and molar volume are lower for the deuteriated species. On the basis of the Flory–Huggins lattice model for χ and with the use of the London equation to describe the intersegmental dispersion forces, we have calculated the segment–segment interaction parameters for deuteriated and normal polymers. These predictions, which are based on bond polarizabilities taken from the literature and directly measured polymer segment volumes, compare well with the experimentally determined values. Two other published theories for nonideal isotopic polymer mixtures, based solely on the segment volume isotope effect, have also been examined and found to be in qualitative agreement with experiment.

In conclusion, the results of this work, taken together with our previous findings for isotopic mixtures of 1,4-polybutadiene and atactic polystyrene firmly establishes that in general deuteriation and protonated polymers, otherwise of identical chemical structure, do not form ideal solutions, contradictory claims not withstanding.[7]

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Registry No. PVE, 9003-17-2; PVE (deuteriated), 29989-19-3; PEE, 9003-28-5; PEE (deuteriated), 113111-12-9.

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Preparation of Asymmetric Three-Arm Polybutadiene and Polystyrene Stars

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ABSTRACT: The synthesis of three-armed polybutadiene and polystyrene stars is described for the case where one of the three arms differs in molecular weight from the remaining two. The preparative approach involves the reaction of methyltrichlorosilane with the chain end active centers under conditions unfavorable to chain coupling or linking, i.e., the synthesis of linear doublet chains or three-arm stars. Some observations regarding thermal-induced post-polymerization side reactions that distort the near-monodisperse nature of the molecular weight distributions obtainable for polybutadiene are described. Preparative conditions must be selected to avoid such side reactions if "model" branched polybutadienes are required.

Introduction

The behavioral differences of branched and linear polymers of equal molecular weights have been a topic of academic and commercial interest. Polymers that undergo chain transfer events or are prepared in the presence of polyfunctional monomers are randomly branched and have broad molecular weight and branching distributions. These factors contribute to the overall behavior of a polymer. Thus, in order to isolate and interpret the effects of branching on physical properties, the polymer must be composed of only one type of branched structure and this structure must be defined.

Star-shaped polymers prepared by the use of multifunctional chlorosilane compounds,[2–39] divinylbenzene,[40–47] or other linking agents[48–54] represent the simplest type of branched structures and, therefore, have received detailed

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Table I
Molecular Characterization Results for the Short-Arm Star Polystyrenes

	$10^{-4}M_n$,[a] g mol^{-1}			$10^{-4}M_w$, g mol^{-1}		star heterogeneity indices		
sample	short arm	long arm	star	star[b]	star[c]	M_z/M_w[c]	M_w/M_n[c]	M_w/M_n[d]
SAS-1	0.2_0	0.5_0	1.1	1.1	1.1	1.08	1.06	1.05
SAS-2	0.7_0	1.3	3.3	3.4	3.2	1.02	1.02	1.05
SAS-3	1.3	2.9	6.9	7.1	6.8	1.03	1.02	1.03
SAS-4	2.1	4.2	10.5	10.9	9.5	1.02	1.04	1.04
SAS-5	2.3	4.5	11.9	12.4	13.0	1.01	1.02	1.04
SAS-6	2.9	6.2	15.4	16.3	16.0	1.02	1.03	1.06
SAS-7	4.3	9.3	20.0	21.1	19.0	1.03	1.04	1.06
SAS-8	6.6	13.4	32.9	34.8	34.6	1.03	1.08	1.06

[a] Osmometry. [b] Static LALLS. [c] On line (SEC) LALLS. [d] From Static LALLS and osmometry.

attention. These polymers consist of a central branch unit with homopolymer or block copolymer arms of equal molecular weight and, in the case of the latter, identical compositions. Under termination-free conditions, anionic polymerizations yield polymers having predictable molecular weights and near-monodisperse molecular weight distributions.

In this work these procedures have been extended to prepare a new type of model branched structure: the three-arm asymmetric polystyrene stars were synthesized in this work. The preparation of asymmetric three-arm polybutadiene stars is also discussed.

Experimental Section

The purification and subdivision of initiator (*sec*-butyllithium), solvents, monomers, and linking agents (chlorosilanes) were done under vacuum line conditions as were the subsequent polymerizations and star preparations. Benzene was the solvent for the polymerization of styrene (Aldrich) while cyclohexane was used for butadiene (Matheson, 99.9%). Handling procedures and safety precautions are described elsewhere.[55,56] Polymer fractionation was done by using the procedure given previously.[14]

Polymer characterization was done with a combination of size exclusion chromatography (SEC), Waters Ana-Prep and 150C instruments, membrane osmometry (Hewlett-Packard 503), static low-angle laser light scattering (LALLS), Chromatix KMX-6, and the Waters 150C:Chromatix KMX-6 combination for on-line LALLS. This approach was used, in part, for the rapid preliminary characterization of the star arms prior to commencing the coupling reaction. The Ana-Prep instrument had a seven column Styragel set with a nominal porosity range of 7×10^5 to 5×10^3 Å while the 150C had a six column μ-Styragel arrangement with a 10^6–10^2 Å porosity range. Both instruments were operated under identical conditions; i.e., the flow rate was 1 mL min^{-1} with tetrahydrofuran at 30 °C as the mobile phase.

The two sets of light scattering measurements, static and on-line, were done in toluene and tetrahydrofuran, respectively, for the polystyrene stars. Static measurements, using cyclohexane, were done on the polybutadiene materials. The on-line LALLS measurements were done by coupling the KMX-6 photometer with the Waters 150C instrument and interfacing the two with a Digital computer. The Chromatix MOLWT-2 program collected, stored, and processed the data from the photometer and the refractometer of the Waters 150C. This led to the evaluation of the various moments of the near-monodisperse molecular weight distributions of the asymmetric stars. Spectroscopic analysis was done by using a Perkin-Elmer 559 spectrometer. Quartz cells having 0.1-cm path length were used.

Results and Discussion

The polystyrene asymmetric stars prepared in this work consisted of two series: where the third arm possessed a molecular weight of either half or twice that of the remaining two identical arms. These materials with the third arm equal to half the molecular weight of the other two arms are referred to as short-arm stars (SAS) whereas the second series are designated long-arm stars (LAS).

In essence, the preparation of the asymmetric stars relies on the inability[2,8,24] of poly(styryl)lithium to undergo complete reaction with a stoichiometric quantity of chlorosilanes containing three to four chlorines per silicon atom. This lack of reactivity is apparently at least partly due to steric hindrance[57] and is not caused by an attenuated reactivity of the styryl active center toward silicon–chlorine entities (from a semiquantitative standpoint styryl and dienyl anions have been shown[57–61] to exhibit approximately equivalent reactivities toward chlorosilanes). This difficulty has been circumvented via the expedient of converting the styryl active center to a dienyl entity;[8,10,11] e.g., the reaction between silicon tetrachloride and the butadienyllithium active center readily goes to completion when stoichiometric concentrations are used.[3]

The initial step in the asymmetric polystyrene star synthesis involved the exposure at room temperature of the styryl anion to a ca. 10-fold excess of methyltrichlorosilane (SiCl/SLi = 30) where the benzene solutions of the linking agents were added to the rapidly stirred dilute (5%) of poly(styryl)lithium. This approach proved successful for the preparation of the "macromolecular" coupling agent: polystyrene having the methyldichlorosilane unit at one end.

Polystyrenes prepared in this fashion were characterized via the KMX-6 photometer on-line with the 150C instrument. These measurements did not reveal the presence of coupled (linear) or linked (three-arm product) polystyrene. Thus, the foregoing procedure is effective in preparing methyldichlorosilane "capped" polystyrenes minus the detectable presence of higher molecular weight material.

The capped polystyrene was freeze-dried on a vacuum line. The resultant pourous polymer was then heated for at least 72 h at ca. 50 °C. This procedure was found to remove the unreacted methyltrichlorosilane. Purified benzene was then reintroduced into the reactor. This solution of the polystyrene coupling agent was then added to a precharacterized polystyrene solution containing an excess, ca. 20%, of active centers. A step taken in most cases was the addition of a small amount of butadiene to the styryl anions. This, as was noted, enhances not only the effective rate of the coupling event but also its efficiency. Figure 1 displays chromatograms obtained from the synthesis of an asymmetric polystyrene star while Tables I and II show the respective characterization results for the SAS and LAS materials. Within experimental error, the desired degree of branching of three was obtained for all samples. This synthesis procedure can thus be outlined as follows:

$$\mathrm{PsLi} + \text{excess } \mathrm{CH_3SiCl_3} \rightarrow \underset{1}{\mathrm{PsSi(Cl)_2CH_3}} + \mathrm{LiCl} + \mathrm{CH_3SiCl_3} \qquad (1)$$

$$\underset{1}{\mathrm{PsSi(Cl)_2CH_3}} + 2\mathrm{PsLi} \rightarrow \mathrm{(Ps)_3SiCH_3} + \mathrm{LiCl} \qquad (2)$$

This approach, eq 1, was found not to yield detectable (via

Table II
Molecular Characterization Results for the Long-Arm Star Polystyrenes

sample	$10^{-4}M_n$,^{a} g mol^{-1} short arm	long arm	star	$10^{-4}M_w$, g mol^{-1} star^b	star^c	star heterogeneity indices $M_z/M_w{}^c$	$M_w/M_n{}^c$	$M_w/M_n{}^d$
LAS-1	0.2_0	0.5	0.9_6	1.0	0.9_9	1.05	1.07	1.04
LAS-2	0.5_0	1.3	2.2	2.3	2.2	1.04	1.05	1.05
LAS-3	0.7_0	1.8	3.3	3.6	3.4	1.02	1.02	1.09
LAS-4	1.1	2.6	4.8	5.1	4.8	1.02	1.03	1.06
LAS-5	1.7	3.3	6.7	7.1	6.7	1.02	1.03	1.06
LAS-6	2.1	4.2	7.5	8.1	8.5	1.03	1.02	1.08
LAS-7	2.6	4.5	9.5	10.0	9.7	1.01	1.02	1.05
LAS-8	3.8	7.8	15.5	15.8	14.7	1.02	1.03	1.02
LAS-9	5.1	12.0	22.6	22.8	21.0	1.02	1.01	1.01
LAS-10	7.3	14.3	30.3	31.8	31.5	1.02	1.03	1.05

[a] Osmometry. [b] Static LALLS. [c] On line (SEC) LALLS. [d] From static LALLS and osmometry.

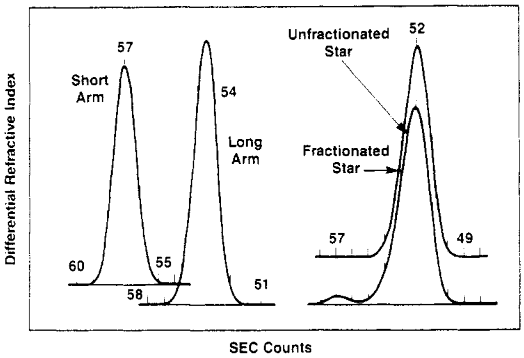

Figure 1. SEC chromatographs of asymmetric polystyrene star (LAS-1) and the constituent arms (Waters Ana-Prep SEC).

SEC) amounts of coupled polystyrene when the mode of addition of the reactants was the chlorosilane solution to that of the capped polystyrene, 1. For the case of poly(butadienyl)lithium, to be discussed later, the reverse made of addition was used in order to minimize the formation of coupled chains.

Subsequently, it was discovered that for three-arm polystyrene stars with molecular weights of <4 × 10^4, the addition of butadiene could be eliminated. This step was replaced by the addition of triethylamine (2–10 vol %); a solvent which serves to at least partially disrupt the dimeric[62–68] association that the styryllithium exhibits in hydrocarbon media. (Similar observations[69] have shown that aprotic polar solvents, e.g., ethers or amines, will decrease the aggregation states of allylic lithium species.) This alteration in the extent aggregation of the styryllithium dimers (coupled with the potential of a change in the polarity of the styryl active center) led to complete linking in certain cases, even when silicon tetrachloride was the linking agent. This was attested to by a spectroscopic evaluation (at 333 nm) of linking events in the absence and presence of triethylamine (Figure 2). Initially, the reaction between poly(styryl)lithium and a near-stoichiometric amount of methyldichlorosilane capped polystyrene (SiCl/SLi = 1) was followed at 35 °C. As is seen in curve A of Figure 2, the reaction rate decreased markedly after about 4 days; the point at which about 50% of the active centers had reacted. Characterization of the fractionated product revealed that the highest molecular weight component present in the mixture was coupled linear polystyrene. Similar results were obtained when methyltrichlorosilane and silicon tetrachloride were used as the linking agents; i.e., coupled linear chains were the primary product. These findings are in accord with those registered by Roovers and Bywater[8] for the case where 1,2-bis(trichlorosilyl)ethane was reacted with styryllithium and found to lead only to four-arm polystyrene stars (two chains per silicon). However, with the presence of triethylamine at 40 °C, this hexafunctional chlorosilane was found to accept the full complement of six polystyrene arms. The efficiency of this general approach to the enhancement of the linking efficiency is displayed in Figure 3. Therein are the chromatograms of the symmetric three-, four-, and six-arm polystyrene stars made by the use of a common arm. In all cases linking was carried out at 40 °C in the presence of triethylamine (~5 vol %). The arm molecular weight (M_n) for this series was 5.8 × 10^3. Within the uncertainty of the molecular weight measurements, the functionalities of these stars were equal to those of the respective linking agents: methyltrichlorosilane, silicon tetrachloride, and 1,2-bis(trichlorosilyl)ethane.

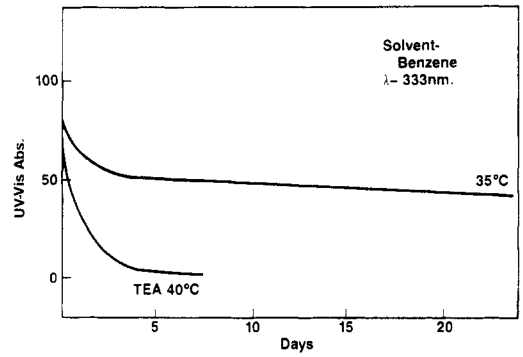

Figure 2. Absorbence of the styryllithium active centers as a function of time in the absence and presence of triethylamine (TEA).

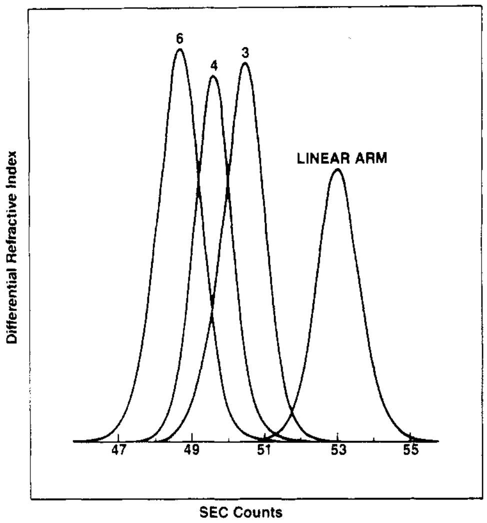

Figure 3. SEC chromatograms of three-, four-, and six-arm polystyrene stars and their common arm (Waters 150C SEC).

Thus, for the case where a polar solvent is used to alter the average degree of association of the styryllithium active centers and where arm molecular weight does not exceed

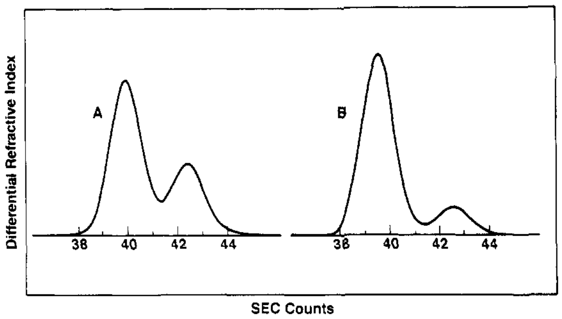

Figure 4. SEC chromatographs of unfractionated three-arm (A) and four-arm (B) polyisoprene stars (Waters 150C SEC).

ca. 1.3 × 10^4, complete linking can be achieved without the necessity of converting the chain end to the butadienyl entity. Several exploratory experiments with polystyrene chains of higher molecular weight failed to give high yields of star materials with the chlorosilanes of choice. These findings indicate that excluded volume effects involving the core of a partially formed star and the polystyrene singlet and dimeric chains may influence the extent of linking. An additional influence on the efficiency of linking is the possibility of a progressive attenuation of reactivity of Si–Cl as the degree of substitution increases, i.e., as the number of chlorines on the silicon atom decrease.

The preparation of four-armed polyisoprene stars by the use of silicon tetrachloride also encounters the problem of incomplete linking.[70] For the polyisoprene case essentially three-arm star is the favored product—not the anticipated tetra-arm product. However, in a fashion parallel to that of polystyrene the addition of a promotor (which serves to decrease the extent of association of the alkenyllithium active centers) will lead to complete linking when silicon tetrachloride is used. This is illustrated by the following. A poly(isoprenyl)lithium solution, to which silicon tetrachloride was added to give a SiCl/active center ratio of ca. 0.9, was divided into approximately equal portions. After division, tetramethylethylenediamine (TMEDA) added to one of the solutions to give a TMEDA/active center ratio of about 1. At this level the association of the active centers would be expected to be completely disrupted.[71] The respective linking reactions were carried out in parallel for 3 days at 20 °C.

The SEC chromatograms of Figure 4 show that the TMEDA modified reaction (B) reached a higher degree of conversion than its unmodified (A) counterpart. In addition to the enhanced linking efficiency subsequent respective extents of branching were, within experimental error three (A) and four (B). Thus, the attenuation of the association state of the poly(isoprenyl)lithium active centers can enhance the extent of linking. In this case the polyisoprene arm molecular weight (M_w) was 2.25 × 10^5.

The preparation of asymmetric polybutadiene stars followed the pattern developed for the corresponding polystyrene materials with the exception that the third arm (B) was of variable molecular weight. The only alteration in the synthetic approach consisted of the addition of the poly(butadienyl)lithium solution to that containing the methyltrichlorosilane (SiCl/BLi $\simeq$ 30). This was done in order to suppress the formation of coupled material as a byproduct. A similar approach has been used by Roovers and Toporowski[72] to prepare polybutadiene star–comb materials where the lithiated arms were functionalized with dimethylchlorosilane units via the use of dimethyldichlorosilane. Parallel to our findings, these authors observed little interstar dimerization.

Table III
Molecular Characterization of Asymmetric Polybutadiene Stars[a]

	arm A		arm B		star	
sample	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_n$	$10^{-3}M_w$
A_2B-1	7.3	7.4	4.4	4.6	$19._1$	$19._3$
A_2B-2	7.3	7.4	2.4	2.4	$17._0$	$17._4$
A_2B-3	7.3	7.4	1.2	1.3	$15._7$	$16._3$
A_2B-4	7.3	7.4	0.8_6	0.9_2	$15._4$	$15._4$

[a] Molecular weights in g mol^{-1}.

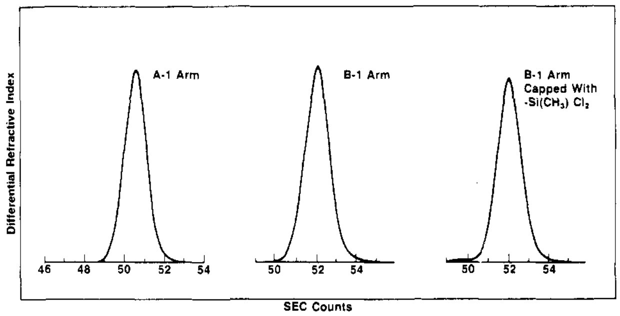

Figure 5. SEC chromatographs of the arms of the A_2B-1 asymmetric three-arm polybutadiene star (Waters 150C SEC).

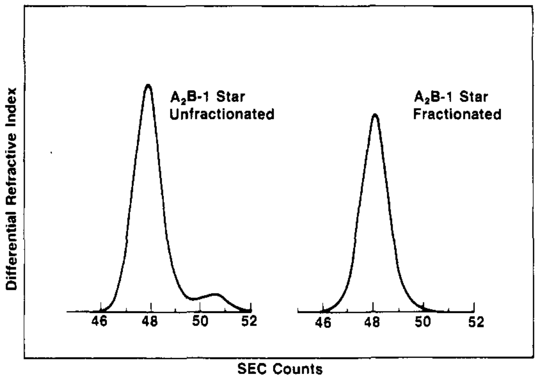

Figure 6. SEC chromatographs of the unfractioned and fractionated A_2B-1 asymmetric polybutadiene star (Waters 150C SEC).

As with the corresponding polystyrene stars, the polymerization solvent and excess dimethyldichlorosilane were removed under vacuum line conditions. After pumping for 3 days at $\simeq$40 °C,[73] the functionalized polybutadiene was redissolved by distilling in purified cyclohexane. This solution was then mixed with poly(butadienyl)lithium chains—the A arms. The characterization results of these asymmetric stars are given in Table III, and representative SEC characterization results in Figures 5 and 6. In all cases the same A arm was used. These samples were then deuteriated for tracer diffusion studies in the hydrogenated linear analogues.[74]

Poly(butadienyl)lithium is susceptible to certain postpolymerization side reactions that can lead to the formation of randomly branched and ultimately gelled product. An example of this is seen in concentrated solution viscosity studies of hydrocarbon solutions of high molecular weight poly(butadienyl)lithium. It was found that after completion of the polymerizations constant solution flow times (at 30 °C) were unobtainable.[64,71] The solutions were found to exhibit continuously increasing flow times until solutions viscosities became too high (after several weeks) to measure in the modified Ubbelohde viscometers.[75] This behavior is in contrast to the constant flow times exhibited under equivalent conditions by hydrocarbon solutions of poly(isoprenyl)- and poly(styryl)lithium[62–66,70] *and* the butadienyllithium chain end formed by reacting several units of butadiene with the active center of either of the

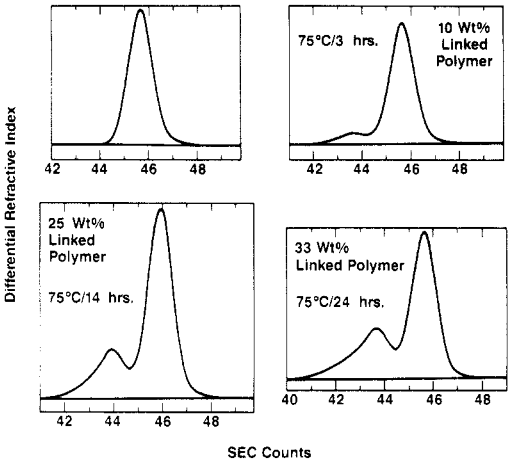

Figure 7. SEC chromatographs of linear polybutadiene (upper left) and the partially branched materials derived from that nonterminated sample by storage at 75 °C (Waters 150C SEC). The molecular weight (M_w) of the linear polybutadiene was 7.1 × 10^4 g mol^{-1} (M_z/M_w = 1.03 and M_w/M_n = 1.04).

foregoing polymers. Thus, the flow time stability of hydrocarbon solutions of polyisoprene or polystyrene tipped with the butadienyllithium entity[65,71] indicates that the post-polymerization increase in the viscosity of poly(butadienyl)lithium solutions is caused by reaction of the active center with the chain. This reaction most likely involves the vinyl units that constitute ca 10% of the polymer. Gelation would be the ultimate outcome of such a reaction, and this observation was reported[64] in 1964.

These observations for poly(butadienyl)lithium parallel the findings[76-79] which show that the dienyllithium active centers in the absence of monomer will undergo the simultaneous side reactions of lithium hydride elimination and metalation which leads to two lithium counterions per terminal unit and chain branching.[80] The facile occurrence of this latter event is shown in Figure 7 for poly(butadienyl)lithium in cyclohexane. Therein SEC measurements show the formation of high molecular weight polymer at 75 °C as a function of exposure time for poly(butadienyl)lithium prepared at 20 °C. Along with branching was the development of a deep red coloration ($\lambda_{max} \simeq 360$ nm). Ankowiak has shown[78] that this formation of color is accompanied by a metalation event leading to dilithiated terminal units.

The branching event can involve the terminal diene unit that evolves from the elimination of lithium hydride.[76,77,79] For polyisoprene this thermally induced process forms three-arm stars.[79] The vinyl units (ca. 8%) in polybutadiene can also react with anionic active centers that in turn would lead to randomly branched structures and ultimately gelation. As has been mentioned, hydrocarbon solutions of poly(butadienyl)lithium at 30 °C exhibit continuously increasing flow times on storage.[64,71] The susceptibility of vinyl groups in polybutadiene chains to anionic attack has been demonstrated in tetramethylethylenediamine-modified polymerizations where the monomer is introduced into the reactor at a rate comparable to its consumption. The resultant polymer can contain as much as 60% 1,2-dialkyl-4-vinylcyclopentane units as a consequence that under such conditions conventional propagation does not effectively compete with the cyclization event. This latter process involves the intramolecular reaction of the active center and the vinyl group of the penultimate unit of the chain.[81-83]

Thus, reactions involving the active centers of the polybutadiene chain must be carried out a temperatures below ca. 50 °C with the avoidance of storage at ambient temperature for any extended period of time. For this reason the poly(butadienyl)lithium chain used as the A arm in the series listed in Table II were stored with dry ice until use.

The synthetic procedures described illustrate the feasibility of preparing asymmetric three-arm stars, for which intrinsic viscosity-based dilute solution properties are presented elsewhere.[84] An obvious extension of this synthetic approach is the preparation of heteroarm stars where polymer arms of different composition are connected at a central unit. These heteroarm stars could consist of amorphous arms (polystyrene and a polydiene) or, after hydrogenation of a material containing at least one 1,4-polybutadiene segment, a mixture of crystalline and amorphous arms. The detailed morphological assay of such materials could, in part, contribute to an examination of the recent proposals of de la Cruz and Sanchez[85] regarding microphase separation in graft and star copolymers.

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Registry No. Cl_3SiCH_3, 373-74-0; polystyrene, 9003-53-6; polybutadiene, 9003-17-2.

References and Notes

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