authors therefore ascribe the very slow rate of polymer formation after addition of fresh monomer to an "equilibrated" system to the slow rate of propagation of the macrosuperacid ester, apparently the only propagating species present. Since our present data demonstrate that there are no measurable quantities of fluorosulfate ester left in such an "equilibrated" system, this conclusion has to be revised. The authors further report a deviation from the macroion $\rightleftarrows$ macrofluorosulfate equilibrium at low temperature and low initiator concentrations in the early stages of the polymerization, since they could not observe the NMR signal which they had assigned to the macrosuperacid ester (SAE). In view of the present discussion it becomes clear that the presumed macrosuperacid ester signal is indeed due to alkyl sulfate, which is formed very slowly at low temperature (see Figure 5). The THF/HFSO$_3$ system therefore approaches a "living" system at low temperature in the early stages of the polymerization, particularly at low initiator concentrations, and deviation from a reversible equilibrium only becomes apparent at higher temperatures and/or longer polymerization times.

Conclusion

We have tried to reconcile some experimental anomalies in the polymerization of THF initiated by strong acid with high resolution NMR results. Based on these and other published results,[13,19] the THF/halosulfonic acid systems cannot be classified as true "living" or even "immortal" systems such as the THF/alkyltriflate systems under ideal conditions. Rather, they should be considered "slowly dying" systems, the "death rate" depending on the type of initiator and on the polymerization conditions.

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Star-Branched Polymers. 1. The Synthesis of Star Polyisoprenes using Octa- and Dodecachlorosilanes as Linking Agents

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ABSTRACT: Star-branched polyisoprenes with near-monodisperse molecular weight distributions containing 8 or 12 arms have been synthesized by anionic polymerization. The linking agents were octa- and dodecafunctional chlorosilanes that were synthesized from tetravinylsilane and the appropriate di- or trichlorosilane. Both the 8- and 12-armed stars were obtained in high yield. Characterization was carried out by light scattering, osmometry, and gel permeation chromatography. The applicability of the GPC universal calibration was also examined.

The use of tri- and tetrachlorosilanes as linking agents for the formation of star-branched polymers was first demonstrated to be a feasible concept by Morton and co-workers[2] in 1962; in this case for polystyryllithium. The polymerization system involved *n*-butyllithium with benzene as the solvent. As a consequence of the termination-free aspects of this polymerization system,[3] these star-branched polystyrenes contained relatively narrow molecular weight distributions. Thus, this synthesis procedure permits the predetermined manipulation of molecular weight and the molecular weight distributions.

This general reaction involving methyltrichloro- and tetrachlorosilane with monocarbanionic chains was subsequently extended to polybutadiene[4–6] with the finding that tri- and tetrachain polymers could be formed in high yield. Roovers and co-workers[7–10] have synthesized and studied a series of 4- and 6-armed polystyrene and polyisoprene stars using 1,2-bis(dichloromethylsilyl)- and 1,2-bis(trichlorosilyl)ethane, respectively. Their work represents the most thorough synthesis and characterization of a series of model star-branched polymers to appear in the literature to date. Thus far, the results of Roovers and co-workers[7–10] involving the hexachlorodisilyl compound represent the highest degree of uniform branching achieved involving the use of an electrophilic linking agent.

The results reported in this paper show that star-branched

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polyisoprenes containing 8 and 12 arms can be synthesized in high yield using tetra(methyldichlorosilylethane)silane and tetra(trichlorosilylethane)silane. These compounds were synthesized following established procedures involving the appropriate chlorosilane and tetravinylsilane. Linking efficiency was found to be virtually 100%.

Experimental Section

All polymerizations and monomer and solvent purifications were carried out under high vacuum conditions using procedures published elsewhere.[11,12] The initiator was *sec*-butyllithium which had been purified by a short-path distillation under vacuum conditions. The resulting benzene solutions of the initiator were colorless. The polymerizations were conducted in benzene at 30 °C. The linking reaction was carried out at 50 °C for 48 h. The residual active chains were terminated under vacuum with methanol. Polymer fractionation was carried out following the procedures published elsewhere.[8]

Light scattering and membrane osmometry were used to determine the molecular weights of the linear and star-branched polyisoprenes. S and S-08 membranes were used in the Hewlett-Packard 503 osmometer with toluene at 37 °C. Prior to use the osmometer was checked with polystyrene standards. Molecular weights were determined by the usual $(\pi/c)^{0.5}$ vs. c plots. Four different concentrations were used for both the osmometry and light-scattering measurements. Cyclohexane (25 °C) and the theta solvent dioxane (34 °C) were used for light scattering. The procedures and techniques used for solvent purification were those reported elsewhere.[7,8]

Gel-permeation chromatography was also used to characterize the linear and star-branched polyisoprenes. Two Styragel column arrangements were used, to wit, a 7-column set (total length of 28 ft) with a continuous porosity range of 10^3 to 10^6 Å (set B) and a 5-column set (total length 20 ft) with a continuous porosity range of 10^4 to 10^7 Å (set A). These two column arrangements had plate counts of 740 ppf and 650 ppf, respectively. A flow rate of near 1 mL min^{-1} was maintained. Tetrahydrofuran was the carrier solvent, at 35 °C, in conjunction with the standard refractive index detector. Full loop (2 mL) injections were used throughout.

The column arrangement was calibrated with standard polystyrenes and polyisoprenes.[13] A universal calibration (log $[\eta]$ M vs. elution volume)[14] was generated using *both* types of polymer standards. Unlike the results of Corbin and Prud'Homme,[15] which were obtained for toluene solutions, we found that the polyisoprene data fitted the universal calibration obtained from the polystyrene standards.

It was noted previously[12] that the elution volume of some star-branched block copolymers can be markedly concentration dependent. Hence, the universal calibration was developed by determining the "zero concentration" elution volume of each standard (12 in all). Each star-branched polyisoprene was examined in an identical fashion with at least three concentrations for each sample used over the range of about $\frac{1}{12}$ to $\frac{1}{3}$ (w/v) %.

The linking agents were synthesized from the appropriate chlorosilane and tetravinylsilane (Petrarch Systems, Inc.) The hydrosilation reaction was carried out with the aid of the chloroplatinic acid (Speiers catalyst). This catalyst has been used previously for the hydrosilation of vinyl groups.[16–19]

The linking agents were synthesized by reacting under dry nitrogen the tetravinylsilane (0.18 mol) with an excess of the appropriate chlorosilane (1.3 mol). The tetravinylsilane was added in a dropwise fashion to the catalyst–chlorosilane solution which was maintained at 40 °C. The catalyst charge consisted of 1 g of $H_2PtCl_6 \cdot 6H_2O$ in 9 cm^3 of dimethoxyethane and 1 cm^3 of ethanol. At the end of the reaction, the excess chlorosilane was removed at a temperature of 60 °C over a 4-h period. Distillation under reduced nitrogen pressure was then carried out to collect the polyfunctional chlorosilanes. ^{1}H-NMR analysis (via the Varian Associates 300-MHz instrument) in perdeuteriobenzene revealed that all the vinyl groups had reacted. It was also apparent that the hydrosilation reaction occurred to a limited extent in a Markownikoff fashion as well as the favored anti-Markownikoff mode of addition. Thus, the octa- and dodecachlorosilane linking agents are a mixture of isomeric species. Base titration of the hydrolyzed linking agents indicated that these species were at least 98% pure.

The linking agents were placed under vacuum and diluted with benzene. The linking agent concentration was determined by adding the benzene solution to a known volume of standard NaOH solution at ~5 °C. Titration of the excess NaOH was then carried out with a standard solution of HCl. Prior to this titration the benzene was removed by distillation.

Results and Discussion

An aspect of star-branched polymer formation (involving carbanionic chain ends) which has been recognized[2,7,20–23] is that steric factors can lead to less than complete linking when chlorosilanes are used. The detrimental aspects of steric hindrance are most noticeable for polystyrene[2,7,23] although the polyisoprenyllithium chain end has also been shown[20] to react in an incomplete fashion with silicon tetrachloride when the two reactants are present in stoichiometric amounts. However, it has been noted[20–22] that the capping of a polystyryl- or polyisoprenyllithium chain end with several units of butadiene is sufficient to apparently minimize the influence of steric factors on linking efficiency. This procedure is based on the observation[4,5] that butadienyllithium chain ends react completely with a stoichiometric quantity of silicon tetrachloride. Thus, the star-branched polyisoprenes synthesized and characterized in this work were prepared (with one exception) by converting the isoprenyllithium chain end to the butadienyllithium species prior to commencing the linking reaction. The amount of butadiene added was enough to ensure that each chain was "capped" with about five butadiene units. In order to eliminate residual isoprene in the void volume of the reactor, the reactor contents were twice frozen in a dry ice–alcohol bath and then allowed to come to room temperature. After completion of the second cycle, the butadiene was added to the solution. The linking reaction stoichiometry was such so as to have an excess of reactive chains to linking sites, a procedure which has been used previously[7,8] to enhance linking efficiency.

Figures 1 and 2 are chromatograms of an 8- and 12-arm star-branched polyisoprene, respectively, after elimination of the residual unlinked parent linear polyisoprene. It has been our observation that the linking reaction seems to go to completion, based on the ratio of linking agent to chain ends and the amount of residual unlinked material (Table I). The results in Table I seemingly demonstrate that virtually all of the butadiene capped chain ends react with the silicon–chlorine sites. Thus the octa- and dodecachlorosilane species apparently possess the necessary linking efficiency needed for the formation of the 8- and 12-armed star polyisoprenes. This conclusion is substantiated by the data in Table II where the molecular weights of the fractionated star-branched polyisoprenes are listed.

We have noted that the linking efficiency is such so as to lead to the formation of virtually no intermediate material, e.g., star-branched polymers containing 3 to 6 or more branches (for the case of the 12-arm stars) or coupled, i.e., linear product. This conclusion is based on a combination of the absolute molecular weight characterization results and the

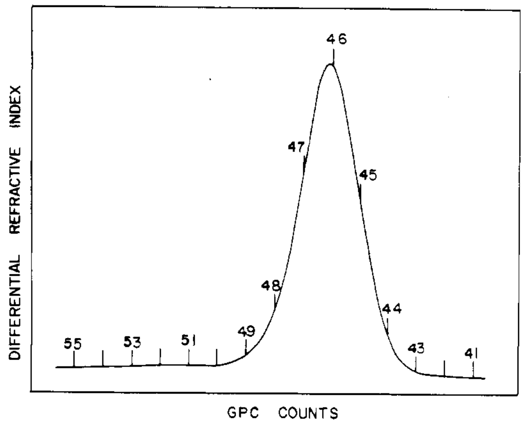

Figure 1. Gel-permeation chromatogram of fractionated star-branched polyisoprene 8-IAA.

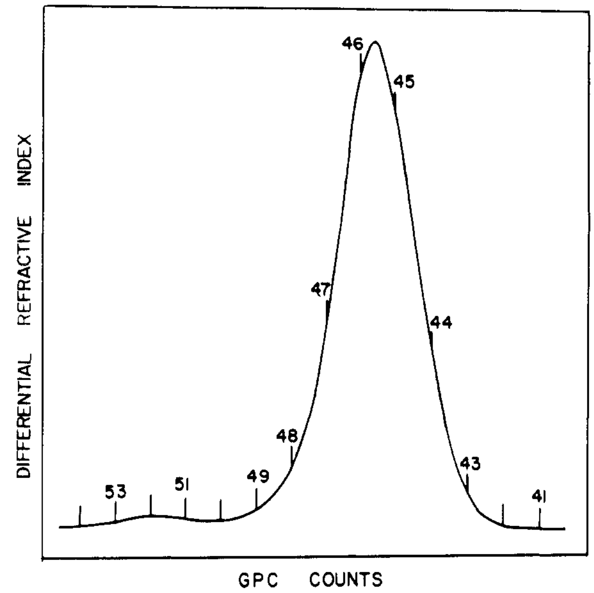

Figure 2. Gel-permeation chromatogram of fractionated star-branched polyisoprene 12-IA.

Table I
Linking Efficiency of the Octa- and Dodecachlorosilanes

Sample	[Si–Cl]/ [RM_jLi]	Wt % unlinked[a] polymer
8-I	0.9_1	9
8-II[b]	0.8_9	13
8-III	0.9_3	7
8-IV	0.4_2	60
12-I	0.9_4	7
12-II	0.8_6	11
12-III	0.9_1	6

[a] Determined from GPC measurements. [b] Chain ends not capped with butadiene prior to linking.

GPC analysis. The latter measurements indicated that branched material containing a relatively small number of arms was not formed since the chromatograms of the unfractionated samples showed no evidence of the existence of intermediate branched polymer between the elution of the unlinked linear polyisoprene and the star-branched species. The elimination of the unlinked parent polyisoprene by fractionation did not result in any detectable change in the shape or half-width of the chromatogram of the star-branched product.

These observations cannot be taken, though, as definite proof that the branched products were exclusively the desired 8- and 12-arm species. The experimental limitations in the accuracy of the respective molecular weight measurements, e.g., about ±5%, mean that some branched polymer could be, and probably is, present in our samples which contain fewer arms than the desired 8 or 12 branches. Nevertheless, the combined characterization methods seemingly indicate that the majority fraction in most of the samples contains the desired degree of branching.

The values of $\overline{M}_w$ for the arms for the star-branched polyisoprenes were determined from GPC measurements with no corrections for column broadening effects. Suffice it to say that previous work with the column arrangement used has shown[24,25] that the values of $\overline{M}_w$ and $\overline{M}_n$ determined in this fashion were in agreement (±5%) with those values determined by absolute measurements.

With the exception of sample 8-IIAAA, the desired degree of branching was achieved for the 8- and 12-armed polyisoprenes. Sample 8-IIAAA was formed from isoprenyllithium chains which were not capped with butadiene prior to the linking reaction. We wish to note, though, that we present this observation merely as an indication that the isoprenyllithium chain end may not react as rapidly nor as completely with the polyfunctional chlorosilanes as the butadienyllithium species. Obviously, additional data are needed before any conclusive indication can be offered pertaining to the relative reactivity of these two dienyllithium species with the branched octa- and dodecachlorosilanes used in this work.

The gel-permeation chromatography universal calibration approach has been used successfully[14,26-28] to characterize random copolymers, block copolymers, and branched homo- and copolymers. It has been shown though that the universal calibration procedure can fail when the degree of branching is "high" for randomly branched polystyrenes[26,29,30] or the rodlike poly(*n*-butyl isocyanates);[30] results which imply that $[\eta]M$ will serve as a universal calibration parameter only when the molecular geometries of all the samples involved are similar. Star-shaped homopolymers with an undefined number of branches have been successfully characterized following this universal calibration approach.[14]

Hence, it was of interest to examine the branched polyisoprenes prepared in this work with regard to the applicability of the $[\eta]M$ parameter. To generate the gel permeation chromatography values for $\overline{M}_w$, the peak elution volume for each star-branched polyisoprene was used to determine the value $[\eta]M$. This was done since the star-branched polyisoprenes exhibited uniform and symmetrical molecular weight distributions.

The GPC elution volume for each branched sample was determined by extrapolation to zero concentration. This value for the elution volume was then used to determine the parameter $[\eta]M$ from the universal calibration. As can be seen from Table III, good agreement between the GPC and light-

Table II
Molecular Weights of Star-Branched Polyisoprenes

		Arm mol wt		Star mol wt		
Sample	f[a]	$\overline{M}_n \times 10^{-4}$,[b] g mol^{-1}	$\overline{M}_w \times 10^{-4}$,[c] g mol^{-1}	$\overline{M}_n \times 10^{-5}$,[b] g mol^{-1}	$\overline{M}_w \times 10^{-5}$,[d] g mol^{-1}	$\overline{M}_w \times 10^{-5}$,[e] g mol^{-1}
8-IAA	7.4	3.74	3.90	2.70	2.76	3.00
8-IIAAA	6.9[f]	8.80	9.20	5.90	6.04	5.70
8-IIIAAA	8.1	9.80	10.4		7.90	8.10
8-IVAAA	8.3	25.0	26.0		20.8	19.8
12-IA	11.7	3.56	3.70	4.10	4.15	4.30
12-IIAAA	12.1	6.90	7.10		8.33	8.43
12-IIIAA	12.1	11.2	12.0		13.6	14.0

[a] The degree of branching; $\overline{M}_w$(star)/$\overline{M}_n$(arm). The $\overline{M}_w$ values were those obtained from dioxane solutions. [b] Membrane osmometry. [c] Gel permeation chromatography; column set B. [d] Light scattering in dioxane. [e] Light scattering in cyclohexane. [f] This sample was not capped with butadiene prior to linking.

Table III
Molecular Weights of Star-Branched Polyisoprenes from Gel-Permeation Chromatography

Sample	$[\eta]M \times 10^6$ Set A	$[\eta]M \times 10^6$ Set B	$[\eta]$,[a] dL g^{-1}	$\overline{M}_w \times 10^{-5}$,[b] g mol^{-1}	$\overline{M}_w$(GPC) × 10^{-5},[c] g mol^{-1}	$\overline{M}_w$(GPC) × 10^{-5},[d] g mol^{-1}	$\overline{M}_w$(GPC) × 10^{-5},[e] g mol^{-1}
8-IAA	0.24	0.24	0.91	2.76	2.6_4	2.6_4[f]	2.6_4[f]
8-IIAAA	1.10	1.10	1.70	6.04	6.4_7	4.7_0	4.4_3
8-IIIAAA	1.60	1.60	2.00	7.90	8.0_0	6.9_2	6.0_0
8-IVAAA	6.00	5.00	3.80	20.8	15.8	9.1_0	7.0_9
12-IA	0.34	0.35		/—5	4.15	4.0_6[f]	4.0_6[f]
4.0_6[f]							
12-IIAAA	1.20	1.15	1.50	8.33	7.8_3	6.8_3	6.4_4
12-IIIAA	3.00	2.90	2.10	13.6	14.0	11.9	9.5_2

[a] Measured in tetrahydrofuran at 35 °C. The intrinsic viscosities were measured in Cannon-Ubbelohde viscometers. [b] Light scattering in dioxane. [c] Average values based on the results from column sets A and B. [d] Values obtained from column set A at a concentration of 2.0×10^{-3} g mL^{-1}. [e] Values obtained from column set B at a concentration of 2.0×10^{-3} g mL^{-1}. [f] Samples 8-IAA and 12-IA did not exhibit a detectable dependency of elution volume on concentration.

scattering molecular weights was obtained for six of the seven samples. The exception, sample 8-IVAAA, is the star polyisoprene that has the highest overall molecular weight and the highest molecular weight arm.

The results contained in Table III indicate that the failure of the universal calibration procedure to correctly characterize sample 8-IVAAA is perhaps not solely related to the degree of branching since the 12-arm stars were successfully characterized. Somewhat similar results have been found[31,32] for a series of polyisoprene stars linked by divinylbenzene. We hope to publish these findings[32] at a later date.

An additional comment to be made pertaining to the application of the universal calibration procedure concerns the necessity of determining the zero concentration elution volume for these star-branched polymers. As can be seen in Figure 3, five of the seven star-branched polyisoprenes prepared in this work showed pronounced dependency of the peak elution volume on concentration. Samples 8-IAA and 12-IA are not shown since their elution volumes were independent of concentration over the concentration range examined. The conclusion drawn from our observations is that the universal calibration procedure yields $\overline{M}_w$ values which are lower than the true values unless extrapolation to zero concentration is done. This is shown in the last two columns where GPC molecular weight values are reported for 0.2% concentration solutions. With the exception of samples 8-IAA and 12-IA, the $\overline{M}_w$ values are lower than the true values.

A comparison of the elution behavior exhibited by samples 8-IIAAA and 12-IIAAA shows that although both samples exhibit nearly identical elution volumes at zero concentration, they fail to do so at finite concentrations in both Styragel column arrangements. Since these two samples differ in both the degree of branching and overall molecular weight, our observations pertaining to their combined elution behavior indicate that the retention time in the GPC instrument of these branched polymers is a function of the arm molecular weight, overall molecular weight, the degree of branching, and solute concentration.

We have also observed that the star-branched polyisoprenes exhibit a more pronounced dependency of elution volume on concentration than do linear polymers which exhibit similar zero concentration elution volumes. This is shown in Figure 3 with regard to PS-25167 which is a polystyrene standard with an $\overline{M}_w$ of 8.7×10^5 and an $\overline{M}_n$ of 7.7×10^5 g mol^{-1}. Similar differences were observed for other linear polystyrene and polyisoprene standards when compared to branched polyisoprenes which exhibited similar zero concentration elution volumes. We do not wish to imply that the elution volume–concentration effects we have observed would be applicable to randomly branched polymers such as comb-shaped homo- or copolymers. Our combined observations, though, regarding star-branched and homo- and block copolymers thus far demonstrate that only by the expedient of determining the zero concentration elution volume can accurate $\overline{M}_w$ values be obtained from the universal calibration.

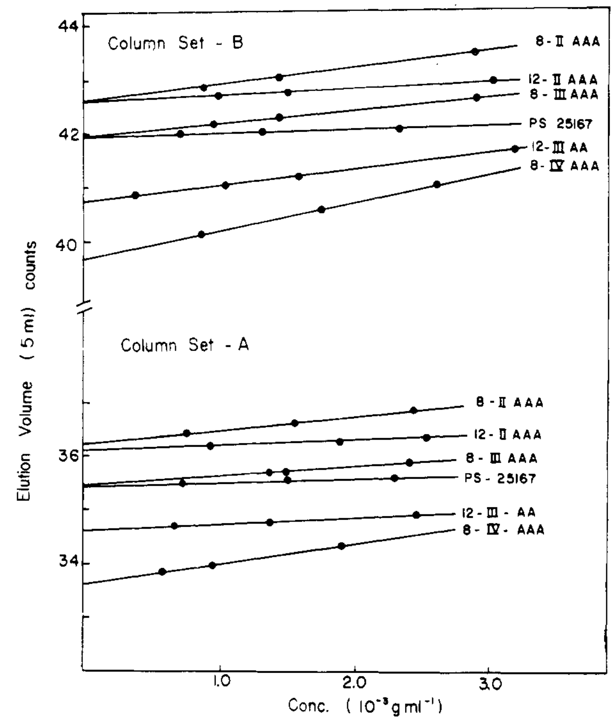

Figure 3. Dependency of elution volume on concentration for star-branched polyisoprenes and a linear polystyrene (PS-25167).

The highest molecular weight star-branched polyisoprene, 8-IVAAA, was found to yield low $\overline{M}_w$ values by the universal calibration for both of the Styragel column arrangements used in this evaluation. The zero concentration elution volume registered by this sample is within the range where the $[\eta]$-M–elution volume calibration is linear for both of the Styragel column sets. Hence, the "failure" of the universal calibration procedure to lead to a valid $\overline{M}_w$ value is not due to the hydrodynamic volume of this sample exceeding the resolution range of the columns used. Rudin[33] has noted that linear high molecular weight polymers do not exhibit a linear dependence of elution volume on concentration. However, we have found that this dependency was linear for sample 8-IVAAA over the concentration range we examined. Hence, our tentative conclusion is that the failure of the universal calibration procedure regarding this one sample is real. However, this "failure"

Table IV
Experimental and Theoretical Values of g' for Star-Branched Polyisoprenes in Tetrahydrofuran

Sample	f	$[\eta]_{br}$,[a] dL g^{-1}	$[\eta]_l$,[a] dL g^{-1}	g' $[\eta]_{br}/[\eta]_l$	$[M_l/M_{br}]^{1.735}$	Z–K[b]	S–F[c]
8-IAA	7.4	0.91	1.77	0.52	0.57	0.65 (0.59)[d]	0.38
8-IIAAA	6.9	1.70	3.14	0.54	0.58		
8-IIIAA	8.1	2.00	3.83	0.52	0.55		
8-IVAAA	8.3	3.80	7.79	0.49	0.28		
12-IA	11.7	0.85	2.38	0.36	0.38	0.52 (0.49)[d]	0.24
12-IIAAA	12.1	1.50	3.98	0.38	0.37		
12-IIIAA	12.1	2.10	5.70	0.37	0.36		

[a] $[\eta]_{br}$ and $[\eta]_l$ are for the star-shaped and linear polyisoprenes, respectively. $[\eta]_l$ is calculated from $[\eta] = 1.77 \times 10^{-4} M^{0.735}$ (ref 36). [b] $g' = (2/f)^{3/2}[0.396(f-1) + 0.196]/0.586$ according to the theory of Zimm and Kilb (ref 35). [c] $g' = f^{3/2}[2 - f + 2^{1/2}(f-1)]^{-3}$ according to the theory of Stockmayer and Fixman (ref 34). [d] $g' \simeq g^{1/2}$ according to Zimm and Kilb where $g = (3f-2)/f^2$ from Zimm and Stockmayer (ref 37).

must be contrasted with the obvious success of this approach regarding the remaining star-branched polyisoprenes examined in this work as well as with most of the divinylbenzene linked stars.[31,32]

Stockmayer and Fixman[34] and Zimm and Kilb[35] have performed calculations on the average segment density in the star system. The parameter g' was defined as $[\eta]_{br}/[\eta]_l$ under theta conditions. Both groups developed methods for calculating g' for the star system. We have presented, in Table IV, the values of g' based on intrinsic viscosities for the star-branched polyisoprenes in tetrahydrofuran. For the case of 3-, 4-, and 6-armed star-branched polymers, it is now well documented[37] that their intrinsic viscosities are lower than those theoretically proposed by Zimm and Kilb[35] while they are higher than those proposed by Stockmayer and Fixman.[34] This has been observed for star-branched polymers under theta conditions and in good solvents. This general trend is continued for the 8- and 12-armed stars listed in Table IV.

We have also determined, following Perchner, Panaris, and Benoit,[39] the parameter g' from the $\overline{M}_w$ values (in dioxane) and GPC data where

$$g' = [M_l/M_{br}]^{a+1}$$

with M_l as the molecular weight of linear polyisoprene having the same elution volume as the corresponding star-branched polymer with a molecular weight M_{br}. The parameter a is the exponent in the Mark-Houwink equation which for our samples was taken as 0.735.[36] Apparently, this GPC approach can yield g' parameters nearly identical to those obtained from intrinsic viscosity measurements. The exception to this trend was sample 8-IVAAA which previously was found to yield low values for $\overline{M}_w$ via GPC measurements. Nonetheless, our data for the remaining six samples seemingly can be taken as a demonstration of the validity, at least in certain cases, of the universal calibration principle regarding star-branched polymers.

The GPC molecular weights for the star-branched polyisoprenes cannot, and should not, be taken as a definitive demonstration that the desired branched samples were synthesized. However, the combination of the data presented in this paper shows that 8- and 12-armed star branched polyisoprenes can be synthesized through the use of the appropriate octa- or dodecachlorosilane. We intend to report at a later date the detailed characterization results regarding radii of gyration and intrinsic viscosities at theta conditions and in good solvents for these 8- and 12-armed polyisoprene stars and for a series of multi-armed materials linked by divinylbenzene.[32]

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