator efficiency. As shown in Table 1, the molecular weights determined from light scattering are very close to the theoretical ones which lead us to the conclusion that all initiator molecules participate in the polymerization and more importantly that all initiation centers are essentially equally efficient. Our last conclusion is supported from viscometry studies discussed below. Only in our first polymerization using the trifunctional initiator a small excess of *sec*-BuLi was used (3-4% compared to the double bonds) and a second peak with higher molecular weight was seen in the SEC eluogram which was attributed to linear PS (Figure 4). The two peaks were separated by fractionation and the star branch structure was confirmed through the measurement of g' .

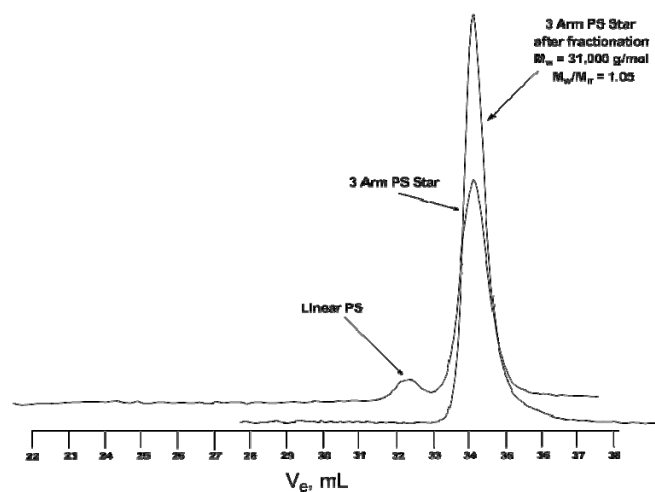


Figure 4. SEC chromatograms for the three-arm star PS before and after fractionation.

Table 1

Entry	Sample	$C_I \times 10^7$ (mol/mL)	M_n (th) $\times 10^{-3}$ (g/mol)	M_w/M_n^b	$M_w \times 10^{-3}$ (g/mol)	$[\eta]_{\text{star}}^f$ (dL/g)	g'	k_H^f
1	PI	3.7	43	1.47	306 ^c	-	-	-
2	PI	7.5	47	1.48	225 ^c	-	-	-
3	PI	55.5	10	1.03	11 ^d	0.163	0.84	0.37
4	PS	12.6	81	1.23	116 ^c	-	-	-
5	PS	21.3	29	1.05	31 ^d	0.148	0.81	0.43
6	PS ^a	62.0	8	1.06	X ^e	0.078	0.82	0.41
7	PS- <i>b</i> -PI	21.3		1.09	X ^d	-	-	-

^a PS end-capped with (CH₃)₃-Si-Cl, determined by ^b Size Exclusion Chromatography in THF, ^c determined by Low Angle Laser Light Scattering in Cyclohexane (PI) and Toluene (PS) at 25 °C, ^d determined by laser light scattering with a laser of 809 nm at 15° and 90° angles using dn/dc values of 0.186 mL/g and 0.128 mL/g for PS and PI, respectively, ^e determined by ¹H NMR, and ^f determined by viscometry in Cyclohexane (PI) and Toluene (PS) at 35 °C.

To further confirm the branched architecture and determine the functionality, g' values were measured and compare to the ones reported in the literature for 3-arm stars. As is well known, star polymers have smaller hydrodynamic volume, smaller radius of gyration, R_g , and smaller intrinsic viscosity, $[\eta]$, as compared to linear polymers with the same composition and molecular weight. So, through measurements of intrinsic viscosity of the branched and the corresponding linear polymers, g' values may be determined from the equation below:

$$g' = [\eta]_{\text{br}}/[\eta]_{\text{lin}} \quad (1)$$

The absolute molecular weights of the polystyrene star in toluene, and of polyisoprene star in cyclohexane were determined by light scattering and through the following equations, the intrinsic viscosities of the linear analogous were determined.

$$[\eta]_{\text{lin}} = 9.27 \times 10^{-3} M_w^{0.734} \quad \text{PS in toluene (2)}$$

$$[\eta]_{\text{lin}} = 1.97 \times 10^{-2} M_w^{0.733} \quad \text{PI in cyclohexane (3)}$$

In Table 1 the values of intrinsic viscosities of the star samples, the g' , and the Huggins coefficients k_H are shown. The k_H coefficient was determined from the slope at the Huggins plot (4) and provides additional proof of the polymer's branched structure.

$$\eta_{\text{sp}}/c = [\eta] + K_H [\eta]^2 c \quad (4)$$

Literature values of g' for three-arm star polymers are in the range between 0.8 and 0.94,² but especially for three arm PS stars the values obtained in toluene at 35 °C are between 0.81 and 0.85. These values are in very good agreement with the ones obtained from viscometry, in the same solvent and at the same temperature, for our two PS samples. Also, g' values are sensitive to the asymmetry of the arms. It has been shown that PS stars with three arms of different molecular weights have increased g' values (~ 0.92). An additional evidence that the obtained polymers have star branch structure comes from Huggins coefficient, k_H . The increased value of the Huggins coefficients for our materials, as compared to the ones obtained for analogous linear polymers in good solvents ($k_H \sim 0.3$), provides additional strong evidence for higher chain segment density as expected for stars.

To confirm the 'living' nature of the polymerization, sequential addition of a second monomer (isoprene) was performed after the polymerization of styrene. Upon addition of isoprene the color of the polymerization solution changed rapidly (a few seconds) from orange to pale yellow, which demonstrates fast initiation of the second block. The polymerization of the 2nd block was left to proceed for one day at room temperature before termination with methanol. The synthesis of three-arm star with diblock copolymer arms was confirmed by SEC (Figure 5) where an obvious shift of the peak corresponding to the diblock copolymer arm star towards higher molecular weights was observed. Also, as it can be seen at the eluogram about 3% contamination at the final star product with the three-arm polystyrene star. Further, confirmation was obtained by ¹H-NMR where resonances of both blocks are present in the spectrum.

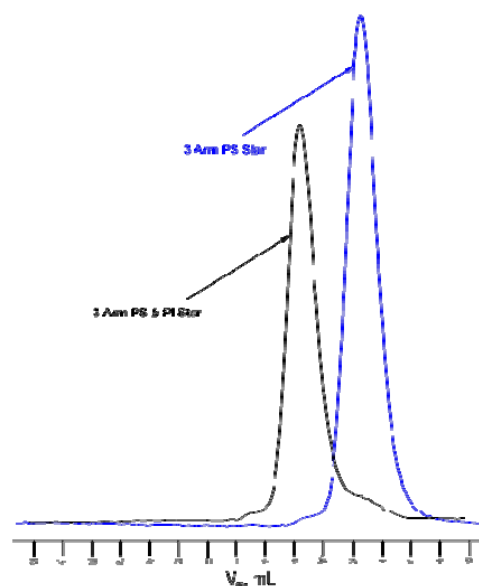


Figure 5: Size exclusion chromatography eluograms of the three-arm PS star and of the corresponding diblock copolymer star after the polymerization of isoprene.

Conclusions

In summary, we carried out the synthesis of a novel trifunctional anionic initiator that is effective in hydrocarbon solvents without the addition of polar additives. Using this initiator, well-defined three-arm star homopolymers of PS and PI were synthesized, as well as star-block copolymers having arms of PS-*b*-PI. Rigorous molecular characterization by a combination of NMR, SEC, light scattering, mass spectrometry, and viscometry confirmed the well-defined

three-arm star architecture of these materials and confirms the highly efficient nature of this initiator.

Future work will report the use of this new initiator for the synthesis of highly complex macromolecular architectures. We also plan to conduct light scattering experiments designed to probe the association behavior of the active trifunctional initiator in hydrocarbon solvents at different concentrations in order to gain insight into the interesting effect of concentration on initiator efficiency.