

Synthesis and Chacterization of
Linear and Star-Branched
Butadiene-Isoprene Block Copolymers
And Their Hydrogenated Derivatives

by

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(ABSTRACT)

The principal purpose of this investigation was to synthesize and hydrogenate well-characterized linear and star-branched block copolymers based on butadiene and isoprene. Sequential anionic addition techniques initiated by homogeneous organolithium species in hydrocarbon solvents were employed to prepare several series of butadiene-isoprene copolymers varying in block size and architecture.

Linear A-B-A poly(butadiene-isoprene-butadiene) triblock copolymers were synthesized by two different living addition techniques, e.g., three-stage process using a monofunctional anionic initiator and a two-stage process using a difunctional anionic initiator. Alternatively, the synthesis of star block copolymers involved the sequential polymerization of poly(butadiene-isoprene) diblock arms which

were then linked into stars via divinylbenzene.

Hydrogenation of unsaturated polymers has widely attracted attention since this provides an alternate method for improving and optimizing the mechanical, thermal, oxidative and chemical resistance properties of these technological important materials.

Homogeneous catalytic hydrogenation was employed to chemically modify these linear and star-branched copolymer into thermoplastic elastomers. Hydrogenation successfully converted the soft polybutadiene blocks into hard semicrystalline polyethylene segments, while the central polyisoprene blocks resulted in the formation of amorphous alternating rubbery copolymers of propylene-ethylene. The hard semicrystalline blocks form morphological domains that serve as physical crosslinking and reinforcement sites.

The presence of semicrystalline segments in both the linear and star-branched copolymers has important significance for processing. Above the endothermic melting temperature of the semicrystalline end blocks, the now amorphous system can approach the melt behavior of a single-phase melt, that is, displaying negligible "physical" network structure in the melt. Overall, these systems display a valuable combination of good melt processability together with physical properties characteristic of A-B-A architectures.

Dedication

This thesis is dedicated to a person who has influenced me
with a lifetime of kindness, encouragement and wisdom, my
grandmother

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Finally, a thanks to the invaluable friendship of my fellow Davidson Hall confrères:

, and ..

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I. Introduction

The principal purpose of this investigation was to synthesize and hydrogenate well-characterized linear and star-branched block copolymers based on butadiene and isoprene that have predictable block lengths and narrow molecular weight distributions. Sequential anionic addition techniques initiated by homogeneous organolithium species in hydrocarbon solvents were employed since this technique allows the best block copolymer synthesis for the control of block integrity, architecture and achieving the ultimate attainable properties (78). Hydrogenation of polydiene polymers is an important method for enhancement of photolytic, oxidative and thermal properties as well as optimizing mechanical strength. Another equally important benefit of hydrogenation has been a synthetic route to prepare sequence distributions that are impossible to achieve through conventional polymerizations.

Linear A-B-A poly(butadiene-isoprene-butadiene) triblock copolymers were synthesized by two different living addition techniques, e.g., a three-stage process using a monofunctional anionic initiator and a two-stage process using a difunctional anionic initiator. The three-stage process involved the polymerization of the first block polybutadiene, followed by the sequential addition of the

second monomer isoprene for the central block, and finally, the addition of butadiene to complete the A-B-A triblock. The second synthetic method utilized the initiation of the central isoprene block by a dicarbanion species, followed by the sequential addition of butadiene to form the two end blocks. Polymerization by difunctional initiation saves one sequential monomer addition step, compared to the three-stage process.

The synthesis of star block poly(butadiene-isoprene) copolymers involved the anionic sequential polymerization of butadiene and isoprene, forming diblock segments for star arms. This step was followed by the addition of divinylbenzene, resulting in a microgel nucleus containing pendant vinyl groups that serve as branch points for the incorporation of the diblock arms. In general, it was observed that increasing the amount of divinylbenzene led to increased number of star arms.

Homogeneous catalytic hydrogenation was employed to chemically modify these linear and star-branched copolymer to essentially complete saturation. Hydrogenation successfully converted the soft polybutadiene blocks into hard crystalline polyethylene segments, while the central polyisoprene blocks resulted in the formation of amorphous alternating rubbery copolymer of propylene-ethylene. The hard crystalline blocks form morphological domains that serve as physical

crosslinking and reinforcement sites.

The principal reason for studying star polymers is because they display low melt and solution viscosities, even at very high molecular weights compared to their linear counterparts. The presence of crystalline segments in both the linear and star-branched copolymers has important significants for processing. Above the endothermic melting temperature of the crystalline end blocks, the now amorphous system can approach the melt behavior of a single-phase melt, that is, displaying negligible network structure in the melt. Overall these systems display a valuable combination of good melt processability together with physical properties characteristic of A-B-A architectures.

A secondary aspect of this investigation was to develop block copolymers for potential application as binders for castable composite propellants. Specifically, the desirable properties of these thermoplastic elastomers are: (1) crystalline hard blocks, (2) a sharp endothermic melting temperature in the range of 90-105°C , (3) a homogeneous melt and (4) a low hard block content.

The strategy employed in this study was to synthesize linear triblocks and star copolymers with hard crystalline end blocks derived from hydrogenated polybutadiene. Block copolymers with crystalline hard block are known to undergo sharp first order melting transition. This type of melt can

be monophasic and therefore less viscous (216) compared to two-phase separated amorphous thermoplastic elastomers. Thus, series of triblocks and stars were prepared with increasing content of polybutadiene in an attempt to find the proper range of crystalline hard block for thermoplastic elastomer and binder applications.

II. LITERATURE REVIEW

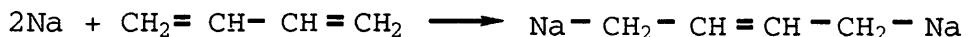
A. Aspects of Anionic Diene Polymerization

1. Historical Overview

Polymerization of olefins by heat and acid catalysts dates back to 1840 (209). However, it was not until the early part of this century that studies describing the phenomenon classified today as anionic polymerization appeared (1). The first patent on anionic polymerizations, issued during the period 1910-1914 for the polymerization of dienes prepared by alkali metals, was described by Matthews and Strange (2) Harries (3) and Schlenk (4). Polymerization by alkali metals and their alkyls became a commercial process for synthetic rubbers of polybutadiene and polyisoprene. But its significance as an anionic chain reaction was not recognized for a long time because of the heterogeneous nature of the reaction materials. The foundations of the modern day concept of anionic mechanism and nontermination of living polymerization was suggested by Ziegler and his co-workers using lithium and organolithiums in the polymerization of dienes and styrene (5-8).

Ziegler demonstrated the "stepwise" addition of the diene to the organometallic species, by the addition of butadiene to a diadduct sodium initiator formed from the reaction of sodium with butadiene. The existence of the diadduct was

shown by adding methylaniline and analyzing the amount of sodium methylaniline produced. For every mole of butadiene consumed, two moles of sodium methylaniline was quantitatively determined. Thus, Ziegler postulated the polymerization was initiated by a disodium adduct:

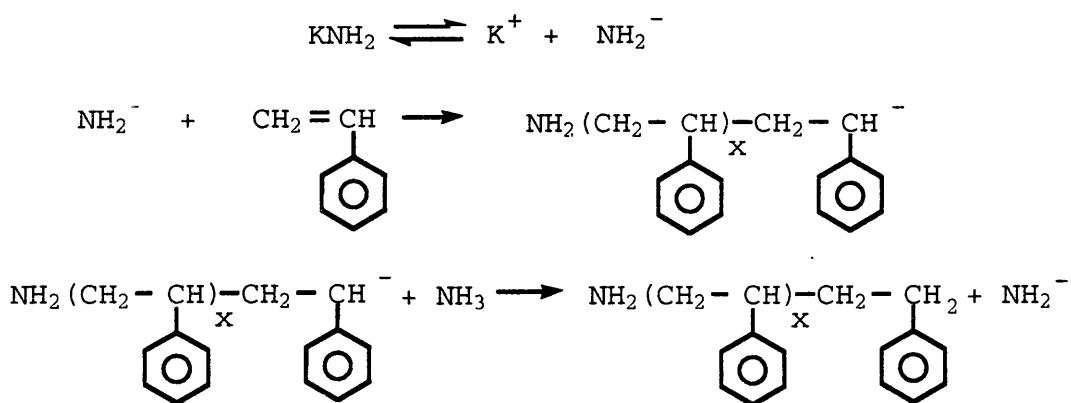


This implied that polymerization occurred by some other mechanism than a free-radical process, however Ziegler did not explicitly suggest an anionic mechanism. He described the propagation of the polymerization as an insertion of a butadiene into the C-Na bond yielding another carbon-sodium bond, a postulation that differ little from our present day understanding. Ziegler also showed that these polymerizations involved 1,4-addition as well as 1,2-addition.

Flory, was the first to considered the important consequences of chain ends that do not undergo termination (9-10). Flory recognized from the reaction of the homogeneous polymerization of ethylene oxide by alkali alkoxides that in the absence of any termination step, such systems should lead to a very narrow molecular distribution. Since all the growing chains have equal access to the monomer, the chains will react to similar lengths. The

polymerization mechanism taking place in these systems was not fully realized until the 1950's, when it was recognized that basic initiators, such as organometallics, actually proceeded by an anionic polymerization mechanism. The propagating ion was now considered to be a carbanion in analogy with the cationic systems, since the counterions in these initiators were metallic in nature.

One of the first proposed anionic polymerization mechanisms was reported by Higginson and Wooding in 1952 (12):



They studied the kinetics of the polymerization of styrene by potassium amide in a homogeneous solution of liquid ammonia. The degree of polymerization was found to be independent of the amide ion and increased with increasing concentration of styrene. The rate of polymerization was proportional to the amide ion concentration and to the square of the styrene concentration. These observations, along with the presence

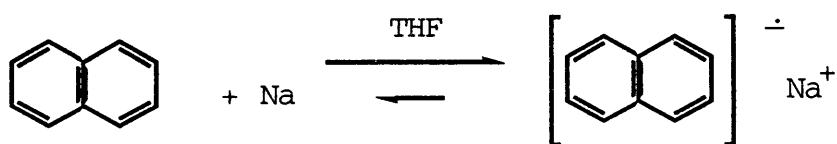
of only one terminal nitrogen atom from the amide ion in each polymer chain led to strong support for the anionic mechanism. From the above mechanism it is seen that the solvent is essentially an active transfer agent with the growing chain, limiting the chain length.

The work done by Higginson and Wooding established two important concepts in the understanding of anionic polymerizations. First, they showed the participation of the three conventional steps in an anionic mechanism: initiation, propagation and termination. Secondly, they raised the importance of free ions and ion pairs as distinct intermediates in solution anionic polymerizations.

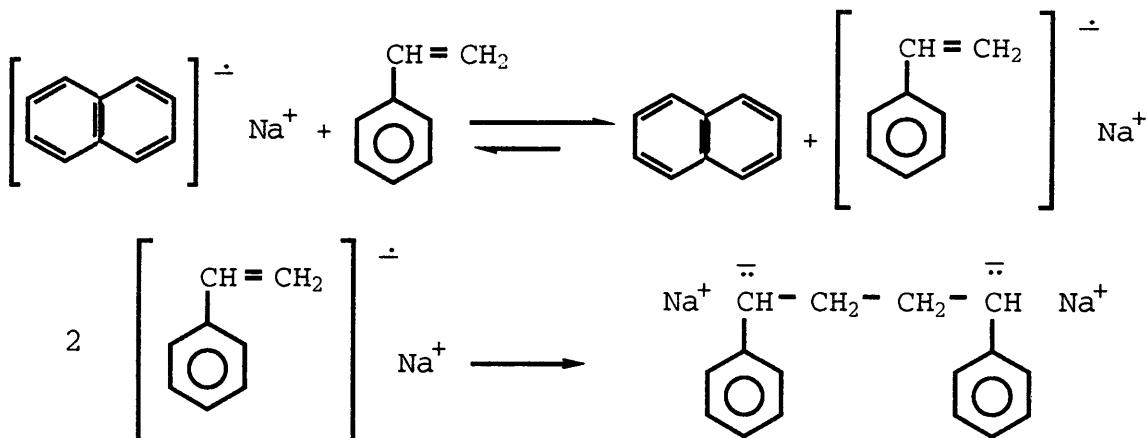
Two major events that occurred at about the same time greatly influenced interest in anionic polymerizations. First, was the discovery by Stavely and coworkers at Firestone that lithium and its organic derivatives could initiate the polymerization of predominantly cis-1,4-polyisoprene in either the bulk or hydrocarbon solvents (13). Thus, virtually copying the structure of natural rubber. The second event was the pioneering work of Szwarc demonstrating that the nonterminating chain addition polymerization was not restricted to the ethylene oxide, but in fact was also possible for vinyl polymers (14-15). Szwarc showed that the homogeneous anionic polymerization of styrene initiated by sodium naphthalene in tetrahydrofuran led to a living

polymer. That is, chains retain their ability to resume their growth whenever more monomer is added. Thus, the chain ends do not die but remain active. Szwarc also demonstrated that block copolymers result if a monomer different from the one previously used was added (16-18).

A detailed understanding of carbanionic polymerization mechanism became apparent from extensive studies of homogeneous systems involving initiators of sodium naphthalene compounds. It was previously known from Schlenk and coworkers that polynuclear aromatic compounds reacted with alkali metals, like sodium, in ether solvents to form highly colored solutions, without involving substitution reactions or evolving hydrogen (4,19). In 1935, Scott first showed that rapid polymerization of styrene and dienes took place with either sodium naphthalene or sodium biphenyl in dimethyloxyethane (20). The structure of these aromatic compounds was determined using electron spin resonance by Lipkin, Weissman and coworkers (21-22). They found these compounds to be radical ions formed by transfer of an electron from the alkali metal to the lowest unoccupied π orbital of the aromatic compound:



Szwarc, Levy and Milkovich demonstrated that the sodium naphthalene complex initiates styrene by an electron transfer, leading to a styrene radical-anion, which immediately dimerizes to form a styrene dianion, as shown below (23,14):



The resulting dianion is then capable of polymerizing styrene by rapid anionic attack. Substituting a diene for styrene, a diene dianion is formed from the coupling of the anionic-radical and polymerization occurs by an anionic mechanism.

Szwarc and colleagues recognized the possibilities of forming polymers from anionic polymerizations with hydroxyl and carboxyl functional end groups and coined the term "living polymer" for these system. Since these systems involved homogeneous polymerization, this made it possible to study them with regards to stoichiometry and kinetics, and therefore determine their mechanism. These unique features

and applications aroused great interest in the chemistry of anionic polymerizations, providing the polymer chemist with a method of preparing "tailor-made" predictable molecular weight homopolymers and copolymers with very narrow molecular weight distributions.

2. Organolithium Initiated Polymerizations

Polymerization reactions involving the opening of carbon-carbon double bonds in which the propagating reactive center is a carbanion can be initiated for the most part by three types of initiators: 1) alkali metals, 2) aromatic complexes of alkali metals and 3) organoalkali compounds (27). The most important and frequently used of the organoalkali compounds are the organolithium initiators, since these are soluble in nonpolar and polar solvents. Alkyl lithiums are extremely reactive with oxygen, moisture, carbon dioxide, alcohols, ethers, ketones and carbon-carbon double bonds (30).

Organolithium initiators function by direct anionic attack on the monomer, rather than by electron transfer, leading to a monopropagating chain in the case of monofunctional alkyl lithium initiators and dipropagating chains by use of difunctional organolithium initiators. Under scrupulously purified systems, avoiding any chain or initiator terminations, the concentration of growing chains corresponds to the concentration of initiator. The

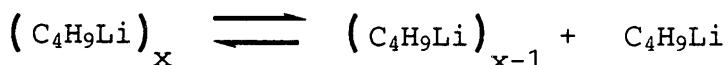
stoichiometric number-average chain length at 100% conversion is given by the following relationship in the case of monofunctional initiation (e.g., only one active lithium per alkyl lithium molecule):

$$\bar{M}_s = \frac{\text{grams of monomer}}{\text{moles of initiator}}$$

while difunctional initiation (e.g., two active lithium per organolithium molecule) leads to the following stoichiometric number average molecular weight prediction (27,35):

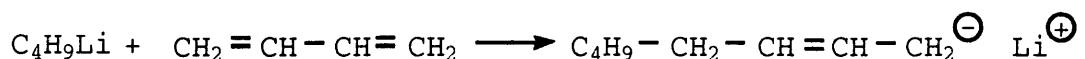
$$\bar{M}_s = \frac{\text{grams of monomer}}{0.5 \text{ moles of lithium}}$$

Alkyllithiums tend to associate in nonpolar solvents to give aggregates as a result of the small size of the lithium cation and the strength of its electric field. For example, n-butyllithium has a degree of association of six. It is believed that the first step in the initiation of polymerization is the dissociation of the alkyllithium aggregate into the corresponding monomeric species (31):



Initiation is then thought of involving the addition of a monomer molecule to a monomeric alkyllithium molecule. This

nucleophilic attack is principally the addition of a vinyl or diene monomer to a negatively charged entity. The addition of the negative ion to the double bond of the monomer produces a covalent bond on one end and a carbanion on the other end. The generalized initiation process is given by:



where the nucleophilic part of the alkyl lithium initiator is denoted by C_4H_9^- and the alkali metal counterion is Li^+ . The new carbanion may now add more monomer, propagating a living polymer. This mechanistic approach is based on the assumption that only the unassociated initiator molecules are active in initiation. Therefore, if the equilibrium between the hexameric association state of n-butyllithium and the monomeric molecule is small, the rate of initiation will be proportional to $[(\text{C}_4\text{H}_9\text{Li})_6]^{1/6}$. This mechanism has been met with much debate and opposition and remains to be elucidated (27,29,30).

The rate of addition of organolithium to diene and vinyl monomers is much slower compared to the rates of reaction with water, carbon dioxide and alcohols. Hence, the presence of these reactive impurities during polymerization prevents the initiation by destroying the initiator. The importance of very rigorous purification of solvents, monomer,

initiator, and glassware for kinetic studies of anionic polymerizations is of the upmost importance if premature initiator and/or chain end termination is to be avoided. Typically, anionic initiators are used in the concentration range of 10^{-3} - 10^{-5} M, then obviously reactive impurities must be kept below 10^{-6} M (28,29).

The utility of homogeneous organolithium initiators has provided substantial advancements in our understanding about the kinetics and mechanism of anionic polymerization. Diene and vinyl anionic polymerizations initiated by organolithiums has attracted both academic and commercial interest as a result of the potential for obtaining systems lacking termination reactions. The importance of nonterminating chain ends is readily recognized by the preparation of polymers with predictable molecular weights, narrow molecular weight distributions, functionalization of chain end and the synthesis of block copolymers with precise control of architecture.

Most of the kinetic studies of organolithium initiation have been conducted with 1,3-dienes and styrene in hydrocarbon solvents. The rate of initiation of organolithiums with dienes or styrene is known to be relatively slow to propagation. This is mostly due to the high degree of association of organolithium compounds in hydrocarbon solvents. The kinetics of both initiation and

propagation have consistently been found to be first order with respect to the monomer concentration, without regard to the solvent type and temperature. Nevertheless, both initiation and propagation have been found to show fractional order dependencies on the initiator concentration, depending on the solvent and monomer concentration. The association makes the kinetics of the addition complex and leads to fractional orders of reaction (1). Consequently, a simple correlation between the reactivity and basicity of the alkyl lithium nucleophile is not observed. It is now widely recognized that the kinetic significance of aggregation involving carbon-lithium species is incomplete in our understanding with regards to initiation and propagation (34). A variety of reaction orders can be seen in Table 1 for the reaction of organolithium initiators with butadiene and isoprene.

Slow initiation is known to broaden molecular weight distribution, having an adverse effect on ultimate physical properties. For example, in anionic polymerization of diene and styrene monomers initiated by n-butyllithium in hydrocarbons. Many chemist employ the so-called "seeding technique" to prevent this broadening effect by adding a small amount of monomer to all of the "slow" initiator to be used in the polymerization. After the formation of short chain oligomers the remainder of monomer is added, in hopes

Table 1
 Initiation Studies of Butyllithium Isomers
 in Hydrocarbon Solvents (34)

Initiator	Monomer	Solvent	Reaction Order	T (°C)
n-Butyl	Butadiene	n-Hexane	1.0	50
		Toluene	1.0	50
		Cyclohexane	0.5-1.0	40
		Cyclohexane	1.0	50
	Isoprene	n-Hexane	1.0	50
		Toluene	1.0	50
		Cyclohexane	0.5-1.0	30
		Cyclohexane	1.0	50
s-Butyl	Butadiene	Benzene	0.9	30
		Cyclohexane	1.0	50
	Isoprene	n-Hexane	0.7	30
		Benzene	0.25	30
		Cyclohexane	0.66	25
		Cyclohexane	0.75	30
		Cyclohexane	1.0	50
t-Butyl	Butadiene	Cyclohexane	1.0	50
	Isoprene	Cyclohexane	1.0	50
		Cyclohexane	0.2-0.7	25
i-Butyl	Isoprene	Cyclohexane	1.0	50

of producing polymer of uniform size since the slow initiator has already been consumed.

Recent work by Szwarc and coworkers report that the seeding technique cannot eliminate the undesired broadening of molecular weight distribution in irreversible propagation systems. They present theoretical considerations and empirical findings that neither the amount of the utilized initiator nor the molecular weight or molecular weight distributions of polymers is effected by the order of monomer addition (140). Hsieh has emphasized that narrow molecular weight distribution are obtained by using "fast" initiators (141,142). The short chain alkylolithiums, ethyllithium and n-butyllithium are considered as slow initiators in hydrocarbons with styrene and dienes, while the branched chain alkylolithiums, sec- and tert-butyllithium achieve rapid initiation (69).

Even though many of the initiation reactions listed in Table 1 have been only partially explained, it has been possible to compare the reactivities of the initiators toward diene and styrene monomers in various solvents. Table 2 list the effect of the organic moiety of the alkylolithium in decreasing order of reactivity, with the exception of t-butyllithium, which reacts very slowly with styrene and moderately fast with dienes (32,33).

3. Propagation Kinetics of Dienes

Table 2

Relative Reactivities of Organolithium Initiators (32,33)

Dienes

Methyl > s-Butyl > i-Propyl > t-Butyl > n-Butyl and Ethyl

Styrene

Methyl > s-Butyl > i-Propyl > n-Butyl and Ethyl > t-Butyl

Solvents

Toluene > Benzene > n-Hexane > Cyclohexane

In the kinetic study of polymerization the most significant step to consider is the propagation reaction. The distinction between initiation and propagation is important; under the proper experimental conditions the propagation step can be measured independently of the initiation process. In homogeneous anionic polymerization, the following characteristics may be considered of the propagation kinetics(27):

- a) Propagation should be independent of the mode of initiation, e.g., whether initiation is by alkali metals, aromatic complexes, or organolithium compounds.
- b) Propagation is highly dependent on the type of counterion inaugurated by the initiator, which may be associated with the living chain end.
- c) The kinetics and mechanism of the growing chain end is profoundly affected by the nature of the solvent used.

The rate of polymerization in living systems yielding high molecular weight polymers is expressed simply as the rate of propagation:

$$-\frac{d[M]}{dt} = k_p[P^*][M]$$

where M is a monomer, P^* a growing chain end, and k_p the observed propagation rate constant. The propagation step should be in general, a simple bimolecular reaction between

the living chain and monomer. However, in most cases the propagation reaction does not follow the kinetics of the simple bimolecular reaction, indicating a more complex mechanism. What has been found for studies on dienes and styrene, a first-order dependence on monomer concentration for the propagation reaction and a fractional order relative to the initiator concentration. Again, these two parameters depend on two important factors: solvent and counterion. Consistently, dienes have been found to have kinetic orders between one-fourth and one-sixth, while styrene shows a one-half order in nonpolar solvents. For example, Wang reported kinetic studies at 20, 30 and 40°C for homopolymerizations of butadiene and isoprene by dilatometry in n-hexane using s-butyllithium as the initiator. Wang observed the propagation rate having a first-order dependence on the monomer concentration and a one-fourth fractional order on initiator concentration as shown in Table 3 (58,59).

Morton suggest the first-order dependencies indicate a direct reaction between chain ends and monomer, but orders less than unity indicate the presence of a dissociation phenomenon (27). Table 3 summarizes propagation rates and orders for butadiene and isoprene in hydrocarbon solvents.

If the initiation rate is of the same order of magnitude as the propagation rate for homogeneous organolithium polymerization and the initiator is efficiently mixed into

Table 3
 Propagation Rate Studies in Hydrocarbon Solvents
 of Butyllithium Isomers (35)

Solvent	Initiator	[Initiator] (moles/liter)	Order M	Order I	Ref.
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Butadiene

n-Hexane	n-Butyl	$(0.9-12) \times 10^{-3}$	1	0.5	36-38
	s-Butyl	$(0.68-2.54) \times 10^{-3}$	1	0.25	58
n-Heptane	n-Butyl	$(0.07-6) \times 10^{-3}$	1	0.25	39
		$(0.4-10) \times 10^{-3}$	1	0.17	50
Cyclohexane	s-Butyl	$(1.5-6.0) \times 10^{-2}$	1	0.50	40
		$(0.7-15) \times 10^{-3}$	1	0.33	40

Isoprene

n-Hexane	n-Butyl	$(2.4-57) \times 10^{-4}$	1	0.5	36-38
		$(2-140) \times 10^{-5}$	1	0.5	41
		$(2-16) \times 10^{-3}$	1-2	0	42
		$(5-100) \times 10^{-4}$	1	0.25	29
	s-Butyl	$(0.70-2.51) \times 10^{-3}$	1	0.25	58
	t-Butyl	$(1-10) \times 10^{-3}$	1	0.5	43
n-Heptane	n-Butyl	$10^{-6} - 10^{-2}$	1	0.17-0.5	44
		$<5 \times 10^{-3}$	1-2	0.25	39
		$(5-20) \times 10^{-3}$	1-2	0-0.25	39
Cyclohexane	n-Butyl	$(2.6-6.5) \times 10^{-3}$	1	0.17	45
	s-Butyl	$(2.6-6.5) \times 10^{-3}$	1	0.17	45
		$(1.5-6.0) \times 10^{-2}$	1	0.5	40
		$(0.7-15) \times 10^{-3}$	1	0.33	40
		$(0.06-16) \times 10^{-3}$	1	0.25	46
	t-Butyl	$(2.6-6.5) \times 10^{-3}$	1	0.17	45

the reaction mixture, then all chains should start growing at the same time and add monomer at equal rates. Using an efficient organolithium initiator, the initiation is complete at approximately 10-15% conversion of monomer into polymer (61). Polymers produced under these conditions will have very narrow molecular weight distributions. As predicted by Flory, under termination free conditions, the molecular weight will approach a Poisson distribution (9). That is, the number and weight fraction of j-mers, P_j and W_j , respectively, is defined by:

$$P_j = e^{-x} x^{j-1} / (j-1)!$$

$$W_j = [x/(x+1)] j e^{-x} x^{j-2} / (j-1)!$$

and x represents the number of monomer units which have reacted per initiator molecule. Therefore, the molecular weight distribution is defined as the ratio of the weight average (x_w) to number average (x_n) chain length, given by:

$$x_w/x_n = 1 + 1/x_n$$

The degree of uniformity attained in organolithium polymerizations increases with increasing degree of polymerization. For example, for $x_n = 100$ approximately 70% of the polymers have molecular weights within 10% of their

average value. This corresponds to a $x_w/x_n = 1.01$. The following experimental conditions have to be met to obtain a Poisson molecular weight distribution (30):

- a) The polymerization must be irreversible;
- b) Chain-transfer and termination must be strictly excluded;
- c) There must be virtually instantaneous initiation, or low molecular weight oligomers have to be used for initiation;
- d) Uniform reaction conditions must be maintained throughout the entire reaction, e.g., temperature, concentration and efficient mixing.

A listing of narrow molecular weight distributions obtained for butadiene and isoprene polymers prepared by butyllithium initiators is shown in Table 4. After satisfying the various experimental conditions listed above, we can see from Table 4, that indeed, a Poisson molecular weight distribution is obtained.

4. Mechanism of 1,3-Diene Polymerization

Our present knowledge on the mechanism of organolithium initiated polymerizations has been explained from accumulated studies on the chain structure of dienes along with the properties and kinetics of the propagating chain ends. Nuclear magnetic resonance studies of the carbon-lithium chain ends has been used in organolithium polymerization of

Table 4
 Butyllithium Initiated
 Diene Polymers with Narrow Molecular Weight
 Distributions in Hydrocarbon Solvents (27)

Initiator	Polymer	Solvent	x_w/x_n	Ref.
n-Butyl	Polybutadiene	n-Hexane	1.1	51
n,s;t-Butyl		Cyclohexane	1.10-1.20	52
n-Butyl	Polyisoprene	n-Hexane	1.05-1.18	53,36
n-Butyl		n-Heptane	1.1	54
n-Butyl		Cyclohexane	1.10	55
s-Butyl		n-Hexane	1.1	56
n,s;t-Butyl		Cyclohexane	1.13-1.35	52
s-Butyl		Cyclohexane	1.05	57

dienes to elucidate the character of the propagation mechanism.

In the study of dienes, a mechanistic distinction is made between polymerization in nonpolar and polar solvents. In nonpolar solvents, studies support that the propagating chain ends are associated in pairs, which may be expected for polar species in nonpolar environments. While, in polar solvents, the propagating chain end have an ion pair in equilibrium with a free ionic species. Both types of chain ends are capable of chain propagation, with the free carbanion being several orders of magnitude more reactive than the ion pair. There is no unambiguous evidence whether the active chain ends are the dissociated or associated species, or both, since there is no simple relation between the state of association and the kinetic order, which can vary from one-half to one-sixth, depending on the monomer and solvent used (60).

A mechanistic scheme as proposed by Morton and coworkers is shown in Figure 1 for the propagation of butadiene in nonpolar and polar solvents (62-66). It can be seen, that 1,4-addition occurs from a concerted four-center reaction between butadiene and the σ -carbon-lithium bond, favored in hydrocarbon solvents. While, 1,2-addition results when butadiene reacts with the γ -carbon of the π bond, favored in polar solvents. The σ -bonding is supported for both the α

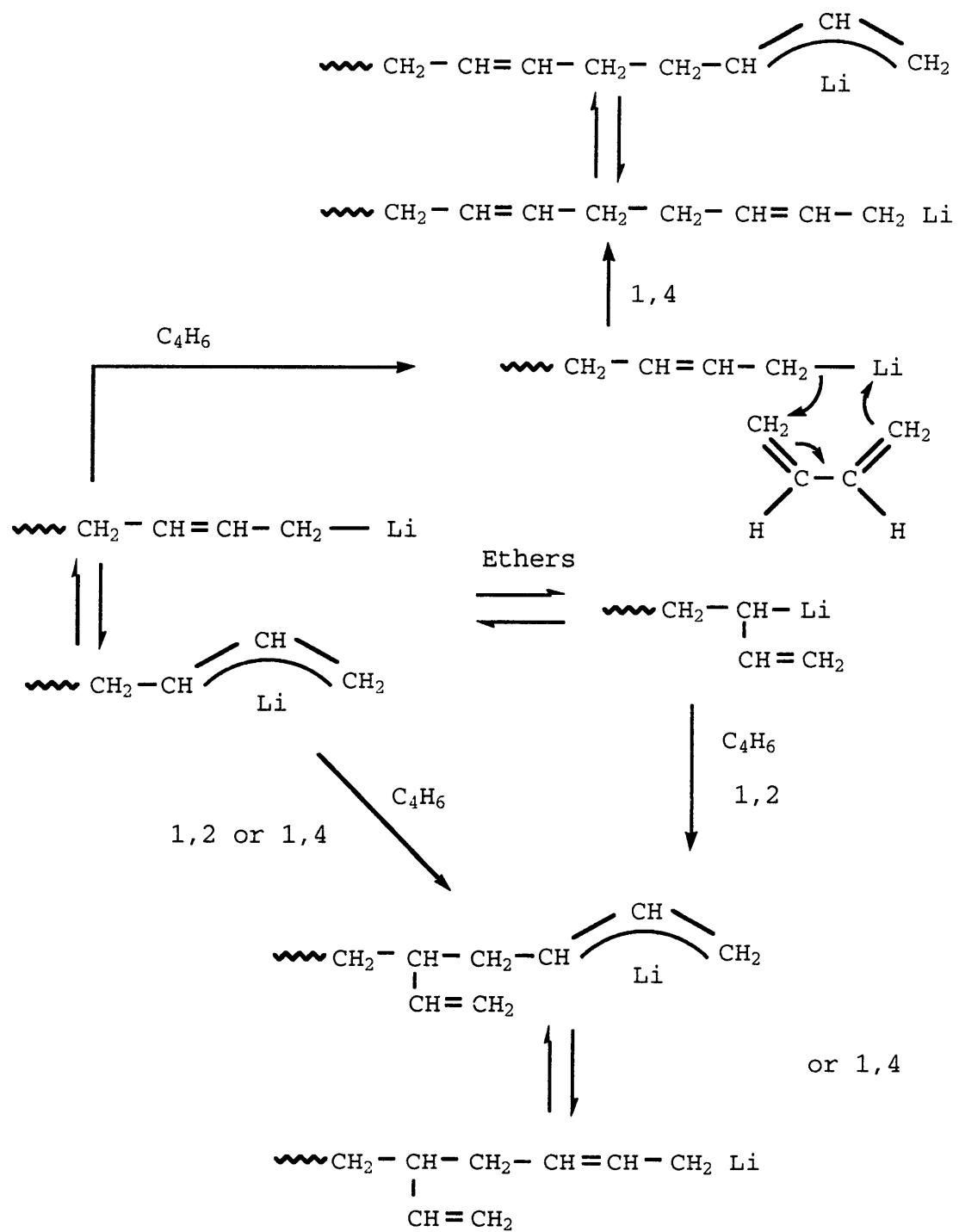


Figure 1. Mechanism for Butadiene Polymerization

and γ carbon of butadiene in polar solvents, however σ -bonding is inclusive to the α carbon in hydrocarbon solvents. Furthermore, the $\sigma-\pi$ equilibrium should lead to a cis-trans equilibrium in the 1,4 propagating chain end in polar solvents only.

5. Microstructure and Association Phenomena

Unlike the previously described aromatic complexes of alkali metals, organolithium compounds are soluble in a variety of solvents. Organolithium compounds hold a special interest among the organic derivatives of alkali metals because they are soluble not only in basic solvents like tetrahydrofuran, but also in hydrocarbon solvents such as cyclohexane (1,24,25). Naturally, this makes organolithium compounds very versatile as diene and vinyl polymerization initiators. In polar solvents, evidence from reaction kinetics as well as physical measurements leave little doubt that the growing chain end can either be a ion pair of some type or a free anion. However, in hydrocarbon solvents, organolithium initiated polymerizations of butadiene and isoprene, the chain ends are associated as dimers, since hydrocarbon solvents do not solvate the metal counterion (27).

One distinguishing characteristic of anionic polymerization is the regulation of the stereoisomeric arrangement of the incoming monomer unit. This mechanism has

little control over tacticity, however it does control the geometric isomerism of polydiene units. The 1,3-dienes can polymerize in four modes of configuration in the variation of the double-bond position: cis-1,4, trans-1,4, 1,2 and 3,4 as well as head-to-tail, tail-to-tail and head-to-head constitutional isomers. The conjugated diene butadiene can become enchainued either as a 1,4-unit or as a 1,2-product, as shown in Figure 2 (68). The 1,4-structure occur when both double bonds in butadiene engage in the polymerization, with a subsequent shift of the remaining double bond to the 2,3-position. The two isomeric structures cis-1,4 and trans-1,4 may then be formed since the remaining double bond does not allow free rotation. While, isoprene a substituted 1,3-diene has the additional microstructure enchainment by 3,4 addition. The 3,4- and 1,2-structure form when isoprene addition takes place across the corresponding double bond only. Both the 3,4- and 1,2-structures can occur in either the isotactic or the syndiotactic stereoregular forms, as shown in Figure 3. The cis-1,4-polyisoprene is identical to that in natural rubber or *Hevea brasiliensis*, whereas trans-1,4-isoprene corresponds to *Gutta percha*.

Organolithium initiated diene polymerizations involve successive insertions of monomers between a macromolecular anion and a more or less tightly associated lithium counterion. The macroion and counterion form an organic salt

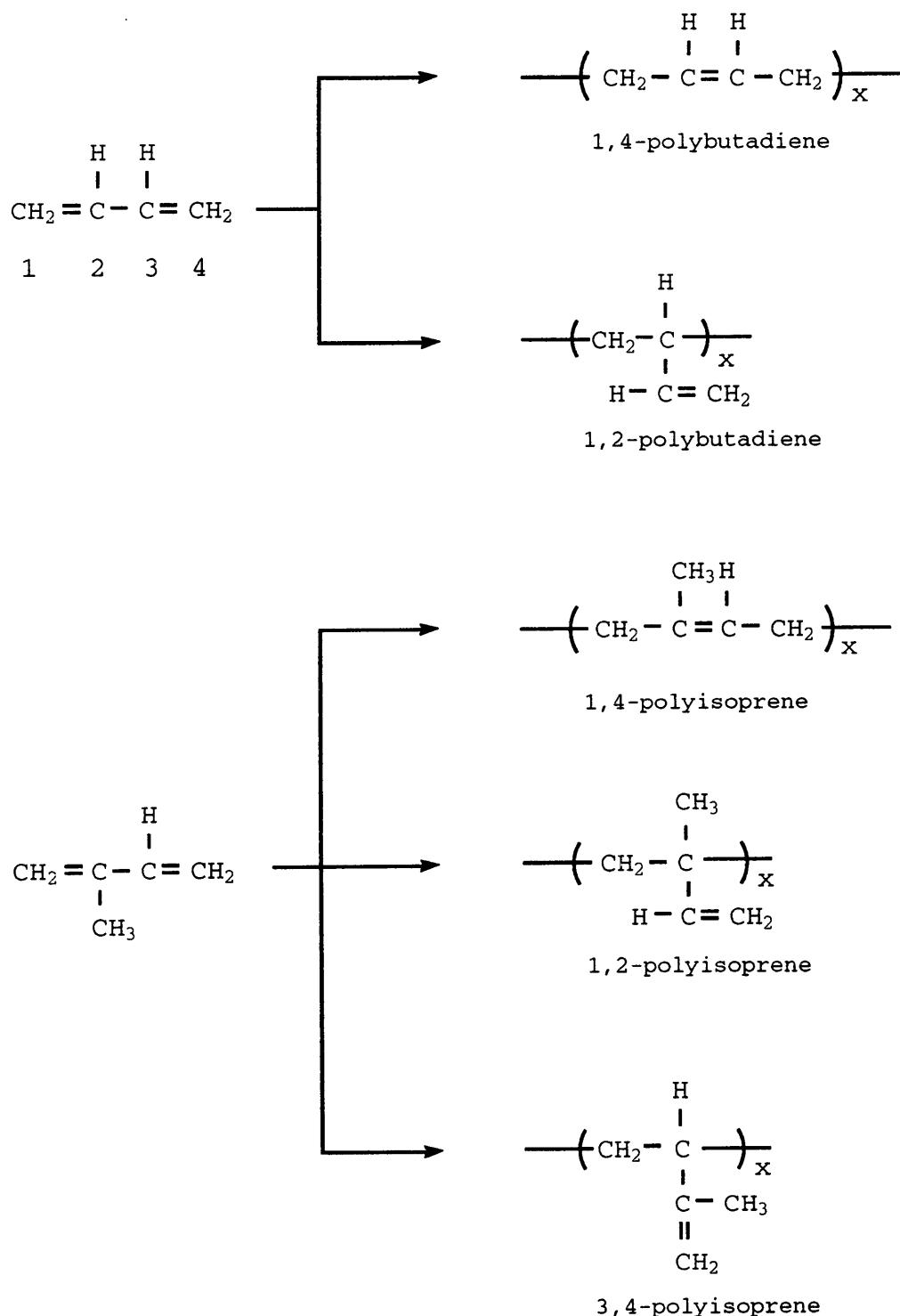


Figure 2. Microstructures of Polybutadiene and Polyisoprene

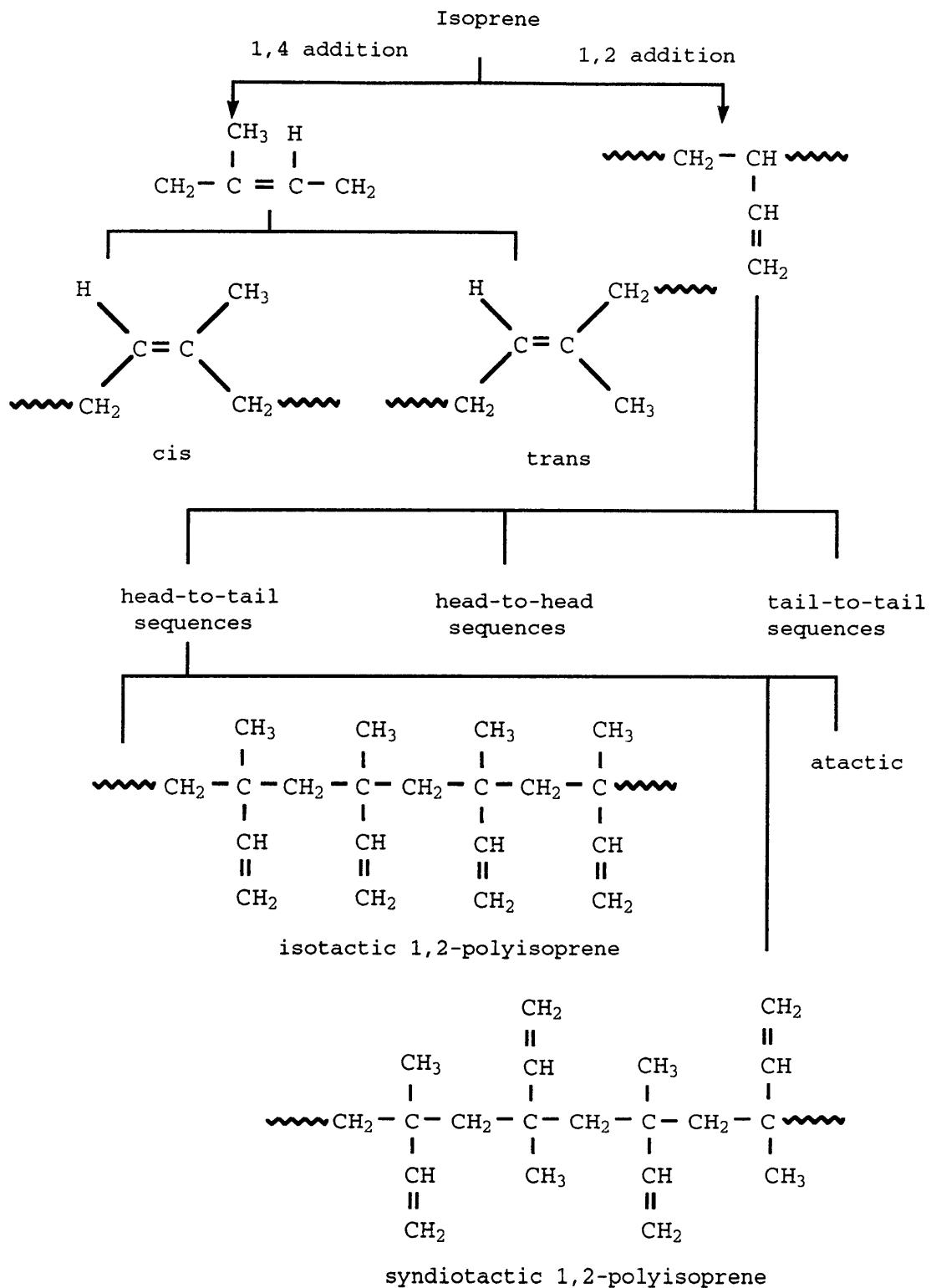
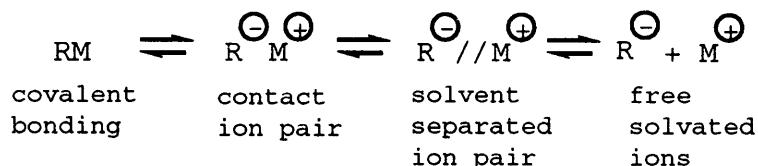


Figure 3. Constitutional Isomers of Polyisoprene

which may exist in various forms depending on the polymerization solvent. The solvent does not actually interrupt the propagation step, but plays an active role in controlling both the rate and mode of the chain growth process (67). There are at least four forms of organic ion pairs in principle to consider:



The forms which are actually encountered in a polymerization will depend of the organic species R, the alkali metal counterion M, the solvating ability of the reaction solvent and the temperature (68).

The slow rates of initiation of butyllithiums in hydrocarbon solvents are most likely due to the fact that these compounds are associated in nonpolar solvents. Table 5 summarizes various association states of butyllithium isomers in hydrocarbons. It is apparent from Table 5 that branched butyllithiums have lower degrees of association (*n*), probably due to steric hindrance. The kinetics and mechanism of chain propagation still remains to be completely determined, undoubtedly because of complications due to association of

Table 5
 Association States of Butyllithium Isomers in
 Hydrocarbon Solvents

Initiator	Solvent	Molar Concentration	n	Ref.
n-BuLi	Benzene	0.5-3.4	6.2	77
	Cyclohexane	0.4-3.3	6.1	77
s-BuLi	Benzene	0.17-0.5	4.1	78
	Cyclohexane	0.11-0.4	4.1	78
i-BuLi	Cyclohexane	0.004-0.02	4.0	79,80
t-BuLi	Benzene	0.05-0.18	3.8	81
	n-Hexane	0.05-0.23	4.0	81
	Cyclohexane	0.0005-0.3	4.0	79,80

chain ends with chain ends and "cross association" of propagating chain ends with the alkylolithium initiator.

The first indications that the microstructure of polydienes could be influenced by the counterion were through studies of polybutadiene polymerized by alkali metals, as shown in Table 6 (69). For both polybutadiene and polyisoprene prepared by alkali metals, the 1,4-structure decreases with increasing electropositivity of the metal (70). As already mentioned, lithium metal or an alkylolithium gives a predominantly 1,4 polymerization of both isoprene and butadiene in nonpolar solvents, e.g., close to that of natural rubber. The type of organolithium initiator does not have any effect on the microstructure of the polydiene, since the organic moiety is not associated with the growing chain-end. However, the concentration of organolithium initiator in nonpolar solvents does effect the microstructure of polydienes. Table 7 shows the effects of different hydrocarbon solvents and s-butyllithium initiator concentrations on the chain structure of polybutadiene and polyisoprene. From these results, the following conclusion can be interpret (74):

- a) The absence of any solvent provides the highest attainable cis-1,4 structure, as a function of monomer concentration (29,75);

Table 6
Effect of Alkali Metal on Polybutadiene Microstructure

Metal	Electro-negativities	Composition, %				Ref.
		cis-1,4	trans-1,4	1,2		
Li	1.0	35	55	10		71
Na	0.9	23	45	32		72
K	0.8	13	49	38		72
Rb	0.8	7	31	62		73
Cs	0.7	6	36	59		73

Table 7
Chain Microstructure of Organolithium Polydienes

Solvent	[s-BuLi]	Microstructure (mole %)			
		cis-1,4	trans-1,4	3,4	1,2
Polybutadiene (29, 75, 76)					
Benzene	8×10^{-6}	52	36	--	12
Cyclohexane	1×10^{-5}	68	28	--	4
n-Hexane	2×10^{-5}	56	37	--	7
n-Hexane	3×10^{-2}	36	62	--	8
None	7×10^{-6}	86	9	--	5
None	3×10^{-3}	39	52	--	9
THF	2×10^{-4}	7	10	--	85
Polyisoprene (29, 75)					
Benzene	3×10^{-4}	69	25	6	--
n-Hexane	1×10^{-2}	70	25	5	--
n-Hexane	1×10^{-5}	86	11	3	--
None	3×10^{-3}	77	18	5	--
None	8×10^{-6}	96	0	4	--
THF	3×10^{-4}	--	26	66	9

- b) The presence of solvent decreases the cis-1,4-structure; aliphatic solvents lead to a slightly higher cis-1,4 content than aromatic solvents (benzene);
- c) Lower initiator concentration leads to an increase in the cis-1,4 content, without any change in side-vinyl content.

In spite of the fact that butadiene, isoprene and styrene polymerizations involving alkali metal initiation in polar solvents have been satisfactorily explained, much remains to be elucidated with regards to polymerization of these systems in nonpolar solvents. Among other studies, it would be necessary to determine the effect of the chain end concentration on the chain end structure. Unfortunately, as of yet NMR studies have not been able to solve these complex problems since conventional techniques are not sensitive enough at the very low concentrations needed to explore these systems.

B. Block Copolymerization

1. Introduction

For the past forty years polymeric materials have been the fastest growing segment of the United States chemical industry. With increasing demands on material application and performance, polymers continue to replace traditional materials. Polymeric materials are constantly being improved and modified for specific needs. Multiphase polymer systems

in recent years have received extensive attention, specifically since the rate of appearance of new polymer types has declined considerably. The development of "block" copolymers has stimulated a great deal of interest, due to the unique physical and mechanical properties obtainable with these materials. This is due largely to the heterophase nature obtainable with block copolymers.

Block copolymers offer several advantages over blending of homopolymers (77): First, the different blocks are covalently bonded together, thereby improving the interfacial adhesion between the separate phases compared to homopolymer blends. Second, novel materials can be synthesized by living techniques to accurately control the molecular architecture. Third, block copolymers can be employed to strengthen blends of immiscible polymers by serving as "emulsifiers," by improving the interfacial adhesion and load transferring capability of homopolymer blends.

Sequential anionic addition techniques initiated by homogeneous organolithium species in hydrocarbon solvents allow the best block copolymer synthesis for the control of block integrity, architecture and achieving the ultimate attainable properties. The success of these techniques merit mainly from three desirable features. First, the location and concentration of the living chain ends are known. Second, homopolymer contamination is minimal, resulting from

the termination-free nature of living systems and from stoichiometry control in the addition-growth process. Finally, block length and placement are controlled (78).

2. Architecture

Architectural control is critical in order to develop the unique properties characteristic in block copolymers. Milkovich first showed the importance of architecture in determining polymer properties of multiblock systems (79). Block copolymers are macromolecules composed of chemically dissimilar covalently bonded segments. Their sequential architecture can be identified by four basic structures, shown schematically in Figure 4 and 5 (78).

The most straightforward architectural example is the two-block structure, generally referred to as an A-B diblock copolymer. The diblock is denoted by two dissimilar chemical repeat units, "A" and "B". The second form is the A-B-A block copolymer, known as the triblock. The triblock consist of a central block of B repeat units, flanked by end segments of A repeat units, or by a reverse in the order of the segments, e.g., B-A-B. The third type is the covalently coupling of four or more blocks together to form $(A-B)_n$ multiblock or segmented copolymers, that is, alternating blocks of A and B repeat units. The first three architectural variations are of linear forms, however the fourth basic type is the radial block copolymer or known as a

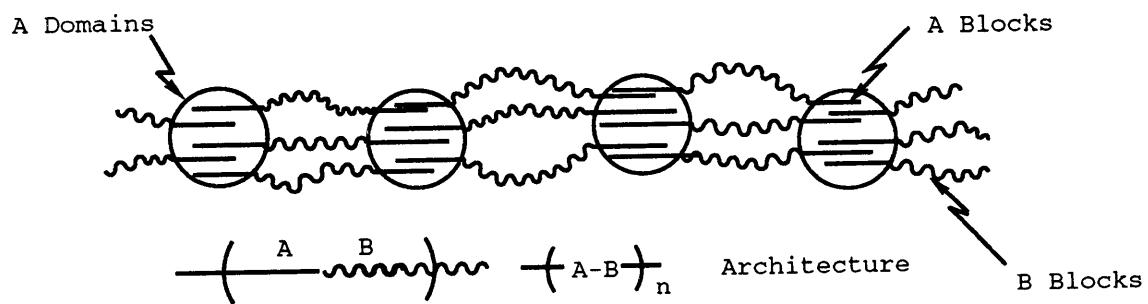
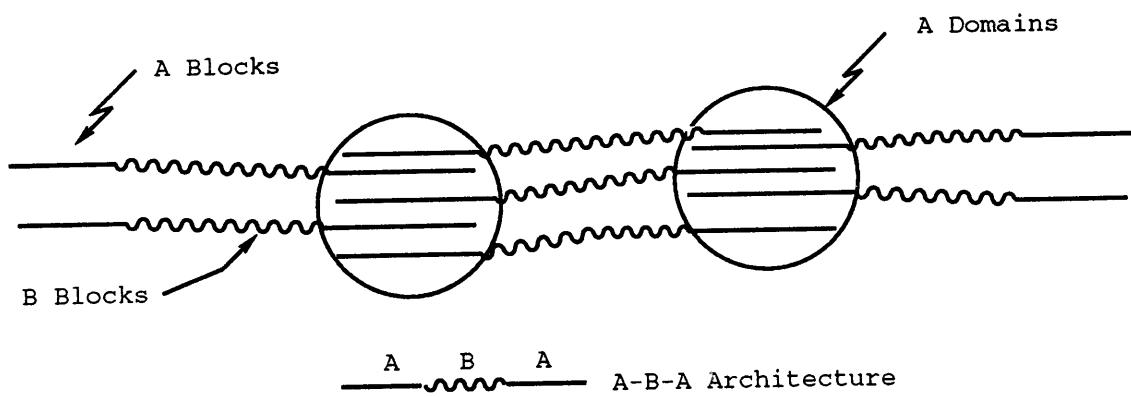
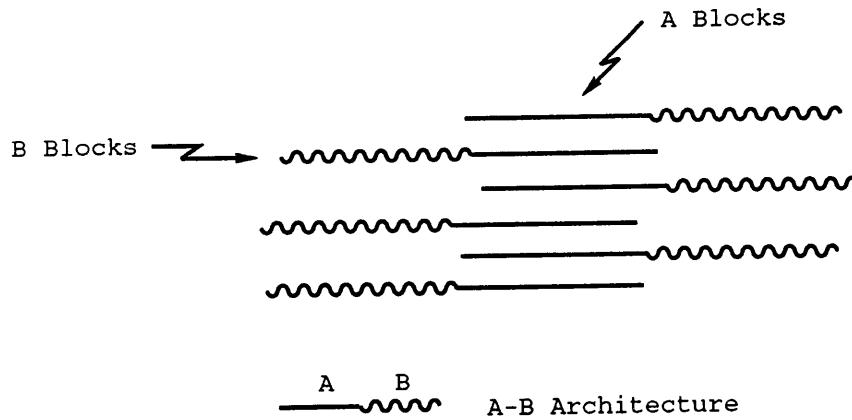
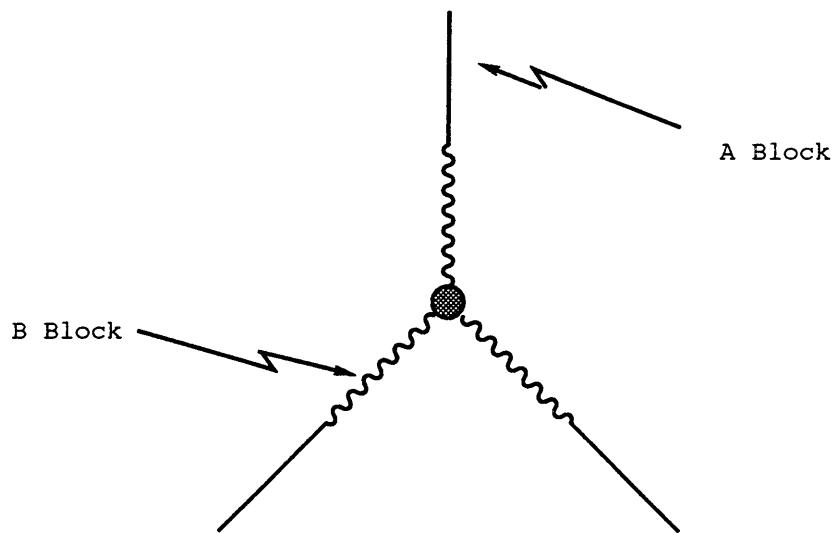
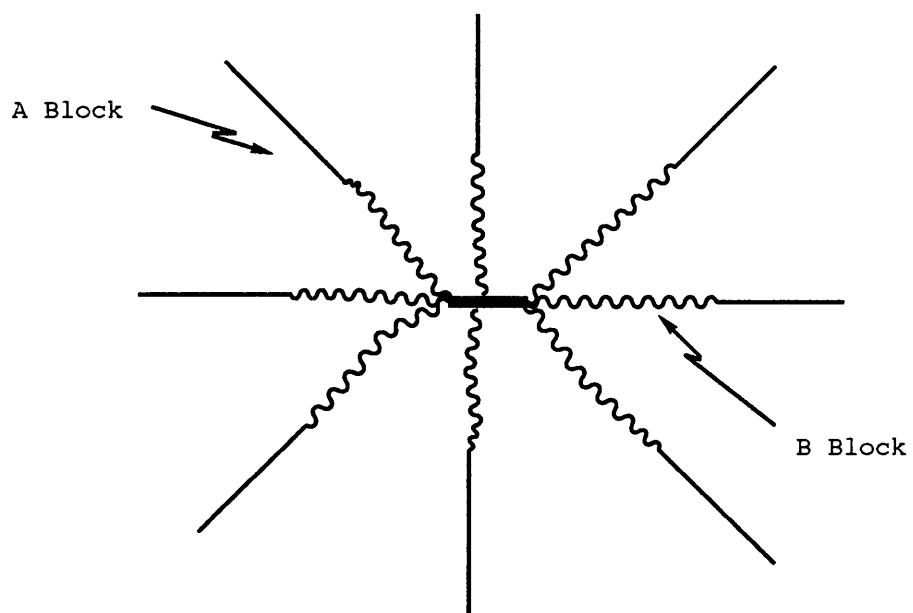


Figure 4. Linear Block Copolymer Architectures (78)



Three Arm Radial



Eight Arm Radial

Figure 5. Star Block Copolymer Architecture (78)

star block copolymer. This architecture consists of three or more diblock copolymers radiating from a central hub as shown in Figure 6.

3. Synthesis by Organolithium Polymerization

The techniques commonly employed to prepare homopolymers by living addition polymerization schemes are also used to synthesize block copolymers. A-B and A-B-A architectures are conveniently made by anionic living polymerizations, however it may be disadvantageous to synthesize well-defined $(A-B)_n$ multiblock copolymers by living addition methods because of chain end "burn out," e.g., premature chain end termination caused by the fortuitous impurities encountered during repeated sequential monomer additions.

Diblock copolymers can be made by two methods, depending on the monomers employed. First, the second monomer can be added to the completed living polymerization of the first monomer. Also, copolymerization of certain monomer mixtures can be achieved without having to resort to sequential monomer addition methods. For example, in the organolithium initiated copolymerization of butadiene and styrene in hydrocarbon solvent, butadiene polymerizes almost preferentially, since the polymerization kinetics favor the addition of polystyryl anion to butadiene monomer rather than to styrene monomer. This is attested visually in the polymerization mixture, since the orange color of the

polystyryl anion does not appear until the butadiene has been depleted.

There are basically four methods which can be employed in the synthesis of A-B-A triblock copolymers, depending on the anionic initiator used (78,80-87):

- a) A three-stage process using a monofunctional initiator;
- b) A two-stage process using a difunctional initiator;
- c) A two-stage process using a monofunctional initiator plus a coupling agent;
- d) A tapered blocks process - polymerization of A block followed by copolymerization of a mixture of A and B monomers.

The three-stage process for preparing A-B-A triblocks involves the organolithium initiation of the first block, followed by the sequential addition of the B monomer, after the first monomer has been polymerized, for the formation of the diblock, and finally, the addition of A monomer. This method requires careful purification of all materials to avoid the formation of homopolymer and diblock contamination that can have detrimental effects on the physical behavior of the final product. However, this process cannot be used if the first block is not reactive enough to initiate the polymerization of a less reactive monomer or if the first block has a low ceiling temperature.

The second method involves initiation of a polymeric dianion center B block by use of a dicarbanion species, followed by the sequential addition of the A monomer to form the two end blocks. This process has several advantages over the three-stage process using a monofunctional initiator. First, this method allows the synthesis of A-B-A triblock copolymers when the A anion is not sufficiently basic to initiate the polymerization of B monomers. Second, this synthesis saves one sequential monomer addition step.

In the two-stage process with a coupling agent, an A-B diblock is formed by living sequential addition using a monofunctional initiator. However, unlike the three-stage approach, the final step is the addition of a difunctional linking agent capable of coupling together the diblocks at the B block chain ends. This is an important pathway to well-defined symmetrical end blocks, which is not always obtained by the three-stage sequential process. This method is useful in systems where the B block chain end cannot initiate the A block. For example, to produce an A-B-A triblock of styrene and methacrylate, the methacrylate chain end is too weakly basic to initiate the polymerization of styrene. Also, this process saves one sequential monomer addition, thus helping to keep the adventitious impurities low. One disadvantage however, it is difficult to get exact stoichiometric coupling of the diblock chains, since only a

small amount of linking agent is needed. Even a small amount of unlinked diblock can adversely effect the mechanical properties of the triblock material.

The last method, triblocks by tapered block process, utilizes monomer mixtures in hydrocarbon solvents that preferentially polymerize one monomer first before addition of the second monomer. The initial A block is formed followed by copolymerization of a mixture of B and A monomers. For example, this process is prominent for the combination of butadiene and styrene. Styrene is first homopolymerized in hydrocarbon solvent, followed by the addition of a styrene-butadiene mixture, since the diene will be preferentially polymerized. This procedure also has the advantage of a two-stage system in that the effects of termination can be minimized. The marked disadvantage of this process is that some of the styrene becomes copolymerized with the diene giving rise to decreased incompatibility of the two phases (80).

Table 8 list several diene and styrene block copolymers prepared by the four processes discussed above (78).

4. Structure-Property Relationships of A-B-A Triblocks

The most significant and interesting of the anionic block copolymers architectures is the A-B-A triblock, since this structure resulted in the rapid development of a new class of polymer materials. Milkovich aroused considerable world wide

Table 8
 Block Copolymers by Organolithium Polymerization of
 Two Monomers

Monomer A	Monomer B	Initiator	Solvent	Ref.
A-B by Sequential Addition				
Butadiene	Isoprene	s-BuLi	Cyclohexane	59
Butadiene	Styrene	EtLi	Ether	88
Isoprene	Styrene	n-BuLi	n-Hexane	89
A-B-A by Three-Stage Sequential Addition				
Butadiene	Isoprene	s-BuLi	Cyclohexane	90
Isoprene	Butadiene	s-BuLi	Cyclohexane	58
Butadiene	Styrene	n-BuLi	Cyclohexane	91
Isoprene	Styrene	s-BuLi	Cyclohexane	92

Table 8
Block Copolymers by Organolithium Polymerization of
Two Monomers (continued)

Monomer A	Monomer B	Initiator	Solvent	Ref.
A-B-A by Two-Stage Process With A Difunctional Initiator				
Butadiene	Styrene	Dilithioisoprene	Benzene	84
Isoprene	Styrene	s-BuLi-DDPE	Cyclohexane	93
A-B-A by Tapered Block Process				
Butadiene	Styrene	n-BuLi	Benzene	80
Isoprene	Styrene	s-BuLi	Benzene	92
A-B-A of Styrene-Diene-Styrene by Coupling Process				
Diene	Initiator	Coupling agent	Solvent	Ref.
Butadiene	s-BuLi	Dicarboxylic acid diesters	Cyclohexane	94
	s-BuLi	Dibromoalkane	Benzene	95
Isoprene	s-BuLi	Carbon monoxide	Benzene	96
	s-BuLi	Dibromoalkane	Benzene	97

interest in the early 1960's due to a combination of attractive properties that had not been observed before in polymer materials. This was Shell's Kraton®, the thermoplastic elastomer composed of 70% butadiene and 30% styrene by weight. Kraton® is a strong rubber capable of large reversible deformation, without requiring crosslinking (vulcanization) or external reinforcing fillers. Kraton® can be processed by molding, extrusion and other fabrication techniques as a thermoplastic, however it has elastomeric properties at room temperature - hence the name "thermoplastic elastomer."

Some properties of block copolymers are dramatically influenced by architecture, for example, elastomeric behavior, toughness in rigid materials and melt rheology. In contrast, some of the properties are independent of sequential arrangement, these include those derived from the chemical nature of the blocks, that is, thermal transition behavior, transport, electrical, chemical resistance and stability properties (77). The properties of A-B-A triblock copolymers differ greatly compared to those of corresponding random copolymer or homopolymer blends with the same net composition. Many of the basic characteristics of triblock copolymers are similar because of the common presence of covalent intersegment chemical bonding, which influences the degree to which the phases can separate.

Triblock systems generally exhibit two-phase morphology on a micro-scale in preference to the macro-scale division seen in incompatible physical blends. This micro-heterogeneous, two-phase structure is a result of separation of dissimilar polymer segments into distinct domains. This system is composed of a minor fraction of a hard rigid block, with the T_g or T_m above room temperature and a major fraction of a soft block, with T_g below room temperature. The hard blocks associate to form morphological domains that serve as physical cross-linking and reinforcements sites for the flexible rubbery continuous matrix. This behavior requires a significant difference in segment solubility parameter and long block lengths.

Compared to conventional cross-linked elastomers, this saves one synthetic step in that the cross-linking reaction is not needed. In contrast, A-B architectures do not show any dramatic improvements in mechanical properties, since this structure does not have any means of forming reinforcement sites.

The segment block length, composition volume and chemical compatibility of the two fractions are important parameters in developing microphase separation and ultimate mechanical properties. Fedors and Meier have presented predictions in regard to minimum molecular weights required to achieve microphase separation (98,99). Variations in block lengths

also effect domain size. Typically, domain sizes range from 100-300Å, resulting in a high degree of transparency, even though these are heterogeneous systems. The type of morphology produced with amorphous two-phase triblocks depends on the volume fraction of segments A and B and on the type of sample fabrication. The effect of molecular weight on properties of A-B-A thermoplastic elastomers is shown in Figure 6 (100).

The unique behavior to achieve a network structure by physical rather than chemical crosslinking is important since the hard domains are thermally reversible, allowing melt processibility at temperatures above the hard block T_g or T_m , while cooling reestablishes the rigid domains. This is unlike vulcanizates, since their chemical crosslinkages do not slip and persist until the temperature is warm enough to cause chemical degradation of the polymer.

However, in some A-B-A systems adverse melt rheology results. Depending on specific chemical structure and block length, to varying degrees the physical networks can persist in the block copolymer melt, resulting in extraordinarily high melt viscosities and elasticities (78).

Two-phase A-B-A triblocks generally exhibit modulus-temperature behavior characteristic of both components, e.g., the glass transition temperatures and/or melting points of each phase. Compositional variations do not significantly

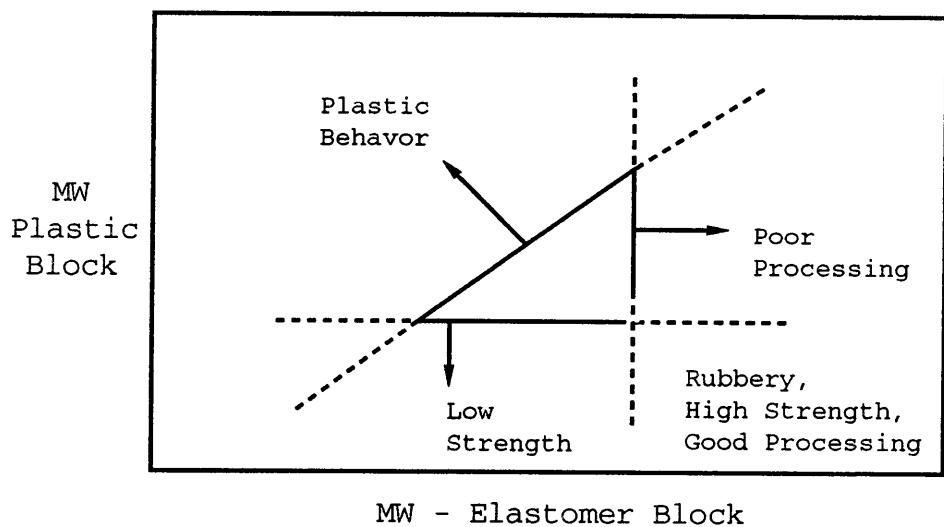


Figure 6. Effect of Block Molecular Weight on Properties of A-B-A Thermoplastic Elastomers (100)

change the location of the two T_g values in a two-phase system. This is in contrast to random copolymers prepared from A and B monomers, which display behavior intermediate to that of the homopolymers A and B. In a random copolymer, a single T_g is observed interposed between those of the corresponding homopolymers, related to the weight fraction of the A and B components. Modulus-temperature and dynamic mechanical loss behavior of the two-phase triblock copolymers are somewhat analogous to those of physical blends.

C. Star-Branched Polymers

1. Background

The synthesis of star-branched polymers provides further illustration of the versatility of living and copolymer techniques. Star-branched homopolymer or copolymer are characterized by a number of arms radiating from a common center, as seen in Figure 5. Schaeffgen and Flory were the first to successfully prepare a star polymer. They synthesized four and eight-armed polyamide stars by condensation polymerization with either a tetrafunctional or an octafunctional acid as the multifunctional reactants (101).

The first feasible preparation of star polymers by living anionic techniques was established by Morton, Helminiak, Gradkary and Bueche in 1962 (102). They were able to prepare three and four-armed polystyrene stars using

methyltrichlorosilane and tetrachlorosilane as polyfunctional linking agents.

More than two decades have passed since Milkovich reported that divinylbenzene could be employed for the synthesis of star macromolecules (103). Latter, Rempp and coworkers demonstrated the utility of this method for the polymerization of star-branched polystyrenes (104). Fetters and el at. also incorporated this procedure for the formation of multi-arm star-branched polyisoprene homopolymers and polystyrene-polydiene block copolymers (105-108). Recently, Pennisi and Fetters reported preparing asymmetric three-arm polybutadiene and polystyrene stars (109). Also, interesting "double diamond" morphologies have been reported (110).

Star-branched polymers form a class of macromolecules between the strictly linear and network polymers. Because of their finite size, star polymers resemble linear polymers rather than infinite networks. For example, star polymers are generally soluble in the same solvents as their linear homologues, in contrast to the insoluble crosslinked systems. Branching reaction occur inadvertently in many industrially important polymerizations and independently of the polymerization mechanism (111). In most cases it is difficult to define the number and types of branches and therefore correlate the changes in physical properties. There is a obvious need to elucidate the type and degree of

branching in a polymer and correlate these effects with the physical properties of the polymer.

While star branching is quite removed from branching found in commercial linear polymers, the study of star macromolecules of well defined structure allows a more quantitative study of the effects of branching in one architectural form. Stars also provides an example to check current theories of polymer solutions (113). Theoretical models have been set up for simple branched architectures, however calculations involving these systems can be quite complex. The attempts to describe a system of a mixture of branched polymers gets even more complicated. It is logical to test models with the simplest possible system. For branched polymers, this is a polymer with a single branching point with all of the arms having equal lengths, e.g., a star-branched macromolecule (112).

Living anionic polymerization techniques are the most effective process for producing homopolymer and copolymer star-branches with well defined structures, e.g., predictable molecular weights and narrow molecular weight distributions. Postpolymerization linking reactions with the living chain can then produce in some instances star polymers with predetermined number of arms. In model studies of branching effects in star polymers there are three variables to consider: the macromolecule type, the number of arms, and

the molecular weight of the arms. The effects of branching can therefore be deduced from comparing the characteristics of star polymers to those for linear polymers of the same type and molecular weight. A practical incentive for studying star block copolymers appears to be since they display very low melt and solution viscosities, even at high molecular weights (78).

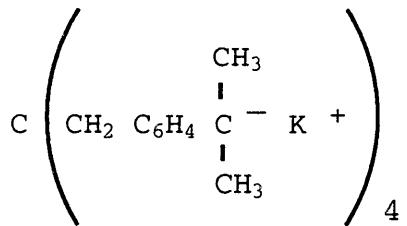
2. Synthesis of Star-Branched Polymers

Most of the star polymers reported in the literature have been synthesized by anionic polymerization techniques. Undoubtedly, this is due to the unique features obtainable through living anionic techniques previously discussed. Three distinct routes leading to star homopolymer and copolymers formations through anionic techniques can be described:

- a) Application of multifunctional initiators;
- b) Use of polyfunctional terminating linking agents with homocarbanionic polymers;
- c) Utilization of divinylbenzene as a linking agent for homocarbanionic polymers.

The approach of multifunctional initiators comprises the polymerization of polymer chains from one common axis. In principle, by appropriate techniques all the arms should grow to the same length and all the star macromolecules should be identical. For example, the following tetrafunctional

initiator may initiate the polymerization of styrene, forming four arms radiating from a central point (1):

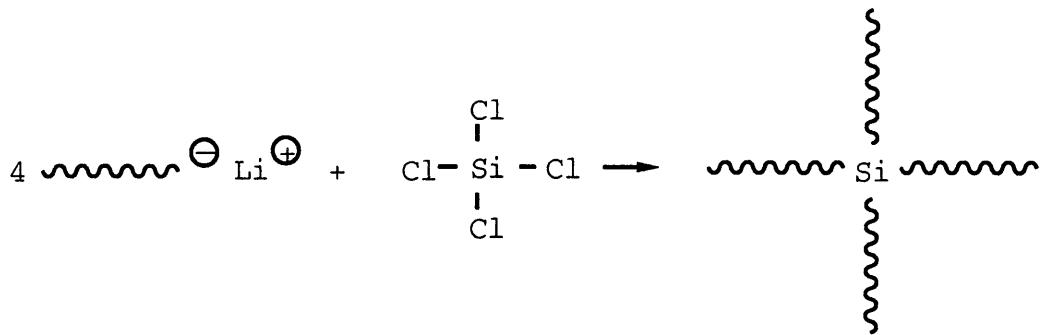


Burchard and coworkers have synthesized star polystyrenes by first forming a polyfunctional initiator from the reaction of technical grade divinylbenzene (11% p-, 22% m-divinylbenzene and 66% o-, m-, and p-ethylvinylbenzene) with n-butyllithium followed by the addition of styrene monomer (128,129,130). This system, however results in slow initiation probably due to steric factors.

In the second process, the synthetic route involves the organolithium polymerization of either homopolymers or copolymers followed by linking of the lithium chain ends by a polyfunctional linking agent. Table 9 contains star branched polymers synthesized by linking agents (35,112). A typical scheme as shown below, could be by the addition of a chlorosilane linking agent after the polymerization of either styrene or a diene by s-butyllithium (102,119):

Table 9
 Synthesis of Star Polymers via Polyfunctional
 Linking Agents (35,112)

Monomer	Initiator	Solvent	Linking Agent	# Arms
Butadiene	n-BuLi	Cyclohexane	Silicon tetrachloride	4
			Methyltri-chlorosilane	3
			Tin tetrachloride	4
Isoprene	s-BuLi	Cyclohexane	Methyltri-chlorosilane	3
			Silicon tetrachloride	3
			Octa- and dodeca-chlorosilanes	8-12
Styrene	n-BuLi	Benzene	Silicon tetrachloride	3, 4
		Benzene-THF	1,2,4-Tri(chloromethyl)benzene	3
			1,2-Bis(tri-chlorosilyl)ethane	3; 4
			Cyclic trimer of phosphonitrilic chloride	2, 4; 6
			1,2,4,5-Tetra-(chloromethyl)benzene	2-10
			Hexa[p-(chloromethyl)phenyl]benzene	6
	s-BuLi	Benzene	1,2-Bis(methyl-dichlorosilyl)ethane	4



Analogous reactions involving Si_2Cl_6 , $(\text{PNCl}_2)_3$, CH_3SiCl_3 , $(\text{ClCH}_2)_4\text{C}$ and tri(allyloxy)-2,4,6-triazine can be used to produce stars with six, six, three, four and three arms, respectively (1,114).

It can be noted from Table 9 that the linking reaction between silicon tetrachloride and polystyryllithium produces a mixture of tri- and tetra-armed stars (115). The same results were found also for SiCl_4 and poly(isoprenyllithium) (116). However, poly(butadienyllithium) reacts in a quantitative conversion with silicon tetrachloride (117). Apparently, steric hindrance influences the efficiency and extent of linking in the reactions of polystyryllithium and poly(isoprenyllithium) with silicon tetrachloride. Unlinked linear homopolymer or copolymer result in many cases, with the inevitable need to fractionate in order to obtain pure star polymer (118).

One approach in overcoming the problems of steric interference has been to "cap" either the polystyrene or polyisoprene chain ends. When several units of butadiene are

added to either polystyrene or polyisoprene before the addition of silicon tetrachloride, quantitative linking occurs (120,121). Hadjichristidis, Guyot and Fetters also had success in applying the capping method for the synthesis of eight- and twelve-armed polyisoprene stars using octa- and dodecachlorosilane. They found that the addition of approximately five butadiene units to each polystyryllithium chain end was sufficient for efficient linking (122).

Side reactions for halogen-carbon linking agents can also hinder the efficiency of star formation. For example, in Table 9 the tetrafunctional linking agent 1,2,4,5-tetra(chloromethylbenzene) was found to produce stars with up to eleven arm (123). This was believed to be cause by competing lithium-chloride exchange:



since RCl_x can react with $RM(Cl)_{x-1}$, yielding a new linking agent with higher functionality. Although metal-halogen exchange is not a problem with chlorosilanes, it does interfere with halogen-carbon linking agents. This exchange is a competing reaction of the interchange and displacement of the halogen. Wenger and Yen found that they could maximize the displacement reaction relative to the

interchange at elevated temperatures and using a solvent mixture of benzene and tetrahydrofuran (50/50 v/v) (124).

Linking reactions involving carbon-lithium chain ends with chlorosilanes have been found to be much more efficient than the halogenated hydrocarbon agents. Similar success of linking diene chains has been reported with PCl_3 and dimethylphthalate (119).

The third distinct route of star-branched polymer formation involves the utilization of divinylbenzene as the linking agent (103,125). These are prepared by first synthesizing either a homopolymer or a copolymer by organolithium sequential techniques, forming linear segments for the star arms. This is followed by the addition of divinylbenzene. The addition results in a microgel nucleus incorporating pendant vinyl groups that serve as branch points for the star polymer, e.g., arms are formed when the linear chain ends react repeatedly with pendant double bonds. This method has produced star-branched polyisoprenes containing up to 56 weight-average number of arms (106,126).

The success of the divinylbenzene linking process depends on the relative rates of the crossover reaction and subsequent self polymerization of the divinylbenzene (meta and/or para) vinyl groups (112). Young and Fetters studied the crossover of butadienyl- and isoprenyllithium reactions in benzene with m- and p-divinylbenzene. They determined

through UV spectroscopy that the p-divinylbenzene react slightly faster with the dienyllithium chain ends than the meta isomer (127). However, m-divinylbenzene was found to be more effective in linking the dienyllithium chains in the star-branched macromolecule than the para isomer. They concluded this behavior could be explained since the overall self polymerization reaction (of both vinyl groups) of the para isomer was slower than that of the meta isomer of divinylbenzene. Wiley, Jin and Ahn found that the rates of polymerization of the pure meta isomer was faster than that of the para isomer in toluene by free radical initiation (131).

Commercial divinylbenzene generally contains a dilute mixture of meta and para isomers as well as a mixture of three ethylvinylbenzene isomers (132). Therefore, the linking process is more complex compared to the pure divinylbenzene isomers. In this case there would be at least three separate crossover reaction and "terpolymerization" of the vinyl species (112). Bi and Fetters have noted that efficient linking (>95%) can be achieved when moderately high temperatures (60°C) are used with commercial divinylbenzene (108).

Generally only a small amount of divinylbenzene (2-10 mole% DVB to RLi) is used when linking arms. However, unlike the predetermined number of arms obtained using

polyfunctional linking agents, the stoichiometry is not exact in predicting the number of branches with divinylbenzene as the linking agent (27). As might be expected for a mixture of polymers having varying number of arms, the polydispersity increases. Polydispersity of star polymer can originate from the polydispersity of the individual branches and/or from variations in the number of arms within a sample (134). It should also be noted that the divinylbenzene linking reaction with polystyrene and polydiene stars result in polydispersities of 1.3 or less (126,134).

Martin synthesized star-branched homopolymer of butadiene and isoprene by linking living dienyllithium chain ends with commercial divinylbenzene. He studied the nature of the star-branching reaction with regards to: the molar ratio of divinylbenzene (DVB) to alkylolithium (RLi), reaction temperature, reaction time and the nature of the polydienyllithium chain end. In general, Martin observed that a higher number of arms were achieved with an increased concentration of DVB to RLi; an increased reaction temperature and through the choice of polydienyllithium chain ends (135,138).

Martin found that the poly(isoprenyllithium) anions reacted faster with divinylbenzene than with poly(butadienyllithium) anions, under similar reaction conditions (136). These rate observations may help explain

the fact that poly(butadienyllithium) anions link into higher branched star molecules than the corresponding poly(isoprenyllithium) anions, in addition to the influence of steric hindrance from the methyl group on the polyisoprene chain end. However, the poly(isoprenyllithium) anions generally resulted in a more efficient star formation than poly(butadienyllithium) anions (139).

3. Properties of Star-branched Polymers

The properties of star-branched polymers can be quite different from those of linear polymers of the same molecular weight. Dilute and concentrated solution viscosities as well as bulk viscosities can be lower for star polymer than for a linear material of equivalent molecular weight. For example, by alterations in the number average molecular weight, molecular weight distribution and the length of long arms, the melt processing behavior of stars can be manipulated (112). Fetters and coworkers noted from rheological studies of star-branched block copolymers that in the melt state the viscosity is independent of the extent of branching and depends on the arm molecular weight (108,127).

Thus, a principal reason for studying star polymers is because they display very low melt and solution viscosities, even at very high molecular weights compared to their linear counterparts. Typical melt flow and solution viscosity behavior are shown in Figure 7 for poly(styrene-butadiene)

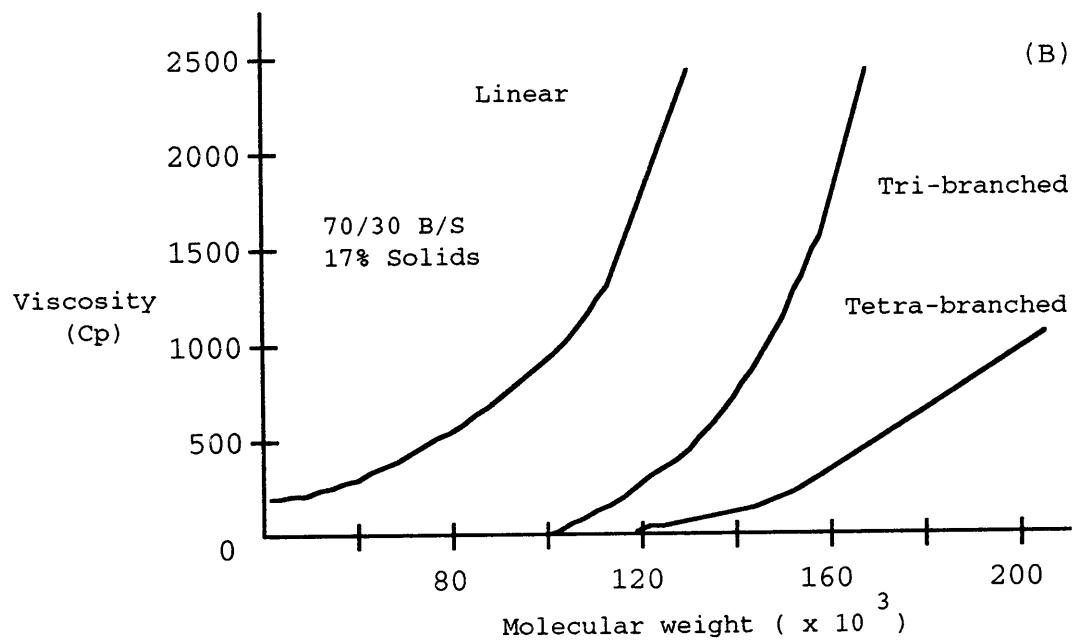
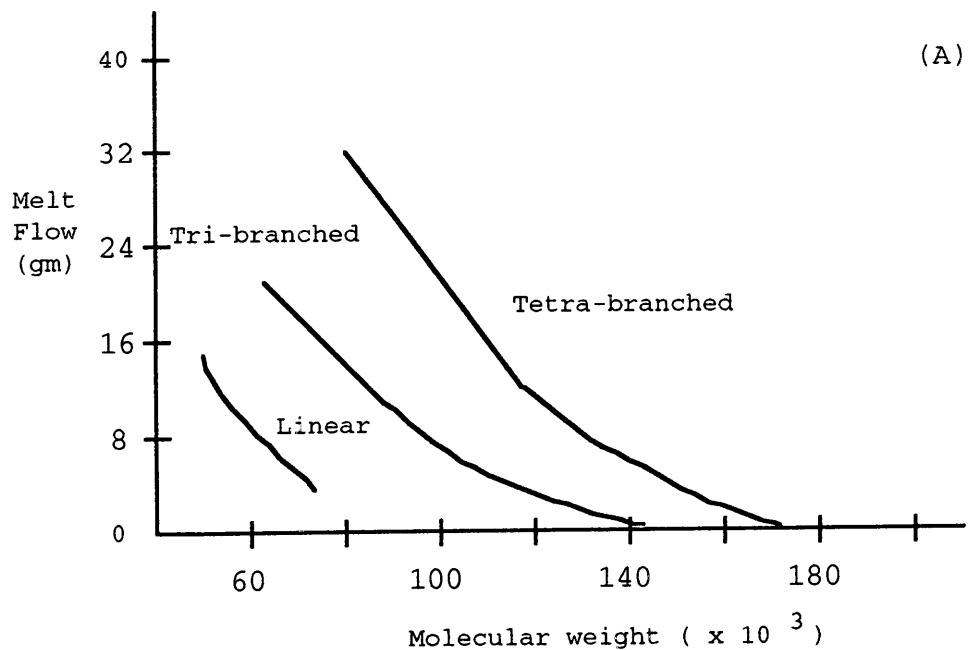


Figure 7. (A) Melt Flow of Star Polymers (30% Styrene);
 (B) Solution Viscosity of Star Polymers
 in Toluene-Naphtha (145)

star block copolymers (78,145). This is obviously important in processing for commercial application. Noshay and McGrath point out it is also perhaps less apparent that one may prepare much higher molecular weight polymers than are easily obtainable with linear systems (78). This behavior is important in adhesive applications.

Star-branched butadiene-styrene block copolymers have been used as hot melt and pressure sensitives adhesives (143,144). Meyer and Widmaier studied the adhesion behavior of 2-13 armed styrene-isoprene diblock linked copolymer stars and styrene-isoprene-styrene linked triblock stars. The star diblock arms consisted of approximately 50% polystyrene while the triblock was composed of 70% polystyrene. Various linking agents were used, e.g., divinylbenzene, silicon tetrachloride and 1,2,4,5-tetra(chloromethyl)benzene. It was found that the stars were better adhesives than the corresponding linear polymers. They attributed the difference to the relatively high cohesive strength of the triblock stars as a result of physical cross-linking and the formation of a large central glass domain consisting of divinylbenzene plus polystyrene (146).

Bi and Fetter et al. have prepared star block copolymers of styrene and isoprene with up to 30 arms using divinylbenzene as the linking agent (107,108,112,133,137). These polymers exhibit both different mechanical properties

Table 10
 Properties of Star-Branched and Linear SIS
 Block Copolymers (137)

Type	Molecular weight of S block (x 10 ⁻³)	Avg. no. Wt% S branches	Tensile strength (MPa)	Strain at break(λ)
Star	20	25.2	6	41.0
	21	32.3	7	40.0
	20	31.2	9	43.0
Linear	20	32.4	2	34.0
	14	30.0	2	34.5

and morphologies than their linear counterparts. A comparison of some of these differences is shown in Table 10 (137). The authors found the mechanical behavior of the stars to be different from the linear counterparts in four respects. The stars exhibited yielding and had higher strengths, smaller extension ratios and less permanent set. They attributed these features to the presence of physical cross-links due to the divinylbenzene microgel in the system.

LeBlanc made comparative studies on the processing properties relationships of four-armed stars based on styrene-butadiene Solprene® resins made by Phillips Petroleum Co., in contrast to the conventional linear triblock Kraton® resins produced by Shell Oil Co.(147). This investigation found that the star samples showed a higher Youngs' modulus, a greater dependence of molecular weight on modulus, a yield stress and strain and ultimate stress and strain and also a greater tendency to exhibit yielding.

Considerable research has been reported on the mechanical properties, morphology, compatability and general behavior of linear styrene-diene diblock and triblock copolymers. For these block copolymers the commonly found morphologies are spheres, cylinders, or lamellae of the minor hard styrene component in a matrix of the major soft diene component. However, relatively little work has been done on the corresponding star-shaped polymers (110,148). For star block

copolymers having 30 wt % polystyrene contained in the outer block of 10^4 molecular weight and six or more diblock arms, the equilibrium structure is composed of two translationally displaced mutually interwoven but unconnected three dimensional networks of polystyrene rods embedded in the polydiene matrix (110,148,149,150).

Fetters and coworkers investigated the morphology of a series of 18-arm poly(styrene-isoprene) star diblock copolymers as a function of composition, as shown in Table 11 (110). Each sample in Table 11 is designated by a two letter code and three numbers. SI represents polystyrene outer blocks in the diblock arm and IS indicates to polyisoprene outer blocks. The first number designates the number of diblock arms in the star molecule and the second refers to the weight percent of polystyrene in the diblock arm while the last number indicates the number average molecular weight of the polystyrene component.

Interesting, the ordered bicontinuous double diamond structure was observed at compositions of 30 and 35 wt % polystyrene. The double diamond structure was also found at 76 wt % polystyrene when the minor component polyisoprene was the outer segment of the diblock arm. In addition, for a fixed number of arms (i.e., 18) it was confirmed experimentally that the predictions of the microphase separation theory of de la Cruz and Sanchez for star diblock

Table 11
Characteristics of 18-Arm Star Block Copolymers

Sample	$10^{-4} M_n$, g/mol		Morphology
	Poly-Styrene ^a	Diblock Arm ^b	
SI-18:10:10	1.0	10.0	PS spheres
SI-18:19:10	1.0	5.3	PS cylinders
SI-18:23:12	1.2	5.0	PS cylinders
SI-18:30:10 ^c	1.0	3.3	PS double diamond ^c
SI-18:35:10	1.0	2.8	PS double diamond
SI-18:40:10	1.0	2.5	Lamellae
SI-18:43:10	1.0	2.3	Lamellae
SI-18:56:10	2.6	4.6	Lamellae
SI-18:66:30	3.0	4.3	PI cylinders
SI-18:81:30	3.0	3.7	PI cylinders
SI-18:92:30	3.0	3.3	PI spheres
IS-4:76:47 ^d	4.7	6.2	PI cylinders
IS-18:76:47 ^d	4.7	6.2	PI double diamond ^d
IS-18:30:10 ^d	1.0	3.3	PS cylinders

^aVia size exclusion chromatography. M_w/M_n of 1.06 or less.

^bBased on composition and polystyrene segment molecular weight.

^cData from ref 148. ^dThe outer segments of the star arms are polyisoprene.

copolymers holds true. That is, the observation of a maximum in the scattered intensity from these copolymers in the homogeneously disordered state and that the squared product of the diblock arm radius of gyration and the scattering vector of this maximum goes through a minimum as the content of core block polymer increases and lastly the squared product of the core block polymer radius of gyration and the scattering vector of the maximum shows a systematic increase as the content of core polymer increases (151).

Furthermore, styrene-rich rigid star copolymer have been developed under the trade name K Resins®. The important quality of these materials is their impact strength for packaging applications and a combination of transparency (152,153). McGrath and Fetters note that preliminary results with rigid star structures suggest these materials are more ductile than their linear high molecular weight counterparts of similar composition (78).

D. Hydrogenation of Unsaturated Polymers

1. Introduction

Hydrogenation of polymers, principally homo- and copolymers of dienes in the presence of a catalyst offers an alternate method for improving and optimizing the mechanical and chemical resistance properties compared to the parent unsaturated macromolecule (154). Polymer modification by hydrogenation has proven to be an important technique for

producing new materials as well as an assistant in polymer characterization and molecular elucidation (155,156,157). Destructive hydrogenation have been employed in molecular determinations, while nondestructive hydrogenation techniques have been used to increase stability of parent materials.

Hydrogenation of unsaturated polymers has received unique attention due to the technological importance of the parent materials and is one of the oldest polymer modification reactions (158,159,160). Many macromolecules with novel monomer sequence distributions and compositions which are laborious or impossible to synthesize directly through conventional polymerization techniques can be easily obtained by the hydrogenation of polymers (161). In general, hydrogenated linear polymers are thermoplastic in nature and hydrogenated branched polymers are rubbery.

Most of the early hydrogenation studies were limited to natural rubber for the most part in destructive molecular characterization (159). Wicklitz has reviewed the status of hydrogenation of polymers up to the early sixties (155). Berthelot used hydroiodic acid to hydrogenate natural rubber, latter Hinrichsen and Kempf et al. employed platinum catalyst in their studies of natural rubber (162). While, with the development of synthetic polymers of dienes and copolymers, the objective became more to preserve the high molecular weight and increase their stability by nondestructive

hydrogenation. Ipatieff and Schaad reported hydrogenation of polybutadiene with no decomposition using black nickel oxide as the catalyst at 100°C while at 250°C they depolymerized to liquid products (162).

Hydrogenation of butadiene elastomers and copolymers using nickel-on-kieselguhr catalyst at hydrogen pressure of 500 psi and temperatures ranging from 200-250°C were performed by Jones et al. (163). However, these severe conditions caused chain scission and crosslinking. Most of the early hydrogenation studies involved dienes produced in emulsion systems, free-radically or polymerized using sodium. These techniques generally require the polymers to be purified before hydrogenation to prevent poisoning of the hydrogenation catalyst. However, with the discovery of organolithium polymerization of dienes and copolymers, novel synthesis and hydrogenations have become common.

Hydrogenated polymers have been employed for a number of applications including plastics for severe environments, wire and cable coverings, extruded and molded products, fibers and filaments, sheets and films, adhesives and bonding agents and vulcanizable products such as weather stripping, sealing rings, hose, and tires (160). In general, postpolymerization modifications cannot compete with direct polymerization routes, especially for commodity type polymers. For example, low density polyethylene obtained by the Ziegler-Natta

polymerization of ethylene is much less expensive to produce than by the hydrogenation of 1,4-polybutadiene.

However, hydrogenation is commercially competitive for specialized products unable to be synthesized by direct routes. Examples include block and functional polymers, e.g., Kraton G® (Shell), Zeon® (Nippon) and the hydrogenated nitrile rubber Therban® (Bayer AG and Mobay Corp.) (158,164). The hydrogenated nitrile rubbers are proving successful in the demanding environment of oil field wells (164).

2. Catalytic and Noncatalytic Hydrogenation

Molecular hydrogen is relatively unreactive chemically, especially at low temperatures (below 100°C). This is partly accounted for by the fact that the dissociation of gaseous hydrogen into atoms is endothermic to the extent of 104 kcal mole⁻¹ (165). Many reactions involving molecular hydrogen have been recognized which involve catalysis of various substances. Early hydrogenation systems were largely confined to heterogeneous techniques involving metals, metal oxides and salts. Currently, a wide range of metal ions and complexes have been found to catalyze hydrogenation reactions homogeneously in solution.

Hydrogenation of unsaturated polymers can be described by two distinct schemes: catalytic and noncatalytic techniques. In general, these methods vary in selectivity, yield, side reactions, catalyst poisoning, reaction conditions, and

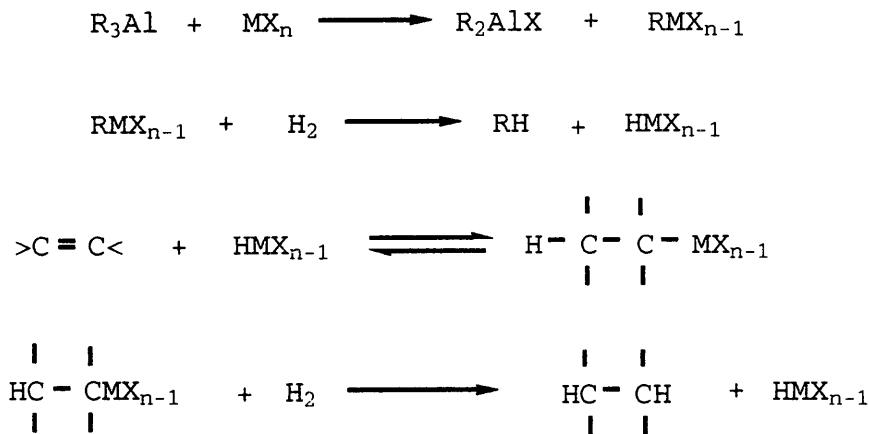
catalyst removal.

Catalytic hydrogenation can be achieved by either homogeneous or heterogeneous catalysts. The hydrogenation of polymers in the presence of heterogeneous catalysts is difficult and generally unsatisfactory, because of the high tendency of polymer molecules to become absorbed on the catalysts, rendering the catalyst inefficient or ineffective (166). Due to the low reactivity of molecular hydrogen, catalytic hydrogenation by transition-metal complexes has become an valuable pathway to saturated species (167,168). Homogeneous hydrogenation catalysts are principally of the organotransition metals (Co, Ni) plus a reducing agent (*n*-BuLi or R₃Al) and a hydrocarbon activator (cyclohexane) (154,169,170,171). The activator serves as a stabilizer by coordinating the site of unsaturation to Ni-H (171).

Ziegler's catalyst used for dimerization and polymerization of olefins are prepared from the reaction of transition metal halides with alkyls of aluminum, alkaline earth and alkali metals. In general, these systems are heterogeneous, however homogeneous systems have been developed by modification of the ligands coordinated to the transition metal and have been found to be effective for catalytic hydrogenation (165).

Homogeneous catalytic hydrogenation catalyst derived from organometallic compounds and transition metal compounds have

been employed by Sloan and by Laporte and Schuett in the hydrogenation of dienes and aromatics (177,178). These preformed combinations appear to have higher activity and are assumed to be subcolloidal in size (160). Sloan and coworkers have presented a speculative mechanism shown below for hydrogenation synthesis. The transition metal complex is first alkylated, followed by the reaction of the alkylated transition metal to form a hydride and the transfer of hydrogen to the double bond:



Trialkylaluminum compounds result in the highest activity and are generally utilized in 3 to 4 molar ratio to the transition metal compound. Catalytic activity of the metals has been found to follow the order $Ni \geq Co > Fe > Cr > Cu$.

Homogeneous nickel catalysts have been widely used, these include nickel complexes of octanoate, carbonyl, carboxylate,

ester compounds, stearate, acetate, propionate, formate, benzoate and naphthenate (172,173,174). Additional catalysts include bis(hippurato) nickel and nickel chelates with phenols (175,176).

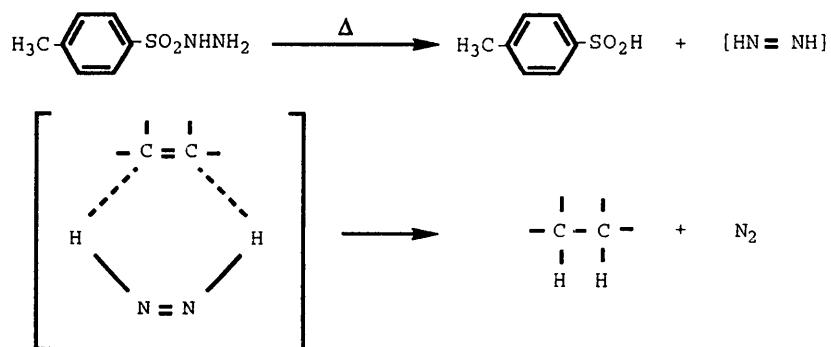
Cobalt homogeneous hydrogenation catalysts include the complexes of carboxylates, amides, pyridine, lactams, ureas, hydroxylamine, octoate, and benzoate obtained by the addition of trialkylaluminum or n-BuLi (154). Interesting, Halasa reports using the catalyst formed from the reaction of cobalt-caprolactam reduced by tri-isobutyl aluminum to hydrogenate polybutadiene. This homogeneous catalyst reduces the 1,2 double bonds at a rate four times faster than it reduces the 1,4 double bonds (179).

Other homogeneous catalyst systems for hydrogenation of polymers include rhodium catalyst such as $(PPh_3)_2RhCl$ and $(PPh_3)_3RhHCO$ (180,181,184,187,188,189), amine boranes and tin or chromium tetraalkylboron compounds (182,183). Due to the inherent problems with heterogeneous catalytic methods, most chemist prefer to work with homogeneous systems, however Rachapudy, Fetters et al. have reported clean and complete hydrogenation with heterogeneous systems based on transition metals (Ni, Co) on kieselguhr or palladium or calcium carbonate (185,186).

Another useful method of polymer hydrogenation has been by noncatalytic techniques. Diimide has been shown to be a

convenient species for the selective hydrogenation of nonpolar unsaturated groups in low molecular weight olefins (190,191,192). Harwood and others found diimide to be very practicable for polymer hydrogenations due to the simple experimental apparatus and technique of this method (166,193,194). Several attributes of the diimide technique make this method appealing for hydrogenation of polymers. The reaction is homogeneous and can be used at moderate temperatures at atmospheric pressure, under nitrogen.

From studies on diimide reagents, p-toluenesulfonylhydrazide (TSH) appears to offer the best features. Aromatics like toluene and xylene are good solvents for the mutual solubility of TSH, and the unsaturated and hydrogenated polymer. Under proper conditions high levels of hydrogenation are obtained (193). The thermal unimolecular decomposition of p-toluenesulfonylhydrazide and subsequent hydrogenation of unsaturated site by the transitory species, diimide N_2H_2 is believed to proceed by the following mechanism (191,193,195):



Furthermore, TSH is air stable at room temperature and the reaction byproduct salts are methanol soluble and easily filterable.

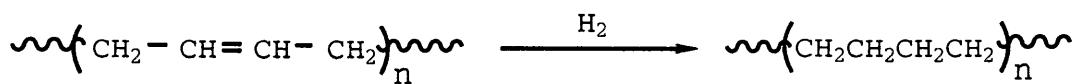
The diimide technique has been applied to a number of polydiene and copolymer systems, for example, polybutadiene, polyisoprene, styrene-butadiene-styrene block copolymers, styrene-butadiene random copolymers and chlorobutadiene (166,193,196,197,198).

Boranes have also been used for noncatalytic hydrogenations of polydienes, however, these generally suffer from chain scission (199,200,201).

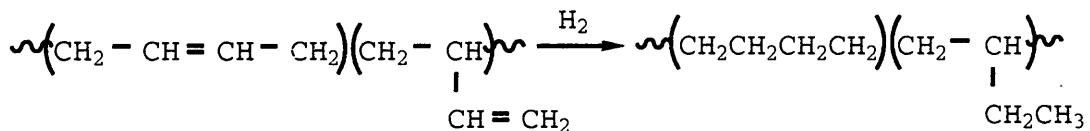
3. Properties of Hydrogenated Products

The structures and properties of hydrogenated polymers depend upon the parent polymer and the extent of hydrogenation. One of the main advantages resulting from hydrogenating polymers is the enhancement of the photolytic, oxidative and thermal properties as well as improved mechanical strength. Another equally important benefit is a synthetic route to prepare sequence distributions that would be impossible to achieve through conventional pathways.

Hydrogenation of elastomeric 1,4-polybutadiene leads to thermoplastic crystalline polyethylene (202-208):



Polybutadiene made in hydrocarbon solvents initiated by organolithiums contains approximately 5-8 mole percent of the 1,2-microstructure (203). This mole percent is equivalent to 1.3 to 2.1 ethyl branches per 100 carbons. Hydrogenation of the 1,2-structure results in the formation of pendant ethyl groups, disrupting the chain symmetry and lowering the degree of crystallinity. This then is essentially atactic polyethylene resembling linear low density polyethylene (LLDPE). While hydrogenation of polybutadiene containing a moderate amount of 1,2 units (e.g., organolithium initiation of butadiene in polar media) produces an elastomer, poly(ethylene-co-butylene):



Some properties of linear low density polyethylene and hydrogenated polybutadiene are listed in Table 12 (163). Low cis-polybutadiene in the raw state is a soft cheeselike material however, depending on the degree of hydrogenation this elastomer is converted into either a tough thermoplastic elastomer or a very tough thermoplastic. Figure 8 illustrate the tremendous influence on tensile strength as the degree of hydrogenation exceeds 50% of the double bonds for polybutadiene (35). The melting temperature for hydrogenated

Table 12

Properties of Hydrogenated Polybutadiene and Low
Density Polyethylene (163)

Property	Hydrogenated polybutadiene	Low density polyethylene
Tensile strength, MPa	16.2	13.1
Elongation, %	750	600
Stiffness modulus, MPa	103.4	137.9
Brittle point, °C	<-73	<-73
Impact strength, Izad	a	a
Refractive Index	1.50	1.51

^aDoes not break

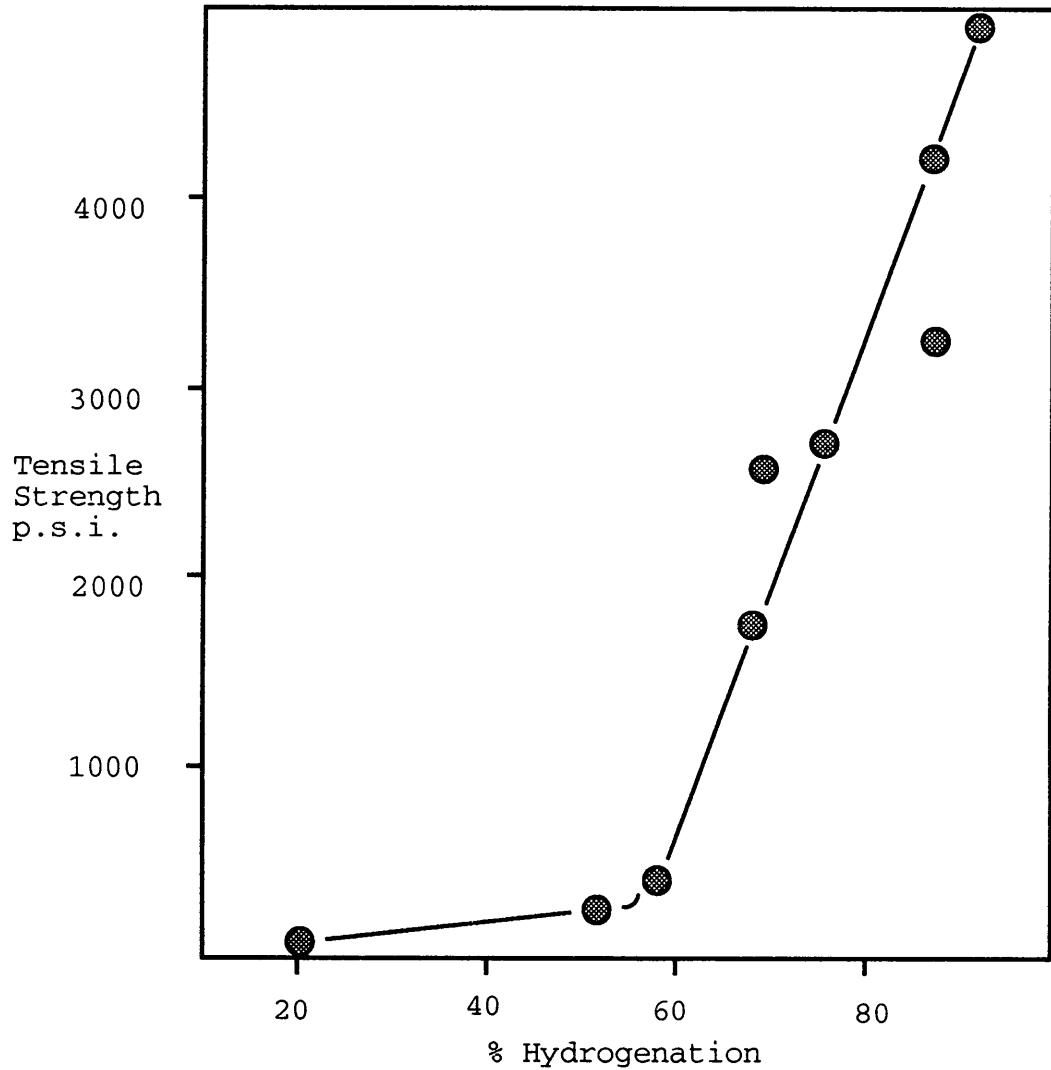
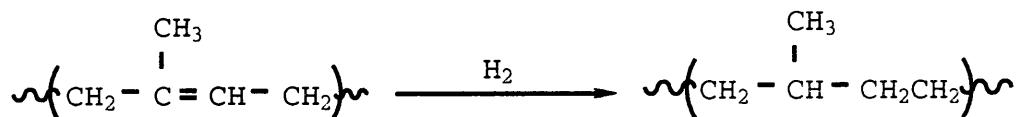


Figure 8. Effect of Hydrogenation on Tensile Strength of Raw Polybutadiene (35)

polybutadiene is approximately 100°C and for molecular weights near 10^5 , hydrogenated polybutadiene is approximately 50% crystalline when cooled slowly from the melt (185).

Wang studied the effect of the degree of hydrogenation on the thermal transition behavior by differential scanning calorimetry (DSC) for series of polybutadiene and polyisoprene homopolymers (58). For polybutadiene samples with varying degree of hydrogenation two main features were seen from DSC thermograms, these results are tabulated in Table 13. For a degree of hydrogenation of 27.3%, (HB-1), the DSC thermogram showed a broad endotherm. However, when hydrogenation exceeded 60%, (HB-5), the T_g was difficult to locate and a strong melting endotherm was seen. Samples in the intermediate range showed both T_g and a broad endotherm, suggesting some form of developing crystallinity.

Hydrogenation of polyisoprene results in the formation of amorphous alternating copolymer of propylene-ethylene (208):



Hydrogenated polyisoprene is rubbery at room temperature and has a glass temperature of approximately -60°C (198). Wang found for a series of hydrogenated polyisoprene samples ranging in degree of hydrogenation from 14.5 to 100%, that

Table 13
 Effect of % Hydrogenation on the T_g and T_m of
 Hydrogenated Polybutadiene^a (58)

Sample	% Hydrogenation ^b	T_g , °C	T_m , °C (peak)
PB-2	0	-98	
HB-1	27.3	-92	
HB-2	36.8	-84	-25
HB-3	47.0	-76	0
HB-4	52.6	-71	15
HB-5	60.2	-63	25
HB-6	70		42
HB-7	72		56
HB-8	75.2		62
HB-9	84		67
HB-10	100		100

^a Perkin-Elmer DSC-2, 40°K/min., 5 mcal/min, 7 mole % 1,2-unit

^b From Infrared Analysis

only a T_g of approximately -61°C was observed for all samples (58). As expected, for these samples no detectable melting endotherm was observed.

Hydrogenation of copolymers, especially block copolymers is a way of extending the performance range of copolymers. The hydrogenation of copolymers reported so far have included either hydrogenated diene-diene systems or hydrogenated diene-aromatic copolymers. Architectures based on A-B-A triblock copolymers of the styrene-diene type are well known and owe their unique properties to their phase separated systems. The hydrogenation of the center block of a poly(styrene-butadiene-styrene) copolymer results in an oxidatively stable thermoplastic elastomer (179).

Recently there has been considerable interest in an alternative type of A-B-A triblock structure, where the end blocks could form crystalline domains, by crystallization, rather than amorphous domains by phase separation (210).

These systems are important since such a crystallization process does not depend on the incompatibility between blocks. Therefore, the presence of crystalline segments has important significance for processing in addition to the physical properties characteristic of A-B-A triblocks with high degree of phase separation. Above the T_m of the crystalline end blocks, the now amorphous system can approach the melt behavior of a single-phase melt (78).

Thus, these A-B-A systems should exhibit a much lower viscosity and be much easier to process than the amorphous domain phase separated triblocks.

The anionic synthesis of A-B-A triblock copolymers with crystalline end blocks can be achieved by the hydrogenation of poly(butadiene-isoprene-butadiene) (HBIB) polymers (211,212). Mohajer et al. found that HBIB polymers were thermoplastic elastomers, whereas hydrogenated poly(isoprene-butadiene-isoprene) (HIBI) polymers behaved like an uncured particulate filled rubber (198). Hence, the crystalline end blocks in the HBIB material act as a physical crosslinks resulting from the anchorage of the HB end blocks in the continuous rubbery matrix of the "ethylene-propylene" block. While the HIBI and HBI polymer do not show crosslinked elastomer behavior since they are not capable of forming permanent endblock anchorages.

The dynamic mechanical behavior of HBIB triblocks indicated that the glass transition of the rubbery block is independent of the butadiene content. In addition, the melting temperature of hydrogenated butadiene block does not show any dependence on composition or architecture of the block copolymer (198).

III. Experimental

A. High Vacuum System

1. High Vacuum Line and Techniques

Anionic polymerizations are chain-growth reactions whereby successive monomers add to active centers which are negative ions associated with positive counterions. Initiation and propagation proceeding by anionic mechanisms require the rigorous purification of all solvents, monomers, initiators and polymerization reactors. This is because reactive impurities such as water, carbon dioxide and oxygen can destroy the carbanionic active centers causing premature initiator and/or chain end termination. Typically, anionic initiators are used in the concentration range of 10^{-3} - 10^{-5} M; then obviously reactive impurities must be kept below 10^{-6} M (28,29).

An all glass high vacuum apparatus ($\leq 10^{-6}$ torr) was utilized in this investigation to achieve the stringent purification of solvents, linking agent, initiator and initiator precursor. The high vacuum system used in this study is shown schematically in Figure 9. The vacuum line was composed of a hierarchy of manifolds, each with its own specific function. All manifolds were constructed with heavy wall pyrex glass tubing, while interconnecting valves and drops were made with normal pyrex tubing. The primary

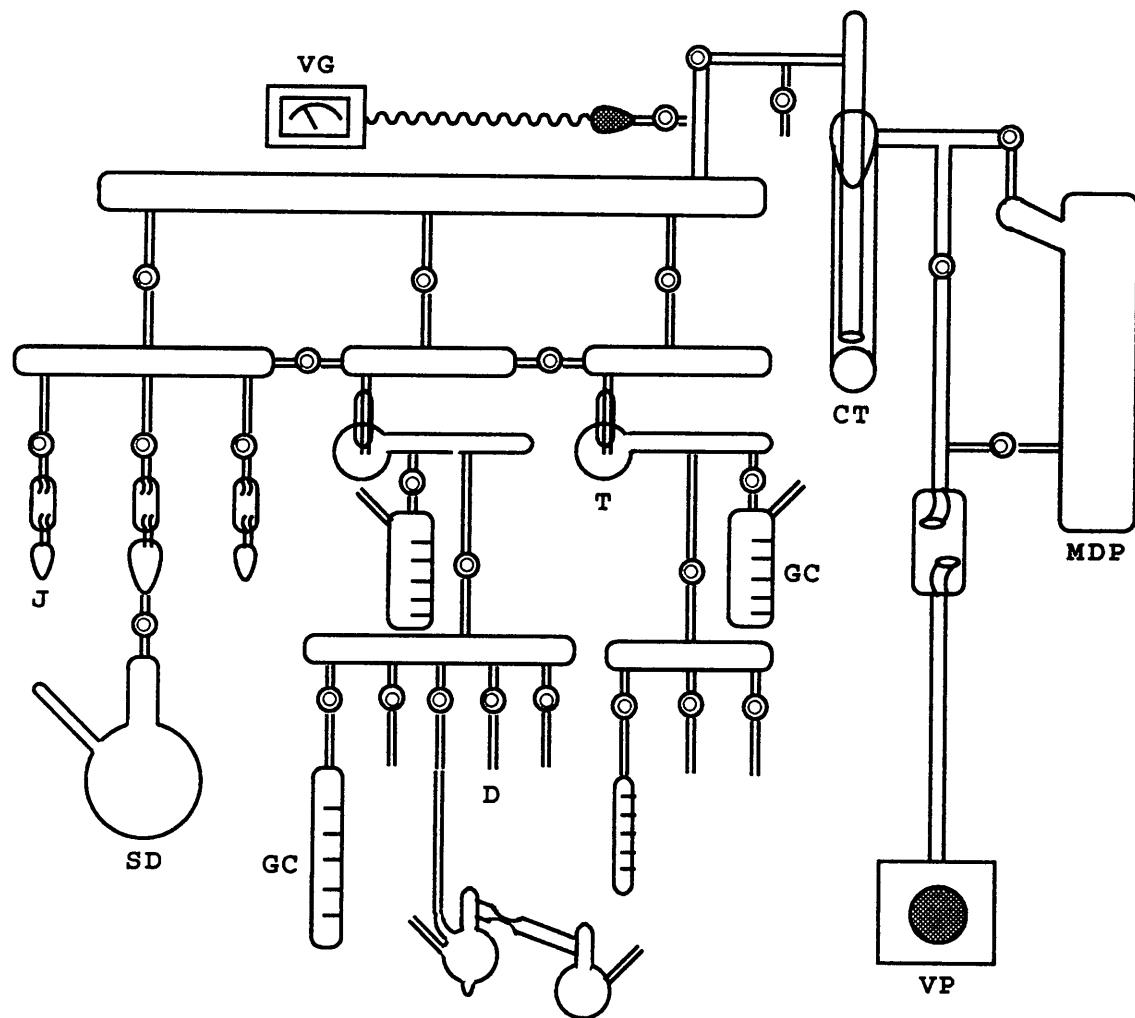


Figure 9. High Vacuum System

manifold was constructed of 40mm diameter tubing while the secondary manifold of 25mm tubing. The entire vacuum system can be isolated by sections using in line Teflon Rotaflow Stopcocks®.

The secondary manifold was conveniently divided into several sections. Several male ground glass 24/40 joints (J) served as attachments for round bottom flasks for solvent distillations (SD). Various graduated cylinders (GC) used for solvent measuring and temporary storage are also seen attached to the third and fourth level manifolds. The fourth or lowest level manifold serves the working manifold where glass apparatuses can be attached to drops (D). The third and fourth level sections are separated from the secondary manifold by grease traps (T), since silicone grease is used on the cold trap and ground glass joints on the secondary manifold. All glass apparatuses are attached to the drops by glass blowing the joints together, with the exception of the male ground glass joints. A distillation apparatus can be seen in Figure 9 attached to one of the drops on the fourth level manifold.

The rest of the vacuum system consists of a large cold trap (CT), cooled with liquid nitrogen, a Hastings-Teledyne high vacuum gauge (VG), a mercury diffusion pump (MDP) and a Sargent-Welch mechanical vacuum pump (VP). Argon gas inlets are attached to the back of each of the third level manifolds

(not shown in Figure 9). The argon is passed through a series of three Drierite® columns before entering the high vacuum system.

All vessels and apparatuses for high vacuum applications were constructed from pyrex glass and were cleaned with dilute hydrofluoric acid, rinsed with dilute sodium hydroxide and distilled water. The clean glassware was then oven dried over night at $\geq 120^{\circ}\text{C}$ prior to sealing to the high vacuum line. After insuring there were no pinhole leaks by using a Tesla coil, all vessels were flamed with a glass blower's hand held torch using a medium blue flame while pulling a vacuum to remove any moisture or volatiles present.

2. Purification of Solvent, Linking Agent and Initiators

a. Solvent Purification

1. Cyclohexane Cyclohexane (Fisher, reagent grade) was first stirred over concentrated sulfuric acid (10% v/v) for one week at room temperature to remove olefinic impurities, i.e., converting olefins to sulfonates, which are soluble in the acid layer. The cyclohexane layer was then decanted from the dark brown acid layer into a 24/40 round bottom flask containing a sodium dispersion in paraffin wax. The cyclohexane/sodium dispersion flask was then connected to a distillation apparatus and refluxed while stirring for one day, under a nitrogen blanket. Next, the cyclohexane was distilled under nitrogen onto a sodium dispersion contained

in a 24/40 round bottom flask fitted with a Teflon Rotaflow Stopcock® as shown in Figure 10. The stopcock was closed under nitrogen after distillation to prevent air and moisture contamination when disconnecting the round bottom flask from the distillation apparatus.

The solution flask was then connected to one of the male ground glass joints on the high vacuum line. The cyclohexane was degassed by freeze/thawing the solution using a dry ice/isopropanol or liquid nitrogen bath. The freeze/thaw cycle was repeated three to four times. During each freeze sequence, repeated evacuations were performed and upon complete freezing of the cyclohexane a vacuum was pulled to $\leq 10^{-6}$ torr for 10-15 minutes.

After thawing, the cyclohexane was distilled into another round bottom flask fitted with a Teflon Rotaflow Stopcock® on one of the ground glass joints using a dry ice/isopropanol bath. This receiving flask contained polystyryllithium used as a drying agent and as a colorimetric indicator of solvent purity. Polystyryllithium is a deep red-orange color when reactive impurities such as water and oxygen are not present and colorless when these species are present. The polystyryllithium was formed from the addition of a small amount of n-butyllithium and styrene. This solution was stored on the vacuum line until needed. The polystyryllithium was made in a round bottom flask as shown

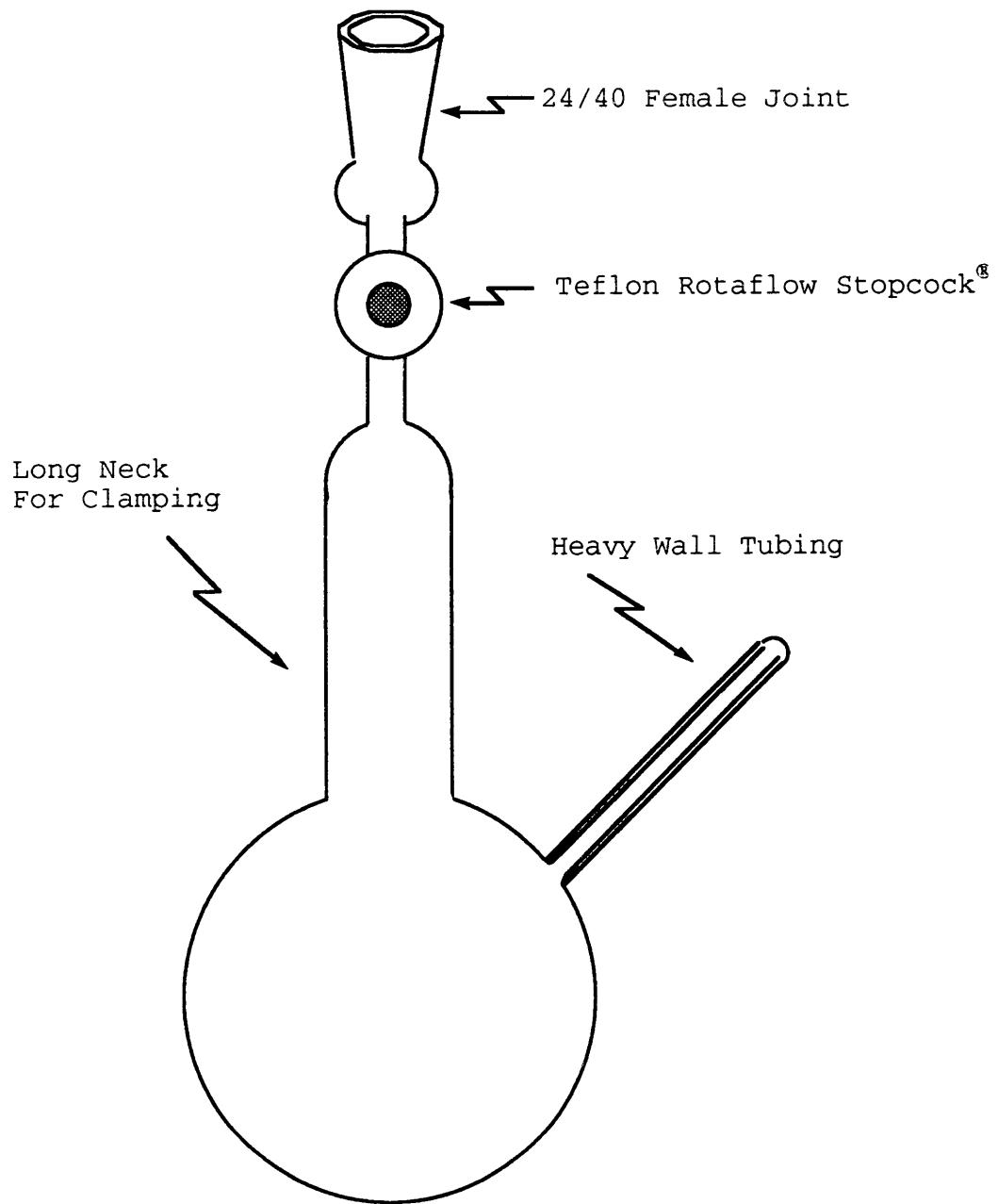


Figure 10. Solvent Flask

in Figure 10, fitted with a Teflon Rotaflow Stopcock®, which was equipped with a heavy wall pyrex sidearm as a convenient means of syringing in styrene and n-butyllithium under a argon blanket.

2. Hexane Hexane (Fisher HPLC grade) was purified in the same manner as described above for cyclohexane.

b. Linking Agent

1. Divinylbenzene Practical grade divinylbenzene (DVB) (MCB) was purified by stirring over finely ground calcium hydride in a Teflon Rotaflow Stopcock® fitted round bottom 24/40 flask as shown in Figure 10. The divinylbenzene/calcium hydride solution was then attached to one of the high vacuum ground glass joints and periodically degassed for twenty-four hours, removing hydrogen gas produced from the reaction of calcium hydride with moisture. The linking agent was then distilled transferred to a distillation apparatus attached to one of the drops on the high vacuum line, as shown in Figure 11. Divinylbenzene was stirred over dibutylmagnesium for several hours and then distilled from dibutylmagnesium. Prior to DVB being distilled into the distillation flask, dibutylmagnesium (in heptane; generously provided by Lithium Corp.) was introduced by syringing through a heavy wall sidearm tube into the distillation flask under a dry argon blanket. The sidearm

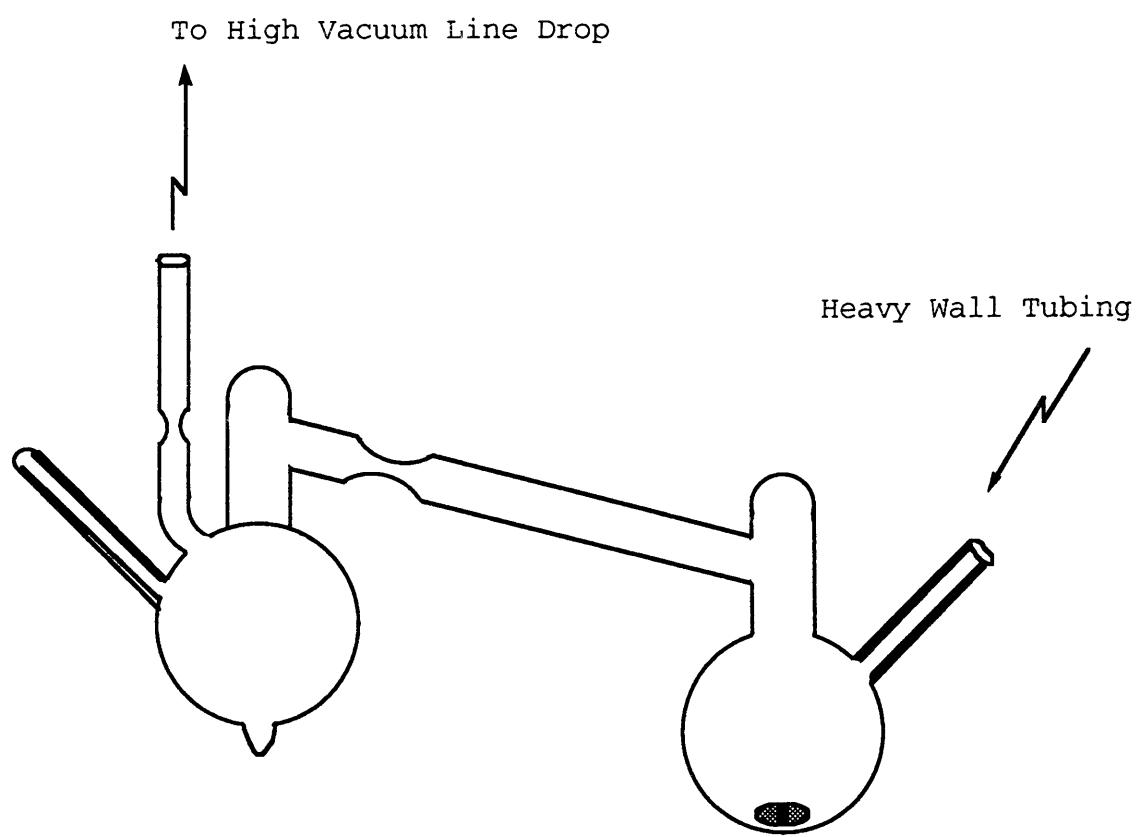


Figure 11. High Vacuum Apparatus for Distillation

was then covered with a septum, a vacuum pulled and the dibutylmagnesium solution cooled with liquid nitrogen. Next, the sidearm was sealed using a glass blowing torch and checked for pinholes using a Tesla coil. Heptane was stripped from the dibutylmagnesium by pulling a vacuum overnight while stirring, before distilling DVB into the dibutylmagnesium.

Divinylbenzene was then diluted to a working concentration of 0.2 to 0.8N, while in the receiving flask of the distillation apparatus by distilling hexane from one of the graduated cylinders on the high vacuum line. Next, the distillation apparatus was pressurized with argon. The sidearm of distillation receiving flask was scored approximately 2cm from the end and the end section of the sidearm removed by touching the score with a hot glass rod under a flow of argon gas from the distillation flask. This then allowed the sidearm to be capped with a rubber septum and the divinylbenzene to be removed by transferring the diluted DVB through a double ended needle into a dried rubber septum reagent bottle. The receiving flask was equipped with a nipple well making it easier to transfer the DVB solution. The DVB was stored in a freezer at -20°C under dry argon pressure.

The divinylbenzene (MCB, practical grade) consisted of 56% of a mixture of para- and meta-DVB and 44% by weight, of

a mixture of ethylvinylbenzene isomers (136).

c. Initiator Purification

1. sec-Butyllithium sec-Butyllithium was purified by vacuum distillation using the apparatus shown in Figure 11. Purification of sec-butyllithium by distillation has been discussed in the literature by Graze et al. (213,25). The distillation vessel was heat sealed to one of the drops on the high vacuum line, adding a small magnetic teflon stirring bar to the distillation flask. A rubber septum was added to the heavy wall sidearm of the distillation flask and a vacuum pulled. After insuring there were no pinhole leaks by using a Tesla coil, the distillation vessel was flamed with a hand torch while pulling a vacuum to remove any moisture inside the apparatus.

When a constant vacuum of $\leq 10^{-6}$ torr had been obtained after repeated flamings, the vessel was allowed to cool and pressurized with dry argon. sec-Butyllithium (1.5N in hexane, generously supplied by Lithium Corporation of America) was then syringed through the heavy wall sidearm into the distillation flask under an argon blanket. The heavy wall sidearm was recapped with a rubber septum and the sec-butyllithium was cooled with liquid nitrogen. After pulling a vacuum to $\leq 10^{-6}$ torr the sidearm was sealed closed using a hand torch.

The distillation flask was then warmed in a water bath

(40°C) stripping the hexane solvent off overnight, with constant stirring, under vacuum. sec-Butyllithium was distilled under continuous vacuum with a 65°C water bath while using a liquid nitrogen bath for the receiving flask. The distillation path was wrapped with a heating tape, heating to 65°C during distillation. With the completion of distillation both the receiving and distillation flask were cooled with liquid nitrogen and the distillation flask removed by sealing the constriction joint on the distillation column while under vacuum.

The receiving flask containing the distilled sec-butyllithium was then diluted with the appropriate volume of cyclohexane (0.5 to 1.3N) from one of the graduated cylinders on the high vacuum line by distillation using dry ice/isopropanol bath or liquid nitrogen.

The sec-butyllithium was transferred from the receiving flask by first pressurizing the flask with argon. Now, the sidearm of distillation receiving flask was scored approximately 2cm from the end and the end section of the sidearm removed by touching the score with a hot glass rod under a flow of argon gas from the distillation flask. This allowed the sidearm to be covered with a rubber septum and the sec-butyllithium to be transferred through a double ended needle into a dry rubber septum round bottom flask. The sec-butyllithium was stored in a freezer at -20°C under dry argon

pressure in order to minimize the slow decomposition that takes place at room temperature.

The concentration of sec-butyllithium was determined by titration with standardized alcoholic HCl (0.1N) to a phenolphthalein end-point. For example, 1ml of sec-butyllithium syringed into 50ml of distilled water was titrated with 13ml of alcoholic HCl, resulting in a normality of 1.3. This titrimetric method determines the concentration of total base present. This method was found to be satisfactory for freshly distilled samples that were properly refrigerated. However, any sec-butyllithium solution left out at length at room temperature or which shows any discoloration should be titrated by the Gilman double titration method (213). sec-Butyllithium concentration was also periodically determined using 2,5-dimethoxybenzyl alcohol as a self-indicating primary standard and the organolithium as the titrant (214).

2. 1,3-Bis(α-phenylethenyl)benzene 1,3-Bis(α-phenylethenyl)benzene or simply called double diphenyl ethylene (DDPE) was purified by high vacuum distillation from n-butyllithium (93). DDPE was supplied by Dow Chemical Co. (Midland, MI) as large pale yellow crystals and transferred to a dry 500ml round bottom flask. The DDPE flask was then equipped with a rubber septum and degassed with dry argon. The crystals were then melted by placing the

flask in a 65°C water bath.

DDPE was purified by vacuum distillation using the apparatus shown in Figure 11. The distillation vessel was sealed to one of the drops on the high vacuum line, adding a medium size magnetic teflon stirring bar to the distillation flask. A rubber septum was added to the heavy wall sidearm of the distillation flask and a vacuum pulled. After insuring there were no pinhole leaks by using a Tesla coil, the distillation vessel was flamed with a hand torch while pulling a vacuum to remove any moisture inside the apparatus.

When a constant vacuum of $\leq 10^{-6}$ torr had been obtain after repeated flamings, the vessel was allowed to cool and pressurized with dry argon. The sidearm septum was then removed and approximately 50ml of DDPE was then syringed through the heavy wall sidearm into the distillation flask under an argon blanket. The distillation flask was heated with a water bath to 40°C.

DDPE could then be titrated slowly through the sidearm with rapid stirring using n-butyllithium (1.4N in cyclohexane, supplied by Lithium Corp.) under an argon blanket. n-Butyllithium was added until the solution turned red, then a small excess of n-butyllithium was added, typically 5-6ml total n-butyllithium. The heavy wall sidearm was recapped with a rubber septum and the DDPE was cooled with liquid nitrogen. After pulling a vacuum to $\leq 10^{-6}$ torr

the sidearm was sealed closed using a hand torch. Cyclohexane solvent from the organometallic was stripped off into the cold trap overnight with rapid stirring at 40°C.

DDPE was then distilled by continuous vacuum, replacing the water bath under the distillation flask with a silicone oil bath warmed to 135-145°C and a liquid nitrogen bath around the receiving flask. The distillation column was heated to 135°C using a heating tape. The distillate was a clear colorless liquid. With the completion of distillation both the receiving and distillation flask were cooled using liquid nitrogen and the distillation flask removed by sealing the constriction joint on the distillation column while under continuous vacuum.

DDPE was transferred from the receiving flask by first pressurizing the flask with argon. The sidearm of distillation receiving flask was scored approximately 2cm from the end and the end section of the sidearm removed by touching the score with a hot glass rod under a flow of argon gas from the distillation flask. This then allowed the sidearm to be covered with a rubber septum and DDPE to be removed by transferring through a double ended needle into a dry 24/40 round bottom flask equipped with a rubber septum. DDPE was stored in a freezer at -20°C under dry argon pressure. In this way, DDPE could conveniently be obtained, after warming in a 65°C water bath, either by transferring

with a double ended needle or by syringing.

The distillation apparatus used for DDPE was similar to the one used for sec-butyllithium, except the distillation path for DDPE was found to perform better if its length was longer (40-50cm) than that of the sec-butyllithium apparatus (20-30cm). This was primarily due to a slight refluxing of DDPE. In general, it was also useful to have the distillation flask made such than it was lower in height than the receiving flask for distilling DDPE.

B. Low Pressure Glass Bowl Reactor

1. Reactor System Design and Operation

The most rigorous method for anionic polymerization is by high vacuum techniques. However, this procedure is limited by its lack of ease in routine experimental convenience. Especially in procedural time, glass blowing skills, efficient stirring, sample size and sampling with time. Low pressure (<100psi) glass bowl reactors offer many favorable advantage over classical vacuum techniques, greatly in convenience and ease of operation.

The reactor design used in this study can be seen in Figure 12 (215). Efficient stirring was provided by two propellers shaft driven by a magadrive motor assembly. Monomer, solvent and initiator introduction to the reactor and polymer sampling are extremely simplified and time efficient. The temperature control of the reactor was

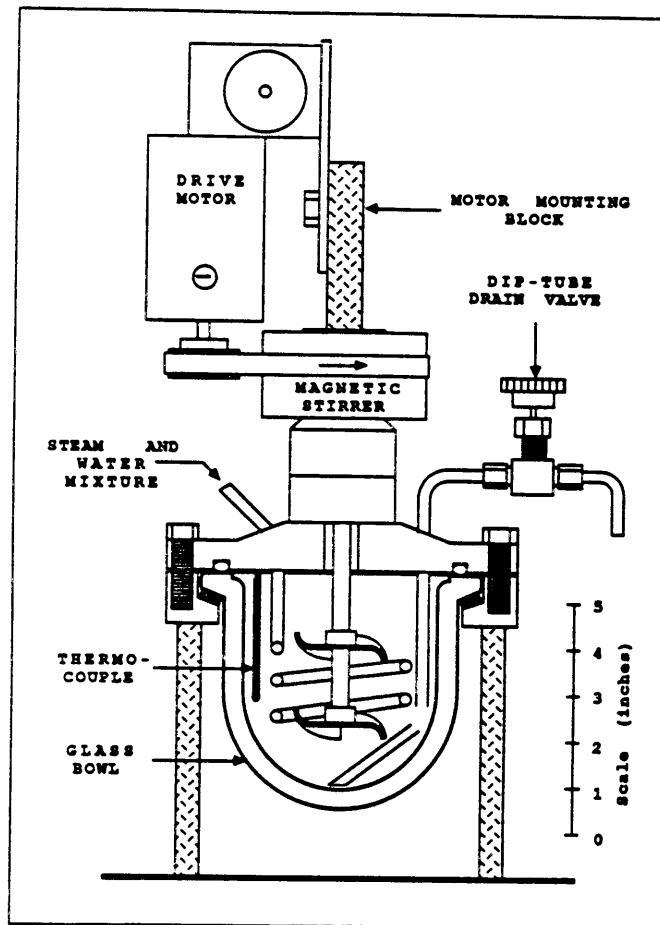


Figure 12. Cross-Sectional View of Glass Bowl Reactor

regulated by a steam/tap water mixture flowing through a stainless steel coil inside the reactor's glass bowl by means of a solenoid/relay equipped thermistor controller (YSI model RC63). Constant temperature control in the range of $\pm 0.5^{\circ}\text{C}$ of the desired setting was achieved.

Monomer and solvent were conveniently transferred from liquified propane gas (LP) storage tanks under dry prepurified nitrogen gas (50psi) through series of stainless steel pipes and Swagelok® valves to the reactor. Measurement of monomers and solvent was accomplished volumetrically by the use of on line stainless steel holding tanks equipped with graduated capillary sight glasses. While, initiators were easily syringed through a rubber septum port located on the top of the reactor.

Prior to polymerization, the reactor was conditioned with diphenylethylene and sec-butyllithium in cyclohexane to neutralize any reactive impurities that may cause premature initiator and or polymer chain end terminations. The reactor was then rinsed several time with cyclohexane before loading the reactor for a polymerization.

Sample removal was performed by attaching a syringe needle fitted with a Swagelok® nut to the dip tube drain valve on the reactor. In this manner samples could be taken without exposure to oxygen by injecting the sample into dry degassed rubber septum capped vials.

2. Purification of Solvent and Monomers

a. Solvent Purification

1. Cyclohexane Cyclohexane, (Fisher, reagent grade) was first stirred over concentrated sulfuric acid (10% v/v) for one week at room temperature to remove olefinic impurities, i.e., converting olefins to sulfonates, which are soluble in the acid layer. The solution was stirred in a 30 liter Nalage® carboy equipped with an electric motor driven shaft propeller.

The cyclohexane was then transferred to a LP storage tank by decanting through a series of dried basic alumina (Fisher) and 4Å molecular sieves columns. The LP tank was then connected to the reactor's stainless steel pipe lines and degassed with dry prepurified nitrogen. Cyclohexane was then pressurized through basic alumina and 4Å molecular sieves columns, in succession prior to reaching the on line cyclohexane stainless steel measuring tank.

Alumina and molecular sieves were dried prior to use in a vacuum oven at 150°C for three days (215). The steel columns were then packed with alumina or molecular sieves while exposing them to the atmosphere. Care was taken to thoroughly degas the reactor lines and columns when putting on new columns or cyclohexane tanks, in order to exclude the detrimental effects of oxygen and moisture.

b. Monomer Purifications

1. Isoprene Isoprene or 2-methyl-1,3-butadiene (The Goodyear Tire and Rubber Company) was conveniently received in a 20 pound LP tank and connected to the reactor's pipe lines. Isoprene was purified by passing through basic alumina and 4Å molecular sieves columns in succession under dry prepurified nitrogen pressure. An activated basic alumina column was effective in removing inhibitors placed in the isoprene by the manufacturer to prevent premature polymerization, while molecular sieves insured dryness. Alumina and molecular sieves were dried prior to use in a vacuum oven at 150°C for three days.

2. 1,3-Butadiene Butadiene (Phillips Petroleum Co., Rubber Grade 99 Mole%) was purified in the same manner as described above for isoprene, with the exception that nitrogen pressure was not necessary to transfer butadiene.

3. Polymerization Techniques

a. Linear Triblocks

The polymerization reactor utilized for the anionic synthesis of linear triblock copolymer is shown in Figure 12. The linear triblocks polymerized in this study were based on isoprene and butadiene, where isoprene was the central block and butadiene the end blocks. Sequential anionic addition techniques initiated by homogeneous organolithium species in hydrocarbon solvent was the method used in polymerizing the

living triblocks.

Two methods were employed in the synthesis of these A-B-A triblocks: a) a three-stage process utilizing sec-butyllithium as a monofunctional initiator; Table 14 shows the calculated molecular weight parameters for poly(butadiene-isoprene-butadiene) triblocks prepared in this manner and b) a two-stage process using a difunctional initiator (DFI) formed from the addition of two equivalents of sec-butyllithium to 1,3-bis(α -phenylethenyl)benzene (DDPE). The calculated molecular weight parameters are shown in Table 15 for poly(butadiene-isoprene-butadiene) triblocks polymerized with DFI.

The three-stage process involved the sec-butyllithium initiation of the first block butadiene in cyclohexane followed by the sequential addition of isoprene for the central block and finally, the addition of butadiene to complete the triblock architecture. For example, thirty one grams of sample III72C in Table 14 required 6.21g (10ml) of butadiene to be initiated with 1.86×10^{-4} mole (0.13ml of 1.42M) of sec-butyllithium, followed by the addition of 18.65g (27ml) isoprene and finally the same amount of butadiene to complete the triblock.

In the two-stage process, the central isoprene block was polymerized first by dicarbanion initiation using DFI, followed by the sequential addition of butadiene to form the

Table 14
Molecular Weight Parameters for
Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

Prepared by:

A-B-A by Sequential Addition of Monomers Using s-BuLi

Sample	Target Triblock Mn	Total wt% PBd
	PBd-PI-PBd	
III60C	5,600-100,000-5,600	10
III64C	12,500-100,000-12,500	20
III68C	21,400-100,000-21,400	30
III72C	33,300-100,000-33,000	40

Table 15
Molecular Weight Parameters for
Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

Prepared by:
A-B-A by Sequential Addition of Monomers Using DFI

Sample	Target Triblock Mn PBd-PI-PBd	Total wt% PBd
IV18B	12,500-100,000-12,500	20
IV98B	21,400-100,000-21,400	30
IV06B	33,300-100,000-33,300	40

two end blocks.

The DFI was made *in situ* and difunctionality characterized by gas chromatography (GC) as discussed by Broske (93). High vacuum purified 1,3-Bis(α -phenylethenyl)benzene or double diphenylethylene (DDPE) was transferred by syringing into a dry degassed 25ml volumetric flask equipped with a rubber septum. The total amount of DDPE was determined by weighing and diluting to volume with high vacuum distilled cyclohexane.

A known volume of DDPE solution was then syringed into the low pressure reactor. The reactor had previous been filled with a predetermined amount of polymerization solvent (cyclohexane) at 60°C. High vacuum distilled sec-butyllithium was added drop-wise to the reactor until a pale yellow color appeared to titrate out the impurities. Next, a stoichiometric amount of sec-butyllithium was added. This resulted in a dark red color change.

The disappearance of unreacted DDPE and monoadduct and the appearance of diadduct, i.e., addition of sec-butyllithium across the double bonds of DDPE were followed by GC. Samples were taken from the reactor by the same methods described below for polymers and terminated with degassed methanol. The reaction was allowed to proceed for two hours at 60°C before injecting a 2 μ l sample into the GC. Additional aliquots of sec-butyllithium were added to the

reactor until just under 1% unreacted DDPE was left.

The sequential polymerizations were synthesized at 60°C for two hours. Typically 20 to 40 grams of triblock were polymerized for each run, at a total concentration of 5 - 10% (w/w). At the end of each sequential monomer polymerization a sample was taken by injecting a syringe needle attached to the reactor's dip tube valve into a dry nitrogen degassed rubber septum vial.

An adequate amount of polymer was first removed from the reactor dip tube before taking the actual sample to insure that sampling was representative of the current status of the reactor and not the dip tube volume. The living sample was then terminated with degassed methanol (Fisher, HPLC grade) and stabilized with the antioxidant Irganox® (Ciba-Geigg). The antioxidant was added by syringing into the sample vial a 0.6% (w/w) solution of Irganox® in cyclohexane for a 0.5% (w/w) of Irganox® to polymer. It was important to add an antioxidant in order to avoid a lightly crosslinked insoluble polymer gel.

After the methanol addition to a triblock polymerization a decrease in viscosity was immediately observed due to the cessation of chain end association. Polymer yield were always quantitative.

b. Star Block Copolymers

Star-branched block copolymer synthesized in this work

were based on butadiene-isoprene diblocks linked into a star architecture by divinylbenzene. The diblocks were synthesized by first homopolymerizing butadiene in cyclohexane with sec-butyllithium then sequentially adding isoprene monomer to form the diblock followed by the addition of divinylbenzene. The divinylbenzene addition resulted in a microgel nucleus incorporating pendant vinyl groups that served as branch points for the star polymer, e.g., arms are formed when the linear diblock isoprenyllithium chain ends react repeatedly with pendant double bonds. The calculated molecular weight parameters for the poly(butadiene-isoprene) diblock copolymers before linking with divinylbenzene (DVB) are shown in Tables 16, 17 and 18, in addition to the mole ratio of DVB to isoprenyllithium chain ends. The moles of isoprenyllithium was based on the number of moles of sec-butyllithium charged.

The sequential polymerizations and divinylbenzene linking were each executed at 60°C for two hours. Typically 20 to 40 grams of star block copolymer were polymerized for each run, at a total concentration of 5-10% (w/w). Each sequential step and star copolymer were sampled in a similar manner as previously described above for linear triblock systems. The mole ratio of divinylbenzene to isoprenyllithium chain ends linked in this study were varied from 1 to 10.

4. Hydrogenation of Unsaturated Polydienes

Table 16
Molecular Weight Parameters for
Poly(butadiene-isoprene) Star Block Copolymers
10 wt% Polybutadiene
2/1 mole ratio of DVB to RLi

Sample	Target Diblock Arm Mn PBD - PI
II85B	3,000-25,000
II83B	4,200-37,000
II74B	5,600-50,000
III10B	7,000-62,500
III09B	8,300-75,000

Table 17
 Molecular Weight Parameters for
 Poly(butadiene-isoprene) Star Block Copolymers
 2/1 mole ratio of DVB to RLi

Sample	Target Diblock Arm Mn PBd - PI	Total wt% PBd
II74B	5,600-50,000	10
III27B	12,500-50,000	20
III47B	21,400-50,000	30
III77B	33,300-50,000	40

Table 18
 Molecular Weight Parameters for
 Poly(butadiene-isoprene) Star Block Copolymers
 10 wt% Polybutadiene

Sample	Target Diblock Arm Mn	
	PBd - PI	DVB/RLi mole ratio
III30B	5,600-50,000	1
II74B	5,600-50,000	2
III15B	5,600-50,000	4
III16B	5,600-50,000	6
III19B	5,600-50,000	8
III21B	5,600-50,000	10

The above linear poly(butadiene-isoprene-butadiene) triblocks and star-branched poly(butadiene-isoprene) block copolymers were hydrogenated *in situ* in the glass bowl reactor with a homogeneous organotransition metal hydrogenation catalyst. The catalytic hydrogenation catalyst used in this study was preformed by the reduction of nickel octoate with triethylaluminum in cyclohexane.

A working solution (0.10M) of nickel octoate (provided by Shepherd Chemical Co.) was prepared by dissolving the dark green crystals volumetrically with cyclohexane. The solution was then transferred to a large round bottom flask with finely ground calcium hydride and a teflon stirring bar. The round bottom flask was then capped with a rubber septum and degassed with dry nitrogen gas. The nickel octoate solution was then dried by rapid stirring for 2-3 weeks, while periodically venting evolved hydrogen gas from the reaction of moisture and calcium hydride.

The completion of dryness was observed when venting with a hypodermic needle through the rubber septum ceased to vent hydrogen gas. The solution was then passed through a Gelman Acro 50AS 0.2 μm disposable filter into a dry degassed reagent bottle equipped with a rubber septum. As a further check of dryness a few drops of water were added to the decanted calcium hydride to observe if it was active or not by the rapid evolving of hydrogen gas.

A 0.3M working solution of triethylaluminum (generously supplied by Ethyl Corp., 25 wt% in hexane) was made volumetrically in cyclohexane. The triethylaluminum (TEA) was received in a steel cylinder and the appropriate amount was transferred to a dry degassed rubber septum volumetric flask by syringing, then diluting to volume with cyclohexane.

The catalyst was prepared by syringing the working solution of nickel octoate into a 100ml dry degassed rubber septum serum bottle. Prior to adding the nickel octoate, a small teflon coated stirring bar and 25ml of cyclohexane were added to the serum bottle. Now, the nickel octoate was reduced by slowly dripping in the triethylaluminum working solution by syringing with rapid stirring at room temperature. This immediately resulted in a black subcolloidal suspension. The reduced catalyst was always made up fresh, approximately one hour before use.

The amount of nickel octoate used for either the linear triblocks or star-branched copolymers was based on 0.1 mole% per total moles of double bonds derived from both the butadiene and isoprene blocks. While, the amount of triethylaluminum used was calculated at two to one moles of TEA to nickel octoate.

For example, from Table 14 a poly(butadiene-isoprene-butadiene) linear triblock copolymers prepared by sequential addition of monomers using sec-butyllithium required the

following amounts of hydrogenation reagents: Thirty one grams of sample III72C contained a total of 0.50 moles of double bonds. This sample then required 5.0ml of the nickel octoate working solution, 3.3ml of the TEA and approximately 25ml of cyclohexane.

The preformed hydrogenation catalyst could then be syringed *in situ* into a polymerization that had just been terminated with methanol. The hydrogenation was carried at 65°C for 24 hours at a constant hydrogen pressure of 50psi and moderate stirring.

The hydrogenated polymer was then drained into several large glass bottles and washed with hot 1% (w/v) citric acid (Fisher, reagent grade) in distilled water at 65°C in a water bath with constant stirring. The polymer to citric acid volume ratio was 2 to 1. The polymer was decanted from the aqueous layer and centrifuged. Again this was decanted and the polymer was vacuum oven dried.

C. Instrumental Analysis

1. Gas Chromatography

A Varian 6000 capillary chromatograph equipped with a flame ionization detector was used. Hydrogen gas mixed with breathing air was used for flame gases, while the carrier gas was helium. A summary of the chromatographic conditions as developed by Broske are listed below (93):

Column Temperature:

195°C for 0.5min

195°C to 235°C at 5°/min

Column Type: Hewlett-Packard Capillary column,
crosslinked methyl silicone

Flow Rate: 2ml/min He

Split ratio: 50/1

Injector Temperature: 260°C

Detector Temperature: 275°C

Attenuation: 8

Range: 10^{-12} (Auto Zero On)

Air Flow Rate: 300ml/min

H₂ Flow Rate: 25ml/min

2. Proton Nuclear Magnetic Resonance

Proton Nuclear Magnetic Resonance (¹H-NMR) were performed on a Bruker WP-270-SY mutinuclear NMR using a super conducting magnet. NMR spectra of poly(butadiene-isoprene) copolymers was used in conjunction with FTIR spectra to confirm their microstructure and degree of hydrogenation. Samples were dissolved in deuterated chloroform at 10 wt% (w/w) and NMR's were determined at room temperature.

Polybutadiene 1,4 and 1,2 content were determined from the olefinic peaks appearing approximately at 5.45 and 5.15ppm, respectively. While, the polyisoprene 1,4 and 3,4 structures were obtained from the peaks at 5.15 and 4.75ppm, respectively.

3. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet 10-DX FTIR. Films of unhydrogenated and hydrogenated polymer were cast from cyclohexane directly onto sodium chloride plates and vacuum oven dried. Typically, scan were taken from $4000-600\text{cm}^{-1}$ with a resolution of 4cm^{-1} . Generally, 27 scans were accumulated for a FT spectra.

4. Gel Permeation Chromatography

Molecular weight distributions (M_w/M_n) and number average molecular weights (M_n) were determined by gel permeation chromatography (GPC) using the universal calibration method. GPC measurements were carried out on a Waters 150-C ALC/GPC Chromatograph equipped with Waters ultrastyragel columns of 100, 500, 10^3 , 10^4 , 10^5 and 10^6\AA porosities. Samples were run at 0.9ml/min in tetrahydrofuran at 30°C . A Waters differential refractive index detector and a Viscotek differential intrinsic viscosity detector, Model 100 were utilized in parallel.

5. Thermal Analysis

A Perkin-Elmer DSC-2C differential scanning calorimeter was used for the determination of glass transitions (T_g) and endothermic melting temperatures (T_m). Measurements were made a 5°C/min on samples of 5-10mg sealed in aluminum pans. Dynamic mechanical thermal analysis (DMTA) were performed on

a Polymer Laboratory instrument. Log storage modulus and tangent delta were plotted as a function of temperature at 1Hz.

IV. Results and Discussion

A. Linear Triblock Polymerization

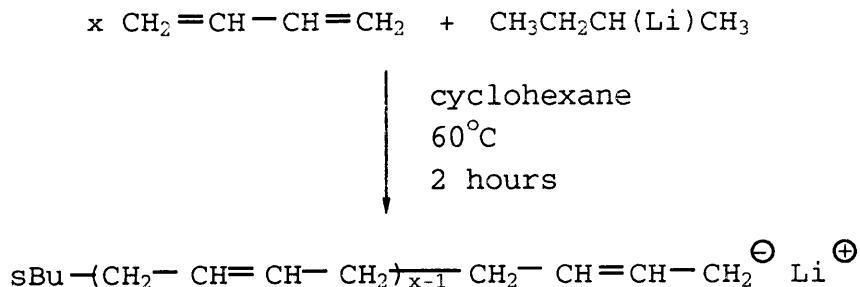
1. Poly(butadiene-isoprene-butadiene) by Monofunctional Anionic Initiation

Sequential anionic addition techniques were employed to prepare poly(butadiene-isoprene-butadiene) linear triblock copolymers in cyclohexane using sec-butyllithium as the organoalkali initiator. The synthetic approach used is outlined in Scheme 1, where isoprene was sequentially added to a living homopolymer of polybutadiene to form the diblock follow by the addition of butadiene to complete the linear triblock.

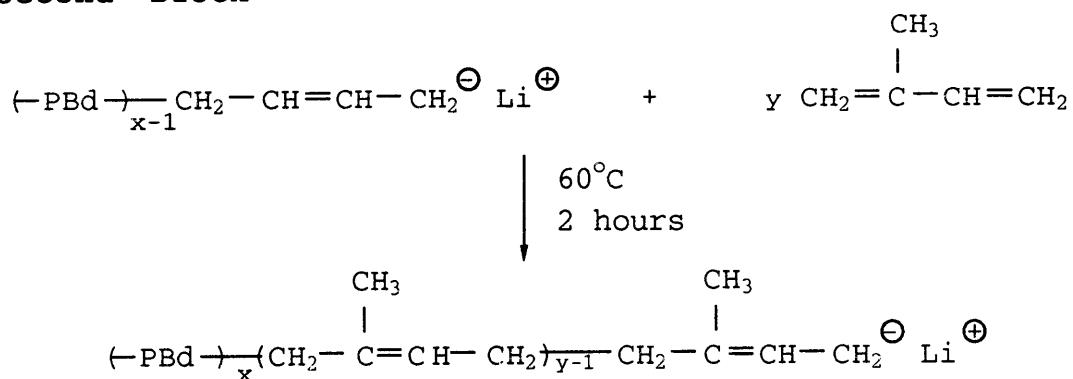
The theoretical molecular weight parameters for poly(butadiene-isoprene-butadiene) triblocks are summarized in Table 14. The goal here was to prepare a series of triblocks with a constant number average molecular weight (M_n) polyisoprene central block while increasing the weight percent of polybutadiene from 10 to 40. This method requires the careful purification of solvent and monomers, since each sequential addition can introduces impurities which can have detrimental effects on predetermined block structure.

Samples of each homo-, di- and triblock were taken to determine molecular weight control in this three-stage sequential addition process. Size exclusion chromatographic

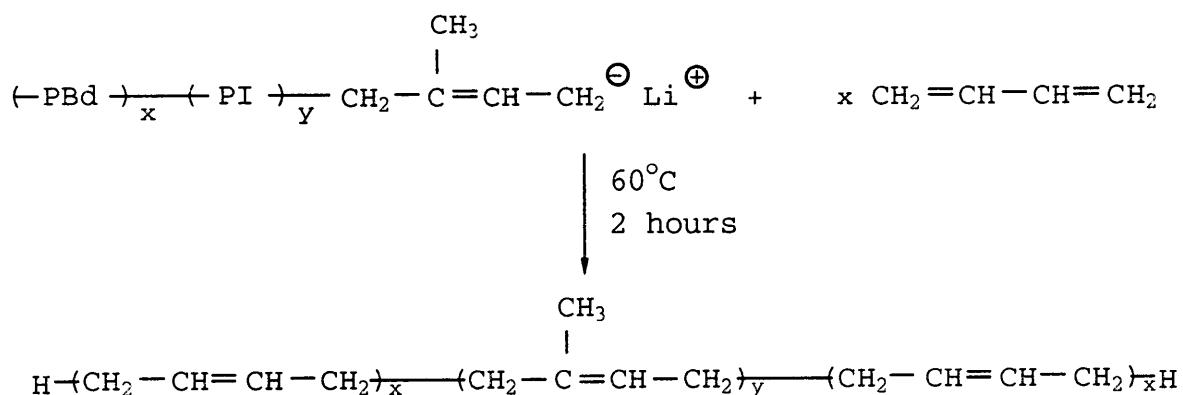
First Block



Second Block



Third Block



Scheme 1. Synthesis of Poly(butadiene-isoprene-butadiene) Triblock by Three Stage Sequential Addition Utilizing a Monofunctional Initiator

(GPC) results for these poly(butadiene-isoprene-butadiene) triblock copolymers are given in Table 19, where sample A represents the homo-polybutadiene block, sample B the poly(butadiene-isoprene) diblock and sample C the poly(butadiene-isoprene-butadiene) triblock. It is evident from the increase in polydispersity (M_w/M_n) going from the homo- to the triblock the detrimental effects of premature chain termination caused by impurities encountered during repeated sequential monomer addition.

Also, evident from GPC results is the trend of obtaining average molecular weights (M_n) higher than the predicted value for the first and second block as summarized in Table 19 and 20. In Table 20 triblock average molecular weights were determined from GPC results listed in Table 19. The first block was taken directly from the obtained GPC M_n , while the central block M_n was determined by subtracting the GPC M_n of the first block from GPC M_n of the diblock (i.e., the B samples in Table 19). And the final butadiene block M_n by the difference of the sample C from sample B GPC M_n in Table 19.

Several reasons can account for the higher than predicted average molecular weights for the first and second blocks. First, is the precision at which an accurate small amount of monomer (several milliliters for the butadiene additions) can be volumetrically introduced from the graduated monomer

Table 19
 Gel Permeation Chromatography (GPC) Results for
 Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

Prepared by:

A-B-A by Sequential Addition of Monomers Using s-BuLi

Sample A = First Block
 Sample B = Diblock
 Sample C = Triblock

Sample	GPC Mn	M_w/M_n
III60A	13,000	1.09
III60B	200,000	1.33
III60C	210,000	1.60
III64A	25,000	1.05
III64B	218,000	1.23
III64C	229,000	1.38
III68A	63,000	1.06
III68B	165,000	1.29
III68C	171,000	1.45
III72A	39,000	1.09
III72B	157,000	1.65
III72C	183,000	1.79

Table 20
Gel Permeation Chromatography (GPC) Results for
Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

Prepared by:

A-B-A by Sequential Addition of Monomers Using s-BuLi

Sample	GPC Triblock M _n	Total wt % PBd
	PBd-PI-PBd	
III60C	13,000-193,000-4,000	8
III64C	25,000-194,000-10,000	15
III68C	36,000-129,000-6,000	25
III72C	39,000-119,000-25,000	40

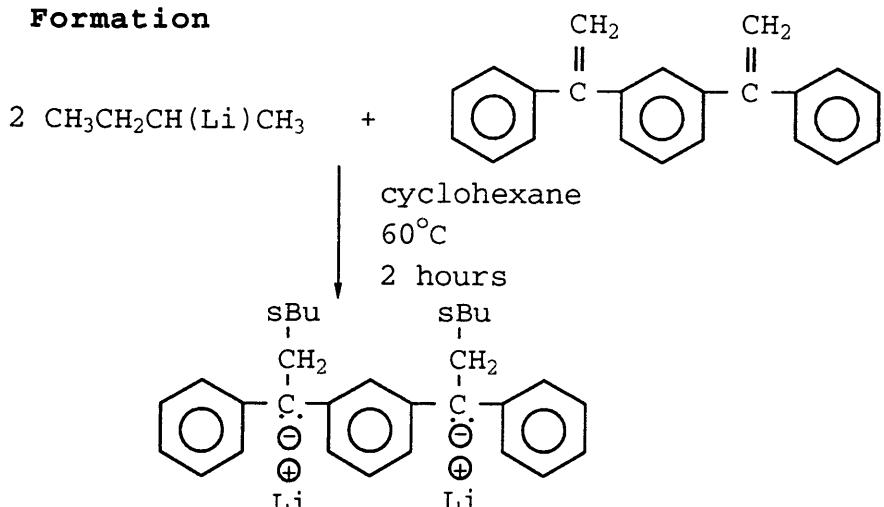
measuring cylinder to the reactor. Another reason would be the effect of impurities terminating the initiator and/or active chain ends by each sequential addition. The general trend of lower than calculated M_n for the last block may also be expected, due to impurities introduced by each sequential step. Also, the GPC universal calibration method used to characterize the average molecular weights and molecular weight distribution is not valid for block copolymers, since different blocks can have differences in their hydrodynamic volumes.

2. Poly(butadiene-isoprene-butadiene) by Difunctional Anionic Initiation

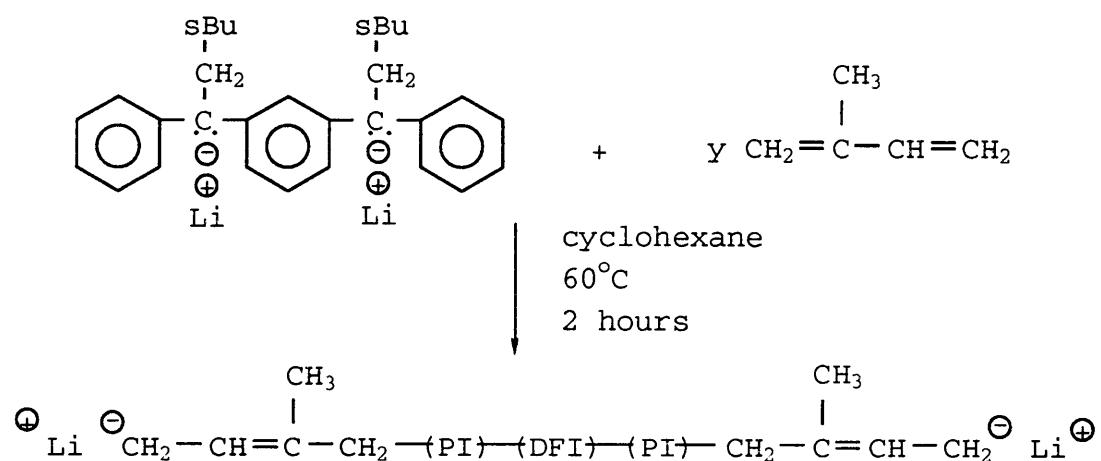
Triblock poly(butadiene-isoprene-butadiene) were prepared by the two-stage sequential addition method using dicarbanion initiation as shown schematically in Scheme 2. This synthetic method involves two steps, first the *in situ* formation of a difunctional anionic initiator (93) and second the addition of monomers to form the triblock.

In Scheme 2 it can been seen that the difunctional initiator (DFI) was formed from the addition of two equivalents of high vacuum distilled sec-butyllithium to 1,3-bis(α -phenylethenyl)benzene (DDPE) and difunctionality characterized by gas chromatography as described by Broske (93). Initiator formation was then followed by the polymerization of the central polyisoprene block and the

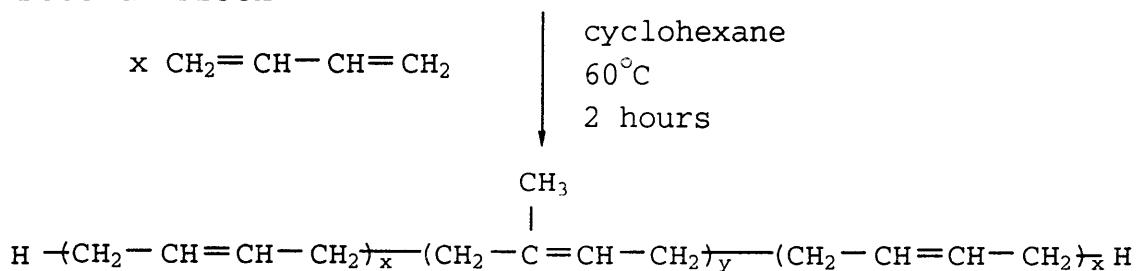
Initiator Formation



Polymerization of First Block



Second Block



Scheme 2. Synthesis of Poly(butadiene-isoprene-butadiene) Triblock by Two Stage Sequential Addition Utilizing a Difunctional Initiator

sequential addition of butadiene to form the two end blocks.

The calculated number average molecular weight parameters for poly(butadiene-isoprene-butadiene) triblocks prepared by DFI are shown in Table 15. The strategy here was to prepare a series of triblocks with a constant M_n polyisoprene central block while increasing the weight percent of polybutadiene from 20 to 40. The gel permeation chromatographic (GPC) results are summarized in Table 21, where sample A represents the M_n of the central polyisoprene block and sample B the M_n of the triblock. Table 22 summarizes in a similar manner as just described above for Table 20 the number average molecular weights of each triblock segment.

B. Star-Branched Block Copolymerizations

1. Poly(butadiene-isoprene) Star-Branched Block Copolymers Using Divinylbenzene

Star-branched block copolymers were synthesized as outlined in Scheme 3. Poly(butadiene-isoprene) diblocks based on the sequential addition of isoprene to sec-butyllithium initiated polybutadiene were linked into star formation utilizing divinylbenzene (DVB). This technique allows the incorporation of known molecular weight diblock arms with narrow molecular weight distributions into high molecular weight stars.

Schemes 4 and 5 illustrate the resulting microgel nucleus incorporating pendant vinyl groups that serve as branch

Table 21
Gel Permeation Chromatography (GPC) Results for
Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

Prepared by:
A-B-A by Sequential Addition of Monomers Using DFI

Sample A = Central Block

Sample B = Triblock

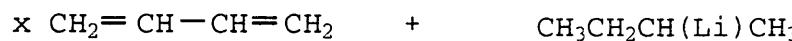
Sample	GPC M _n	M _w /M _n
IV18A	136,000	1.13
IV18B	143,000	1.30
III98A	125,000	1.14
III98B	150,000	1.28
IV06A	210,000	1.18
IV06B	253,000	1.31

Table 22
Gel Permeation Chromatography (GPC) Results for
Poly(butadiene-isoprene-butadiene) Linear Triblock Copolymers

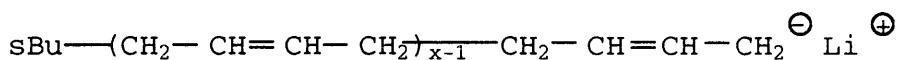
Prepared by:
A-B-A by Sequential Addition of Monomers Using DFI

Sample	GPC Triblock Mn	Total wt% PBd
	PBd-PI-PBd	
IV18B	3,500-136,000-3,500	6
IV98B	12,500-125,000-12,500	17
IV06B	20,000-210,000-20,000	16

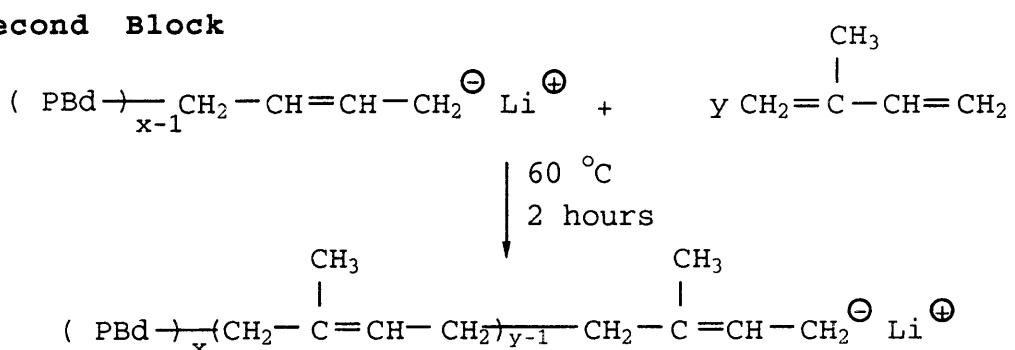
First Block



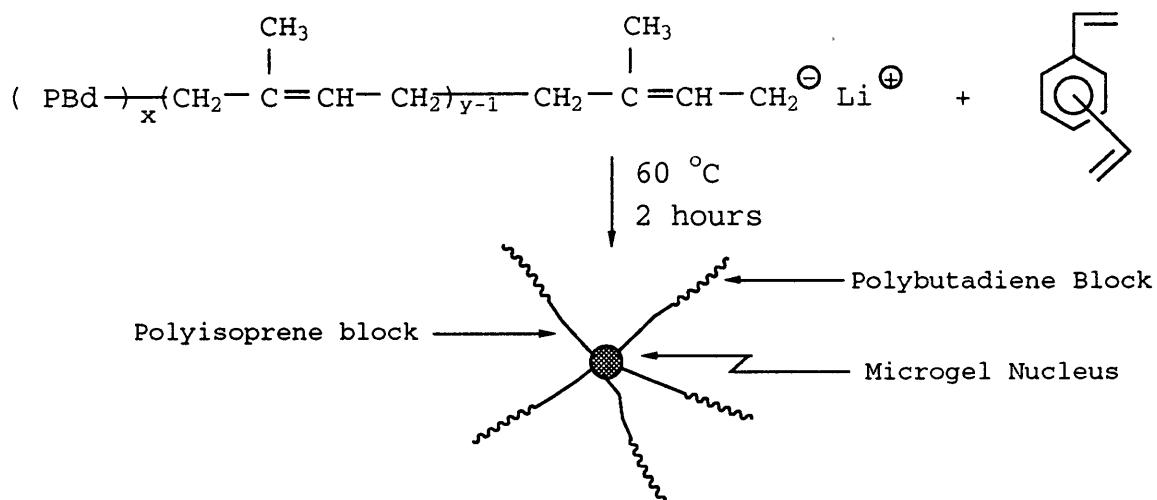
↓
cyclohexane
60 °C
2 hours



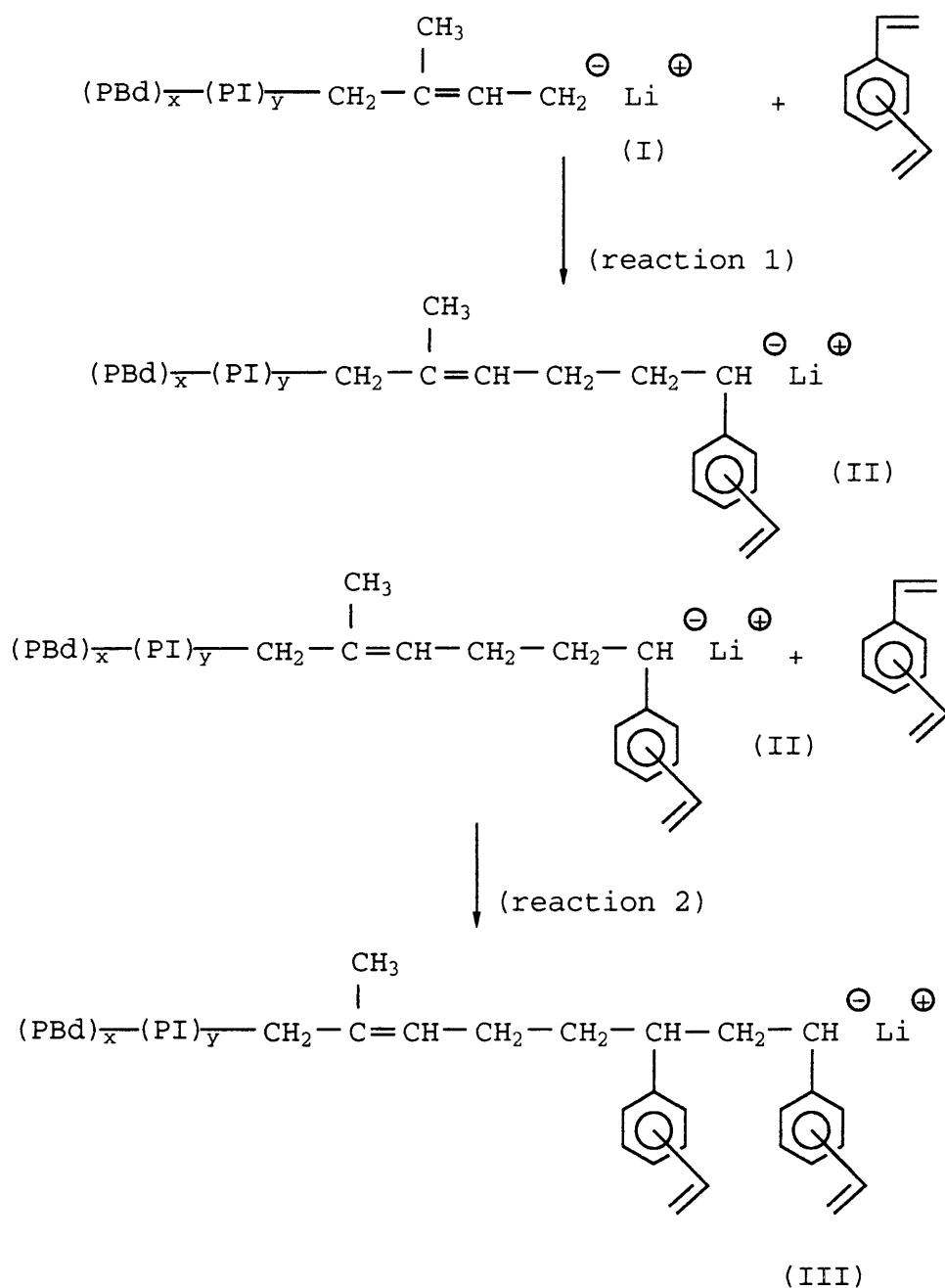
Second Block



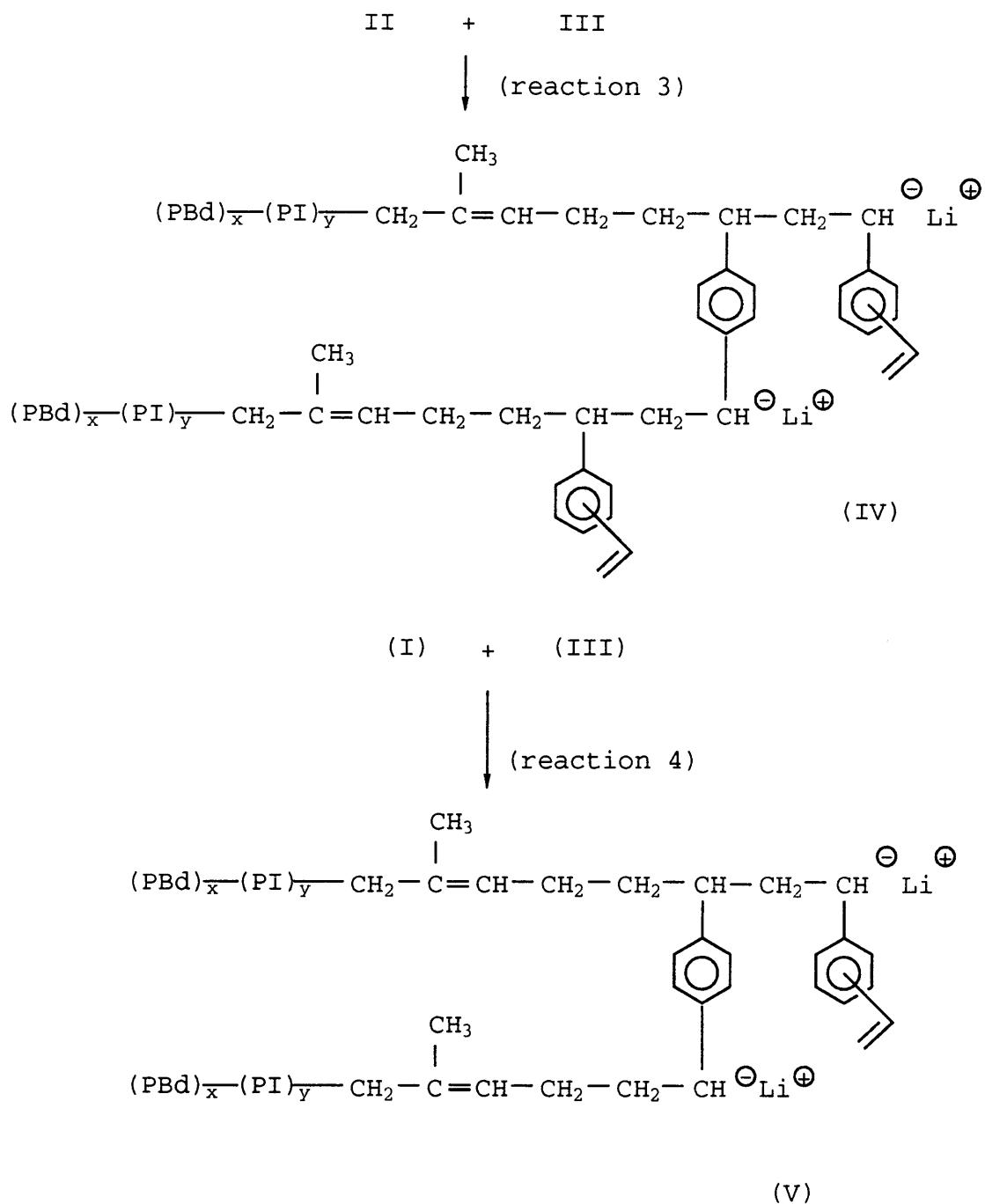
Star Formation



Scheme 3. Synthesis of Star Poly(butadiene-isoprene) Copolymers by Linking Diblocks with DVB to Form Stars



Scheme 4. Poly(butadiene-isoprene) Diblock Linking via Divinylbenzene



Scheme 5. Pendant Vinyl Formation

points for star arms. In Scheme 4 the poly(butadiene-isoprene)-isoprenyllithium anions can add across pendant vinyl groups of DVB to form the vinylbenzylanions (II) (reaction 1). The vinylbenzylanions (II) can then homopolymerize with more DVB (reaction 2), resulting in pendant vinyl groups. Scheme 5 shows that the pendant groups (III) can then serve as points for addition of more chains terminated with vinylbenzylanions (reaction 3, Scheme 5) or for the addition of poly(butadiene-isoprene)-isoprenyllithium anion (I) chains (reaction 4). Again, DVB can add across active polymer chain ends formed in reactions 1-4. Finally, after many combinations of isoprenyllithium anions and vinylbenzylanions across the pendant vinyl groups; DVB additions to active chain ends, multiarm diblock stars can be formed.

Table 16, 17 and 18 outline the targeted molecular weight parameters for poly(butadiene-isoprene) star block copolymers as described in Schemes 3 through 5. Three strategies were employed in the molecular architecture.

The first strategy was to prepare a series of stars with increasing M_n of both blocks, while holding a constant 10 weight percent content of polybutadiene, linking with a 2/1 mole ratio of DVB to chain ends (RLi) as illustrated in Table 16. Next, in Table 17 a series of stars was made by holding the M_n of the polyisoprene block constant while increasing

the polybutadiene weight percent from 10 to 40, also at a 2/1 mole ratio of DVB to RLi . Finally, in Table 18 the mole ratio of DVB to RLi was varied from 1 to 10 while holding both blocks at a constant M_n with a 10 weight percent content of polybutadiene.

Samples of each homo-, diblock and star were taken to establish structural control in this synthetic method, where sample A represents the homo-polybutadiene block, sample B the poly(butadiene-isoprene) diblock and sample C the poly(butadiene-isoprene-butadiene) star. Table 23 and 24 give GPC molecular weights for homo-, diblocks and stars prepared at a 2/1 mole ratio of DVB to RLi. In Table 24 the M_n of the isoprene block was determined from Table 23 by subtracting the M_n of the first block from the M_n of diblock.

Tables 26 and 27 list the GPC results for the stars made where the DVB/RLi mole ratio was varied from 1 to 10. In Table 27 the M_n of the polyisoprene block was determined in the same manner as they were in Table 24 as just mentioned. It should be noted that a sample was mistakenly not taken for III15A, as a result the M_n in Table 27 is the total M_n of the diblock.

Reasonably good molecular weight control of diblock arms was obtained with narrow molecular weight distributions as shown in Tables 23 and 26 for star polymers. As expected the

Table 23
 Gel Permeation Chromatography Results for
 Poly(butadiene-isoprene) Star Block Copolymers
 2/1 mole ratio of DVB to RLi

Sample A = First Block
 Sample B = Diblock
 Sample C = Star

Sample	GPC M _n	M _w /M _n
II85A	7,000	1.05
II85B	58,000	1.19
II85C	392,000	1.75
II83A	8,000	1.03
II83B	68,000	1.09
II83C	741,000	1.50
II74A	9,000	1.04
II74B	65,000	1.06
II74C	741,000	1.38
III27A	17,000	1.02
III27B	74,000	1.05
III27C	545,000	2.12
III47A	29,000	1.04
III47B	123,000	1.16
III47C	962,000	1.63
III77A	43,000	1.07
III77B	102,000	1.22
III77C	441,000	2.56
III10A	9,000	1.03
III10B	81,000	1.08
III10C	594,000	1.23
III09A	11,000	1.03
III09B	87,000	1.06
III09C	747,000	1.15

Table 24
Gel Permeation Chromatography Results for
Poly(butadiene-isoprene) Star Block Copolymers
2/1 mole ratio of DVB to RLi

Sample	GPC Diblock Arm Mn PBd - PI
II85B	7,000-51,000
II83B	8,000-60,000
II74B	9,000-56,000
III27B	17,000-57,000
III47B	29,000-94,000
III77B	43,000-59,000
III10B	9,000-72,500
III09B	11,000-76,000

Table 25
 Average Number of Arms and
 Percent Unlinked Diblock for
 Poly(butadiene-isoprene) Star Block Copolymers

2/1 mole ratio of DVB to RLi
 $N_{\text{arms}} = M_n \text{ (Star)} / M_n \text{ (Diblock)}$

Sample	N_{arms}	% Unlinked Diblock
II85C	7	5
II83C	11	7
II74C	11	8
III27C	7	16
III47C	8	18
III77C	4	28
III110C	7	3
III09C	9	4

Table 26
 Gel Permeation Chromatography Results for
 Poly(butadiene-isoprene) Star Block Copolymers

Sample A = First Block
 Sample B = Diblock
 Sample C = Star

Sample	GPC M _n	M _w /M _n
III30A	8,000	1.04
III30B	56,000	1.05
III30C	424,000	1.37
II74A	9,000	1.04
II74B	65,000	1.06
II74C	741,000	1.38
III15A	-	-
III15B	69,000	1.06
III15C	920,000	1.20
III16A	10,000	1.01
III16B	74,000	1.06
III16C	1,070,000	1.25
III19A	12,000	1.03
III19B	72,000	1.19
III19C	1,190,000	1.31
III21A	10,000	1.02
III21B	90,000	1.03
III21C	1,560,000	1.38

Table 27
Gel Permeation Chromatography Results for
Poly(butadiene-isoprene) Star Block Copolymers

Sample	GPC Diblock Arm Mn PBd - PI	DVB/RLi mole ratio
III30B	8,000-48,000	1
II74B	9,000-56,000	2
III15B	69,000	4
III16B	10,000-64,000	6
III19B	12,000-60,000	8
III21B	10,000-80,000	10

Table 28
 Average Number of Arms and
 Percent Unlinked Diblock for
 Poly(butadiene-isoprene) Star Block Copolymers

$$N_{\text{arms}} = M_n \text{ (Star)} / M_n \text{ (Diblock)}$$

Sample	N _{arms}	% Unlinked Diblock	DVB/RLi
III30C	8	7	1
II74C	11	8	2
III15C	13	6	4
III16C	14	5	6
III19C	16	6	8
III21C	17	12	10

polydispersity of the second block increases slightly due to the to impurities introduced by each sequential step. In going from the diblock to the star polymer the polydispersity increased as a result of the contributions of polydispersity of individual arms and/or from variations in the number of arms (134) as well as an intermolecular coupling reaction between different star nodules (136). However, the obtained star polydispersities were in good agreement with literature values (126,134).

Tables 25 and 28 list the average number of arms for star block copolymers which were determined from the GPC M_n of the star divided by the GPC M_n of the diblock. Figure 13 represents a typical series of GPC chromatograms. Sample A and B illustrate the narrow molecular weight distribution of the homo-polybutadiene and poly(butadiene-isoprene) diblock, respectively. While one can observe in Sample C for the star, a portion of unlinked diblock at a retention volume of 40.9ml. This was determined from GPC analysis to be unlinked diblock and not coupled diblock as a result of having the same retention volume as the diblock.

This is in good agreement with Martin who found that poly(butadienyllithium) anions can form coupled dimers (at low ratios of DVB to RLi) not incorporated into the stars, while poly(isoprenyllithium) anions do not form dimers unlinked from the stars (136). Table 25 and 28 also

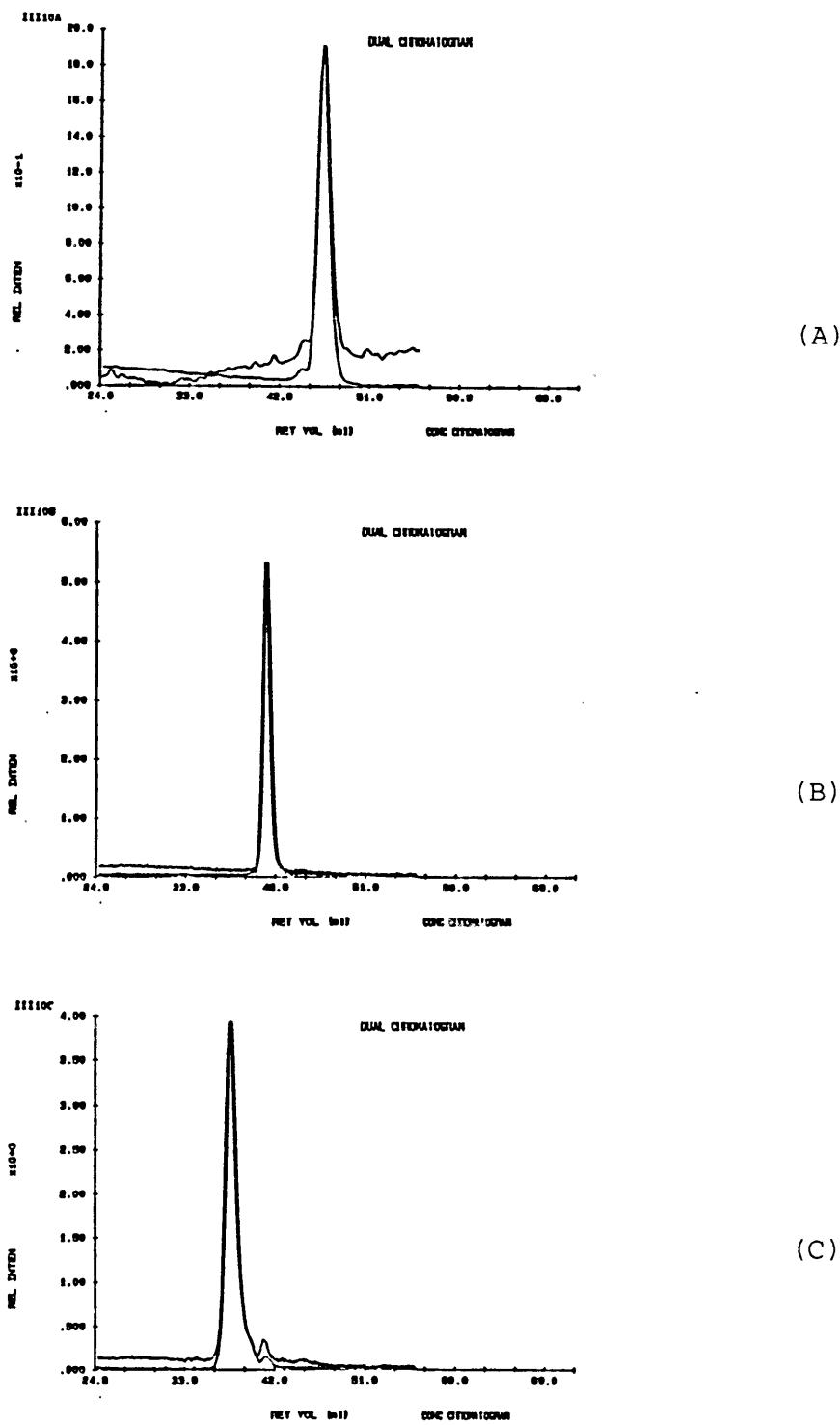


Figure 13. GPC Chromatogram of Sample III10: (A) First Block, Polybutadiene, (B) Diblock, Poly(butadiene-isoprene); (C) Star Block Copolymer with 3 wt% Unlinked Diblock

summarize the percent of unlinked diblock which was determined by the area under their respective GPC peaks.

It is evident from Table 28 that increasing the DVB/RLi mole ratio resulted in stars having an increase in the number of arms. Data from Table 28 is plotted in Figure 14 as the DVB/RLi mole ratio v.s. the number of star arms. The series of stars prepared in Table 28 have diblocks arms composed of approximately the same Mn for each block.

C. Polymer Modification

1. Catalytic Hydrogenation of Polydienes

The previously mentioned linear poly(butadiene-isoprene-butadiene) triblocks and star-branched poly(butadiene-isoprene) block copolymers were hydrogenated *in situ* with a homogeneous organotransition metal hydrogenation catalyst. The catalytic hydrogenation catalyst used in this study was preformed by the reaction of nickel dioctoate and triethylaluminum as illustrated in Scheme 6.

The nickel dioctoate was first alkylated using triethylaluminum, then nickel octoate hydride was formed by the reaction of hydrogen gas with the alkylated nickel octoate. This was follow by hydrogen transfer to an unsaturated site and subsequent hydrogenation as outlined in Scheme 7.

Hydrogenation of triblocks and stars proceeded as outlined in Schemes 8 and 9, respectively. Hydrogenation of

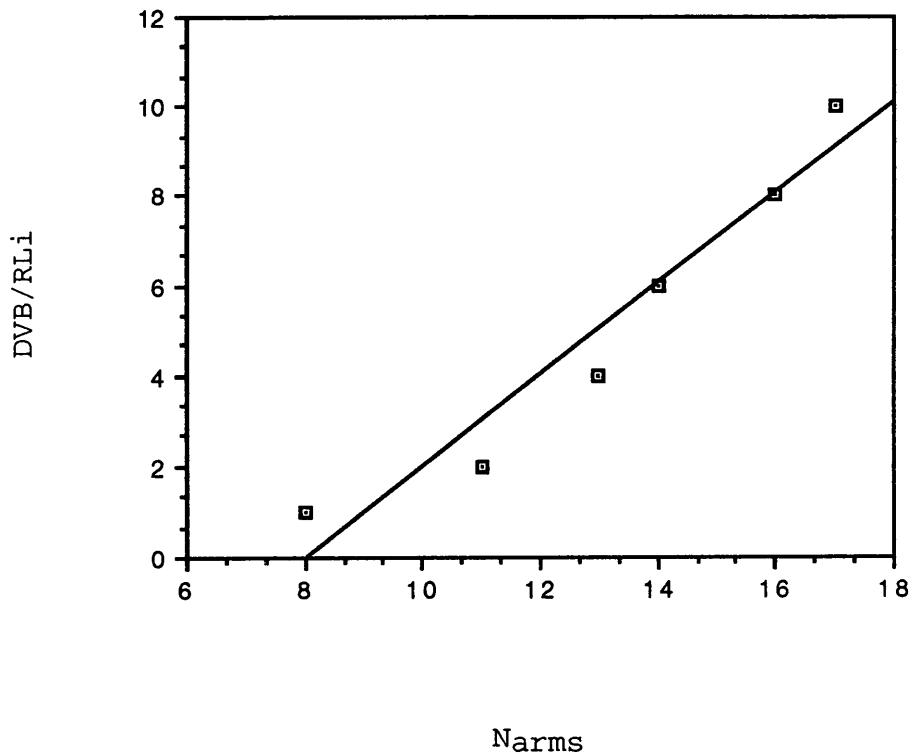
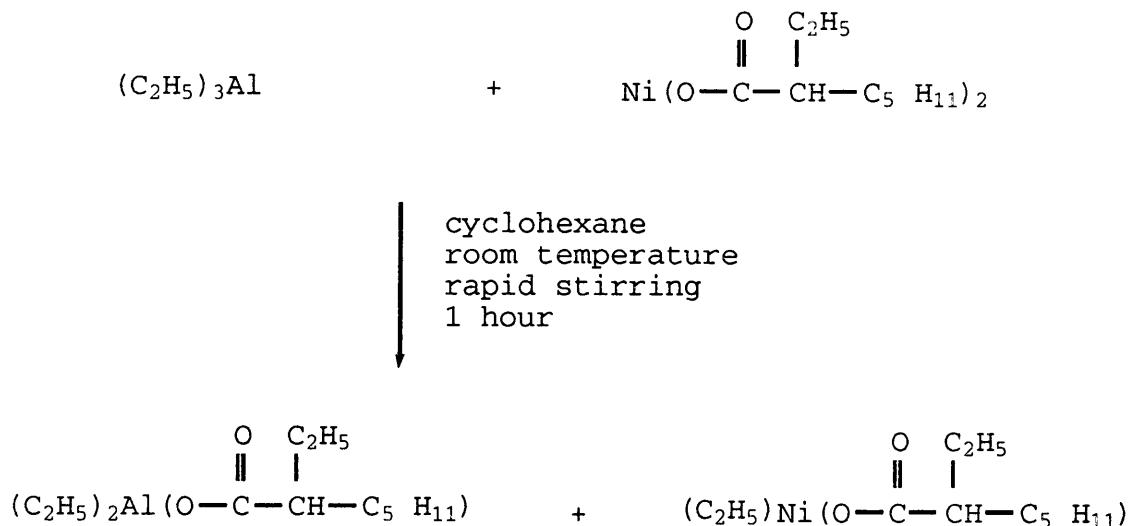
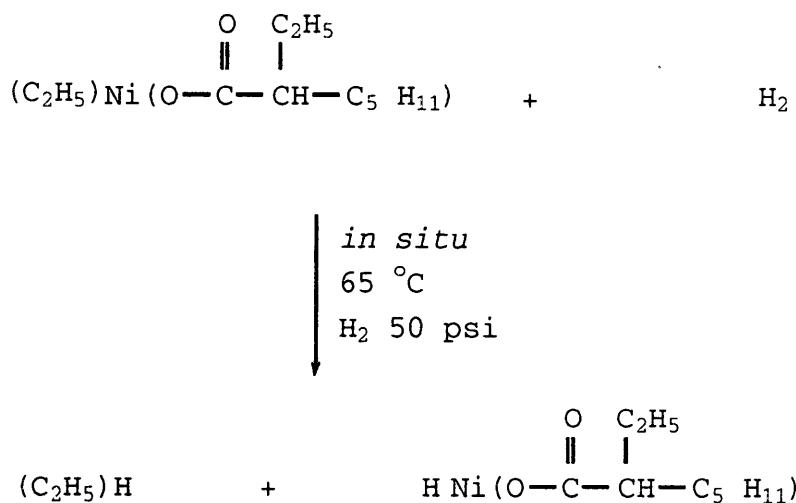


Figure 14. The Influence of DVB/RLi Mole Ratio to the Number of Star Arms (Narms)

Transition metal complex alkylation

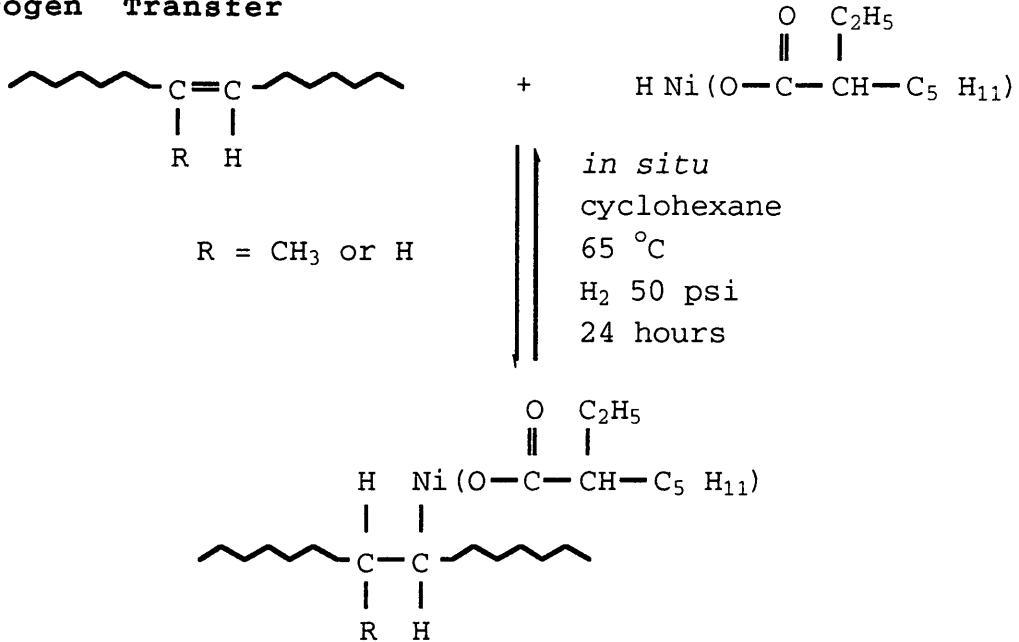


Hydride Formation

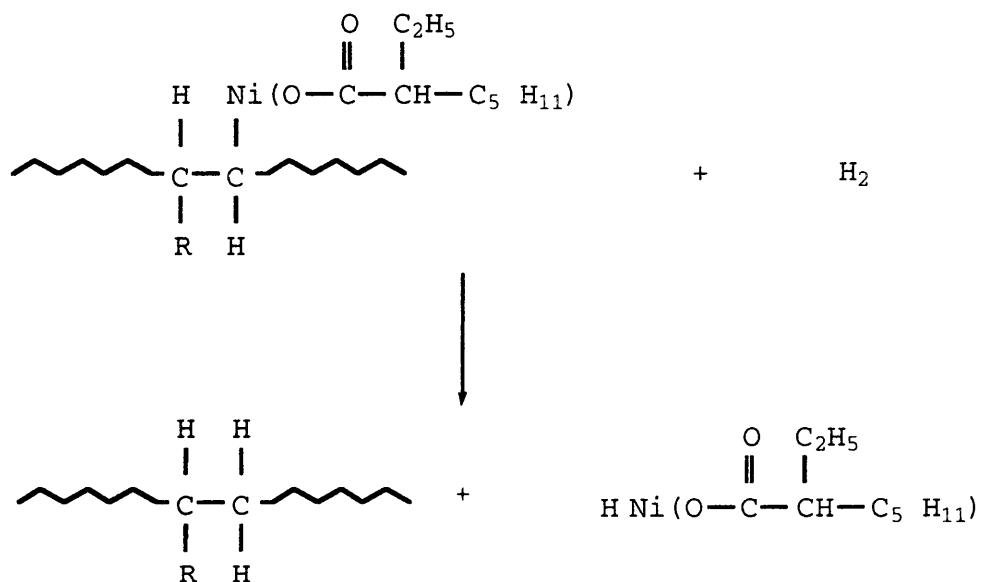


Scheme 6. Homogeneous Catalytic Hydrogenation Catalyst Formation

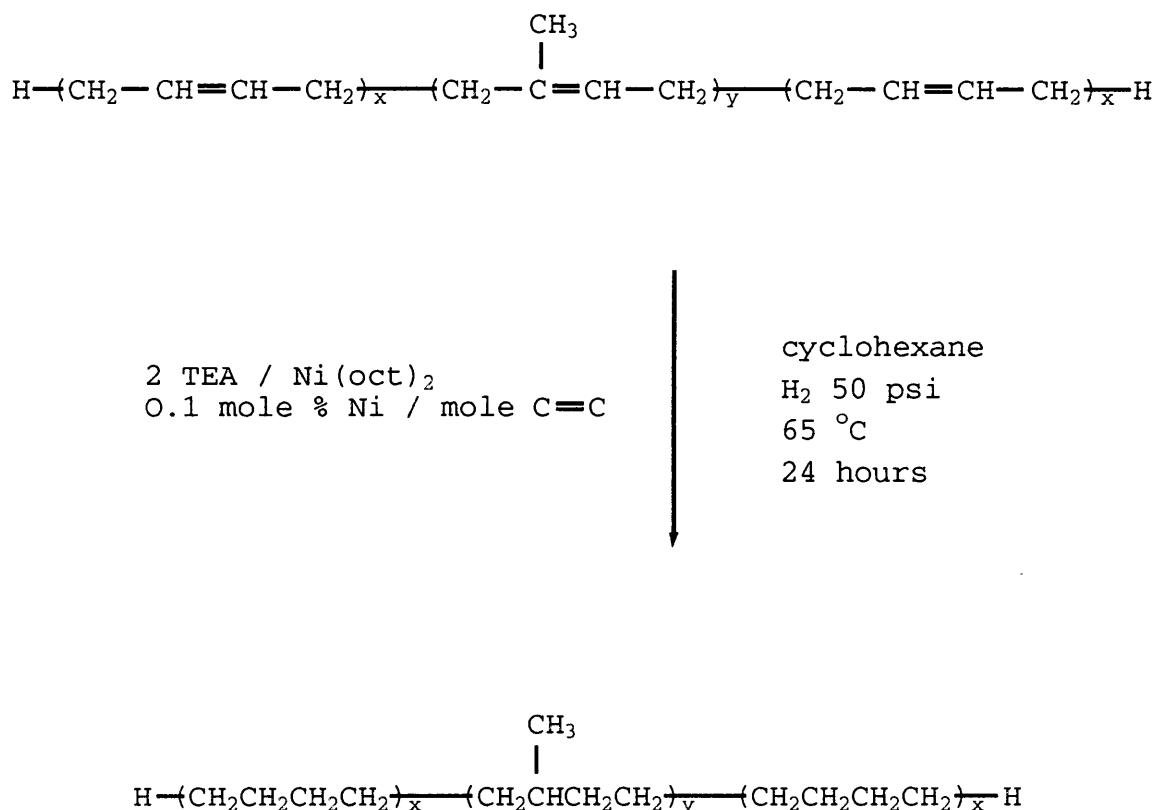
Hydrogen Transfer



Hydrogenation

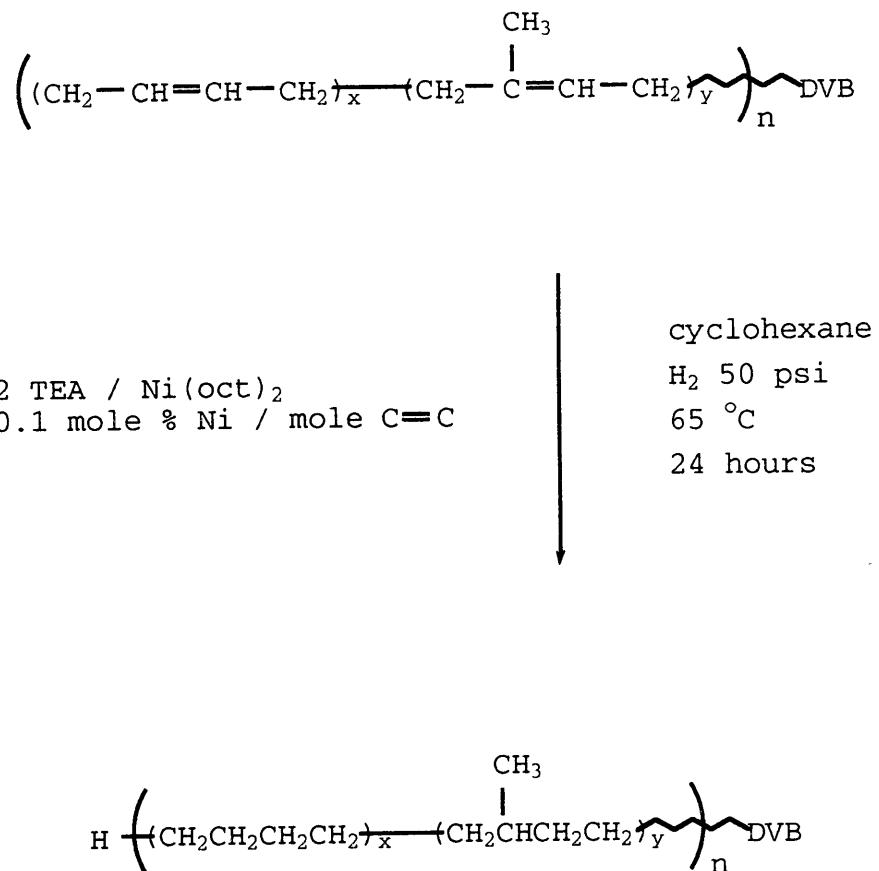


Scheme 7. Homogeneous Poly(diene) Catalytic Hydrogenation



Scheme 8. Catalytic Hydrogenation of Poly(butadiene isoprene-butadiene) Linear Triblock Copolymer via Homogeneous Nickel Catalyst

v



Scheme 9. Catalytic Hydrogenation of Star Poly(butadiene-isoprene) Block Copolymer via Homogeneous Nickel Catalyst

1,4-polybutadiene blocks resulted in the formation of semicrystalline polyethylene like end blocks (202-208). While, hydrogenation of 1,2-microstructure resulted in the formation of pendant ethyl groups (i.e., poly(butylene-co-ethylene)). Hydrogenation of 1,4-polyisoprene lead to the formation of amorphous alternating copolymer of propylene-ethylene (208) as shown in Scheme 8 and 9.

One of the main purposes of this study in preparing series of linear triblock and star-block copolymers was as the amount of polybutadiene end blocks was increased, the hydrogenated derivatives lead to increasing levels of crystalline hard blocks. These types of triblocks are important since they acquire their thermoplastic elastomers nature by crystalline domains rather than amorphous domains by phase separation, for example the Kraton® materials.

This is significant, since above the T_m of the crystalline end blocks, the now amorphous system can approach the melt behavior of a single-phase melt. Therefore, these A-B-A stars and linear triblocks should exhibit lower viscosities and simplified processing compared to the amorphous domain phase separated systems. These materials also show enhanced chemical resistance relative to the amorphous thermoplastic elastomers.

Fourier transform proton nuclear magnetic resonance ($^1\text{H-NMR}$) and fourier transform infrared spectroscopy (FTIR) were

used to observe the degree of hydrogenation as previously described by Wang and Hoover (59,215). $^1\text{H-NMR}$ and FTIR analysis compared the parent polydiene to the hydrogenated derivative for the degree of unsaturation to saturation. These methods indicated > 99.9% saturation of the polydiene copolymers after 24 hours.

The nondestructive nature of this hydrogenation method is demonstrated in Figure 15 for GPC chromatograms of a star-branched copolymer. One can observe by comparing the GPC peak for the nonhydrogenated poly(butadiene-isoprene) star (sample III21C) to the hydrogenated derivative (sample III21D) that the only difference between the two is a slight shift due the increase in M_n of the hydrogenated derivative.

D. Thermal Analysis

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) results are summarized in Tables 29 through 31 for hydrogenated poly(butadiene-isoprene-butadiene) triblocks and poly(butadiene-isoprene) stars. While Figures 16 and 17 represents typical DSC and DMTA traces.

Dynamic mechanical thermal analysis showed that the hydrogenated poly(butadiene-isoprene-butadiene) (i.e., poly(ethylene-[propylene-co-ethylene]-ethylene)) triblocks and poly(butadiene-isoprene) stars all had approximately the same thermal transitions temperatures independent of polymer

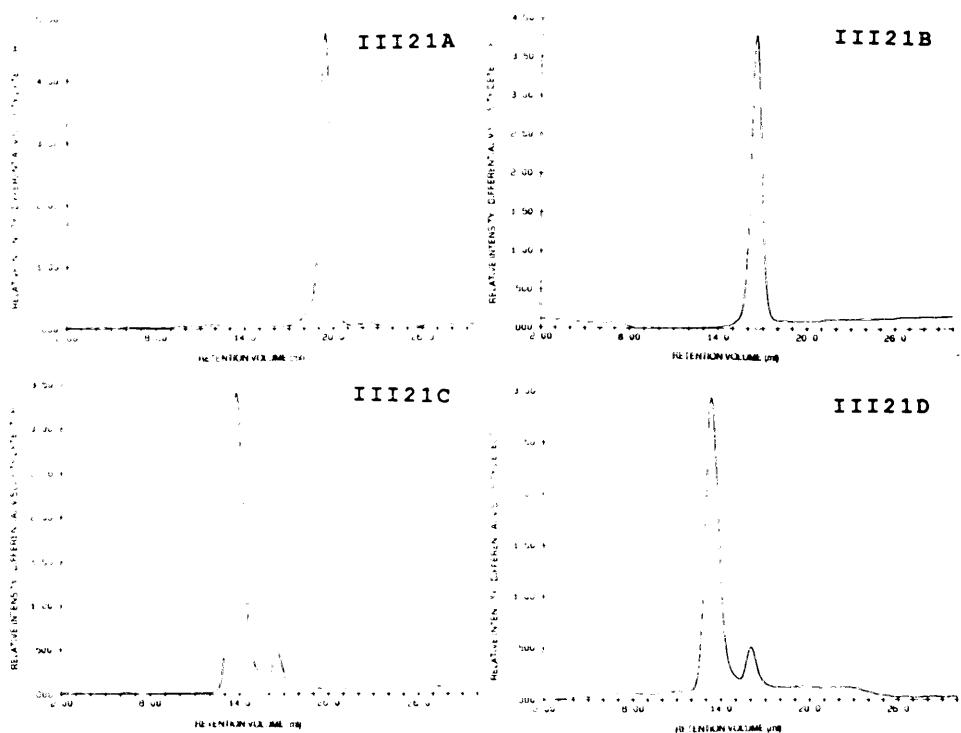


Figure 15. GPC Chromatograms of a Star Copolymer: (III21A) Polybutadiene Segment, (III21B) Poly(butadiene-isoprene) Diblock, (III21C) Unfractionated Poly(butadiene-isoprene) Star and (III21D) Hydrogenated Derivative of III21C. (GPC analysis were analyzed in toluene at 80°C)

Table 29
DSC Endothermic Melting Transitions for Hydrogenated
Poly(butadiene-isoprene-butadiene) Linear Triblocks

Sample	T _m , °C
III60D	99
III64D	100
III68D	96
III72D	87
IV18C	98
IV98C	97
IV06C	96

Table 30
 DSC Results for Hydrogenated
 Poly(butadiene-isoprene) Star Block Copolymers

Sample	Beta Relaxation, °C	T _m , °C
II85D	-60	94
II83D	-61	94
II74D	-60	93
III10D	-60	93
III09D	-62	96
III27D	-	99
III47D	-	99
III30D	-61	95
III15D	-61	94
III16D	-63	95
III19D	-63	94
III21D	-63	93

Table 31
DMTA Results for Hydrogenated
Poly(butadiene-isoprene) Star Block Copolymers

Sample	Beta Relaxation, °C	T _g , °C	T _m , °C
III60D	-106	-48	102
III64D	-106	-49	103
III72D	-107	-48	97
III07C	-100	-48	96

Table 32
 DMTA Results for Hydrogenated
 Poly(butadiene-isoprene) Star Block Copolymers

Sample	Beta Relaxation, °C	T _g , °C	T _m , °C
II85D	-95	-42	93
II83D	-98	-42	99
II74D	-97	-38	93
III10D	-99	-44	93
III09D	-107	-41	100
III15D	-103	-46	93
III16D	-100	-47	99
III19D	-93	-46	98
III21D	-100	-41	93

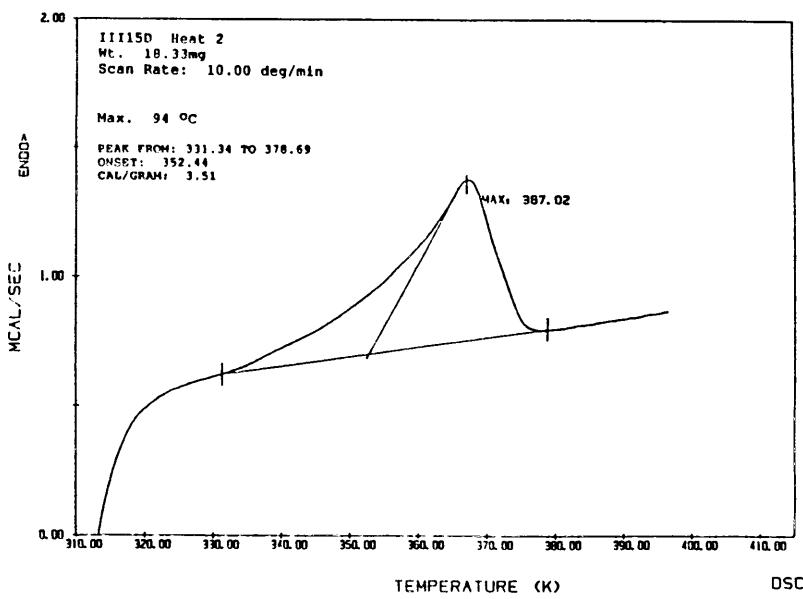
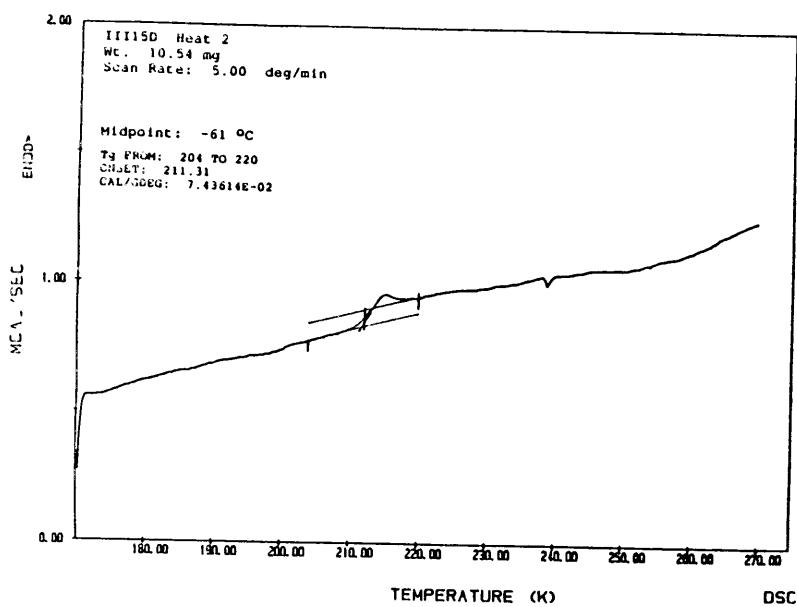


Figure 16. DSC Thermograms of a Hydrogenated Poly(butadiene-isoprene) Star Copolymer, Sample III15D: (A) T_g Region; (B) T_m Region

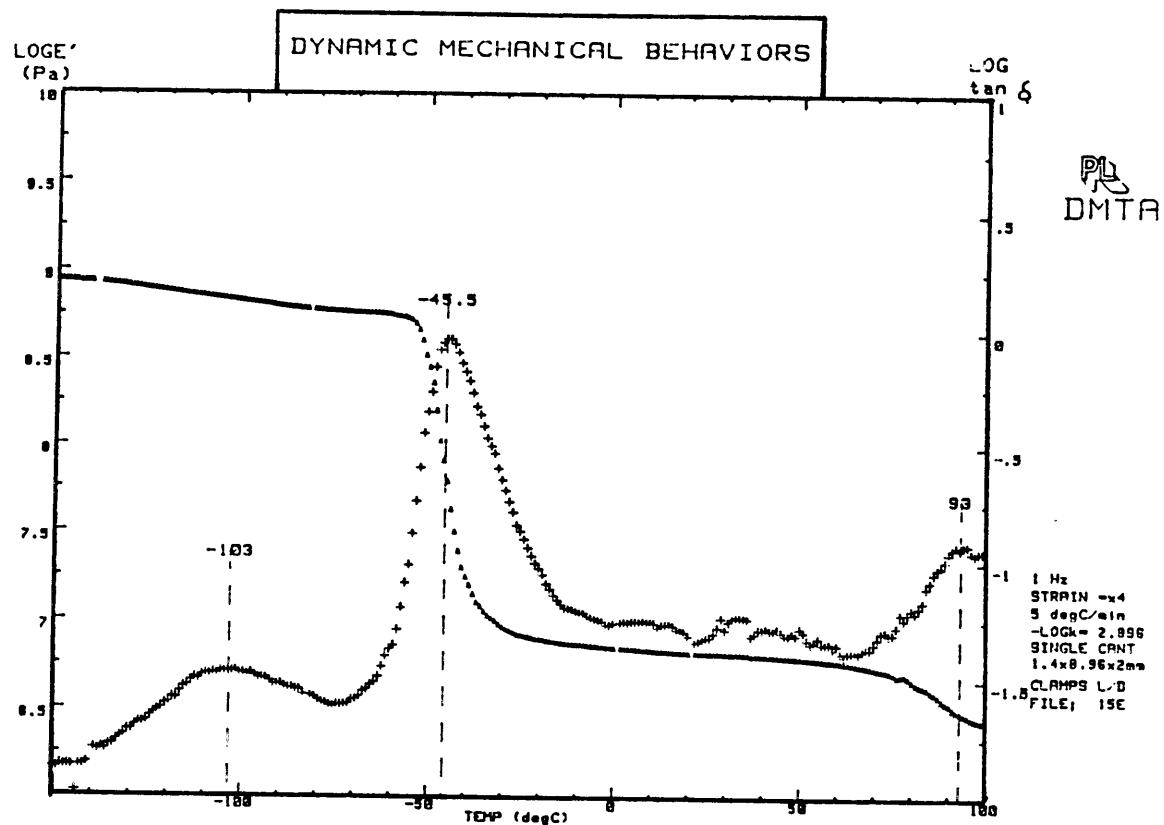


Figure 17. Dynamic Mechanical Behavior of a Hydrogenated Poly(butadiene-isoprene) Star Copolymer, Sample III15D, 4/1 DVB to RLi Mole Ratio

composition and block length (58,161,198). This was expected since in general thermal transition behavior is an architecture-independent property.

The glass transition temperatures ranging from -38 to -47 °C in Table 31 are due to the alternating propylene-ethylene rubbery blocks. While the beta transitions in the vicinity of -100°C are due to the semicrystalline polyethylene blocks. Two-phase block copolymers usually exhibit modulus-temperature characteristics similar to those of physical blends of the two components. In two-phase systems the position of the thermal transitions are not changed significantly by compositional variations (78).

The endothermic melting temperature (T_m) of the triblocks and star remain in the range of 93-100°C regardless of block length and compositional variation. This is a further indication of the incompatibility between the ethylene and alternating propylene-ethylene blocks in the solid state.

The constant T_m of the semicrystalline polyethylene end blocks and constant T_g of the rubbery central block, plus the fact that these material are opaque indicates that these two phase are incompatible in the solid state.

V. Conclusions

The following conclusions have been reached as a result of this investigation.

1. The three anionic living polymerization techniques utilized in this study were successful in the preparation of linear triblocks and star block copolymers that were in reasonable agreement with predicted molecular weights, narrow molecular weight distributions and various ranges of block length incorporation.

2. The synthesis of star-branched block copolymers was efficiently achieved by linking poly(butadiene-isoprene) "living" diblocks with commercial divinylbenzene. In general, it was found that increasing DVB/RLi mole ratios lead to stars with increasing number of diblock arms.

3. Catalytic hydrogenation has provided a successful method for converting poly(butadiene-isoprene-butadiene) linear triblocks and stars into polymers containing hard semicrystalline polyethylene and a soft rubbery alternating propylene-ethylene copolymer segments. Various block lengths of polyethylene were incorporated by varying the M_n of the parent polybutadiene segments.

4. Both hydrogenated linear triblocks and star block copolymers exhibited endothermic melting temperatures in the desired range of 90-105°C for potential applications as

thermoplastic elastomers and as binders for castable propellents.

VI. Suggested Future Studies

1. To study the melt rheology of these hydrogenated poly(butadiene-isoprene-butadiene) linear and poly(butadiene-isoprene) star systems for elucidation of the effects of variation of molecular architecture and composition on the melt behavior.
2. It would be of interest to couple poly(butadiene-isoprene) diblocks into triblocks, since this should be an efficient method of preparing linear triblocks with the same M_n end blocks, thus avoiding the uneven block lengths and broad polydispersities associated with the three-stage process using monofunctional anionic initiation.

It was concluded by Martin (136) and this investigation that low ratios of DVB/RLi did not result in linear chain coupling with poly(isoprenyllithium) chain ends. However, Martin found very efficient coupling of poly(butadienyllithium) chain ends at low ratios of DVB/RLi. It may be possible to cap the poly(butadiene-isoprene)-isoprenyllithium diblock chain ends prepared in this study with a few units of butadiene in the attempt to efficiently couple diblocks using low ratios of DVB/RLi to achieve control of block architecture.

3. To further compare linear and star architectures.

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