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Anionic polymerization of 1,3-cyclohexadiene.

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ANIONIC POLYMERIZATION OF 1,3-CYCLOHEXADIENE

by

KUNLUN HONG

A DISSERTATION

Submitted to the graduate faculty of The University of Alabama at Birmingham,
The University of Alabama and The University of Alabama in Huntsville,
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

BIRMINGHAM, ALABAMA

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ABSTRACT OF DISSERTATION
GRADUATE SCHOOL, THE UNIVERSITY OF ALABAMA AT BIRMINGHAM

Degree Ph. D. Program Material Science

Name of Candidate Kunlun Hong

Committee Chair Jimmy W. Mays

Title Anionic Polymerization of 1,3-Cyclohexadiene

1,3-Cyclohexadiene (1,3-CHD) polymers are very interesting due to their unique structure and potential applications. Many pursuits have been made toward the synthesis of poly(1,3-cyclohexadiene) (PCHD); anionic polymerization strategies have given the best results. Nevertheless, well-defined PCHD polymers have remained an elusive target because of side reactions. In this dissertation, the anionic polymerization of 1,3-CHD is studied in detail. In addition, the synthesis and characterization of 1,3-CHD and styrene block copolymers, PCHD-based three-armed star and star-block copolymers are also presented.

The polymerizations of 1,3-CHD using various anionic initiators without additives or with mono-dentate additives failed to produce PCHD with controlled molecular weight and narrow molecular weight distribution because of chain transfer and termination reactions. However, suitable combinations of specific butyllithium initiators and poly-dentate Lewis-base additives, such as 1,2-dimethoxyethane (DME), N,N,N',N'-tetramethylethylene-diamine (TMEDA), and 1,4-diazabicyclo[2.2.2]octane (DABCO), are effective in minimizing these side reactions. Further studies indicated that the longevity of these "living" polymerizations is quite short by the standard of anionic polymerization.

The copolymerization of 1,3-CHD and styrene was also studied. It was observed that the chain propagation and cross-propagation rates of PSLi and PCHDLi with 1,3-CHD or styrene in benzene are comparable. Well-defined poly(1,3-cyclohexadiene-block-styrene)s with a wide range of compositions have been synthesized and characterized. Near-monodisperse, three-armed star and star-block copolymers based on PCHD were synthesized and characterized. The stars are prepared by the reaction of "living" anionic chain ends of PCHD, polystyrene-b-poly(1,3-cyclohexadiene), and poly(1,3-cyclohexadiene)-b-polystyrene from *sec*-BuLi/DABCO with CH_3SiCl_3 in benzene. DABCO also acts as a promoter during the linking reaction.

DEDICATION

This dissertation is dedicated to my family and friends.

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But the GOD should have all the credits May this glorify HIM!

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LIST OF ABBREVIATIONS

$[\eta]$	Intrinsic viscosity
AIBN	Azobisisobutyronitrile
t-AmOK	Potassium tertiary amyl oxide
t-AmOD	tertiary amyl alcohol-o-d
BenzylK	Benzyl potassium
BHT	Butylated hydroxytoluene
t-BuOK	Potassium tertary butoxide
sec-BuOLi	Secondary lithium butoxide
n-BuLi	Normal butyllithium
sec-BuLi	Secondary butyllithium
t-BuLi	tertiary butyllithium
1,3-BD	1,3-Butadiene
1,3-CHD	1,3-Cyclohexadiene
1,4-CHD	1,4-Cyclohexadiene
$CHCl_3$	Chloroform
p-Chloranil	2,3,5,6-Tetrachloro-1,4-benzoquinone
CS_2	Carbon disulfide
2D-COSY	Two-dimensional correlated spectroscopy

LIST OF ABBREVIATIONS (Continued)

CumylK	Cumylpotassium
DABCO	1,4-Diazabicyclo[2.2.2]octane
DCA	Deoxychloic acid
DME	1,2-Dimethoxyethane
DPPE	1,2-Dipiperidinoethane
DVB	Divinylbenzene
GC	Gas chromatography
LiH	Lithium hydride
HMPA	Hexamethylphosphric triamine
IR	Infrared spectroscopy
MALDI-TOF-MS	Matrix-assisted laser desportion/ionization-time-of-flight/mass spectrometry
MALLS	Multi-angle laser light scattering
MAO	Methylaluminoxane
MgBu$_2$	Dibutylmagnesium
MHS	Mark-Houwink-Sakurada equation
M_w	Weight average molecular weight
M_n	Number average molecular weight
M_v	Viscosity average molecular weight
NBS	N-Bromosuccinimide
$^-$NC$^-$	Naphthalide dianionic
OBDD	Ordered bicontinuous double diamond

PBD	Polybutadiene
PB-PDES	Poly(butadiene-block-diethylsiloxane)
PCH	Polycyclohexane
PCHD	Poly(1,3-cyclohexadiene)
PCHDLi	Polycyclohexadienyllithium
PCHD-PBD	Poly(1,3-cyclohexadiene-block-butadiene)
PCHD-PS	Poly(1,3-cyclohexadiene-block-styrene)
PCHD-PS-PCHD	Poly(1,3-cyclohexadiene-block-styrene-block-1,3-cyclohexadiene)
PCHD-PBD-PCHD	Poly(1,3-cyclohexadiene-block-1,3-butadiene-block-1,3-cyclohexadiene)
PDI	Polydispersity index
PhLi	Phenyllithium
PI	Polyisoprene
PI-PtBMA	Poly(isoprene-block-t-butylmethacrylate)
PI-PSLi	Poly(isoprene-block-styryllithium)
PMDETA	N,N,N',N',N''-Pentamethyldiethylenetriamine
PPP	Poly(paraphenylene)
PS	Polystyrene
PSLi	Polystyryllithium
PS-PCHD	Poly(styrene-block-1,3-cyclohexadiene)
PS-PCHDLi	Poly(styrene-block-1,3-cyclohexadienyllithium)

LIST OF ABBREVIATIONS (Continued)

PS-PCHD-PS	Poly(1,3-cyclohexadiene-block-styrene-block-1,3-cyclohexadiene)
PS-PPP	Poly(styrene-block-paraphenylene)
PS-PPP-PS	Poly(styrene-block-paraphenylene-block-styrene)
SEC	Size exclusion chromatography
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMEDA	N,N,N'N'-Tetramethylethylenediamine
UV	Ultraviolet

INTRODUCTION

The pace of change of today's world is truly incomprehensible, with computers and related industries being clearly the driving forces shaping all aspects of our society. While science is enjoying tremendous advances on all fronts, material science in general and polymer science in particular, in all its permutations, has been a vital component of high technology.[1] Despite magnificent advances, polymer science is far from completely developed. Polymers with well-defined architecture and structural (molecular weight and composition, in the case of copolymers) homogeneity are essential for establishing structure/properties relationships. These relationships are necessary to achieve one of the ultimate goals of polymer science: designing molecules with predetermined properties. Even though an increasing number of tools are at our disposal for the synthesis of polymeric materials, few other methods are as versatile as anionic polymerization for controlling molecular weight, giving narrow molecular weight distributions, and providing access to functional polymers, to block copolymers, to branch polymers, and to other special architectural species.[2]

Anionic polymerizations have been known for decades, but it was Szwarc who emphasized the "living" characteristics of those polymerizations and who inspired the extensive investigation of this methodology.[3] Anionic living polymerization is a chain polymerization in which kinetic chain transfer and termination are negligible, with the chain growth centers being anions (most often carbanions). For an ideal living polymerization, the molecular weight is controlled by stoichiometry of the reaction and the degree of conversion, and the resultant polymers exhibit narrow molecular weight distributions (Poisson distribution).[4] However, the high reactivity of anionic centers toward atmospheric (water, oxygen, and carbon dioxide) and other contaminants dictates use of specially designed apparati and appropriate techniques to purify the reagents in order to avoid premature living chain termination. Both inert atmosphere and high vacuum techniques have been successfully used for anionic polymerization, with each having their own merits.

The most versatile and useful initiators in anionic polymerizations are alkyllithium compounds. They are soluble in a wide array of solvents, including hydrocarbons due to their unique structural characteristics. Namely, the C-Li bond in organolithium compounds exhibits properties of both covalent and ionic bonds,[5] because lithium has the smallest radius, the highest electronegativity, and the highest ionization potential of all alkali metals. However, alkyllithiums tend to aggregate in solvents, which complicates the initiation reactions. Moreover, they are preferred for the polymerization of styrene and acyclic dienes, since they are too reactive for some monomers (such as methacrylates) and not active enough for other monomers (such as ethylene oxide). Thus many other anionic initiators have also been developed.[4]

A wide variety of vinyl and diene monomers (non-polar or polar) and heterocyclic monomers can be polymerized in a controlled fashion by anionic polymerizations.[6] The key requirement for a monomer to be polymerized anionically in a living manner is to form carbanions with suitable stability. If the carbanions were too stable, the chain growth would be too slow to form high molecular weight material; conversely, if the carbanions are too reactive, the chain could be terminated prematurely. The most studied monomers are styrene, acyclic dienes, and some cyclic heteroatom ring compounds. The living polymerization of monomers with reactive substituted groups is only possible under specific conditions, such as low polymerization temperatures, and using bulky initiators, carefully selected counterions, and Lewis base additives. On the other hand, studies of living anionic polymerization of cyclic dienes are very limited, besides a few on 1,3-cyclohexadiene (1,3-CHD).[7] Since the purpose of this project is to synthesize well-defined polymers, including block, star, and star-block copolymers, containing poly(1,3-cyclohexadiene) (PCHD) blocks, it is logical to review previous work on 1,3-CHD and its polymers in the following.

Properties of 1,3-CHD

1,3-CHD, available commercially in experimental quantities from several chemical companies (Aldrich, ACRO, etc.) is an interesting monomer. 1,3-CHD readily undergoes several chemical transformations, including oxidation, dimerization, disproportionation, and isomeric rearrangement. Like many other conjugated dienes, 1,3-CHD reacts thermally with dienophiles to yield Diels-Alder adducts. The cisoid configuration of the dienes is required for this kind of reaction.[8] Thus, 1,3-CHD, which possesses a locked-in cisoid configuration, exhibits particularly enhanced reactivity as compared to its open chain analogs. Indeed, 1,3-CHD may even react with itself in a Diels-Alder fashion.[9] The cycloaddition process proceeds via a diradical intermediate, which yields both polymeric and disproportionation products in addition to dimmers. The composition of the final product depends only on temperature.

Besides the thermally initiated reactions discussed above, 1,3-CHD can also undergo reactions under other conditions, especially in the presence of organic base. It is very important to understand base-induced transformations if we seek to polymerize 1,3-CHD anionically. Bates et al.[10] found that the same mixtures of 3-d-1,4-cyclohexadiene (1,4-CHD) and 5-d-1,3-CHD (8:1) were formed when either 1,3-CHD or 1,4-CHD was treated with potassium tertiary amyl oxide (*t*-AmOK) in tertiary amyl alcohol-o-d (*t*-AmOD) for 45 min at 95 °C. This indicates that a common anion formed by allylic abstraction was apparently involved. The ratio could be understood by the fact that the abstraction of allylic protons in 1,4-CHD is much faster than that in 1,3-CHD, since the allylic protons of 1,4-CHD, activated by two double bonds, are very acidic. In the gas phase, 1,3-CHD is indicated to be non-planar with C_2 symmetry, while 1,4-CHD is planar with D_{2h} symmetry.[11] Contrary to the linear conjugated dienes, 1,3-CHD is devoid of conjugation, thus the relative stability difference of 1,3-CHD and 1,4-CHD is very small.[12,13] With four allylic protons, 1,4-CHD is an excellent anionic chain transfer agent, and thus it is particularly deleterious in the anionic preparation of 1,3-CHD polymers (resulting in low molecular weight and broad molecular weight distribution). Mango[14] and Mango and Lenz[15] found that benzene and cyclohexene were detected when 1,3-CHD was treated with normal butyllithium (*n*-BuLi). Benzene is thought to arise from aromatization of cyclohexadienyl anions formed originally by abstraction of allylic protons from the monomer by the carbanion.

Oxidation is another kind of side reaction in cyclohexadienes that we should consider. It is well known that compounds containing allylic protons react readily with oxygen to form peroxides either through excited singlet oxygen or auto-oxidation.[8] This should be particularly the case for 1,3-CHD. 5,6-dioxabicyclo[2,2,2]octene-2 was formed when 1,3-CHD was exposed to light induced oxidation.[16] Polymeric peroxide was produced when it was reacted with oxygen at 30 °C /960 mm O_2 in bulk.[17] Polar oxidation products are very detrimental to anionic polymerization.

In conclusion, several important aspects of the chemistry of 1,3-CHD as discussed above make it a difficult monomer for living anionic polymerizations. Therefore, extreme care should be exercised in the purification and storage of this monomer. Furthermore, 1,4-CHD can be a good chain transfer agent because the allylic protons are activated by two double bonds and, hence, its presence prevents the anionic polymerization of 1,3-CHD in a living manner.

Polymerization of 1,3-CHD

Prior Polymerization Methods. The polymerization of 1,3-CHD has attracted much attention both practically and scientifically.[14,18-49] With alicyclic units in the main chain, a dramatic improvement of stabilities (thermal, chemical) and strength is expected in 1,3-CHD based polymers. Through subsequent post-polymerization chemistry, PCHD can be converted to other novel materials. Moreover, the richness in microstructural features provides another parameter to tailor the properties of PCHD-related materials.

In 1926, Hoffmann and Damm[18] treated 1,3-CHD thermally, and they obtained rubber-like oligomers. Marvel and Hartzell polymerized 1,3-CHD using a Ziegler-Natta catalyst system and subsequently aromatized the polymer in 1959.[19] Since then essentially all the conventional polymerization methods have been used to polymerize 1,3-CHD. These included radical,[20] cationic,[21-23] Zielger-Natta,[19-22,24] γ-ray irradiation of 1,3-CHD in bulk[21] or in a deoxychloic acid (DCA) canal,[25] metal complexes,[26-32] electro-oxidation,[33,34] thermal-induced,[35] pressure-induced,[36] and anionic polymerizations.[14,20,37-49] Thiourea canal[46] and cyclophosphazene clathrate tunnel[47] have also been used as substrates to convert 1,3-CHD to PCHD. However, most attempts reported to date give polymers with molecular weights under 20 kg/mol and conversions less than 80%. Typical results are summarized in Table 1 and Table 2. The best molecular weights and conversions obtained were via anionic polymerization in hydrocarbon solvents at low temperatures. This particular technique is the one exploited herein and is now considered in further detail.

Anionic Polymerization Method. Lefebvre and Dawans reported the first anionic polymerization of 1,3-CHD using *n*-BuLi as the initiator,[20] with a subsequent study by Cassidy et al.[37] In these early studies, a wide range of solvents, temperatures, and monomer to initiator ratios were utilized. It was found that the molecular weight and conversion increased as the temperature was decreased, both in polar and non-polar solvents. This is consistent with, and suggests the possibility of, chain transfer reactions occurring, in addition to the desired propagation reactions. The effects of solvent in these studies reveal that generally molecular weight and conversion increase in the order polar solvents < aliphatic solvents < aromatic solvents. The relation of aliphatic < aromatic is reasonable on the basis that particularly slow initiation and propagation occur in aliphatic solvents.[48] In the polar solvents, reactions that lead to chain transfer are facilitated. As to the monomer/initiator ratio, Cassidy et al.[37] studied 1,3-CHD to initiator ratios from 8 to 32 at 25 °C and they found that molecular weight was inversely proportional to the initiator concentration in tetrahydrofuran (THF) with the lithium counter-ion. This behavior is normally anticipated for a living anionic polymerization with rapid initiation and propagation.[48] When the monomer to initiator ratio was increased further, however, only low molecular weight material was obtained, and the conversion was low.[37] It might be that, at high monomer ratios, the monomer consumption is slow, and some monomer could function as a chain transfer agent. Lefebvre and Dawans[20] also attempted to initiate 1,3-CHD polymerization using lithium metal, but no polymer was formed. Lussi and Barman used the naphthalene/alkali initiating system to polymerize 1,3-CHD in various solvents.[39] Inherent viscosities (a measure of molecular weight) were noticed to decrease in the order Na>Li>K in THF and 1,2-dimethoxyethane (DME). The authors explained that this was due to steric effects.[39] When the 1,3-CHD to initiator ratio was varied from 105 to 785 in THF at 0 °C with the sodium counter-ion, there was little effect on the molecular weight. They concluded that "no dissociation of the ion pairs on the chain ends seems to occur." Sharaby et al. [41] reinvestigated the polymerization of 1,3-CHD initiated with $Li^{\pm}$, $Na^{\pm}$, or $K^{\pm}$ naphthalenides. Their experiments were conducted in THF, DME, and hexamethylphosphoric triamine (HMPA) at temperatures ranging from -73 °C to +25 °C. Initiation by lithium naphthalenide in THF at 20 °C yielded polymer with a fairly narrow molecular weight distribution. The molecular weight (obtained from size exclusion chromatography, SEC) of polymers so prepared was about. 20,000 gram/mole or below. Dehydrogenation and disproportionation of the monomer was observed during the polymerizations of 1,3-CHD conducted at room temperature, especially with potassium as the counter-ion. Mango and Lenz[15] also studied the anionic polymerization of 1,3-CHD. However, their main purpose was to probe the mechanism, especially side reactions. The anionic polymerization of 1,3-CHD was re-visited by Zhong and Francois[42] about 10 years ago in order to make polystyrene-block-polycyclohexadiene (PS-PCHD) block copolymers. They initiated 1,3-CHD with polystyryllithium (PSLi) in benzene or cyclohexane at room temperature, and the polymerization was allowed to proceed for 24 h. They claimed that secondary reactions could be avoided at low monomer concentrations and that the intrinsic stability of polycyclohexadienyllithium (PCHDLi) in cyclohexane at room temperature was good in the absence of 1,3-CHD.[42] Zhou[43] also used PSLi to polymerize 1,3-CHD in order to make PS-PCHD block copolymers in benzene/hexane mixtures at -10 °C. David et al.[40] studied the morphologies of those block copolymers. However, the CHD composition in the in PS-PCHD copolymers was limited to less than 40 wt % due to side reactions, and homopolymer contaminants were present in the resulting block copolymers.

Very recently, Natori[44] and Natori and Inoue[45] coworkers reported that anionic polymerization of 1,3-CHD could be controlled using certain additives. They used the *n*-BuLi/N,N,N'N'-tetramethylethylenediamine (TMEDA) initiator system and carried out reactions under nitrogen atmosphere at 40 °C and high pressure (up to ~4 kg/cm^2). According to their findings, the ratio of *n*-BuLi to TMEDA and the method of introducing the chemicals are crucial to obtaining "well-controlled" PCHD (molecular weight distribution, M_w/M_n ~ 1.08). A family of PCHD homopolymers and their copolymers with styrene, butadiene, and isoprene were made using this method. Surprisingly, other additives, even if very similar to TMEDA, were not as effective. The microstructures of the resulting PCHD changed with the nature of the additives.

Kinetics and Mechanism in the Anionic Polymerization of 1,3-CHD. Lefebvre and Dawans[20] found that PCHD, even freshly made and handled under an inert atmosphere, contained not more than 80% of the theoretical level of unsaturation

Table 1. Various Procedures Used for 1,3-CHD Polymerizations (Other Than Anionic Polymerization)

Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	MW([η])	Remarks	Ref.
			Ziegler-Natta				
$TiCl_3$	n-C_7H_{16}	25	24	84	(0.081)	Cocat. Iso-Bu_3Al [a]	20
$TiCl_4$	Cycloh [b]	15	68	55	(0.100)	Cocat. Iso-Bu_3Al [a]	21
$TiCl_4$	n-C_7H_{16}	-75	144	92	(0.140)	Cocat. Iso-Bu_3Al [a]	19
Cp_2TiCl_3 [c]	CH_2Cl_2	25	3	82	2300	Cocat. $Et_3Al_2Cl_3$ [a]	22
			Cationic catalyst				
$TiCl_4$	Ben [b]	30	6	34	(0.095)		20
PF_5	CH_2Cl_2	20	0.5	86.6	(0.100)		21
$SnCl_4$	CH_2Cl_2	25	5			Exclusive 1,4	23
			Miscellaneous				
AIBN [d]	Bulk	80				No polymer	20
Thermal	Bulk	200				Dimer vs polymer	35
r-ray	DCA [e]	100	1	23	2900	100% 1,4 $[\alpha]_D$=-19	25
Ni/MAO [f]	Tolu [b]	50	0.5	96		Insoluble	32
$(ANiTFP)_2$ [g]	CB [b]	55	2	87		Insoluble	28
$X_2Ni(Allyl)_2$	CB [b]	20	24	100		X – F_5PhO, Insoluble	29
$Mo(CO)_5PPh_3$	CH_2Cl_2	25				100% crosslinked	22
Bu_4NClO_4	CH_2Cl_2	25			1300	Electropolym.	34
$PdL_4(BuF_4)_2$	CH_3CN	25	0.5	40	2000	L = CH_3CN	26

[a] Cocatalyst. [b] Cycloh: Cyclohexane, Ben: benzene, Tolu: Toluene, CB: chlorobenzene. [c] bis(cyclopentadienyl) titanium chloride. [d] azobisisobutyronitrile. [e] adduct of 1,3-CHD and deoxycholic acid (DCA) canal. [f] nickel bis-(acetylacetonate)/methylaluminoxane. [g] bis[(ally)trifluoroacetontatonnickel(II)]. [h] unit: dL/g.

Table 2. Summary of Prior Anionic Polymerizations of 1,3-CHD

Initiator	Solvent	Additive	Temp, °C	Yield %	MW([η])[d]	M_w/M_n	Ref
n-BuLi	Benzene		25	98	(0.20)		36
n-BuLi	THF[a]		-80	85	(0.12)		
n-BuLi	n-C_7H_{16}		25	85	(0.29)		20
LiNCLi[b]	THF[a]		-30		(0.18)		
NaNCNa[b]	THF[a]		-29		(0.19)		39
KNK[b]	THF[a]		-30		(0.12)		
n-BuLi	THF[a]		-78		9300		14
n-BuLi	Toluene	TMEDA[c]	-78				
n-BuLi	Benzene		25	93	(0.29)		38
LiNCLi[b]	THF[a]		-20	96	12600	1.19	
NaNCNa[b]	DME[a]		-73	81	38700	1.45	41
KNCK[b]	THF[a]		20	61	2400	1.48	
PSLi[b]	Cyclohexane		25		3000		42
n-BuLi	Cyclohexane	DABCO[c]	40	100	11300	1.69	
sec-BuLi	Cyclohexane	DABCO[c]	40	99	11900	1.79	
tert-BuLi	Cyclohexane	DABCO[c]	40	100	12600	1.40	43, 44
n-BuLi	Cyclohexane	TMEDA[c]	40	100	11200	1.08	
sec-BuLi	Cyclohexane	TMEDA[c]	40	99	10800	1.53	
tert-BuLi	Cyclohexane	TMEDA[c]	40	91	14700	1.59	

[a] THF: tetrahydrofuran, DME: 1,2-dimethoxyethane. [b] LiNCLi: lithium naphthalenide NaNCNa: sodium naphthalenide KNCK: potassium naphthalenide. [c] TMEDA: N, N, N', N'-tetramethylethylenediamine, DABCO: 1,4-diazabicyclo[2,2,2]octane. [d] unit: dL/g.

by iodine experiments. They attributed this to chain transfer since crosslinking was not observed. They postulated the hydride elimination chain transfer mechanism, as shown in Figure 1a. Moreover, the "unsaturation" results obtained from iodine experiments are questionable, since these workers did not run "standard samples" (e.g. polybutadienes). Therefore, it is not conclusive whether the 80% level of unsaturation reported represents lack of olefin content or incomplete titration.

Based on ultraviolent (UV) spectroscopy results, Cassidy et al.[37] proposed a hydride transfer to THF process (shown in Figure 1). These mechanisms can explain the low molecular weight phenomenon but not the low conversion. As an alternative to the "hydride elimination" mechanism, Lussi and Barman[39] proposed an "allylic proton abstraction" mechanism shown in Figure 1b. Once again, the overall process in Figure 1b limits only molecular weight, but not conversion. Mango and Lenz[15] studied the reaction of 1,3-CHD with n-BuLi using NMR, gas chromatography (GC), and UV spectroscopy. In this system, chain propagation and allylic proton/hydride abstractions were competitive reactions.

The cyclohexadienyl carbanion, formed by allylic proton abstraction from the monomer, aromatized to benzene immediately, which explained both the limited molecular weights and conversions. However, they did not consider the possibility that metallated monomer could re-initiate the polymerization.

Sharaby and coworkers[41] studied the kinetics and mechanism of anionic polymerization of 1,3-CHD initiated by the naphthalene/alkali metal system. They proposed that the dianionic adducts formed by the reaction of naphthalenide ($^{-}NC^{-}$) with1,3-CHD constituted the cyclohexanyl and naphthyl carbanionic groups. 1,3-CHD

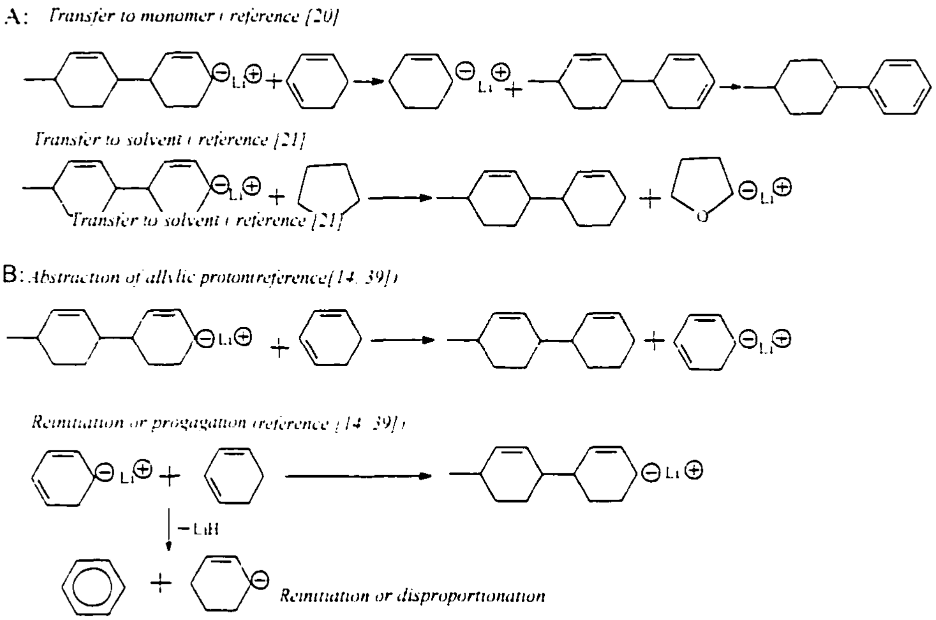

Figure 1. Chain transfer and/or termination reactions of PCHDLi. (a) chain transfer; (b) proton abstractions.

reacts with cyclohexanyl carbanions resulting in chain growth, while naphthyl carbanions are dormant. Again, chain transfer to monomer is the main limitation of the chain growth and thus molecular weight. The isomerization of the cyclohexadienyl anions resulting from chain transfer may be followed by elimination of lithium hydride. This represents a chain termination step. Inspection of the values of the rate constants reveals that the addition of the first monomer to $^{-}$NC^{-} is much slower than the subsequent polymerization. Also, their kinetic data are not accurate because of termination of the chains.

Zhong and Francois[42] addressed the kinetic and mechanistic issues in the PSLi initiated polymerization of 1,3-CHD under different conditions. They concluded that a dimeric association of two living chain ends exists. From viscosity results, Al-Harah and Young[40] reported that the association number of PCHDLi was low (<1.7). Based on the half-order kinetics of propagation, they concluded that part of the metallated monomers formed by chain transfer could reinitiate the polymerization (the ratio of reinitiation to decomposition is about 2 at 20 °C). However, the nature of the homopolymer impurities in the block copolymer is also different from that obtained in this work,[50] which implies that the re-initiation effect was overestimated.

It has been reported that the polymerization of 1,3-CHD initiated by *n*-BuLi TMEDA system leads to well defined PCHD polymers.[43,44] It is believed that the addition and allylic proton abstraction reactions during the polymerization of 1,3-CHD are strongly affected by the extent of the polarization of the Li-carbon bond in PCHDLi. Natori[44] and Natori and Inoue[45] claimed that TMEDA could accelerate chain propagation, while the metalation of the monomer is suppressed. However, the window under which controlled results were obtained is very small, and some polymers obtained by this approach were not really "well controlled" by the standards of anionic polymerization (polydispersities > 1.1), especially at high molecular weights.

Derivatives of PCHD Polymers. PCHD polymers have attracted attention mainly because they can be converted to poly(para-phenylene) (PPP) by aromatization, a material with a high melting point (stable even at 400 °C) and unique electronic and photonic properties, by catalytic or chemical aromatization.[19-21,28,42] The most commonly used chemical to aromatize PCHD is 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil). Other reagents, including palladium, sulfur, and N-bromosuccinimide (NBS), have also been used, combined with pyrolysis. To further increase the thermal properties, Cassidy et al. [37] tried to crosslink dehydrogenated PCHD. They sulfonated the resulting PPP, fused it in molten alkali to generate phenols, and finally crosslinked it with formaldehyde. The final product showed excellent heat stability (only 30% loss at 900 °C). But none of these processes resulted in complete aromatization of the polymer. Moreover, it is difficult to characterize the dehydrogenation products owing to their insolubility in common solvents and their high melting points. Francois and Zhong took a different approach to obtain PPP.[50-53] They aromatized PS-PCHD diblock or poly(1,3-cyclohexadiene-block-styrene-block-1,3-cyclohexadiene) (PS-PCHD-PS) tri-block (obtaining by linking PS-PCHDLi with α,α'-dibromomethylbenzene) to generate poly(styrene-block-paraphenylene) (PS-PPP) or poly(styrene-block-paraphenylene-block-styrene) (PS-PPP-PS) using p-chloranil and followed by removing the PS block with thermal treating at 400 °C. However, the PPP blocks were found to be made of short sequences of about 10 units separated by defects. Natori and Inoue[54] synthesized diblock and ternary block copolymers of 1,3-CHD with styrene, isoprene, or butadiene using the n-BuLi/TMEDA initiating system.

PCHD can also be converted to polycyclohexane (PCH), a polymer with high hydrolytic stability, by hydrogenation. Mango and Lenz[55] used in-situ produced diimide as the H_2 source to hydrogenated PCHD to PCH. They used. The hydrogenation was quantitative, and no chain scission was observed based on molecular weight measurements. Besides PCHD homopolymers, Natori and coworkers[56] also studied the hydrogenation of 1,3-CHD copolymers, such as poly(cyclohexadiene-block-polybutadiene-block-polycyclohexadiene) (PCHD-PBD-PCHD), PS-PCHD, PS-PCHD-PS, Poly(1,3-cyclohexadiene-block-styrene-block-1,3-cyclohexadiene) (PCHD-PS-PCHD). By using palladium (Pd) on barium sulfate ($BaSO_4$) catalyst (55 kg/cm^2 H_2 at 160 °C), the hydrogenation was non-selective with regards to PCHD block or polybutadiene (PBD) block. The PBD block in poly(1,3-cyclohexadiene-block-butadiene) (PCHD-PBD) copolymer could be selectively hydrogenated by using $Cp_2Cl_2/(i\text{-}Bu)_2AlH$ under 8 kg/cm^2 H_2 pressure at 100 °C. However, the characterization data generated on the hydrogenated products were limited.

Concluding Points. In summary, 1,3-CHD has been polymerized by numerous techniques and under different conditions. Anionic polymerization is the most advantageous method in regard to molecular weight and conversion. However, slow initiation and chain transfer to monomer (metallation) and solvent characterizes the anionic polymerization of 1,3-CHD. All the studies so far suggest that the living chains may terminate either through the abstraction of hydride (which limits molecular weight) and/or allylic protons (which limits the molecular weight and conversion). Attempts to overcome these side reactions by using additives (typically TMEDA) have demonstrated some success. The polymerization conditions have a great impact on the microstructures of the final product, as for linear diene analogs. Block copolymers of 1,3-CHD with styrene, butadiene, and isoprene have been prepared sequentially, though the compositions of the blocks are limited. The aromatization and hydrogenation of PCHD polymers has also been reported. Few of these polymers reported so far have been thoroughly characterized.

Structure of PCHD Polymers

Microstructure of PCHD Polymers. PCHD polymers with cyclohexene as the recurring units are rich in microstructure. The possibilities for tacticity and structural and geometrical isomers are shown in Figure 2.

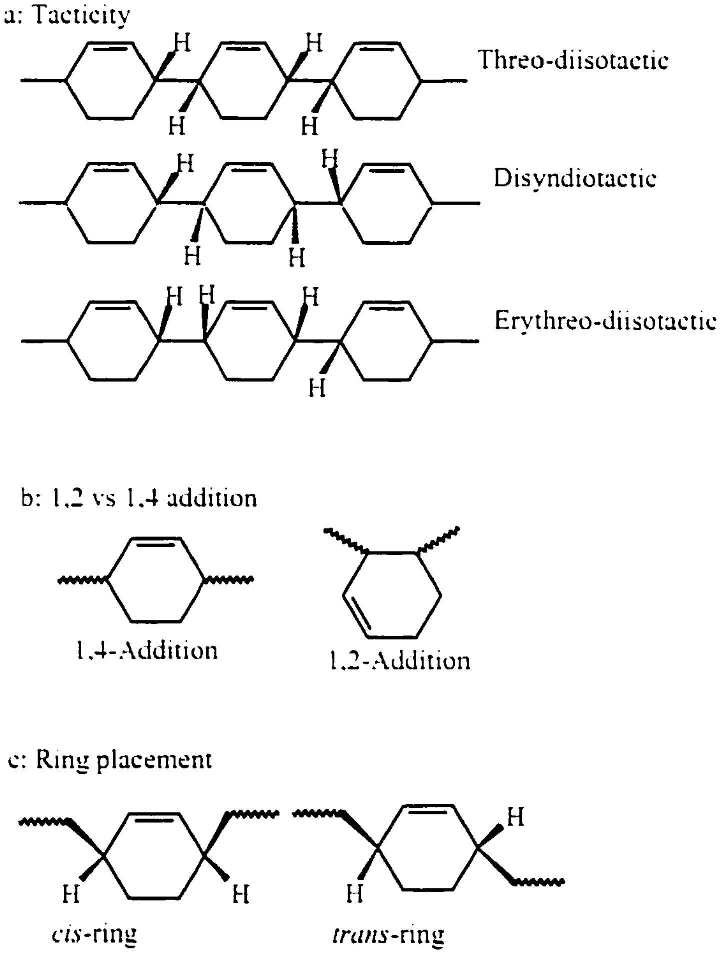

Figure 2. Microstructures of PCHD polymers. (a) tacticity; (b) 1,2 vs 1,4 addition; (c) ring placements.

IR Analysis. Infrared spectroscopy (IR) was widely employed for characterizing PCHD in early studies. IR spectra contain some useful information about repeating units. Lefebvre and Dawans[20] assigned the absorption at 975 cm^{-1} (a small peak) to the double bonds being in *trans* configurations and the absorption at 725 cm^{-1} to *cis* configurations. The calculated *cis-trans* ratios remained constant in all their polymers, and therefore they concluded that the *cis-trans* isomerization of the double bond seems to be independent of the polymerization mechanism. However, these assignments are highly questionable because the residual double bond in the repeating units (cyclohexene) is always locked into a *cis* conformation. Mango and Lenz[15] also studied the C-H out-of-plane stretching infrared absorption region (625 cm^{-1}-900 cm^{-1}) carefully using various model compounds.[14] They ascribed the bands at 785 and 800 cm^{-1} to 1,4-addition and assigned the pair at 721 and 765 cm^{-1} to 1,2-addition. According to their IR results, exclusive 1,2-addition was obtained in polar media or in the presence of solvating additives. The use of non-polar conditions caused partial 1,4 content to be formed, but predominant 1,2-content remained. Again, these conclusions are doubtful since the C-H out-of-plane stretching is very sensitive to its adjacent molecular structure, and model compounds used do not accurately represent the polymer itself. Moreover, it is not possible to get exclusively 1,2-addition PCHD according to Sharaby et al.[57] (based on NMR) and Zhong and Francois[42] (based on IR results on aromatized PCHD). Apparently, Mango and Lenz[14] were misled by their implicit assumption that the molar absorption of the vibrational modes due to different structural forms does not differ significantly.

NMR Analysis: NMR spectroscopy is the most powerful tool for characterization of polymer microstructure. It seems very clear that for complete 1,4-addition H_a/H_b equals to 2/4, while for only 1,2-addition H_a/H_b = 3/3 (H_a: protons adjacent to vinyl protons; H_b protons distant to vinyl protons). But, in reality, the ^{1}H-NMR spectra of PCHD are much more complicated due to the richness of microstructural features. It is not surprising that early ^{1}H-NMR spectra only gave strongly overlapped peaks in the aliphatic region.[14,56] Sharaby et al.[57] studied the microstructure of PCHD using ^{1}H-NMR and ^{13}C-NMR spectra in considerable detail. In their study, it was found that the solvent effects on the microstructure of the anionically polymerization of 1,3-CHD are essentially similar to those of the acyclic analogues. However, even in polar solvents, the fraction of 1,2-isomers did not exceed 50%. The formation of intermittent 1,2 and 1,4 sequences was demonstrated to be feasible, and their content increased with temperature. Even with much better instrumentation relative to prior studies (270 MHz NMR), the resolution was still very low, and the assignment of the ^{13}C-NMR spectra was not very clear. Recently, Natori et al.[56] used two dimensional correlated spectroscopy (2D-COSY) technique to separate H_a and H_b. They attributed the peaks from 1.90 ppm to 2.35 ppm to H_a and the upper field to H_b All these studies provided little information about the *cis-trans* isomers and no information about 1,2/1,4 sequence distributions.

Molecular Weight Determination of PCHD Polymers

Many properties of a polymer depend critically on its molecular weight and molecular weight distribution. A large number of methods have been used to measure these parameters. Light scattering (weight average molecular weight, M_w), dilute solution viscometry (viscosity average molecular weight, M_v), colligative properties based methods (number average molecular weight, M_n) and SEC (molecular weights and molecular weight distribution) are the most often used methods. With the development of mass spectrometry, colligative properties based methods have started to be less used. Even though only providing relative molecular weight, SEC is by far the most commonly used method because of convenience. Viscosity data on PCHD (in benzene or chlorinated solvents; surprisingly, all these data recorded without specifying the temperature) were reported in early studies, mainly as a rough measure of the molecular weight.[14,20,36-39,58] Mango[14] gave the following Mark-Houwink-Sakurada (MHS) equation without specifying under what conditions these data were obtained: $[\eta] = KM^{\alpha}$, with $K = 3.2\times10^{-4}$ (dL/g) and $\alpha = 0.73$. Erofeev at al.[58] studied the relationship between $[\eta]$ and molecular weight of PCHD oligomers in benzene. They established the following equation: $[\eta] = KM^{\alpha}$, where $K = 1.48\times10^{-4}$ (dl/g) and $\alpha = 0.873$. However, the molecular weights of the samples used were low and no microstructure information was given. All the molecular weight data given by Natori[44] and Natori and Inoue[45] were from SEC based on standard PS calibration, thus they are not the true values.

Properties and Applications of PCHD Polymers

Homopolymers. Relatively few studies have reported the properties of PCHD polymers. Thermal properties and some mechanical properties were also studied by Natori et al.[56] They found that the glass transition temperature (T_g) of PCHD rose with the molecular weight or with ratios of 1,2/1,4 content. PCHD with high 1,2 contents or high molecular weight showed high flexural strength, high heat distortion temperature, and high Vicat softening point temperature. They concluded that the PCHD chain is rigid, and the 1,2-unit was considered to impart rigidity to the polymer chain. However, no chain parameters, such as persistence length, were measured to support their assumptions. UV spectra of PCHD in THF solution between 225 and 300 nm were also obtained.[14,42] The results showed UV absorption in the region from 250 to 270 nm. The aromatized PCHD showed continuous UV absorption from 250 to 330 nm, which indicates the presence of two to six conjugated double bond sequences.[42] There was no correlation between the peak position and microstructure. Thermal and oxidative stability of PCHD (from *n*-BuLi/THF, molecular weight~3500) were also reported.[59]

Block Copolymers. The first PS-PCHD block copolymer was synthesized, and subsequently the PCHD block was converted to PPP under different conditions by Zhong and Francois.[50] The PS-PPP polymers formed aggregates in solution with the PPP sequences in the core of these micelles. UV and IR results revealed that the PPP sequences (about 10 units long) were separated by defects. This copolymer could be doped in solution with potassium, after which the UV absorption band of the doped PS-PPP moved from ~320 nm to 900-1500 nm, indicating n-doping of the PPP sequence. The solution properties and morphologies of PS-PPP or PS-PPP-PS were studied by Francois' group.[60-67] PS-PPP thin films cast from carbon disulfide (CS_2) under a flow of moisture gas formed an unusual honeycomb morphology, which was thought to be a non-equilibrium morphology.[60,61] PS-PPP copolymer formed a "flower-like" morphology constituted of a PPP "core" surrounded by PS "petals" was found in PPP-PS-PPP copolymer in THF.[62-64] The conducting and light-emitting properties were studied by Francios' group.[65-67] Functionalized oligo(*para*-phenylene)s were also synthesized by reactions of PCHDLi with various functional groups, such as succinic anhydride and chlorotriethoxysilane, followed by aromatization.[67] However, the degree of functionality obtained was not very high.

The morphology of PS/PCHD block copolymers has also been reported.[56] Natori et al. [56] observed essentially lamellar structures in all PCHD-PS (50/50), PS-PCHD-PS (25/50/25) and PCHD-PS-PCHD (25/50/25) polymers only with slightly different lamellar thickness. However, we recently discovered novel core-shell (cylinder-in-cylinder) morphologies in PCHD-PS (35/65) diblock copolymers.[49] The 1,2/1,4 ratios in Natori et al.'s polymers were around 50/50, while ours were around 7/93.

Concluding Points

The microstructures of PCHD have been studied by using IR and NMR. IR provides some useful information, but much work remains to be done to complete the peak assignments. It seems certain that the CH_2 peaks in ^{1}H-NMR spectra could be assigned to H_a and H_b unambiguously, though the resolution is not very good even with a 600 MHz instrument. However, the contributions to the multi-peaks in H_a and H_b regions and the ^{13}C peaks are still not clear. These peaks may contain important information about the tacticity, ring placement, and sequence distribution.

Little has been done to investigate the properties of PCHD homopolymers, especially the solution properties with respect to persistence length, radius of gyration and their relationship with microstructure. The self-assembly properties of PS-PCHD diblock and triblock copolymers, both in the solid state and solution, deserve much more attention. Since it is anticipated that PCHD chains are quite stiff, the incorporation of PCHD segments into block copolymers may provide a new means to uncouple the morphological dependence of block copolymers on volume fraction.

Outline of Dissertation

In the first paper, the polymerization of 1,3-CHD using various anionic initiating systems with or without additives will be discussed. In the second paper the synthesis of block copolymers of 1,3-CHD and styrene under various conditions will be presented. The influence of additives on the control of the polymerizations, and the cross-over reactions are also discussed. In the third paper we will report the results of the synthesis of well-defined, near-monodisperse, three-armed star and star-block copolymers containing PCHD blocks. We also studied, but have not included in this dissertation, the polymerization kinetics, solution properties (viscosity), and chain parameters of PCHD homopolymers.

GENERAL EXPERIMENTAL PROCEDURES

Anionic centers (initiators and living polymer chains) are very reactive to air (oxygen, moisture, and carbon dioxide) and other contaminates. Thus it is necessary to use specially designed apparati and appropriate techniques to avoid premature termination of the living chains. All the anionic polymerizations in this study were done under high vacuum conditions, and a brief description of the high vacuum line and polymerization reactors is given in the following. The detailed procedures are reviewed in the literature.[69-72]

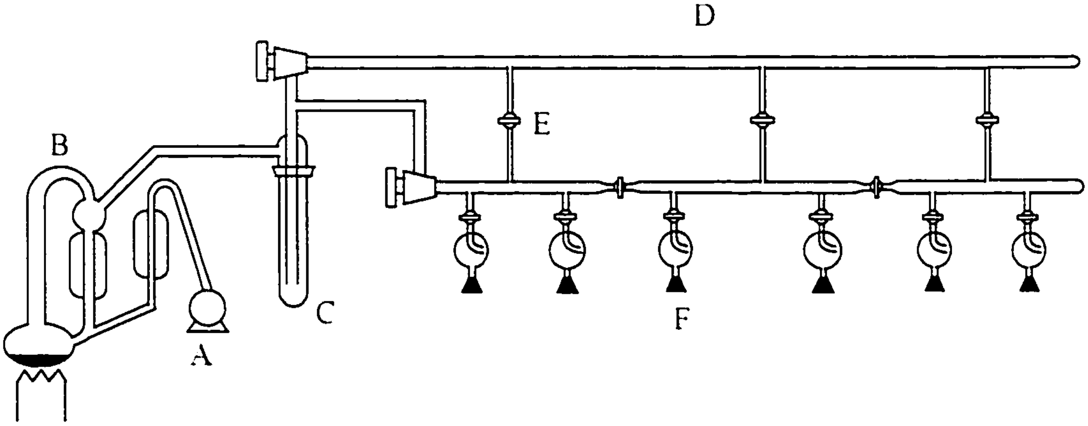

Figure 1. Typical high vacuum line.

High Vacuum Line

The vacuum line we used is shown in Figure 1. The main parts of the high vacuum line are the mechanical pump (A), a mercury diffusion pump (B), the liquid nitrogen trap (C), and the manifold (D). After mercury distillation is achieved, the pressure in the entire system can be as low as 10^{-6} mm Hg. The liquid nitrogen trap is used to condense any volatile substances in the system and in this way protect the mechanical and mercury pumps from contamination. Another dry ice trap (not shown) between the mercury pump and the mechanical pump is used to prevent the toxic mercury from getting into the mechanical pump. The various ground joints (E) and J. Young stopcocks (F) allow the purification and storage of solvents, purification of monomers, distillations, and performance of two or more procedures simultaneously. A Tesla coil is used to check the quality of the vacuum and test for pinholes. The sound of the Tesla coil is the least noisy if the vacuum line is leak-free and properly evacuated.

Polymerization Reactors

A typical reactor for anionic polymerization is shown in Figure 2. Ampoules containing all necessary purified reagents are connected to the main reactor. The apparatus is attached to the vacuum line through the ground joint A, checked for pinholes, flame dried, and pumped until high vacuum is achieved. Then *n*-BuLi (concentrated) is introduced through the septum on B, followed by removing the septum by heat-sealing at the constriction. The desired amount of solvent (final polymer concentration 5~10%) is condensed into the reactor after degassing. The apparatus is then removed from the vacuum line by heat-sealing at C. The inner walls of the whole system are washed using a solution of *n*-BuLi, and the solution is then collected into the purge section. The reactor section is rinsed of trace *n*-BuLi or other species at least seven times by condensing the solvent in the proper places through use of a liquid nitrogen soaked towel. After distilling all the solvent from purging section (25 °C water) into the reactor (ice water), the purging section is removed by heat-sealing through constriction E, leaving a scrupulously clean reactor filled with the

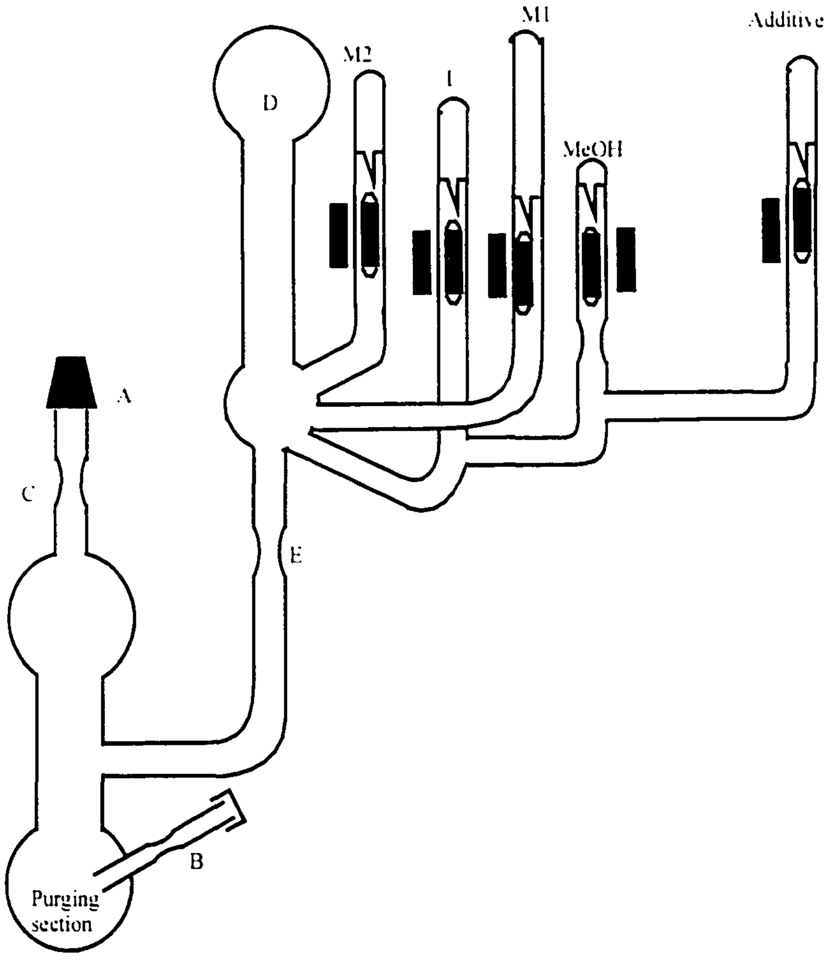

Figure 2. General glass apparatus for anionic polymerization

proper amount of pure solvent. The polymerization can then be started by introducing the reagents in a proper order through use of magnetic breakers.

If the targeted molecular weight of the final polymer is not very high or if the molecular weight generated does not need to be tightly controlled, a simpler reactor (shown in Figure 3) can be used. Most of the operations are the same as those in Figure 2, except the purging process is omitted. Extra initiator (5~10% extra depending on the amount of initiator required for the polymerization) is needed in order to destroy some residual impurities. The initiator, consequently, must be introduced first. Most of the anionic polymerizations in this study were done using this simplified reactor design.

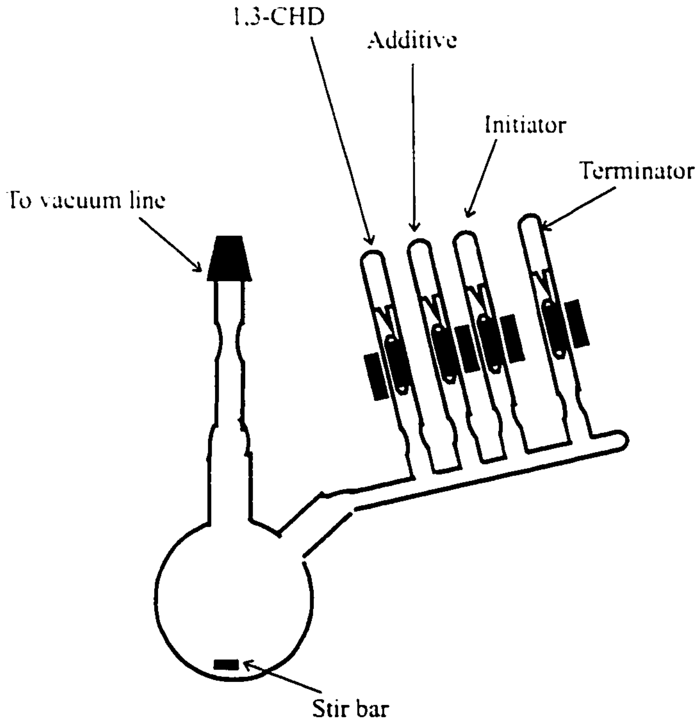

Figure 3. Simplified glass apparatus for anionic polymerization.

1,3-CYCLOHEXADIENE POLYMERS: I. ANIONIC POLYMERIZATION

by

KUNLUN HONG AND JIMMY W. MAYS

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Format adapted for dissertation

Abstract

The polymerization of 1,3-cyclohexadiene (1,3-CHD) using various anionic initiating systems and with or without additives was studied. In contrast to the situation with linear conjugated dienes, common anionic initiators without additives fail to produce poly(1,3-cyclohexadiene) (PCHD) with controlled molecular weight and narrow molecular weight distribution because of side reactions during initiation and chain propagation. However, addition of certain additives changes the nature of the polymerization dramatically. Mono-dentate additives do not yield controlled polymerization, while some poly-dentate additives, such as N,N,N',N'-tetramethylethylenediamine (TMEDA), 1,2-dimethoxyethane (DME), and 1,4-diazabicyclo[2,2,2]octane (DABCO), are effective in minimizing the side reactions, if combined with the suitable butyllithium isomer. Synthesis of PCHD samples with narrow molecular weight distribution and reasonable molecular weight control was possible using the *n*-BuLi/DME/0 °C or *sec*-BuLi/DABCO/20 °C systems. The "living" character of these polymerizations is discussed.

Introduction

Synthetic polymers are an indispensable and remarkably versatile class of materials. The suitability of a polymer for a particular application is controlled by its specific structural and molecular properties such as molecular weight, molecular weight distribution, local and global architecture, and functionality. To understand the relationship between polymer structure and properties there is great interest in well-defined polymers made by living addition polymerization processes. Tremendous progress has been achieved in living polymerizations over the past two decades, thanks to the development of new polymerization methodologies.[1-4] Nevertheless, living anionic polymerization is still the most versatile technique for the synthesis of polymers with well-defined structures.[5,6] Many new materials with controlled architectures, functionalities, and narrow molecular weight distribution have been made using anionic polymerization.[7-9] However, most of the studies are limited to several well behaved, mostly hydrocarbon, monomers (such as styrene, 1,3-butadiene, isoprene, etc).

1,3-cyclohexadiene (1,3-CHD) polymers (PCHD) are of interest from both scientific and practical standpoints.[10-18] The richness of microstructural control combined with post-polymerization chemistry can be used to tailor the properties of PCHD polymers. PCHD and its derivatives are expected to have higher mechanical strength and better thermal and chemical stability as compared to common, such as vinyl, polymers due to the alicyclic structures (six-membered rings) in the main chain. PCHD can be modified by various dehydrogenation procedures,[10-13] such as bromination, followed by dehydrobromination,[10] aromatization by p-chloranil[11,12] or catalytic dehydrogenation.[13] The C=C bond in PCHD can also be hydrogenated by either diimide[14] or using $Pd/BaSO_4$ under H_2 pressure.[15] It is reported that hydrogenated PCHD has the highest glasas transition temperature (T_g, 231 °C) of all hydrocarbon polymers.[15] Hydrogenated PCHD polymers have good heat, weather, impart, abrasion, and chemical resistances, low water absorption and birefringence; they also serve as good optical materials[16] due to their excellent transparency and rigidity. The copolymer of 1,3-CHD with cyclopentadiene has been used as an active element in photomicrolithographic devices, and the optical resolution is greatly enhanced by the addition of PCHD blocks.[17] It has also been proposed that PCHD may be useful as a plastic material for undersea applications because of its high hydrolytic stability.[18]

There have been many reports on the synthesis of PCHD polymers. Essentially all conventional polymerization procedures have been applied to the polymerization of 1,3-CHD. These include cationic,[10] radical,[12] Ziegler-Natta,[19] transition-metal complexes,[20,21] and anionic[22-26] polymerizations. Only low molecular weight or insoluble materials were obtained in most cases due to various side reactions. The anionic mechanism has proven to be the best way to polymerize 1,3-CHD with high conversion and molecular weight control, although side reactions, such as chain transfer and termination, limit the attainable molecular weight of PCHD. In general, the observed molecular weights are independent of conversion and do not depend on monomer or initiator concentrations under anionic polymerization conditions.[16,21,26] The formation of benzene,[21-24] cyclohexene,[21-23] and 1,4-cyclohexadiene[23] has been observed during the polymerization. Using difunctional alkali naphthalenides as initiators, molecular weights as high as 19 kg/mol (Li^-) and 38.7 kg/mol were obtained in 1,2-dimethoxyethane (DME), in which the polymer precipitates.[24] Very recently, Natori and coworkers reported that polymerization of 1,3-CHD anionically could be controlled using certain additives.[27-29] They used the normal butyllithium (*n*-BuLi)/N,N,N',N'-tetramethylethylenediamine (TMEDA) initiation system and carried out the reaction under nitrogen atmosphere at 40 °C and pressure up to 3.92 bar. According to their findings, the ratio of *n*-BuLi to TMEDA and the method of introducing the chemicals are crucial for obtaining "well-controlled" PCHD (molecular weight distribution, M_w/M_n = 1.08). A family of PCHD homopolymers and their copolymers with styrene, butadiene, and isoprene has been made using this method. However, all the samples with narrow molecular weight distribution were less than 15 kg/mol in molecular weight. Surprisingly, other additives, even if structurally very similar to TMEDA, were found to be less effective.

In this paper we report the results of polymerization of 1,3-CHD by using various anionic initiators with or without additives. The differences in the polymerization processes with regard to initiation and propagation are also discussed.

Experimental

Materials. Benzene (Fisher), cyclohexane (Fisher) tetrahydrofuran (THF Aldrich), and methylcyclohexane (Aldrich) were purified according to the anionic polymerization standards, as described in the literature.[6,30] TMEDA (Aldrich), N,N,N',N',N'-Pentamethyldiethylenetriamine (PMETEDA), DME (Acros), and 1,2-dipiperidinoethane (DPPE, Sigma) were stirred over freshly crushed CaH_2 powder for at least 24 h and distilled from potassium (K) mirror twice and finally from potassium / sodium alloy under high vacuum. Naphthalene and 1,4-diazabicyclo[2.2.2]octane (DABCO) were sublimed under high vacuum three times and then diluted in cyclohexane and benzene, respectively. Potassium *tert*-butoxide (*t*-BuOK, Aldrich), phenyllithium (PhLi, Aldrich), *tert*-Butyllithium (*t*-BuLi, Aldrich) were used as received. 1,3-CHD (Aldrich) was cleaned by treated over CaH_2 followed by exposure to sodium mirrors at room temperature two to three times for 24 h each. The "roughly" purified 1,3-CHD was finally treated with *n*-BuLi or dibutylmagnsium ($MgBu_2$) at 0 °C for 30 min just before the polymerization. Butyllithiums (*sec*-BuLi and *n*-BuLi) was prepared by reactions of the corresponding butyl chloride with lithium powder in hexane under vacuum. Cumyl potassium (CumylK) and benzyl potassium (BenzylK) were made via literature methods.[31,32]

Polymerization and Characterization. All polymerizations were performed under high vacuum using custom-made glass reactors. Break-seals allowed introduction of all reagents sequentially, and constriction seal-offs permitted intermediate removal of products. Typical [additive]/[initiator] = 1.5~3 unless otherwise stated. The polymerizations were allowed to proceed for 2 to 24 h or longer at designed temperature and were terminated with degassed methanol. The polymer solutions were precipitated in a large excess of methanol with trace 2,6-di-*tert*-butyl-4-methylphenol (BHT) added to prevent oxidative degradation. The final polymer was filtered and dried under high vacuum. Size exclusion chromatography (SEC) in THF (flow rate: 1 ml/min, columns: Waters 100 Å, 500 Å, 10^3 Å, 10^4 Å, 10^5 Å) or chloroform ($CHCl_3$, flow rate: 0.3 ml/min, columns: Polymer Laboratory 5 μm PL-gel MiniMIX) was used to measure relative number-average molecular weights (M_n) and polydispersities, based upon calibration with polystyrene (PS) standards.

Results and Discussion

Polymerization of 1,3-CHD Without Additives. 1,3-CHD was polymerized using several anionic initiators under different conditions, and the results are summarized in Table 1. From the table we can see that the "traditional" anionic initiators, isomers of BuLi, do not work very well in controlling the polymerization of 1,3-CHD if used without additives. *n*-BuLi produced only trace amounts of polymer (not shown in Table 1. *sec*-BuLi or *t*-BuLi gave better results, but the molecular weights could hardly be manipulated, and the molecular weight distributions were quite broad, as a low molecular weight tail is clearly seen in the SEC trace in Figure 1a. As polymerization continued, the molecular weight increased, but the tail at the low molecular weight end was still observed (Figure 1). This indicated that some of the anionic chains failed to grow beyond the early stage of polymerization. It is generally agreed that anionic polymerization of 1,3-CHD is difficult to control because of side reactions.[23-26] The side reactions during initiation are isomerization of the monomer to produce its 1,4-isomer and further isomerized to benzene; in some cases cyclohexene was detected. The main side reactions during chain propagation are chain transfer through proton elimination and chain termination via hydride abstraction, as shown in Figure 2. Under anionic conditions (strong base), chain transfer through hydride elimination and/or allylic proton abstraction always competes with chain propagation, as shown in Figure 2. 1,4-cyclohexadiene (1,4-CHD) is almost unavoidably produced during the course of reaction. It should be noted that 1,4-CHD is a very reactive chain-transfer agent for alkyllithium-initiated polymerizations.[22] The ability of 1,4-CHD to decrease strongly the observed molecular weight in the lithium-naphthalenide-initiated polymerization of 1,3-CHD has been demonstrated.[23] Since one of the possible side reactions involves the hydride elimination with the formation of stable lithium hydride (LiH) as the driving force, it is anticipated that using larger counterions, such as potassium, could minimize this process. This is indeed the case when benzylK or cumylK is used (Table 1, runs 6-7): the polydispersities are narrowed, but the molecular weights of these samples are always far lower than expected. Moreover, NMR spectral data revealed that the ratio of vinyl protons to non-vinyl protons is much lower than the theoretical value (1/3). Side reactions other than chain transfer or termination must be involved in these polymerization procedures.

Table 1. Polymerization of 1,3-CHD Using Various Anionic Initiators (without Additives)

Run	Initiator	Solvent/Temp (°C)	[CHD] mole/L	[I] ×10^3 mole/L	Yield %	$M_{n,\,Cal}$ ×10^{-3}	$M_{n,\,SEC}$ ×10^{-3}	M_w/M_n (SEC)
1	*sec*-BuLi	Benzene/20	0.53	1.40	53	29.9	7.6	2.17
2	*sec*-BuLi	Benzene/20	0.59	4.69	59	9.9	7.3	1.49
3	*sec*-BuLi	Ben./Hex./0 [a]	1.04	5.56	68	15.0	13.1	1.22
4	*sec*-BuLi	MeCyclohex./-70 [b]	0.88	3.51	83	20.0	18.8	1.43
5	*sec*-BuLi	THF/-78	1.00	7.36	47	10.9	5.1	4.92
6	BenzylK	THF/-78	1.45	2.63	93	44.1	26.0	1.38
7	CumylK	THF/-78	1.29	5.75	89	17.9	15.1	1.30
8	Naphthalene/K	THF/-78	1.09	6.99	98	25.0	17.4	1.40
9	*t*-BuLi	Benzene/20	1.05	3.65	75	5.8	9.5	2.07
10	*t*-BuLi	Benzene /20	1.14	9.96	49	9.1	7.1	1.77
11	PhLi	Benzene/20	1.05	3.04	71	27.6	10.6	2.06

[a] benzene/hexanes v/v = 9/1. [b] methylcyclohexane.

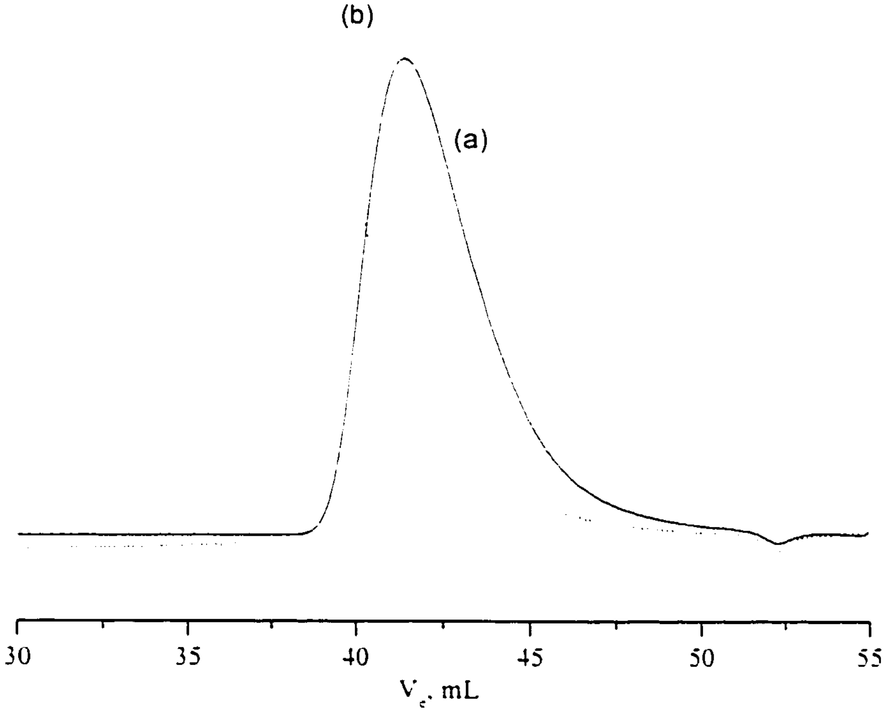

Figure 1. SEC traces of PCHD from *sec*-BuLi in benzene at 0 °C. (a) polymerization time: 2 h, conversion ~ 43%; (b) polymerization time: 6 h, conversion ~ 51%.

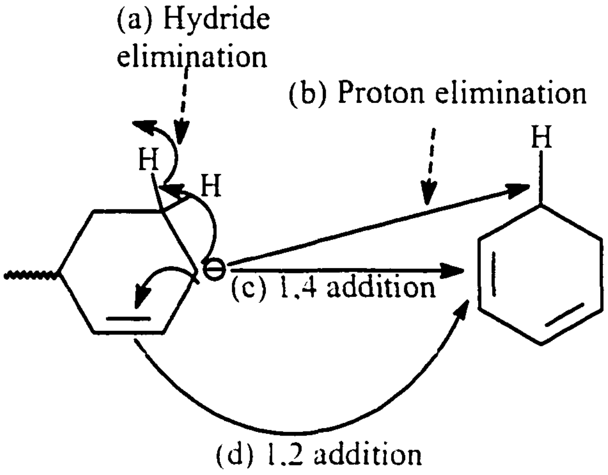

Figure 2. Possible reactions of PCHD anion with 1,3-CHD.

Polymerization of 1,3-CHD With Additives. Additives play an important role in anionic polymerization.[33] They have been widely used to control the microstructures of polydienes and minimize side reactions in acrylate polymerizations.[33] We have employed several mono-dentate additives, and the results are listed in Table 2. THF and secondary lithium butoxide (*sec*-BuOLi), popular additives used to disrupt aggregation in anionic polymerization, failed to give positive results. This suggests that chain aggregation is not the main problem in the anionic polymerization of 1,3-CHD. The *sec*-BuLi /*t*-BuOK system, regarded as a "second generation" super base,[34] yielded polymers with reasonably narrow molecular weight distribution, but the molecular weights were much lower than anticipated. One possible reason is that the polymerization has to be carried out in THF at low temperature (- 78 °C), and chains could not grow very long due to solubility problems (high molecular weight PCHD has

Table 2. Polymerization of 1,3-CHD using BuLi with Additives

Run	Initiator	Solvent/Temp (°C)	Additive	[Add.]/[I]	[CHD] mole/L	[I] ×10^3 mole/L	Yield %	$M_{n, Cal}$ ×10^{-3}	$M_{n\,SEC}$ ×10^{-3}	M_w/M_n (SEC)
				Mono-dentate Additive						
1	*sec*-BuLi	Benzene/0	THF	19.2	1.02	8.16	37	10.0	2.2	4.28
2	*sec*-BuLi	Benzene/20	*s*-BuOLi	1.5	0.82	2.20	78	30.1	4.97	2.21
3	*sec*-BuLi	THF/-78	*t*-BuOK	2.9	1.18	4.86	57	19.4	3.6	1.19
4	*sec*-BuLi	Toluene/-40 [a]	THF		0.97	5.55	23	13.9	3.6	1.77
				Poly-dentate Additive						
5	*n*-BuLi	Cyclohexane/40	TMEDA [b]	1.21	0.70	5.99	100	9.3	18.4	1.38
6	*n*-BuLi	Cyclohexane/40	PMDETA [b]	1.27	0.81	2.62	100	24.6	27.9	1.61
7	*n*-BuLi	Benzene/20	DPPE [b]	2.33	1.05	8.35	100	10.1	5.1	1.07
8	*sec*-BuLi	Benzene/20	DPPE	3.02	1.14	7.80	92	11.7	NOT Soluble	
9	*t*-BuLi	Benzene/20	DPPE	3.09	1.04	7.65	88	10.9	NOT Soluble	
10	*n*-BuLi	Benzene/0	DME [b]	4.43	0.58	6.00	98	7.7	11.3	1.07
11	*sec*-BuLi	Benzene/20	DME	4.80	1.09	3.38	16	25.9	6.3	4.73
12	*t*-BuLi	Benzene/20	DME	4.71	1.75	6.80	9	20.6	4.9	3.18
13	*n*-BuLi	Benzene/20	DABCO [b]	3.19	0.90	5.08	94	14.2	37.8	1.24
14	*sec*-BuLi	Benzene/20	DABCO	2.47	0.79	4.29	100	14.6	20.1	1.04
15	*t*-BuLi	Benzene/20	DABCO	1.54	1.15	5.18	87	17.8	17.6	1.11

[a] THF/toluene ~ ½ (v/v). [b] TMEDA: N,N,N',N'-tetramethylethylenediamine; DME: 1,2-dimethoxyethane; DABCO: 1,4-diazabicyclo[2.2.2]octane; PMDETA: N,N,N',N',N'-pentamethyldiethylenetriamine; DPPE: 1,2-dipiperidinoethane.

limited solubility in THF). Using *sec*-BuLi in THF/toluene (1/2 v/v) at – 40 °C, Zhang and Ruckenstein[35] selectively polymerized the styrene group in 4-(vinylphenyl)-1-butene to generate a polymer with a polystyrene backbone and functional butenyl side chains. However, their targeted molecular weight was only about 4 kg/mol. Not surprisingly, this system does not work well with 1,3-CHD (Table 2, run 4).

Poly-dentate additives can change anionic polymerization processes dramatically due to their chelating effect.[33] Natori and coworkers reported that the polymerization of 1,3-CHD using *n*-BuLi/TMEDA exhibits "living" characters;[27] however, the ratio of *n*-BuLi and TMEDA that gives living characters is crucial. It is believed that chain propagation and abstraction reactions are strongly affected by the extent of the polarization of the Li-carbon bond in PCHDLi, and chelating by TMEDA offers the proper Li-C polarization. We found that the *n*-BuLi/TMEDA initiation system is difficult to handle because the resulting polymers are difficult to dissolve in common solvents for PCHD. Good results could only be achieved for low molecular weight targets. *n*-BuLi/N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA), which is similar to the *n*-BuLi/TMEDA initiation system, failed to produce materials with narrow molecular weight distributions and predictable molecular weights. This is probably because PMDETA does not chelate as effective as TMEDA, since the former is more bulky and has an extra chelating site. Bulkiness alone may not be the sole reason for effective chelating agent since DABCO, also bulky, is quite effective as discussed below.

By using other poly-dentate additives, such as DABCO, DPPE, and DME, in combination with certain butyllithiums, PCHD samples with relatively narrow molecular weight distributions and modest molecular weights were obtained, as summarized in Table 2. DME, a weak chelating agent, can be used as an effective additive under carefully chosen conditions (Table 2). A group of PCHD samples having reasonably well-controlled molecular weights were made from *n*-BuLi/DME and the results are listed in Table 3. One typical SEC trace of PCHD made using this initiating system is shown in Figure 3a. The molecular weight distributions are quite narrow for low molecular weight samples, but at higher molecular weights with narrow molecular weight distribution materials are elusive, at least partially due to the poor solubility of the polymer. The three isomers of butyllithium in combination with DME yield striking differences in the polymerization process. Natori and Inoue[29] observed similar phenomena with TMEDA. It has been reported[13] that the three butyllithium isomers in the presence of TMEDA give very similar results for the polymerization of styrene. With *n*-BuLi, the initiation process proceeds at the same rate as propagation, but with *sec*-BuLi and *t*-BuLi the initiation is faster than propagation. This alone should not cause the observed differences reported by Natori and Inoue[29] in the polymerization of 1,3-CHD. Adequate data to elucidate the differences were not presented. We speculate that the very reactive species generated from *t*-BuLi/TMEDA and *sec*-BuLi/TMEDA must undergo some detrimental reactions other than initiation. For DME these differences are not surprising, since DME has limited stability toward butyllithium.[37] The protons in the β-positions are more acidic than that in TMEDA, thus they are more readily abstracted followed by elimination. This process is fastest with *t*-BuLi and is slowest with *n*-BuLi. Temperature also plays a key role in these polymerizations: lower temperatures reduce side reactions.

DPPE is also a good chelating agent. Some of the characteristics of PCHD obtained from BuLi isomers with DPPE are listed in Table 2. We believe that better results could be achieved if the reactions were carried out under optimal conditions with regard to solvents, temperatures, and the amount of the additive (ratios of BuLi/DPPE). DABCO, a bulky chelating agent, combined with *sec*-BuLi or *t*-BuLi gives the best control of the polymerizations of 1,3-CHD with regard to molecular weight and polydispersity, as indicated in Table 2 and Table 3 (also Figure 3b). Chelation with DABCO effectively minimizes side reactions in initiation and chain propagation; this may be due to the bulkiness of DABCO.

It is a common practice that the linearity of M_n with conversion is used as an experimental criterion to document that a polymerization is living. Unfortunately, this type of plot will only detect chain transfer reactions; it is not sensitive to chain termination.[33] Natori and Inoue[27,29] used this plot to demonstrate that the *n*-BuLi/TMEDA/1,3-CHD system is living. To test if there is any chain termination occurring during the polymerization process, we polymerized 1,3-CHD with *n*-BuLi/TMEDA or DME by sequential addition of the monomer. Figure 4 shows the SEC traces of PCHD obtained by this approach. After adding a second dose of monomer, the peak became significantly broader, as shown in Figure 4b. This indicates that chain termination reactions do occur, both with DME and TMEDA. The large low molecular weight tail may indicate that the chain transferred species could re-initiate 1,3-CHD. Thus the range of conditions conducive to the living polymerization of 1,3-CHD is quite narrow.

Conclusions

The synthesis of poly(1,3-cyclohexadiene (PCHD) polymers using different initiating systems has been studied. Compared to acyclic conjugated dienes, the anionic

Table 3. Poly(1,3-Cyclohexadiene) Homopolymers from BuLi and DABCO or DME

Run	[Additive]/[I]	[CHD](mole/L)	[I] $\times 10^3$ (mole/L)	$M_{n,Cal} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n (SEC)
			sec-BuLi/DABCO/Benzene/20 °C			
1	1.4	1.68	35.11	3.8	4.4	1.06
2	1.7	1.20	12.63	7.6	9.1	1.05
3	1.8	1.13	9.52	10.5	13.8	1.03
4	2.5	0.79	4.29	14.7	20.1	1.04
5	2.0	0.82	2.84	23.1	27.8	1.12
6	2.3	1.14	3.10	29.5	36.0	1.31
7	2.1	1.21	2.10	46.3	42.9	1.34
			n-BuLi/DME/Benzene/0 °C			
8	1.7	1.04	17.6	4.7	4.0	1.13
9	2.39	0.69	6.0	7.1	11.3	1.07
10	1.45	1.05	12.2	9.5	13.8	1.12
11	1.65	1.63	8.91	13.7	17.9	1.21
12	2.09	0.77	2.87	16.3	21.1	1.19
13	1.75	1.75	7.35	19.0	28.2	1.24
14	2.15	1.18	3.28	28.7	36.5	1.51
15	1.74	1.77	3.60	39.4	42.9	1.43
16	4.89	0.95	1.51	50.2	Not soluble	

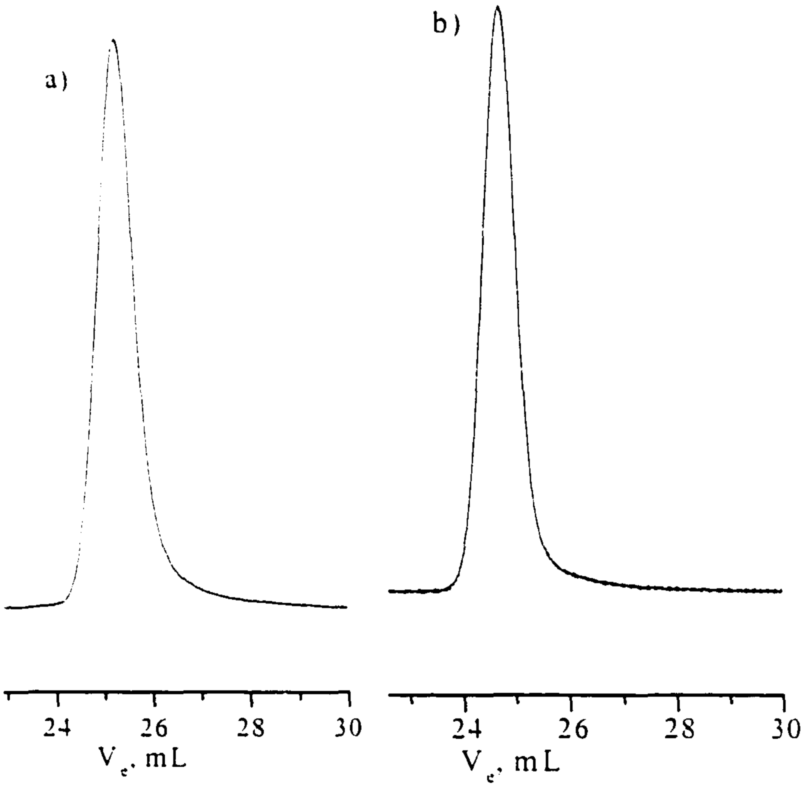

Figure 3. SEC traces of PCHD from (a) *n*-BuLi/DME at 0 °C, M_n = 11.3 kg/mol, M_w/M_n = 1.07 and (b) *sec*-BuLi/DABCO at 20 °C, M_n = 13.8 kg/mol, M_w/M_n = 1.03.

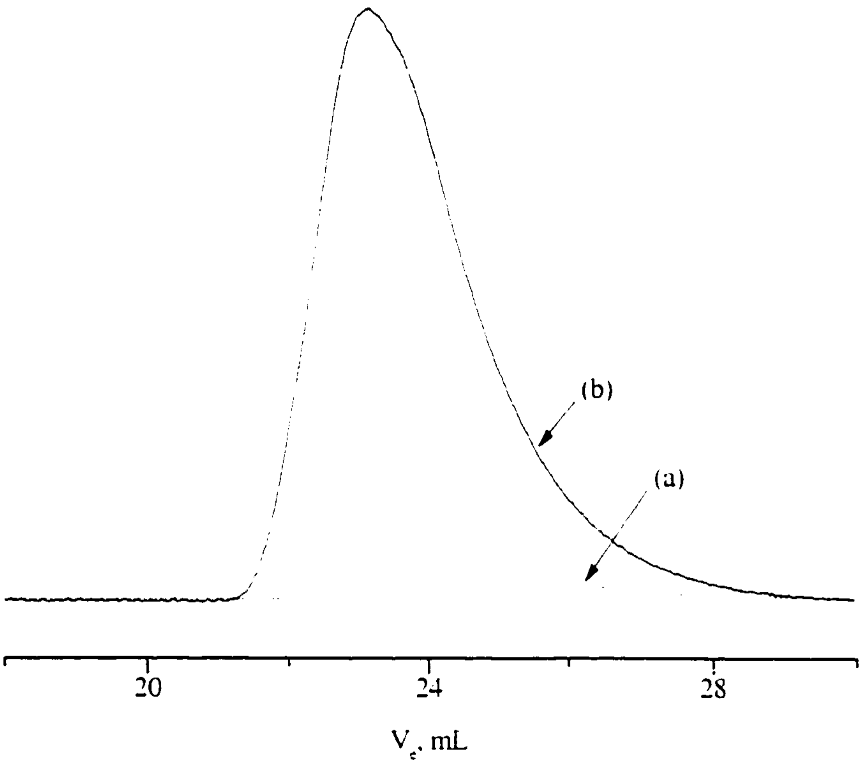

Figure 4. SEC traces of PCHD from *n*-BuLi/DME at 0 °C. (a) aliquot from first dose of monomer, M_n = 18.4 kg/mol, M_w/M_n = 1.08 and (b) aliquot from second dose of monomer, M_n= 19.7 kg/mol, M_w/M_n = 1.68.

polymerization of 1,3-CHD is less controlled with respect to molecular weight and molecular weight distributions. This situation can be improved by using certain additives; there is a bonus that the resulting PCHD exhibits controllable microstructures. Detailed studies of the polymerization kinetics, microstructural and dilution solution characterization of the final products, and the preparation of PCHD star and block copolymers will be published separately.

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SYNTHESIS AND CHARACTERIZATION OF POLY(1,3-CYCLOHEXADIENE-BLOCK-STYRENE)

by

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Abstract

The synthesis of block copolymers of 1,3-cyclohexadiene (1,3-CHD) and styrene under various conditions is reported. *sec*-Butyllithium alone as initiator does not yield living polymerization of 1,3-CHD due to side reactions (chain transfer and termination). However, certain additives, such as tetramethylethylenediamine, dimethoxyethane, and 1,4-diazabicyclo[2,2,2]octane, can be used to improve the control of the polymerizations. Using these additives, well-defined poly(1,3-cyclohexadiene-block-styrene)s with a wide range of compositions have been synthesized and characterized. In addition, the rate of cross-over reactions during block copolymer formation and the "random" copolymerization of 1,3-CHD and styrene have been investigated.

Introduction

Block copolymers, composed of thermodynamically incompatible blocks covalently bonded together, can self-assemble into well-ordered nano-domains because of the mutual repulsions and the constraints imposed by the connectivity of the blocks.[1] In the strong segregation limit, even the simplest linear AB diblock copolymers consisting of two flexible chains can exhibit a rich variety of morphologies depending on their volume fractions.[2] However, it is highly desirable to be able to control the micro-phase morphology and the composition separately in applications. Consequently, this dependence limits the flexibility in designing new materials for specific applications. For example, if for a certain purpose it was desired to have a material with a cylindrical morphology in which the component comprising cylindrical domain makes up over 50 vol % of the material, traditional neat block copolymers are not useful. This is because in this composition range only lamellar phase-separated domains will form typical diblocks.

Two approaches have been used to uncouple this rigorous dependence of block copolymer morphology on volume fraction.[3] One approach is to introduce architectural asymmetry into the block copolymer (i.e., change the connectivity of different blocks).[4] Non-linear architectures, such as miktoarm stars and grafted block copolymers, have been demonstrated both theoretically and experimentally to allow control of morphology independent of the familiar composition windows found in linear AB diblock morphologies.[5-8] For instance, PI (polyisoprene) in a three-miktoarm star of $(PI)_2PS$ (polystyrene) with about 0.81 volume fraction of PS formed a randomly orientated worm micelles dispersed in a continuous PS matrix.[8] Moreover this morphology was demonstrated to be the equilibrium state of the system. It is believed that the unusual morphology is due to the graft architecture of the molecule and unique relationship between the particular volume fraction and the concavity of the PS/PI interface on which the two PI chains per molecule must reside. At the same volume fraction and molecular weight, a linear PS-PI diblock would have PI spheres distributed in the PS matrix. For a regularly spaced, tetrafunctional multi-grafted block copolymer (PI backbone and PS grafts) with ~9 vol % PS, instead of producing PS sphere/PS cylindrical structure as predicted by Milner's theory, an unusual new morphology was formed.[6] The morphology can be described as a microphase-separated mesh of PS struts or wormlike domains in a PI matrix.

The other approach, which is to introduce conformational asymmetry into the copolymer, has attracted considerable interest recently.[3] In a sense, most block copolymers can better be considered as flexible-semiflexible block copolymers due to conformational asymmetry caused by differences in the statistical segment length (chain stiffness) of each block. Conformational asymmetry can shift the volume fraction range in which various morphologies are observed because of different space-filling characteristics of the two blocks.[9] AB diblock copolymers consisting of a flexible coil and a rigid rod block (so-called rod-coil block copolymers) represent the extreme case of conformational asymmetry. These materials have stimulated much research interest over the past decade, and a variety of supramolecular architectures have been observed for rod-coil block systems.[10-11] The unique aggregation behavior of rod-coil systems arises from two different ordering phenomena: (i) the microphase-separation of the coil and rod blocks into ordered periodic structures, and (ii) the tendency of the rod block to form anisotropic, ordered structures. Even though many fantastic structures have been observed, [11] the phase behavior, hence the properties, of rod-coil systems are difficult to tailor because of the complexities of the interactions in the system.

However, if stiffness of one block can be systematically varied, the phase behavior can be tuned in a controlled manner. Lai et al.[12] studied the phase separations of styrene-isoprene diblock copolymers and their hydrogenated derivatives (styrene-ethylene-*alt*-propylene and vinylcyclohexane-ethylene-*alt*-propylene copolymers). They found that the phase behavior did evolve as the conformational asymmetry parameter, ε, was varied, but not in a simple fashion. Pochan and coworkers studied phase-separation in poly(isoprene-block-*tert*-butylmethacrylate) (PI-PtBMA) diblock copolymers.[3] For samples with volume fraction (ϕ) >0.30 of the "stiff" block, PtBMA, small phase boundary shifts were found, consistent with theoretical predications. However, discrepancies were observed in the volume fraction dependence of experimentally determined morphological behavior and that calculated theoretically when $\phi_{PtBMA}<0.30$.

Recently, we observed an unusual core-shell microphase-separated morphology in poly(styrene-block-1,3-cyclohexadiene)(PS-PCHD) systems,[13] which suggests that conformational asymmetry exists in PS-PCHD block copolymers. It is our motivation to elucidate the micro-phase separation morphologies of PS-PCHD block copolymers by studying a wide spectrum of compositions. Thus, our focus in the present work is to better understand the anionic copolymerization behavior of styrene and 1,3-cyclohexadiene (1,3-CHD) under various conditions.

1,3-CHD polymers are a very interesting class of materials because of their unique structures and expected advantageous properties.[14] Zhong and Francois[15] synthesized PS-PCHD block copolymer using secondary butyllithium (*sec*-BuLi) in a non-polar solvent by first polymerizing styrene, followed by addition of 1,3-CHD to the living anions. During the 1,3-CHD polymerization, they found that chain transfer to monomer was unavoidable and some of the metallated monomer reinitiated polymerization. Francois and Zhong[15] eventually converted the PCHD block to poly(p-phenylene) (PPP). Zhou also synthesized a series of PS-PCHD block copolymers using *sec*-BuLi.[17] He used benzene/hexane mixtures as the solvent (v/v = 9/1) and ran the polymerizations at low temperatures (<5 °C) in order to minimize side reactions. Even so, chain transfer and termination reactions limited the PCHD composition in the final products. Recently, Natori[18] and Notori and Inoue[19] reported that polymerization of 1,3-CHD anionically could be controlled using the normal butyllithium (*n*-BuLi)/N,N,N',N'-tetramethyl ethylene diamine (TMEDA) initiation system. Various block copolymers of 1,3-CHD with styrene, butadiene, and isoprene were made by sequential addition of the monomers. According to their findings, polystyryllithium

(PSLi) and polycyclohexadienyllithium (PCHDLi) species had similar reactivity towards styrene, whereas PSLi hardly reacted with 1,3-CHD.

In this paper, we report the synthesis and characterization of a series of PS-PCHD diblock copolymers. The behavior of various initiating systems and the nature of the cross-over reactions are discussed. Under appropriate conditions, narrowed distributed high molecular weight, block copolymers with high 1,3-CHD content (up to 85 wt %) can be prepared. "Random" copolymerization behavior of 1,3-CHD and styrene is also reported.

Experimental

Materials. Benzene (Fisher), tetrahydrofuran (THF, Aldrich), hexane (Fisher), and styrene (Aldrich) were purified to anionic polymerization standards, as described in the literature.[20,21] The details of purification and dilution of 1,4-diazabicyclo [2,2,2] octane (DABCO, Aldrich), TMEDA (Aldrich), and 1,2-dimethoxyethane (DME, Acros) and the purification of 1,3-CHD (Aldrich) were described elsewhere.[14] *sec*-BuLi and *n*-BuLi were prepared from the reaction of the corresponding butyl chloride with lithium powder in hexane under vacuum. Naphthalene (Aldrich) was sublimed three times on the vacuum line and diluted in THF. The potassium naphthanide was made by reacting naphthalene with a potassium mirror in THF at −78 °C for 2 h just before the polymerization.

Polymerization and Characterization. All polymerizations were carried out under high vacuum using custom-made glass reactors. Detailed procedures are described in the literature.[21] Poly(1,3-cyclohexadiene-block-styrene) (PCHD-PS) and

PS-PCHD block copolymers were synthesized by sequential addition of monomers. Following the completion of the first block, a small amount of sample was taken and used for characterization. After the polymerization was finished, degassed methanol was added to terminate the polymer. The polymer was precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (Butylated hydrotoluene, BHT) added as antioxidant. The polymer was isolated by filtration and dried under high vacuum. For some samples, solvent/non-solvent (toluene/methanol) fractionation was used to remove homopolymer contamination. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% wt/vol) until turbidity appeared. The solution was then heated gently while stirring to eliminate turbidity, and it was then transferred to a warm separatory funnel. This system was kept undisturbed overnight to allow phase separation. This procedure was repeated until no undesirable products could be detected by size exclusion chromatography (SEC).

SEC experiments in THF were carried out at 30 °C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 ml/min, columns: 100 Å, 500 Å, 10^3 Å, 10^4 Å, 10^5 Å Waters Styragel column set or 100 Å plus linear Waters Ultrastyragel column set). SEC experiments in chloroform ($CHCl_3$) were done using a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode array detectors. This system was also connected to a Wyatt DAWN DSP multi-angle laser light scattering (MALLS) detector. Two Polymer Laboratories 5 μm PL-gel MiniMIX columns were used, and the flow rate was 0.3 ml/min. ^{1}H-NMR experiments were carried out in $CDCl_3$ at 30 °C using a Bruker ARX 300 instrument. Matrix-assisted laser desportion/ionization-time-of-flight mass spectrometry (MADLI-TOF-MS) data were obtained using a PerSeptive Biosystems Voyager Elite DE instrument. $CHCl_3$ solutions were prepared using Dithranol as matrix and silver trifluoroacetate as the ionizing salt.

Results and Discussions

Block Copolymerization Using BuLi Without Additives The successful control of the anionic polymerization of 1,3-CHD using certain initiating systems, as described in our previous paper,[14] suggests the possibility of making well-defined PS-PCHD diblocks having a wide range of compositions and molecular weights. Some of our preliminary results were presented earlier.[22] We have employed several initiating systems and different polymerization sequences. The conditions used and the characteristics of the resulting polymers are listed in Table 1. When styrene is polymerized by *sec*-BuLi in benzene followed by addition of 1,3-CHD without any additive, the PSLi can rather rapidly initiate 1,3-CHD. The fast crossover was confirmed by the color changing from orange-red to yellow within 1 min. This simple procedure works well for making PS-PCHD block copolymers with short PCHD segments and thus low PCHD content in the copolymer. As shown in Figure 1a (solvent: THF), the SEC trace of a PS-PCHD diblock copolymer (wt % of 1,3-CHD = 5.4) is symmetrical and monomodal. However, when the targeted 1,3-CHD composition in the PS-PCHD block copolymer is high (> 20%), this polymerization is not well-controlled, as indicated by the low molecular weight shoulder in the SEC chromatogram (Figure 1c; Solvent: THF). These low molecular weight by-products arise from side reactions such as chain transfer and/or chain termination.

Table 1. Characteristics of PS-PCHD Block Copolymers from BuLi with Various Additives

Run	Additive	[Add]/[I]	[ST] mole/L	[CHD] mole/L	[I] $\times 10^3$ mole/L	M_n [a] $\times 10^{-3}$	M_w/M_n [a]	wt % [b] PCHD	Remarks
1 [c]	No additive		0.449	0.646	2.78	22.7	1.22	38.4	St first
2 [c]	No additive		0.321	0.777	15.4	8.0	1.25	70.7	CHD first
3 [c]	THF	16.8	0.294	0.266	4.13	15.8	1.15	43.7	St first
4 [d]	TMEDA	1.25	0.551	1.083	3.52		Multi-modal		CHD first
5 [e]	TMEDA	1.27	0.637	0.625	3.47	23.7	1.09	45.1	St first
6 [e]	TMEDA	1.33	0.803	1.015	8.53		bimodal		CHD first
7	Naphth./K/THF/-78 °C		0.737	0.620	11.15	19.3	1.25		St first
8	Naphth./K/THF/-78 °C		0.656	0.959	8.01	23.4	1.41		CHD first
9 [f]	DME	5.71	0.240	1.354	7.01	27.0	1.04	82.2	St first
10 [f]	DME	5.60	0.321	0.900	5.52	33.2	1.07	81.5	CHD first
11 [g]	DABCO	1.74	0.719	0.539	4.88	6.21	1.06	34.7	St first
12 [g]	DABCO	1.63	0.564	0.501	5.47	44.2	1.07	39.4	CHD first

[a] From SEC in THF. [b] From ^{1}H-NMR. [c] *sec*-BuLi in benzene at room temperature. [d] *n*-BuLi in benzene at room temperature. [e] *n*-BuLi in cyclohexane at 40 °C. [f] *n*-BuLi in benzene at 5 °C. [g] *sec*-BuLi in benzene at room temperature.

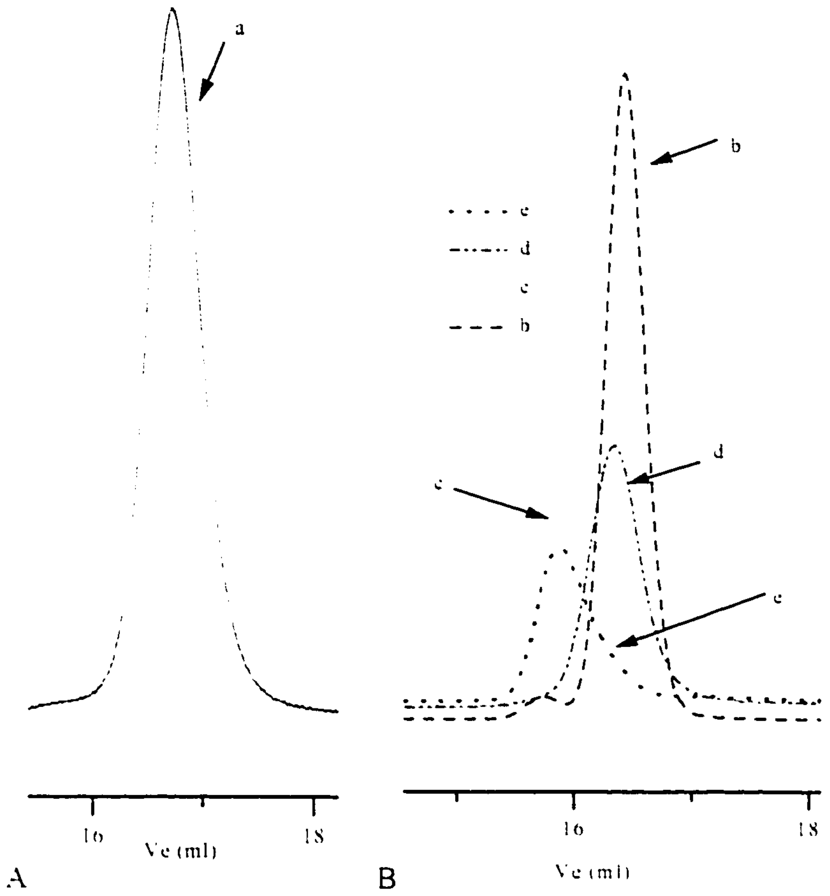

Figure 1. SEC traces (eluent THF) of PS-PCHD from *sec*-BuLi in benzene (styrene polymerized first). (A) monomer charge: styrene/1,3-CHD = 93/7 (mole): (a) M_n = 14.1 kg/mol M_w/M_n = 1.06; (B) monomer charge: styrene/1,3-CHD = 53/47 (mole): (b) PS block, M_n = 15.1 kg/mol M_w/M_n = 1.05; (c) PS-PCHD block before fractionation, M_n = 22.4 kg/mol M_w/M_n = 1.22; (d) fractionation supernatant, M_n= 16.4 kg/mol M_w/M_n = 1.08; (e) fractionation precipitate, M_n = 28.2 kg/mol, M_w/M_n = 1.05.

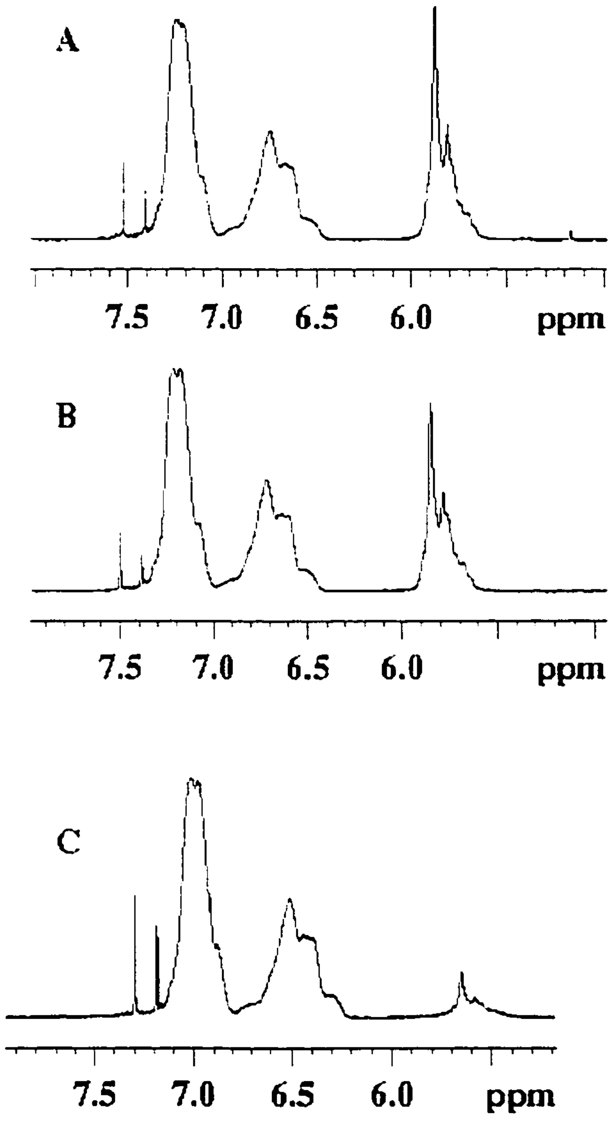

Figure 2. ^{1}H-NMR spectra of PS-PCHD SEC from *sec*-BuLi in benzene. (A) before fractionation, PCHD wt % = 38.4; (B) fractionation precipitate, PCHD wt % = 43.1; (C) fractionation supernatant, PCHD wt %= 12.9.

Since 1,3-CHD can also undergo several detrimental reactions under anionic polymerization conditions (strong base) besides the desired propagation,[14] the maximum attainable composition of PCHD in the copolymers with high molecular weight (>10 kg/mol) is restricted regardless of the initial monomer ratio. The low molecular weight contaminants can be removed easily by solvent (toluene)/non-solvent (methanol) fractionation. These results are similar to those reported by Francois and Zhong.[10] Based on infrared spectra, Zhong and Francois[15] found that the low molecular weight shoulder was pure PCHD. Consequently they claimed that the metallated monomer formed by chain transfer could re-initiate the polymerization of 1,3-CHD. Conversely, we find that the fractionated low molecular weight material contains substantial amounts of PS, as revealed by the ^{1}H-NMR spectra shown in Figure 2. This is not surprising, since the initiation and chain propagation rates in the PSLi initiated systems are not fast enough to avoid the side reactions. In addition to chain termination by hydride abstraction, one of the chain transfer reactions, 1,4-CHD, which is always present at some level in 1,3-CHD, is a very effective chain terminator.[14] Even though we can not evaluate the possible re-initiation quantitatively here, it is clear that this procedure does not play a major role in our studies. Thus, the results presented above show that it is very difficult to prepare PS-PCHD samples with high 1,3-CHD content by using *sec*-BuLi alone as initiator. Table 1 also gives the characteristics of block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene. PCHDLi chains can very rapidly initiate the polymerization of styrene under these conditions, as demonstrated by the yellow color turning to red-orange instantly upon addition of styrene. The SEC traces (in THF) are shown in Figure 3. As reported earlier,[14] the polymerization of 1,3-CHD by initiated *sec*-BuLi in the absence of additives does not proceed in a controlled manner. It is observed that the PCHD blocks are moderately polydisperse (M_w/M_n >1.2) and hence so are the final PCHD-PS diblocks. With a short PCHD block, the resulting PCHD-PS block copolymer is monomodal (Figure 3a). However, bimodal PCHD-PS is formed when the PCHD block is longer (higher molecular weight) (Figure 3b). It is difficult to remove the low molecular weight shoulder from this material by conventional toluene/methanol fractionation. This is probably because part of the PCHDLi was deactivated before all the monomer (1,3-CHD) was consumed, and toluene is not a very good solvent for the PCHD block.[14] More importantly, our experiments show that PCHDLi can rapidly initiate the polymerization of styrene in hydrocarbon solvents even without polar additives. This is in contrast to the copolymerization behavior of styrene and acyclic dienes.[23]

When styrene and butadiene are simultaneously added to anionic initiators in hydrocarbon solvents, tapered block copolymer is formed because of the differences in reactivity ratios.[23] Based upon our observations concerning the cross-over reactions (as noted previously), we used *sec*-BuLi to copolymerize styrene and 1,3-CHD in benzene at room temperature. The composition of the polymerization products was monitored by ^{1}H-NMR as a function of conversion, and the results are summarized in Figure 4. The monomodal character of the polymerization products as evidenced by SEC traces (Figure 5, solvent: THF) strongly suggests that they are not simple mixtures of PCHD and PS homopolymers. From Figure 4 one can see that the 1,3-CHD content in the polymerization products reach a rather high level quickly (30.5 mol % of 1,3-CHD in 20 min and 34.3 mol % in 120 min). All the monomers were consumed in about 4 h. The composition does not change much after 120 min, and it is always lower than anticipated

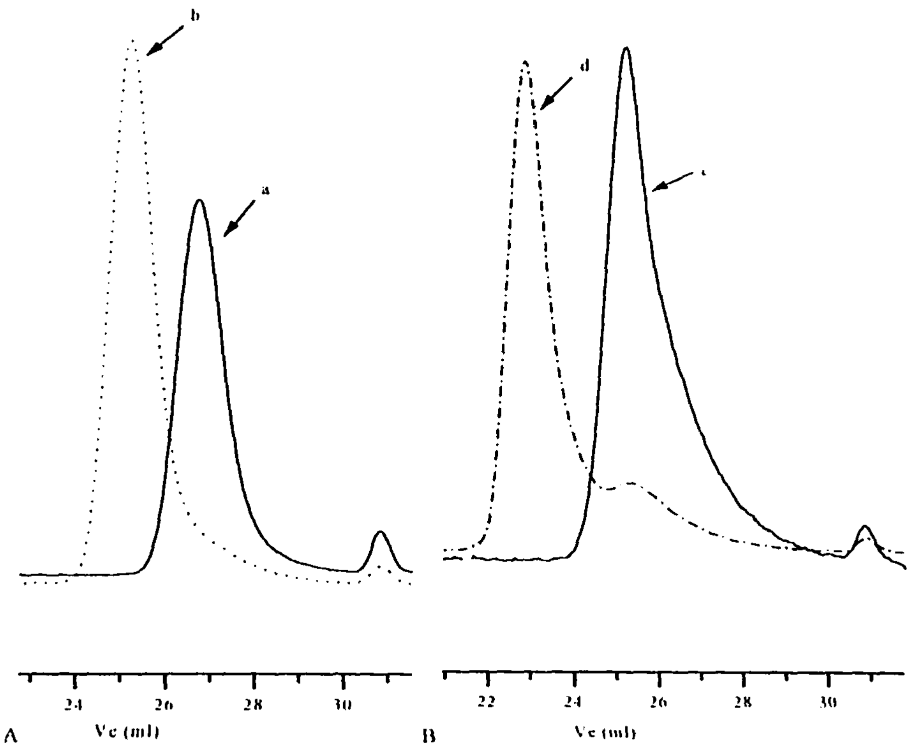

Figure 3. SEC traces (eluent THF) of PS-PCHD from *sec*-BuLi in benzene (1,3-CHD polymerized first). (A) monomer charge: styrene/1,3-CHD = 35.2/64.8 (mole): (a) PCHD block, M_n = 5.8 kg/mol, M_w/M_n = 1.07; (b) PCHD-PS diblock, M_n = 10.1 kg/mol, M_w/M_n = 1.09; (B) monomer charge: styrene/1,3-CHD=38.6/61.4 (mole): (c) PS block, M_n = 8.1 kg/mol, M_w/M_n = 1.13; (d) PS-PCHD block, M_n = 13.3 kg/mol, M_w/M_n = 1.28.

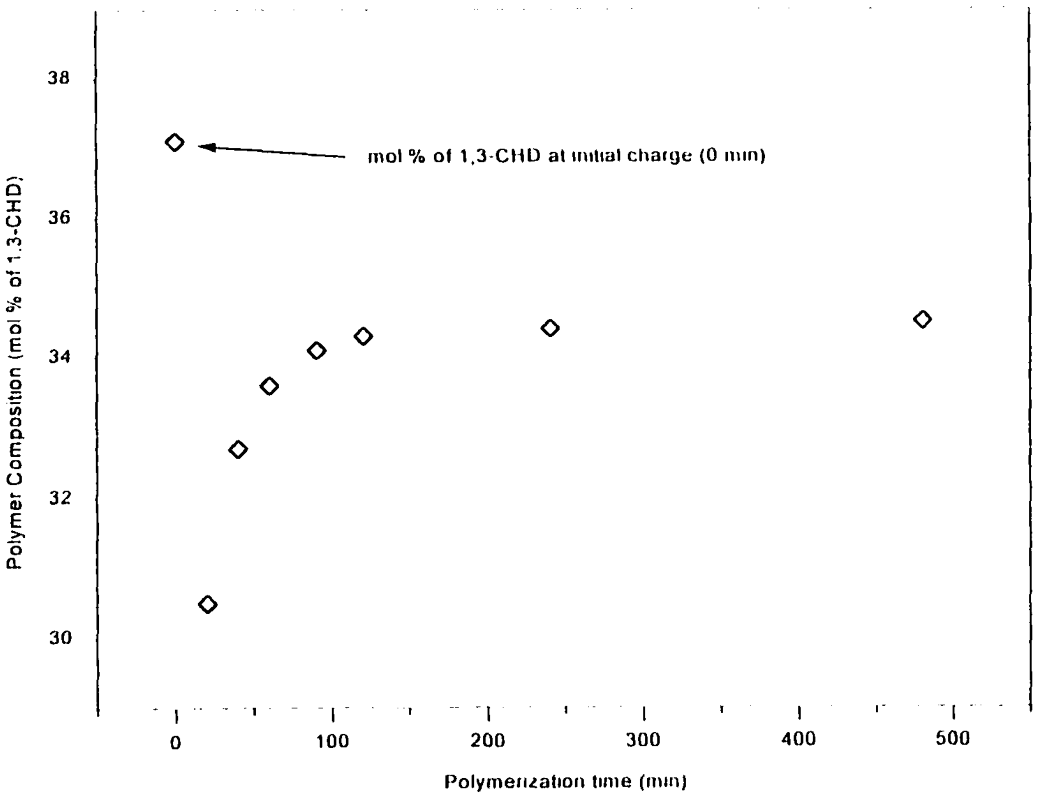

Figure 4. Compositions of PCHD in PS-PCHD copolymer (from the polymerization of 1,3-CHD and styrene simultaneously using *sec*-BuLi in benzene) versus time.

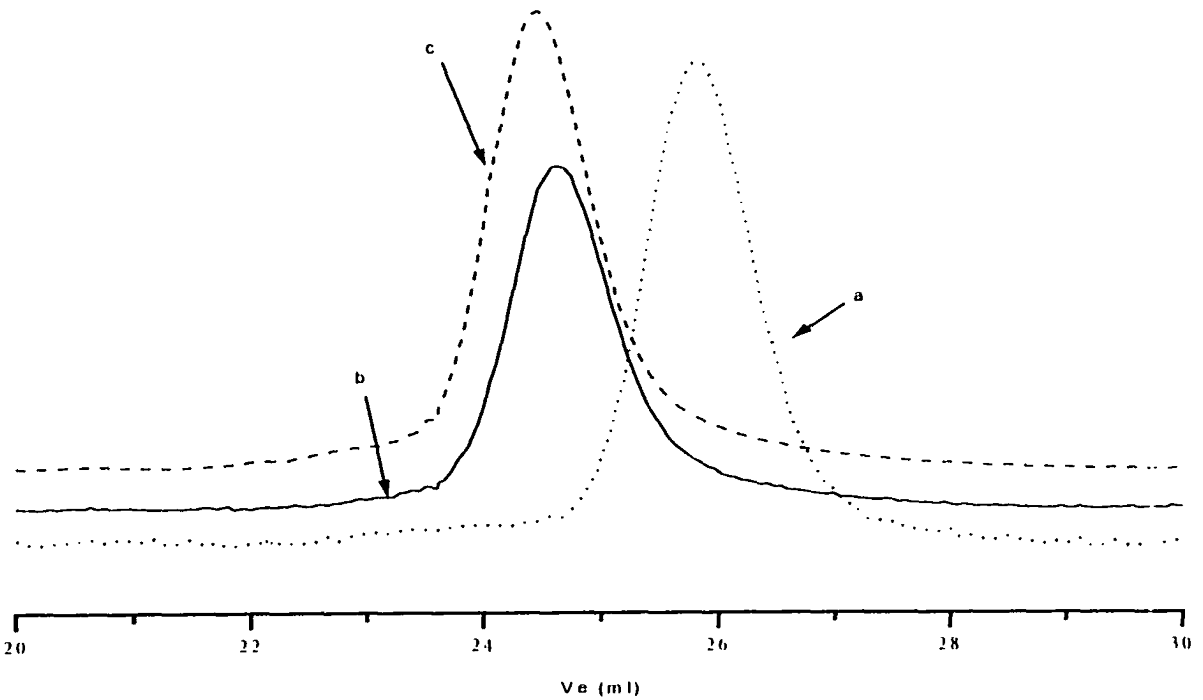

Figure 5. SEC traces (eluent THF) of PS-PCHD from the polymerization of 1,3-CHD and styrene simultaneously using *sec*-BuLi in benzene. (a) first sampling (20 min), M_n = 5.6 kg/mol, M_w/M_n = 1.07 (b) third sampling (60 min), M_n = 13.2 kg/mol, M_w/M_n = 1.11; (c) final product (6 h), M_n = 14.2 kg/mol, M_w/M_n = 1.14.

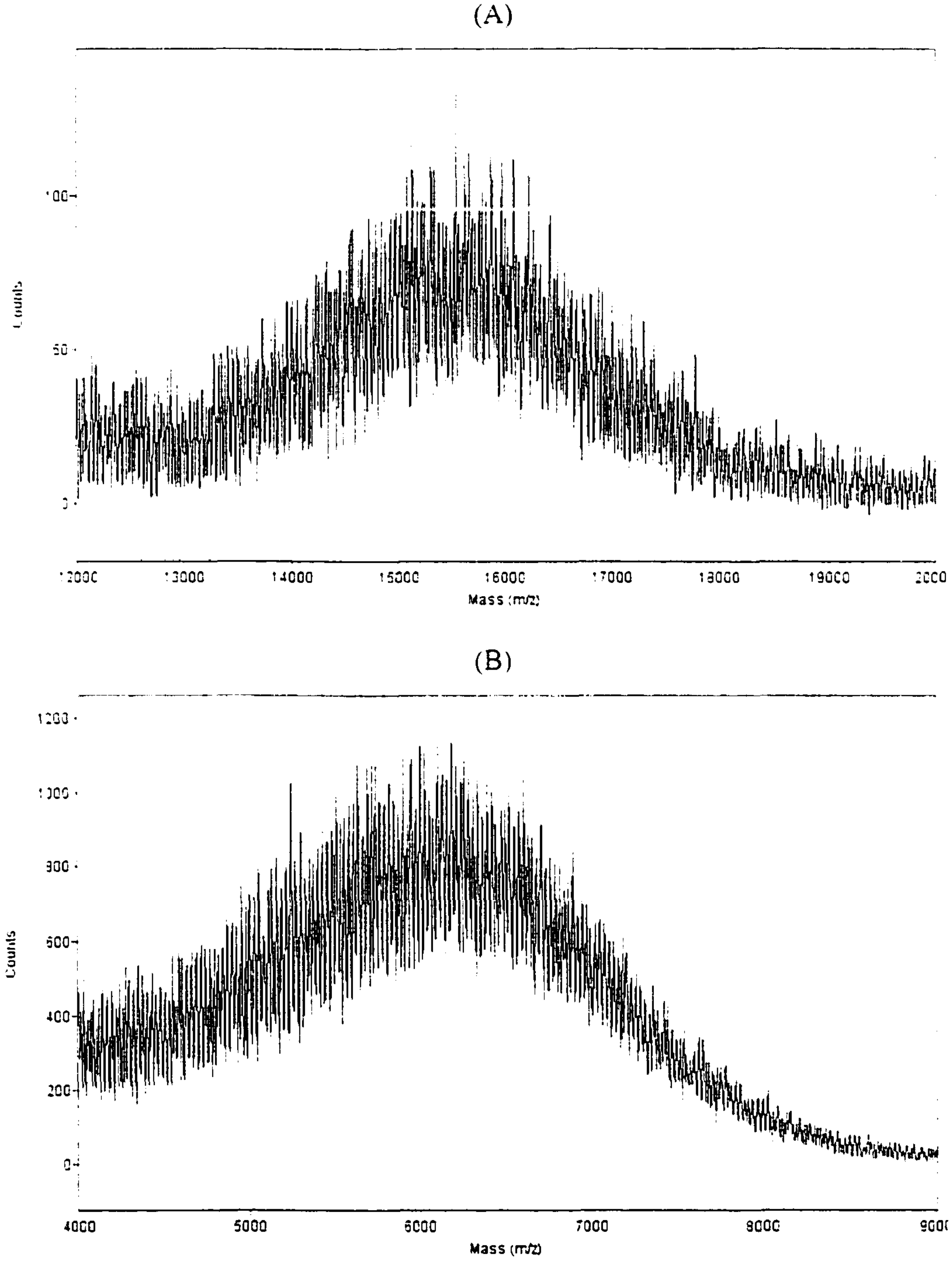

Figure 6. MALDI-TOF-MS spectra of PS-PCHD polymers. (a) "random" coplymer, M_n = 5.9 kg/mol, M_w/M_n = 1.03; (b) diblock copolymer. M_n = 15.4 kg/mol. M_w/M_n = 1.01.

(based on monomer charge) ratio. This is likely caused by the above-mentioned side reactions. These findings suggest that the rate of reaction of PSLi with 1,3-CHD in benzene at room temperature is comparable to that of PCHDLi with styrene. Natori reported[19] the copolymerization behavior of 1,3-CHD with styrene in cyclohexane using the *n*-BuLi/TMEDA (4/5) initiating system at 40 °C. He found that styrene was preferentially polymerized in the initial stages, and the polymerization of 1,3-CHD started only when most of the styrene was consumed. The reason for the higher reactivity of styrene in their study may be attributed to the presence of TMEDA, which can change the polymerization behavior dramatically because of its strong chelating effects with the growing chain ends.[24] Attempts to determine the sequence distribution in the copolymers by NMR were not successful because the spectra were too complex.

The MALDI-TOF-MS spectrum of the polymerization product from the first sampling of the "random copolymerization" is shown in Figure 6a, along with a PS-PCHD diblock spectrum with similar composition in Figure 6b. The single peak around 6 kg/mol and the mono-modal SEC traces (Figure 5) suggest that the copolymerization is of a statistical nature. One must notice the drastic intensity differences in the two spectra. We have observed that the MALDI-TOF-MS signals for PS-PCHD block copolymers are very weak.[25] A possible reason for the low response of PS-PCHD block copolymers in MALDI-TOF-MS is that PCHD segments are rather rigid and tend to aggregate during the preparation of MALDI specimens. MALDI requires that individual polymer chains be dispersed in matrix crystals.[26] Consequently, only a small portion of the polymer could be ionized. However, the intensity for the copolymerization product is much higher than that for PS-PCHD diblock copolymers. This may imply that the styrene and 1,3-CHD units are statistically arranged, which also suggests that the crossing-over reaction rates from

PCHDLi to styrene and vice versa are basically the same. More data are needed to prove this admittedly speculative interpretation. Using naphthalene/potassium initiation system in THF at −78 °C, we can obtain PCHD-PS-PCHD and PS-PCHD-PS triblock copolymers with mono-modal molecular weight distributions; however the molecular weight distributions are broad (runs 7-8 in Table 1).

Block Copolymerizations by BuLi with Additives. As discussed above, *sec*-BuLi alone does not polymerize 1,3-CHD in a controlled manner in hydrocarbon solvents. Therefore, it is difficult to synthesize PS-PCHD block copolymers with broad compositional ranges and high molecular weights, which are necessary for morphological studies, using this approach. Certain additives can improve the situation.[14,17] As shown in Table 1 (run 3), a small amount of THF can have a favorable impact on block copolymer formation via polymerization of 1,3-CHD followed by the addition of styrene. However, further attempts to target higher 1,3-CHD compositions and higher molecular weights were not successful. Because THF does not control the side reactions well enough; moreover, THF may react with *sec*-BuLi at the polymerization temperature. Natori[18] found that the *n*-BuLi/TMEDA initiating system could polymerize 1,3-CHD in a "living" manner. We polymerized 1,3-CHD and styrene sequentially by using this initiator system; the results are listed in Table 1 (runs 4-5) and Figure 7. When styrene was polymerized first, the SEC trace exhibited a tail at the high molecular weight end (Figure 7a). On the other hand, a low molecular weight shoulder was observed in the SEC chromatogram (solvent in THF) when 1,3-CHD was polymerized first (Figure 7b). The shoulder might arise from deactivated PCHDLi. A peak with extremely high molecular weight (~1300 kg/mol calibrated with PS standards) was observed in both cases. Upon diluting the concentrations, these peaks shifted to lower molecular weight (about 970 kg/mol calibrated with PS), and the fractions of the high molecular weight peak also decreased. When the SEC ran in $CHCl_3$, higher molecular weight peaks were also observed, but the positions moved to lower molecular weight (~500 kg/mol, calibrated with PS). Variations of the molecular weight and the fraction of high and low molecular weight components upon changing the SEC sampling concentration or elution solvent suggest that closed associations or micelles exist in these PS-PCHD block copolymers. Natori and Inoue[19] reported that PCHDLi "living" chains could continue to grow by adding either styrene or 1,3-CHD. But tailing can be seen clearly in some of their published SEC traces.

We reported previously[14] that the *n*-BuLi/DME or *sec*-BuLi/DABCO initiating systems could polymerize 1,3-CHD in a controlled manner with regard to molecular weight and molecular weight distribution. Thus it is natural to try and extend those approaches to the synthesis of PS-PCHD diblock copolymers. Typical results are listed in Table 1 (run 9-12), and complete characterization data are given in Tables 2 and 3. Under these reaction conditions, PCHDLi can efficiently initiate the polymerization of styrene and vice versa, as shown in Figure 8.

When the targeted composition for PCHD is either lower than 30 wt % or higher than 85 wt %, the resulting PS-PCHD block copolymers are unimodal and the molecular weight distribution are low (<1.1). However, a shoulder corresponding to the first block is always seen in the SEC traces of the diblocks when the designed composition of PCHD is from 30 to 85 wt %. If styrene is polymerized first, this low molecular weight shoulder can be removed easily by solvent/non-solvent fractionation, and it mainly contains PS as revealed by ^{1}H-NMR (Figure 9b). This is because 1,3-CHD terminates some PSLi and

Table 2. Characteristics of PS-PCHD Diblock Copolymers from *sec*-BuLi/DABCO/Benzene/20 °C

Run	[ST] mole/L	[CHD] mole/L	[I] ×10^3 mole/L	M_n [a] ×10^{-3}	M_w/M_n [a]	M_w [b] ×10^{-3}	M_n [c] ×10^{-3}	wt% [d] (PCHD)
1	1.07	0.225	7.38	15.7	1.04	17.7	16.5	11.4
2	0.719	0.539	4.88	22.9	1.03	26.1	23.8	34.7
3	0.673	0.542	8.33	15.3	1.03	19.3	17.0	38.2
4	0.492	0.340	4.02	26.7	1.06	32.9	28.4	52.7
5	1.05	1.23	7.00	16.9	1.03	18.6	15.4	66.0
6	0.175	1.64	10.64	17.1	1.04	21.9	19.1	85.1

[a] From SEC. [b] From SEC-MALLS. [c] From MALDI-TOF-MS. [d] Via ^{1}H-NMR in $CDCl_3$

Table 3. Characteristics of PS-PCHD Diblock Copolymer from *n*-BuLi/DME/Benzene/5 °C

Run	[ST] mole/L	[CHD] mole/L	[I] $\times 10^3$ mole/L	M_n [a] $\times 10^{-3}$	M_w/M_n [a]	M_w [b] $\times 10^{-3}$	M_n [c] $\times 10^{-3}$	wt% [d] (PCHD)
1	0.599	0.221	4.15	20.6	1.05	25.7	24.4	21.7
2	0.932	0.596	6.92	27.8	1.04	30.5	29.5	36.8
3	0.519	0.525	5.06	46.1	1.08	43.8		41.7
4	0.553	0.546	5.15	23.5	1.05	27.1	26.6	42.3
5	0.745	0.766	7.89	28.7	1.04	28.9	27.8	46.0
6	0.502	0.538	5.00	28.9	1.05	31.3	28.2	51.0
7	0.705	0.850	7.61	30.1	1.05	32.1	31.0	52.3
8	0.635	0.925	7.76	30.0	1.07	33.9	30.4	62.1
9	0.240	1.354	7.02	27.0	1.06	28.4	26.7	82.2

[a] From SEC. [b] From SEC-MALLS. [c]: From MALDI-TOF-MS. [d]: Via ^{1}H-NMR in $CDCl_3$

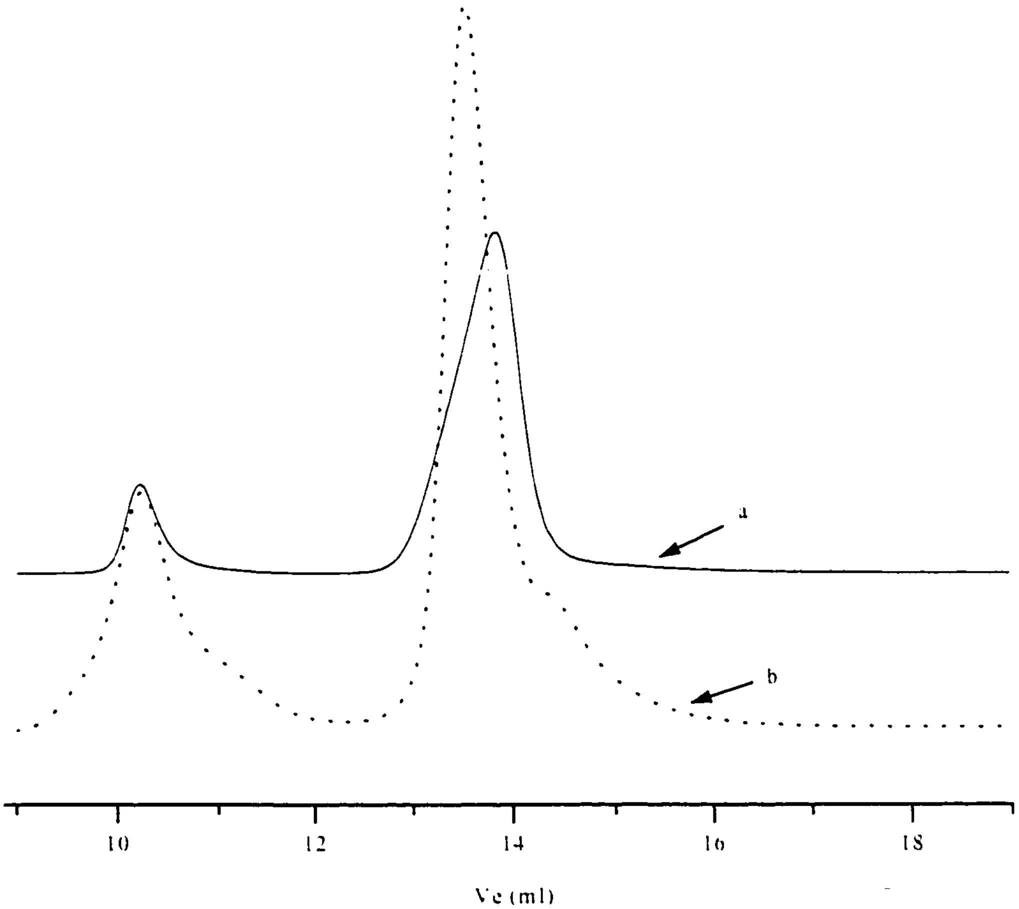

Figure 7. SEC traces (eluent THF) of PS-PCHD from *n*-BuLi/TMEDA /cyclohexane at 40 °C. (a) styrene polymerized first, M_n = 23.7 kg/mol, M_w/M_n = 1.09; (b) 1,3-CHD polymerized first.

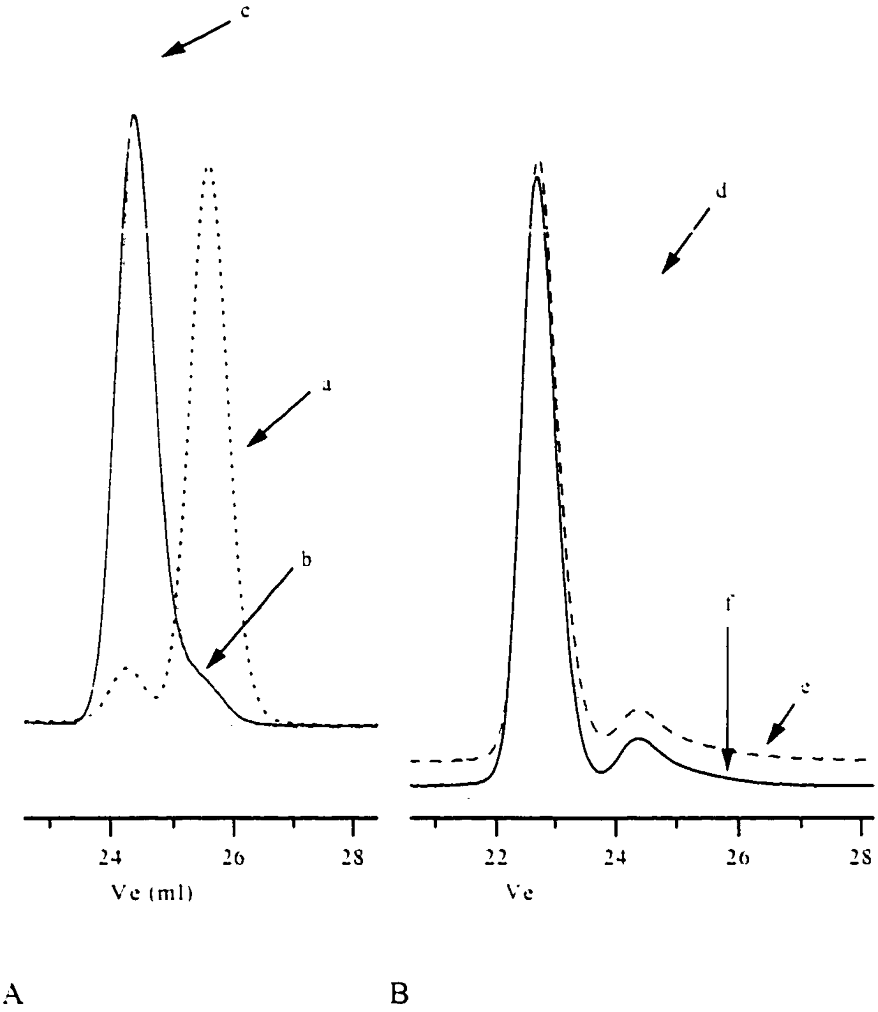

Figure 8. SEC traces (eluent THF) of PS-PCHD from *sec*-BuLi/DABCO/benzene. (A) styrene polymerized first: (a) PS block M_n = 8.3 kg/mol, M_w/M_n =1.07; (b) PS-PCHD diblock before fractionation, M_n = 15.1 kg/mol, M_w/M_n = 1.05; (c) PS-PCHD after fractionation, M_n = 15.3 kg/mol, M_w/M_n = 1.03; (B) 1,3-CHD polymerized first: (d) PCHD block, M_n = 15.7 kg/mol, M_w/M_n = 1.09; (e) PS-PCHD diblock before fractionation, M_n = 43.2 kg/mol, M_w/M_n = 1.10; (f) PS-PCHD diblock after fractionation, M_n = 44.3 kg/mol, M_w/M_n = 1.08.

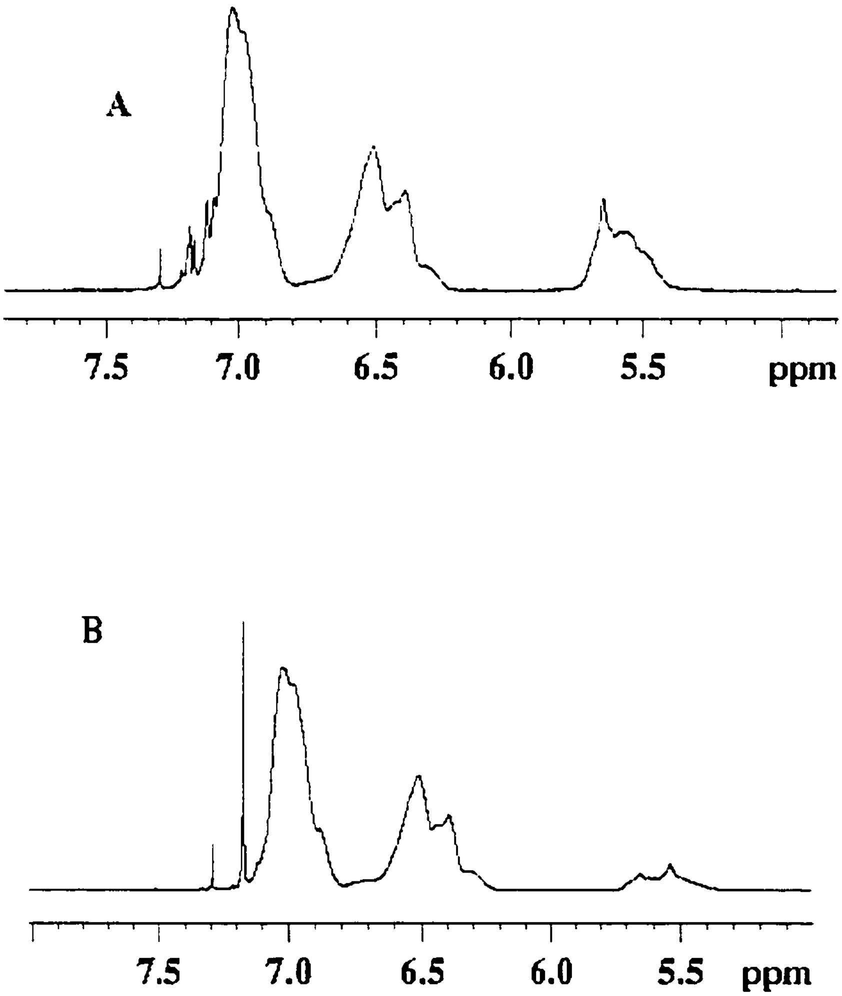

Figure 9. ^{1}H-NMR spectra of PS-PCHD SEC from *sec*-BuLi/DABCO/benzene. (A) styrene polymerized first, fractionation supernatant, PCHD wt %= 26.1; (B) 1,3-CHD polymerized first, fractionation supernatant, PCHD wt %= 11.1.

PS-PCHDLi chains. On the other hand, the low molecular weight shoulder is very difficult to remove by toluene/methanol fractionation if 1,3-CHD is polymerized first. The shoulder is probably formed by the self-termination of the PCHDLi chains, since we assume the possibility of PCHDLi chains terminated by styrene is low. The difficulty in removing the low molecular weight component by toluene/methanol fractionation may arise from the poor solubility of PCHD in toluene. The fractionated solution part of a PS-PCHD block copolymer (1,3-CHD polymerized first) contains significant amounts of PS (Figure 9a), which indicates the inefficient fractionations. However, we cannot exclude the possibility of PS formed by the polymerization of styrene initiated by the metallated 1,3-CHD species (formed by chain transfers).

Conclusions

We have studied the copolymerization behavior of 1,3-CHD and styrene under various reaction conditions. *sec*-BuLi alone as initiator does not give controllable polymerization of 1,3-CHD due to side reactions. Certain additives improved the controllability of the polymerizations. However, under all investigated conditions the PCHDLi chains have limited stability. Well-defined PS-PCHD block copolymers having a wide range of compositions and molecular weights were synthesized and characterized. Materials with polydispersities less than 1.1, compositions as high as 85 wt % 1,3-CHD, and molecular weights as high as 44 kg/mol could be generated, even though some fractionation is needed when the targeted molecular weight is higher than 20 kg/mol and the compositions range from 30 wt % to 85 wt %. The study of their morphologies is currently underway and will be reported in a future publication. Furthermore, the polymerization rates and cross-over rates for styrene and 1,3-CHD were found to be comparable in benzene at room temperature using *sec*-BuLi as initiator. This behavior is in stark contrast to the well-known copolymerization behavior of styrene with acyclic conjugated dienes (e.g., isoprene, butadiene).

Acknowledgements

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NEAR-MONODISPERSE STAR AND STAR-BLOCK POLYMERS BASED ON POLY(1,3-CYCLOHEXADIENE)

by

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Abstract

The synthesis of well-defined, near-monodisperse, three-arm star and star-block copolymers based on poly(1,3-cyclohexadiene) (PCHD) is described. The stars were prepared by the reaction of living anionic chain ends of PCHD, poly(styrene-1,3-cyclohexadiene) (PS-PCHD), and poly(1,3-cyclohexadiene-styrene) (PCHD-PS) with CH_3SiCl_3 in benzene. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was used to control the anionic polymerization of 1,3-CHD, and it also acted as a promoter during the linking reaction. The star polymers were fractionated to remove excess arm material and thoroughly characterized by size exclusion chromatography, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and light scattering.

Introduction

Constituting the simplest form of branching, star polymers are ideal for investigation into the structure–property relationships of branched polymers.[1] The first star polymers were synthesized in 1948 through condensation chemistry.[2] Since then virtually all polymerization methods have been used to make various star polymers; however, all these methods may be considered as variations of two more general methodologies.[3,4] The first method involves the polymerization of a monomer 'out of' a multifunctional initiator. This can be an experimentally expedient and clean approach, but common practical difficulties with this method involve synthesis of an appropriate initiator and adequately promoting its efficiency (to obtain narrow molecular weight distribution materials all initiating sites must react quickly). The second general method for making stars involves linking of pre-polymerized living polymer chains 'into' a coupling reagent. This is by far the more extensively studied procedure. This latter approach provides the opportunity to sample and thus characterize the "arm" material before forming the star polymer, and often allows mixed arm incorporation.[5,6] Divinylbenzene (DVB) and chlorosilanes have been the most popular linking agents used with this approach. Chlorosilanes have become the classic linking agents for the synthesis of star polymers using anionic polymerization because of the clean and quantitative nature of the linking reaction (assuming steric effects are adequately considered). DVB provides robust but relatively less well-defined branched materials, since precise control over the number of arms is not possible and stars produced by this method are always mixtures of materials having different numbers of arms.

Compared to the number of publications on the synthesis and properties of star homopolymers, the number of studies published on star-block copolymers, which have block copolymer arms, is quite small. Price et al. [7] synthesized three- and four-armed star-block copolymers of styrene and isoprene (with styrene as the outer block) using chlorosilanes as linking agents. The styrene volume fractions of their samples were fixed at about 0.24. Even though about 25% excess of living arms was used, significant amounts of three-armed (for $SiCl_4$) and two-armed (for CH_3SiCl_3) species were formed. Bi and Fetters[8] synthesized six- and nine-armed DVB-linked poly(styrene-block-isoprene) (PS-PI) stars containing ~25 vol % PS. Extending this work, they[9] synthesized and studied two series of chlorosilane- and DVB-linked styrene-butadiene and styrene-isoprene star-block copolymers containing up to 29 arms and having approximately 27 to 40 vol % PS (outer block). They found that the synthesis of four-armed star-block copolymers was facilitated by adding several units of butadiene to the isoprenyllithium chain ends prior to the addition of tetrachlorosilane. The linking of the diblock chains by DVB was found to proceed to virtual completion in benzene without a polar promoter or end capping. Thomas et al.,[10] Alward et al.,[11] and Kinning et al.[12] studied a family of PS-PI star-block copolymers (having up to 18 arms) made from the reaction of living diblock arms with chlorosilane linking agents. A new equilibrium microdomain morphology, thought to be ordered bicontinuous double-diamond (OBDD), was found in certain cases. Even though the nature of the morphology was subsequently re-evaluated,[13] the salient morphological features of star-block copolymers had been clearly demonstrated by this group. Inverse star block copolymers, $(AB)_2Si(BA)_2$, with A as PS and B as PI, were prepared by the chlorosilane method using $SiCl_4$.[14] In these materials, two arms are connected to the central silicon by their PS ends, and the other two arms are connected via their PI ends. The linking agent $SiCl_4$ was titrated with living poly(isoprene-block-styryllithium)(PI-PSLi) solution until two arms were linked to $SiCl_4$, as determined by size exclusion chromatography (SEC). The difunctional macromolecular linking agent was then treated with a small excess of the living (PS-PI)Li solution to prepare the inverse star-block copolymer. The order of the addition was dictated by steric factors. Tsiang[15] synthesized several four-armed stars with three polybutadiene (PBD) arms and one poly(styrene-block-butadiene) (PS-PBD) arm, $(PS\text{-}PB)Si(PB)_3$. The key step for this method is the successful synthesis of the pure $(PB)_3SiCl$ intermediate, which is obviously demanding. Molenberg and coworkers[16] synthesized four-armed poly(butadiene-block-diethylsiloxane) (PB-PDES) star-block copolymers by the reaction of living PB-PDES chains with 1,4-dimethyl-1,1-4,4-tetrachloro-1,2-disilyethane. The star-block copolymers were cross-linked by hydrosilylation of the PB double bonds with chlorodimethylsilane followed by condensation of the chlorosilane groups with water. The resulting rubbers showed elastomeric behavior in tension- and stress-induced mesophase formation. All the studies of star-block copolymer noted above focused on well-behaved monomers, mostly styrene, butadiene, and isoprene.

Poly(1,3-cyclohexadiene) (PCHD) and its derivatives are a structurally interesting class of polymer.[17] Polymerization of this monomer results in incorporation of a ring directly into the backbone of the polymer. In the case of PCHD, the cyclohexene ring may subsequently be aromatized, hydrogenated, or subjected to other chemical reactions in order to modify chemical or physical properties. Kara et al.[18] very recently presented a preliminary account of the synthesis of PCHD stars having up to 19 arms. To produce these materials they synthesized PCHD anions using normal butyllithium (*n*-BuLi)/N,N,N'N'-tetramethylethylenediamine (TMEDA) and linked them using DVB. In this work, we report the synthesis and characterizations of three-arm star polymers having PCHD, poly(styrene-block-1,3-cyclohexadiene) (PS-PCHD) or poly (1,3-cyclohexadiene-block-polystyrene) (PCHD-PS) arms. These near-monodisperse star and star-block materials, linked using methyltrichlorosilane, were subjected to rigorous molecular characterization using mass spectrometry and light scattering.

Experimental

Materials. Benzene (Fisher), tetrahydrofuran (THF, Aldrich), hexane (Fisher), 1,3-butadiene (1,3-BD, Aldrich), and styrene (Aldrich) were purified to anionic polymerization standards, as described in the literature.[19,20] 1,3-BD was diluted in hexane. The purification and dilution of 1,4-diazabicyclo[2,2,2]octane (DABCO, Aldrich) and the purification of 1,3-CHD (Aldrich) were described elsewhere.[17] Secondary butyllithium (*sec*-BuLi), prepared from the reaction of secondary butyl chloride with lithium powder in hexane under vacuum, was used as the initiator. Methyltrichlorosilane (CH_3SiCl_3, United Chemical Technologies, Inc.) was stirred over CaH_2 overnight, followed by fractional distillation on the vacuum line (collecting the middle 1/3 fraction), and then subdivided into ampoules. It was diluted to the desired concentration (typical 1×10^{-4} mole/ml) with purified hexane.

Polymerization and Characterization. All polymerizations were carried out under high vacuum using custom-made glass reactors with *sec*-BuLi/DABCO (1/2) as the initiating system and benzene as the solvent. Detailed procedures are outlined in the literature.[20] PCHD-PS and PS-PCHD arms were made by sequential addition of monomers. Following the completion of each polymerization stage, an aliquot was taken for characterization. After the linking agent was added to the arm solutions, aliquots were taken on a scheduled basis. After the linking reaction was completed, degassed methanol was added to terminate the excess arm. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (BHT) added. The final polymer was filtered and dried under high vacuum.

Solvent non-solvent (toluene/methanol) fractionation was used at room temperature to remove the excess unreacted arm material. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% wt/vol) until turbidity appeared. The solution was heated gently to eliminate turbidity while stirring. The solution was then transferred to a warm separatory funnel. This system was left undisturbed overnight to allow phase separation. This procedure was repeated as necessary.

SEC experiments in THF were carried out at 30 °C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 ml/min, columns: Waters 100 Å, 500 Å, 10^3 Å, 10^4 Å, 10^5 Å). SEC experiments in chloroform ($CHCl_3$) were done on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. This system was also connected to a Wyatt DAWN DSP multi-angle laser light scattering (MALLS) detector. Two Polymer Laboratories 5 μm PL-gel MiniMIX columns were used, and the flow rate was 0.3 ml/min. ^{1}H-NMR experiment was carried out in $CDCl_3$ at 30 °C using a Bruker ARX 300 instrument. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were obtained using a PerSeptive Biosystems Voyager Elite DE instrument. $CHCl_3$ solutions were prepared using dithranol as matrix and silver trifluoroacetate as the ionizing salt.

Results and Discussion

The synthesis of the 3-arm PCHD homo-star polymers was performed according to the following reactions in benzene.

1,3-CHD + *sec*-BuLi/DABCO →PCHDLi (A)

(A) + 4-7 units 1,3-BD→ PCHD-BDLi (B)

(excess) (B) + CH_3SiCl_3→ $(PCHD)_3SiCH_3$ (3-arm PCHD star)

The molecular characteristics of the resulting polymers are summarized in Table 1. Both arms and purified stars had very narrow molecular weight distributions (polydispersity < 1.1). The key step of this synthetic route was the linking procedure. It was anticipated that the PCHDLi chain end, without end capping with 1,3-BD,was

Table 1. Characterization of Three-Armed PCHD Stars

Polymer	PCHD arm		3-Armed Star	
	M_w ^{a} $\times 10^{-3}$	M_w/M_n ^{b}	M_w ^{a} $\times 10^{-3}$	M_w/M_n ^{b}
KH5-033	7.3	1.04	21.4	1.06
KH5-041	5.8	1.07	18.3	1.05
KH5-051	13.6	1.05	41.2	1.06

^{a} From SEC-MALLS. ^{b}: From SEC.

sufficiently bulky that steric hindrance would prohibit its complete reaction with the linking agent, CH_3SiCl_3. To our surprise this reaction did yield a three-arm star, although it required long reaction times (up to 2 weeks) as shown in Figure 1. The two-armed intermediate is clearly seen in the SEC trace of the first sampling. We cannot exclude the possibility that some coupled material remained in the final product due to the limitations of SEC separation. However, the star peak appears to be quite symmetrical. When we capped the PCHDLi anions with several 1,3-BD units, the chain ends became much less bulky and the linking reaction took place much faster, as shown in Figure 2.

The linking reaction was so fast under our reaction conditions that we could not detect the two-arm intermediate after only 15 min of reaction. One possible reason for this very rapid linking reaction is that the additive, DABCO, also functions as a promoter. To check this hypothesis, we polymerized 1,3-BD using *sec*-BuLi/DABCO in benzene and linked the resulting anions with CH_3SiCl_3. The linking reaction did proceed quickly; no two-arm material was detected even at the first sampling (after 15 min of reaction), as shown in Figure 3. Even though the linking reaction was allowed to

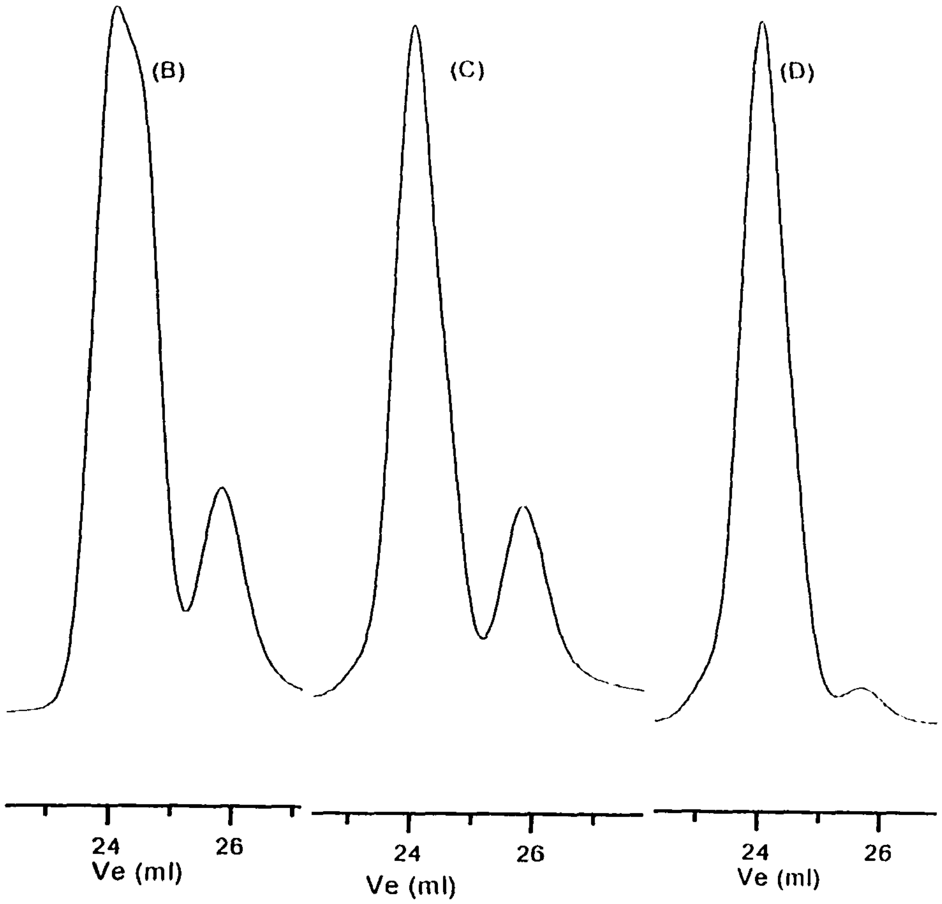

Figure 1. SEC traces of (A) PCHD arm; (B) first sampling (120 min); (C) unfractionated three-arm PCHD star; (D) fractionated three-arm PCHD star.

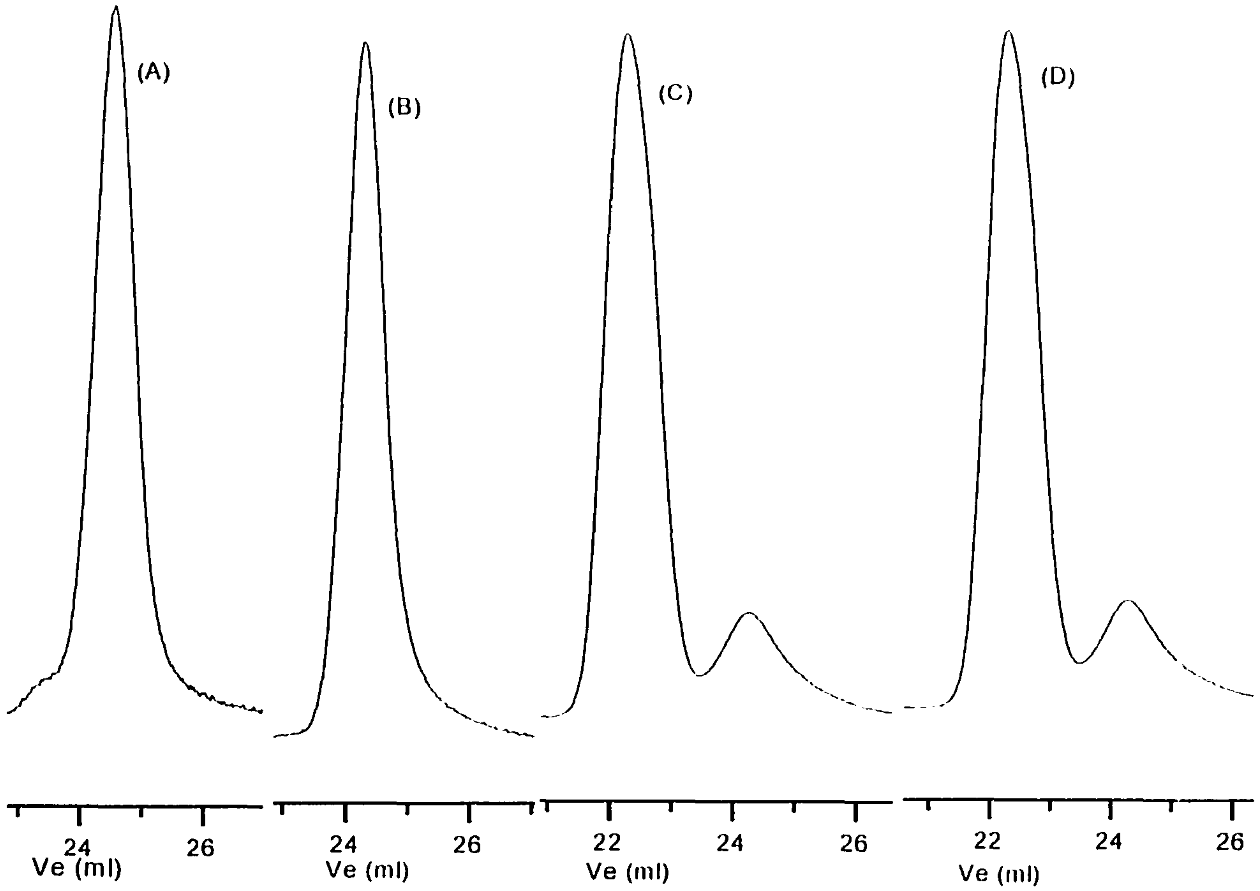

Figure 2. SEC traces of (A) PCHD arm; (B) 1,3-BD end-capped PCHD arm; (C) first sampling (60 min); (D) unfractionated three-arm PCHD star.

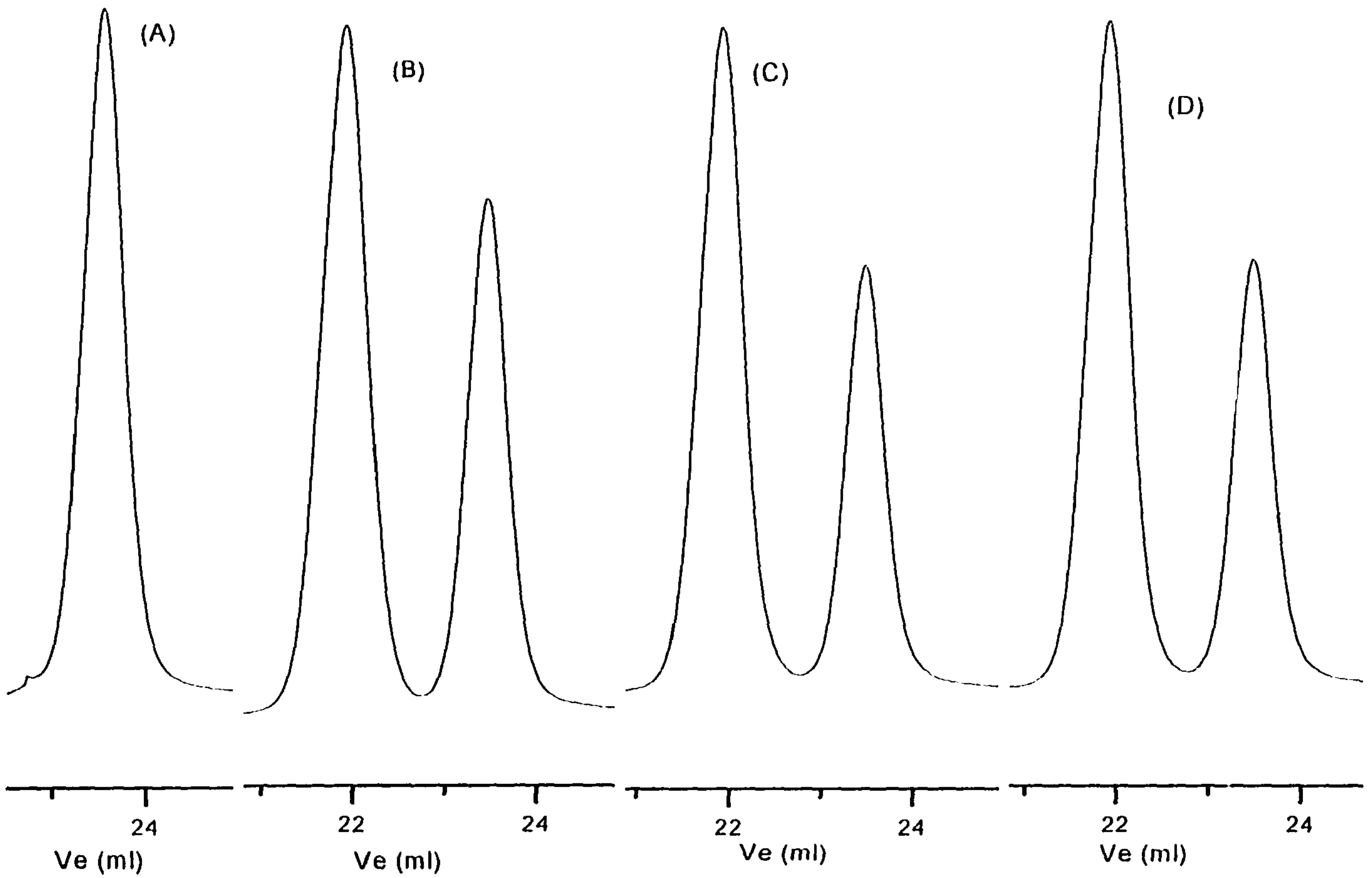

Figure 3. SEC traces of (A) PBD arm; (B) first sampling (15 min); (C) second sampling (60 min);(D) unfractionated three-arm PBD star.

continue, it was virtually finished in 1 h, as can be seen on comparing the SEC traces at 1 h and 1 day (Figure 3c and 3d). Tsiang[15] found that the linking efficiency of $(PB)_3SiCl$ with PS-PBLi was promoted from ~30% without a polar additive to >90% with a polar additive in 10 min, which is consistent with our results. The large arm peak was from the large excess of arm anions used in this experiment.

Removal of the excess arm material from the PCHD stars by solvent/non-solvent fraction has proven to be very difficult (Figure 2d)). This may arise from the modest molecular weights of the PCHD materials investigated. The sol-gel phase separation of a polymer in the solvent/non-solvent system depends on its molecular weight.[21] The higher the molecular weight, the easier the sol-gel phase separates, hence the higher the fractionation efficiency. However, there was one factor that prevented us from pursuing PCHD star homopolymers with higher molecular weight: polymers of 1,3-cyclohexadiene (1,3-CHD) are difficult to dissolve in common organic solvents if the molecular weight is high (> 30 kg/mol). It was expected that a block copolymer arm composed in part of PS would improve the solubility. Thus, we were motivated to synthesize PS/PCHD star-block copolymers.

The synthetic procedures for the star-block copolymers are summarized by the following reactions:

Arm Synthesis:

1,3-CHD + *sec*-BuLi/DABCO →PCHDLi (I)

(I) + Styrene → PCHD-PSLi (II)

(II) + 4-7 units 1,3-BD→ PCHD-PS-BDLi (III)

Styrene + *sec*-BuLi → PSLi (IV)

(IV) + DABCO + 1,3-CHD → PS-PCHDLi (V)

(V) + 4-7 units 1,3-BD→ PCHD-PS-BDLi (VI)

Three-armed Star Synthesis:

(excess) (III) + CH_3SiCl_3→ $(PCHD\text{-}PS)_3SiCH_3$ (3-arm PCHD-PS star)

(excess) (VI) + CH_3SiCl_3→ $(PS\text{-}PCHD)_3SiCH_3$ (3-arm PS-PCHD star)

Several star block copolymers with both PS and PCHD as the outer block were synthesized, and the molecular characteristics of the polymers are summarized in Table 2. Molecular weights determined by light scattering and by MALDI-TOF-MS are in excellent agreement with one another if one considers that the former value is a weight average and the latter is a number average molecular weight (M_n). Both SEC and the absolute methods confirm very narrow molecular weight distributions for the star-block materials. The initial steps for these syntheses involved the preparation of living block copolymers that could be linked to create the desired star-block copolymers. For the arms with PS as the outer block, the polymerization of 1,3-CHD using the living PS chain as initiator has proven to be feasible, and the details are given elsewhere.[22] The progress of the synthesis for one $(PS\text{-}PCHD)_3SiCH_3$, as monitored by SEC, is shown in Figure 4. The mono-modal nature of the PS block and PS-PCHD arm indicates their homogeneity. The small amount of coupled product seen in the chromatogram of the PS-PCHD arm is due to termination of the sample of this material with methanol in air. The linking reactions are very similar to those of the PCHD three-armed star as discussed above. The excess arm can be removed by solvent/non-solvent fractionation. However, if the targeted PCHD composition was too high, the monomer (1,3-CHD) was not consumed quickly.

Table 2. Star-Block Copolymer Characteristics

Polymer	First block		Block Copolymer			Wt %	Star-Block Copolymer		
	M_n[a] ×10^{-3}	M_w/M_n[b]	M_n[a] ×10^{-3}	M_w[c] ×10^{-3}	M_w/M_n[b]	PCHD[d]	M_w[c] ×10^{-3}	dn/dc[e]	M_w/M_n[b]
				Polystyrene as outer block					
KH5-057	9.8	1.02	14.8	15.7	1.03	26.8	46.2	0.160	1.04
KH5-062	2.3	1.08	15.5	15.7	1.08	80.4	47.3	0.136	1.04
KH5-067	5.6	1.04	13.9	15.3	1.06	54.0	43.9	0.148	1.05
				Poly(1,3-Cyclohexadiene) as outer block					
KH5-071	4.7	1.10	14.2	15.3	1.06	31.2	45.1	0.158	1.05
KH5-077	13.4	1.07	16.6	18.1	1.08	74.1	49.4	0.139	1.06
KH5-081	14.2	1.08	24.9	27.1	1.09	56.3	74.9	0.147	1.07

[a] From MALDI-TOF-MS. [b] Via SEC. [c] From SEC-MALLS. [d] Via ^{1}H-NMR; [e]: Unit: ml/g; and data calculated from the weight composition and the dn/dc data for PS and PCHD in $CHCl_3$ (0.172 and 0.125 ml/g, respectively)

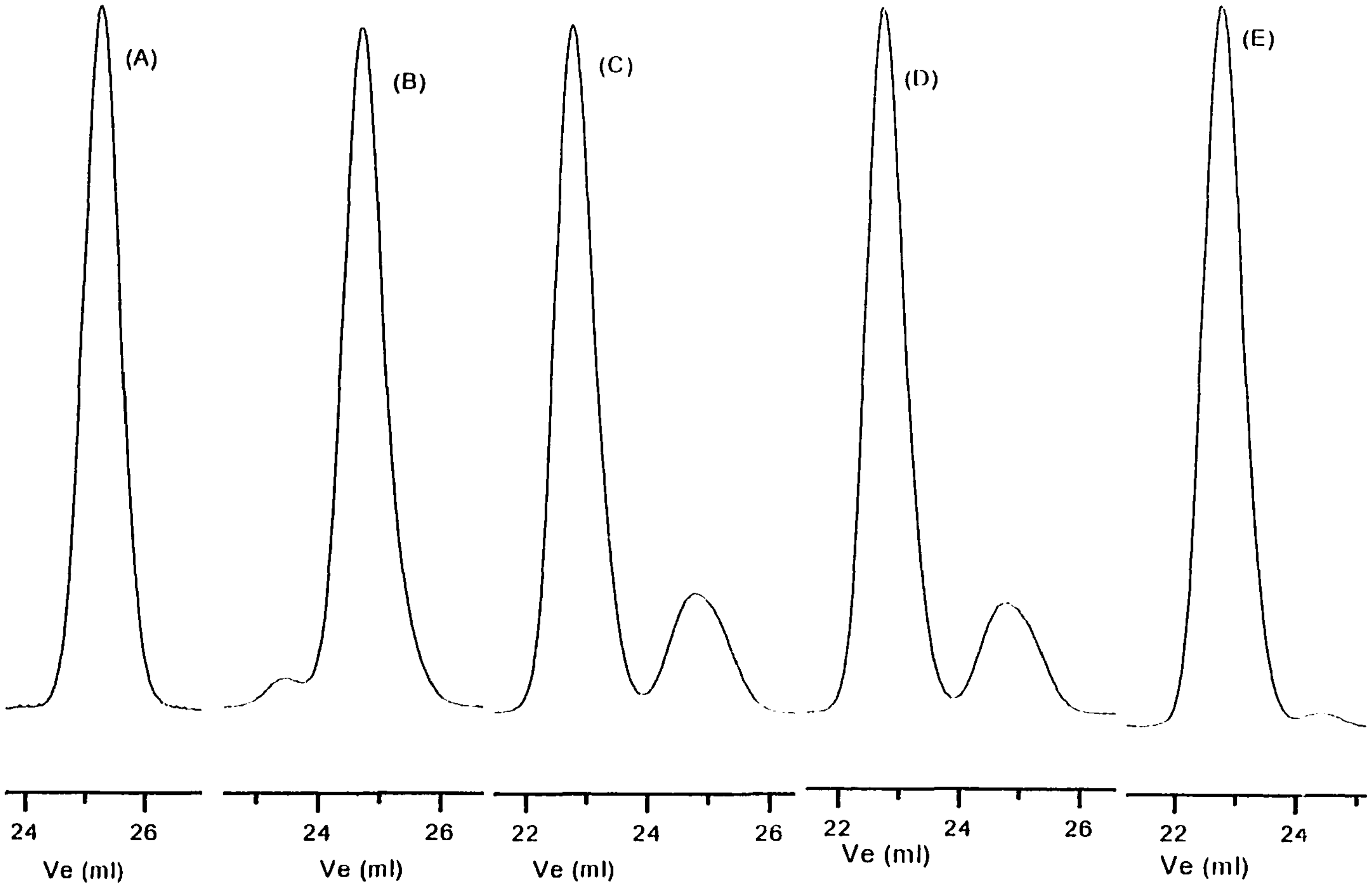

Figure 4. SEC traces of (A) PS segment of diblock arm; (B) PS-PCHD diblock arm; (C) first sampling (60 min); (D) unfractionated three-armed PS-PCHD star block copolymer; (E) fractionated star block copolymer (once).

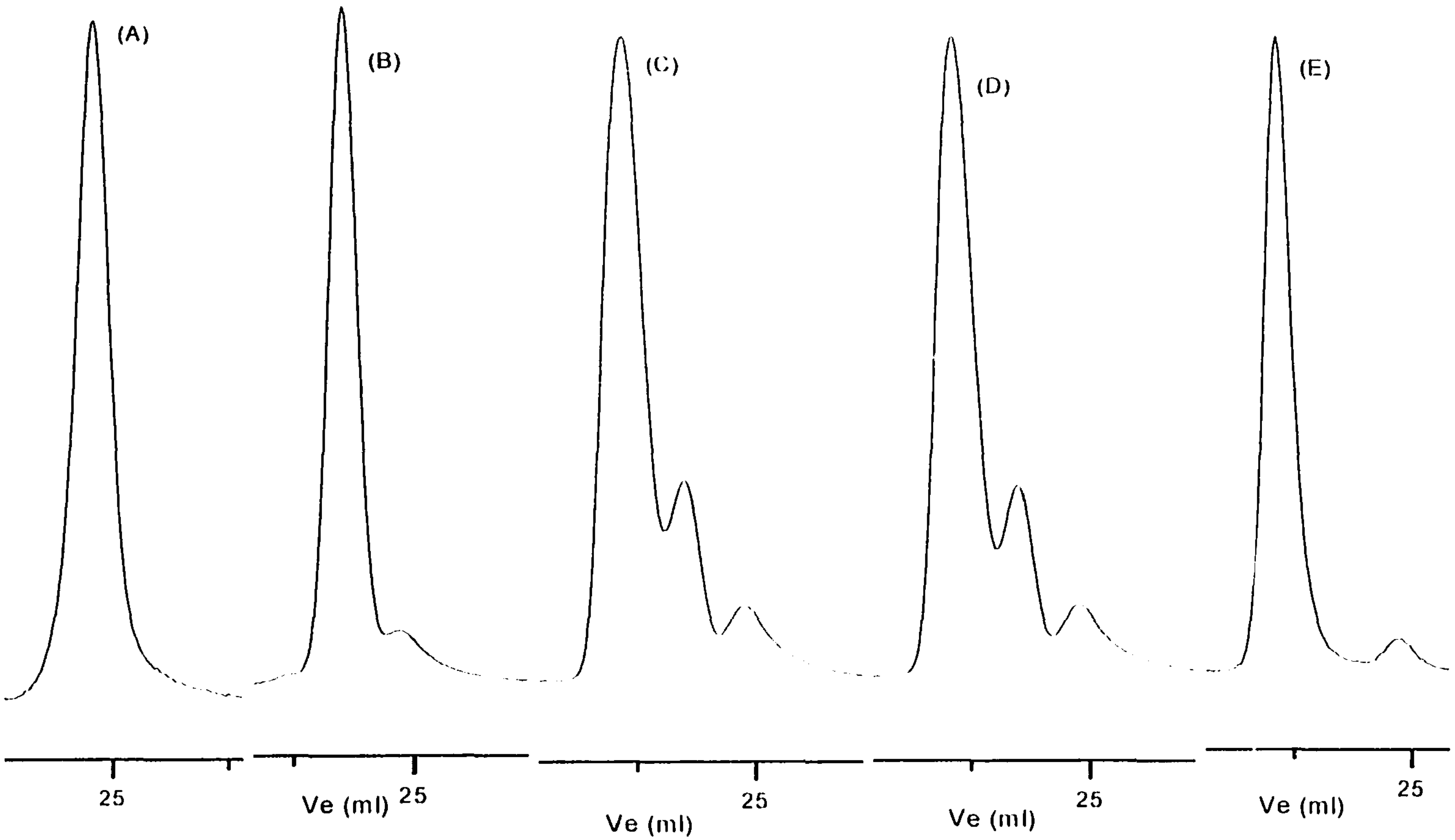

Figure 5. SEC traces of (A) PCHD segment of diblock arm; (B) PCHD-PS diblock arm; (C) first sampling (60 min); (D) unfractionated three-armed PCHD-PS star block copolymer; (E) star block copolymer fractionated (four times) .

quickly. Over time, a small portion of 1,3-CHD molecules may isomerize to its 1,4-isomer, which can terminate some of the living chains (PSLi). Such "dead polymer" can be removed easily by solvent/non-solvent fractionation.

The key to the synthesis of stars with PCHD as the outer block, $(PCHD\text{-}PS)_3SiCH_3$, is an efficient cross-over reaction from PCHDLi to PSLi. This reaction was previously demonstrated to be possible.[22] Figure 5 shows the SEC chromatograms of one of the $(PCHD\text{-}PS)_3SiCH_3$ (run 5 in Table 2). The PCHD block shows a symmetric peak, but the PCHD-PS arm has a small peak at the low molecular weight end, which corresponds to the PCHD block as shown in the Figure 5. There is no such problem when the molecular weight of the PCHD block is low (<10 kg/mol). This indicates that the crossover reaction from PCHDLi to styrene is not 100% complete when the PCHD block is very long. In this case, the cyclohexadiene polymerization takes longer to create high molecular weight PCHD, and during this time some PCHDLi can be terminated or undergo chain transfer. These transferred species are not reactive enough to initiate styrene. We also note that it is very difficult to remove this small peak by fractionation using toluene/methanol as the solvent/non-solvent. This may be because toluene is not a good solvent for PCHD of high molecular weight.

Conclusions

In conclusion, we have synthesized near-monodisperse three-armed PCHD, PCHD-PS, and PS-PCHD stars by linking the corresponding living chains with methyltrichlorosilane. The excess arm material, used to force the linking reaction to completion, can be readily removed by solvent/non-solvent fractionation for PS-PCHD stars and PCHD-PS stars with low PCHD content. Fractionation of the star PCHD homopolymers has proven to be difficult. In addition to their architectural asymmetries (star architecture), the PCHD chains are stiff, thus they also show conformational asymmetry.[23] These star block copolymers are expected to have interesting morphological properties, and these properties will be explored in future work.

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CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Conclusions

The polymerization of 1,3-CHD using the *n*-BuLi/DME/0 °C and *sec*-BuLi/DABCO/20 °C initiating systems in benzene can proceed in a controlled manner with regard to molecular weight and molecular weight distribution. Moreover, the different additives yield different microstructures in the final polymers (PCHD). However, well-defined, very high molecular weight PCHD materials remain elusive due to solubility problems. Without the use of additives, the polymerization of 1,3-CHD, even at low Molecular weights, is plagued by side reactions, such as chain transfer and/or chain termination.

Block copolymers of 1,3-CHD and styrene with a wide range of composition and moderate molecular weight may be synthesized by sequential addition of these monomers. The best block copolymers were obtained using the *n*-BuLi/DME and *sec*-BuLi/DABCO in benzene initiator systems. However, a low molecular weight shoulder was present in addition to the desired PS-PCHD peaks, as revealed by SEC. These low molecular weight peaks can be removed by solvent/non-solvent fractionation. PCHDLi living chains can initiate styrene and vice versa, even without the addition of polar additives. The copolymerization of 1,3-CHD and styrene using *sec*-BuLi in benzene appears to yield statistical copolymers. SEC-MALLS, NMR, and MALDI-TOF-MS were used to characterize the copolymers.

Three-armed PCHD star polymers were prepared by the reaction of PCHDLi and made using *sec*-BuLi/DABCO, with CH_3SiCl_3. The linking reactions were expedited by end-capping the PCHDLi chains with several units of 1,3-butadiene (1,3-BD). Star-block copolymers with PCHD-PS or PS-PCHD as the arms were prepared by the same methodology. After removing the excess arm materials by solvent/non-solvent fractionation, the stars exhibited narrow molecular weight distributions shown by SEC, and their molecular weights were characterized using SEC-MALLS.

Future Work

Compared to isoprene and 1,3-BD, the polymerization of 1,3-CHD and the properties and applications of PCHD-related polymers are largely unexplored. Thus, it is impractical to make very detailed suggestions about the future research concerning 1,3-CHD related polymers. However, based on our results so far the following work can be done, in order to elucidate the detail mechanisms of the polymerization of 1,3-CHD and to develop new materials based on PCHD: (i) Polymerization kinetics studies (partially done); (ii) Characterization of the chain stiffness PCHD polymer (partially done); (iii) Synthesis and polymerization of 5,5,6,6-tetramethyl-1,3-cyclohexadiene (the methyl groups would prevent some side reactions from occurring); (iv) Morphologies of PS-PCHD diblock copolymers (within a certain composition range, PS-PCHD copolymers form core-shell micro-phased separated morphologies (cylinder-in-cylinder morphology). If cleavable linkages were introduced between the PCHD and PS blocks, a route to novel nanotubes is possible. After crosslinking the shell (PCHD block), nano-tubes could be made if the core and the matrix (PS block) are removed after cleaving the bonds connecting the blocks (such as ester groups); (v) Solution properties of PS-PCHD block copolymers (micelles); (vii) Synthesis and characterization of copolymers with monomers other than styrene and/or more complex architectures containing PCHD blocks; (viii) Post-polymerization chemistries (a)ozonlysis for PCHD homopolymers, the ozonolysis products can be used to determine the monomer sequences; it is possible to make novel amphiphilic block copolymers from the ozonlysis of PS-PCHD; (b) hydrogenation of PCHD and its copolymers; (c) aromatization (to make rod-coil block copolymers, possible electro-optical devices based these new materials.

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Title of Dissertation Anionic Polymerization of 1,3-Cyclohexadiene

I certify that I have read this document and examined the student regarding its content. In my opinion, this dissertation conforms to acceptable standards of scholarly presentation and is adequate in scope and quality, and the attainments of this student are such that he may be recommended for the degree of Doctor of Philosophy.

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