

CONTROLLED ANIONIC SYNTHESIS OF FUNCTIONALIZED AND STAR-BRANCHED POLYMERS

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ABSTRACT

The use of living, alkyllithium-initiated anionic polymerization to prepare chain-end functionalized polymers and heteroarm, star-branched polymers is discussed. The scope and limitations of specific termination reactions with a variety of electrophilic species are illustrated for carbonation, hydroxyethylation, amination, and sulfonation. The methodology of using substituted 1,1-diphenylethylenes to provide a general, quantitative functionalization procedure is outlined and illustrated with examples of amine and phenol end-functionalization. A methodology is described for the synthesis of functionalized, star-branched copolymers with compositionally heterogeneous arms of controlled molecular weight and narrow molecular weight distribution using 1,3-bis(1-phenylethenyl) benzene.

INTRODUCTION

One of the goals of synthetic polymer chemistry is to develop methods for the preparation of polymers with control over the major variables affecting polymer properties. These variables include molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity and diene microstructure, chain-end and in-chain functionality, architecture and morphology. Anionic polymerization approaches this goal of synthesizing polymers with predictable, well-defined structures in monomer/initiator/solvent systems which proceed in the absence of chain termination and chain transfer reactions to produce polymers with controlled molecular weight and narrow molecular weight distribution^[1-6]. Under certain carefully controlled conditions, the living anionic polymerizations of styrene, diene, methacrylate, epoxide, and lactone monomers produce polymers which retain their reactive anionic chain-end functionality when all of the monomer has been consumed. In principle, these stable anionic chain ends can undergo controlled termination reactions with a variety of electrophilic reagents to generate a diverse array of functional end groups^[7]. In practice, however, many of the reported functionalization reactions have not been well-characterized^[2]. In the first part of this paper, we will review our recent work on the development of specific methods for the efficient introduction of chain-end functional groups using alkyllithium-initiated polymerization methods. In addition, we will describe the use of substituted 1,1-diphenylethylenes to provide a general, quantitative functionalization method, independent of the specific functional group.

Living polymer chains with stable carbanionic chain ends also react with polyfunctional linking reagents to generate star-branched polymers and copolymers as illustrated with silicon tetrachloride as the linking agent in eq. 1^[8-10]. The resulting homogeneous star-branched polymers can be



formed with arms characterized by well-defined, controlled molecular weights and narrow molecular weight distributions^[8, 9]. Unfortunately, these methods are not readily adaptable to the preparation of star-branched polymers in which the arms differ in either molecular weight or composition^[11]. In the second part of this paper we will describe a methodology for the synthesis of functionalized, star-branched polymers with compositionally heterogeneous arms of controlled molecular weight and narrow molecular weight distribution using 1,3-bis(1-phenylethenyl) benzene^[12, 13].

CHAIN-END FUNCTIONALIZED POLYMERS

One of the most useful and important characteristics of the anionic polymerization of styrene, diene and other vinyl monomers is the generation of polymers with stable carbanionic chain ends. Controlled termination with a variety of electrophilic reagents provides a methodology for the preparation of a diverse array of functional end groups. These end groups can undergo a variety of further reactions, including (a) chain extension, branching or crosslinking reactions with poly-functional reagents; (b) coupling and linking reactions with reactive groups on other oligomer or polymer chains; and (c) copolymerization or initiation with other monomers to form block copolymers. In order to exploit these reactions to their potential, procedures for quantitative chain-end functionalization must be available. Unfortunately, many reported functionalization reactions have not been well defined in terms of careful characterization of the functionalized polymers, side reactions, yields, and optimum experimental conditions^[2]. The following examples of functionalization reactions are taken primarily from results in our laboratories, but they can be regraded as typical of the state-of-the-art in this area.

Carbonation

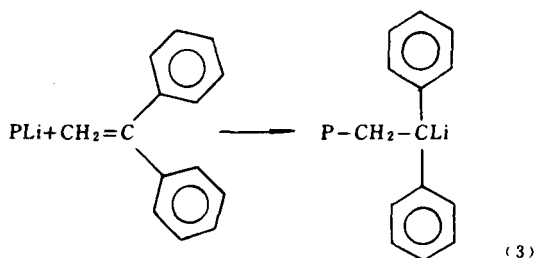
The carbonation of polymeric carbanions using carbon dioxide is one of the most useful and widely used functionalization reactions. We have reported the results of careful investigations of the carbonation reactions of polymeric organolithium compounds using gaseous carbon dioxide^[14, 15]. When these carbonations are carried out in benzene solution at room temperature, the carboxylated polymer is obtained in only 46 — 66% yields. The functionalized polymer is contaminated with dimeric ketone (25 — 30%) and trimeric alcohol (7 — 24%) as shown in eq. 2, where P represents a polymer chain. The dimeric ketone and the trimeric tertiary



alcohol functionalities were confirmed by careful fractionation (toluene/methanol mixtures) followed by infrared and UV-visible spectroscopic characterization of these components^[15]. It was proposed that these side-products are favored relative to the desired carboxylation by aggregation of the chain ends in hydrocarbon solution^[14]. For

example, poly (styryl) lithium is primarily associated into dimers in benzene while the degree of association of poly (dienyl) lithiums is at least dimeric^[2]. It is known that sufficient quantities of Lewis bases such as tetrahydrofuran (THF)^[2,16] and N, N, N', N'-tetramethylethylenediamine (TMEDA)^[2,17] can reduce or even eliminate the association of the chain ends. In accord with these considerations, it was found that addition of either large amounts of THF (25 vol%)^[14] or TMEDA (10-12 molar excess relative to [Li])^[15] were effective in favoring the carbonation reaction to the extent that the carboxylated polymer was obtained in >99% yields for poly (styryl) lithium and poly (isoprenyl) lithium. The actual mechanism of this reaction is complex since the product distribution is dependent on chain end concentration, solvent, temperature, the rate of stirring and the pressure of carbon dioxide^[15]. For example, increasing the chain end concentration or the rate of stirring increased the amount of dimer and trimer products compared to the carboxylated polymer. When the carbonation was carried out on solid living poly (styryl) lithium obtained by freeze-drying the corresponding benzene solution, the carboxylated polymer was obtained in >96% yields in the absence of Lewis base. Quantitative carboxylation was effected by carbonation of analogously freeze-dried poly (styryl) lithium which was complexed with two molar equivalents of TMEDA relative to the lithium chain end^[15].

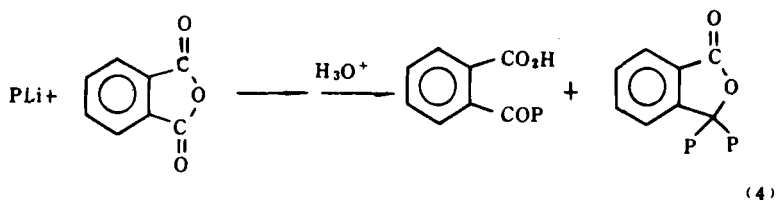
The effect of chain end structure (stability and steric requirements) has also been investigated. The steric and electronic nature of the anionic chain end can be modified by reaction with 1,1-diphenylethylene as shown in eq.3^[18]. When the direct carbonation of the resulting polymeric 1, 1-diphenylalkyllithium species is effected in benzene at



room temperature, the carboxylated polymer can be isolated in 98% yield compared to only 50—60% yields for both poly (styryl) lithium and poly (dienyl) lithiums under the same conditions. These 1, 1-diphenylalkyllithium species are reported to be associated into dimers in hydrocarbon solution^[19], although it would be anticipated that the strength of the association (e. g. K_{assoc}) would be decreased by the increased steric requirements of the chain end. We tentatively conclude that the competing reactions to form dimeric and trimeric side-products are quite sensitive to the steric requirements of the chain end.

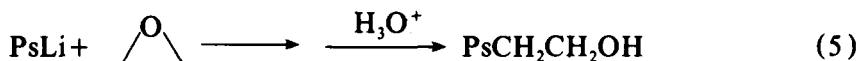
It has been reported that α,ω -disodiumpolystyrene can be functionalized using phthalic anhydride to form the corresponding aromatic carboxyl-functionalized polymer^[20]. When a similar reaction was attempted in our laboratories by addition of poly (styryl) lithium in benzene to a two-fold molar excess of phthalic anhydride in a THF/benzene mixture, the desired carboxyl-functionalized polymer was obtained in only 18% yield (eq.4). Quite surprisingly, the major product was the dimeric lactone (80% yield; ν [IR] = 1774cm^{-1}). In addition, an unidentified trimeric product was obtained in 2% yield. We are currently trying to optimize this functionalization reaction

by varying solvent, temperature, addition mode and the nature of the chain end.



Hydroxylation

In contrast to many other functionalization reactions, the preparation of hydroxyl-terminated polymers from polymeric organolithium compounds by reaction with ethylene oxide is a simple, efficient functionalization reaction. It also serves to emphasize some unique aspects of organolithium-initiated polymerizations. The direct reaction of poly(styryl)lithium with excess ethylene oxide in benzene solution produces the corresponding hydroxyethylated polymer in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks as shown in eq. 5^[21]. This result is surprising in view of the steric strain in ethylene oxide^[22] and the intrinsic

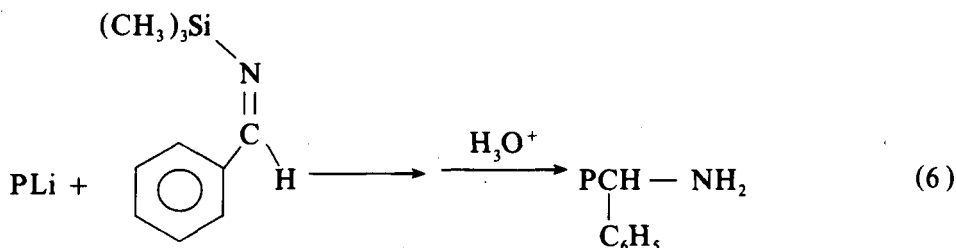


reactivity of ethylene oxide toward nucleophiles^[23, 24]. Among organoalkali compounds, organolithium compounds react the fastest with ethylene oxide^[25], however, the lithium alkoxides are the least reactive among the alkali metal alkoxides for anionic polymerization of ethylene oxide^[26-29]. Apparently the high degree of aggregation of lithium alkoxides and the strength of this association even in polar solvents renders them unreactive^[30]. It is also noteworthy that efficient functionalization of α, ω -dilithiumpolybutadiene in predominantly hydrocarbon media (some residual ether from the dilithium initiator preparation was present) has also been reported to produce the corresponding telechelic polybutadienes with hydroxyl functionalities (determined by infrared spectroscopy) of 2.0 ± 0.1 ^[31].

Amination

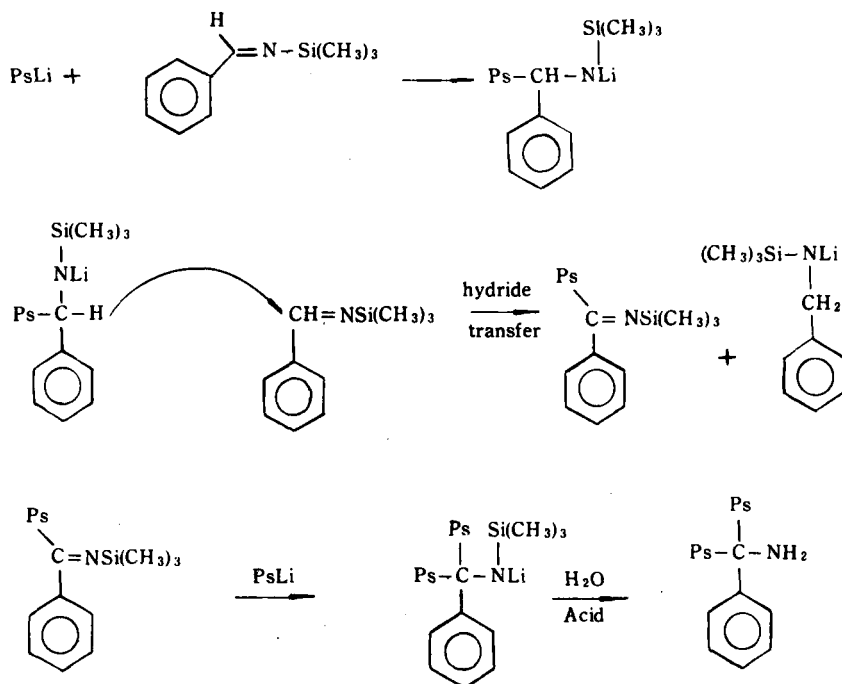
The primary amination of polymeric organolithium compounds is a challenge because of the acidity of nitrogen-hydrogen bonds^[32]. Thus, chain-end amination reactions require indirect methods such as the use of protecting groups^[33]. We have previously reported that poly(styryl)lithium and α, ω -dilithiumpolystyrene can be aminated in 92% and 80% yields, respectively, using the reagent generated from the reaction of methoxyamine and methylolithium at -78°C ^[34, 35], i. e. utilizing the procedure of Beak and Kokko^[36]. Because this reaction requires the use of low temperatures for generation of the aminating agent in the presence of the polymeric organolithium compound, we were intrigued by the reports of Nakahama and coworkers^[37, 38] that high yields (96 — 100%) of primary amine-functionalized polymers could be obtained using the protected imine, *N*-(benzylidene)trimethylsilylamine, in benzene at room temperature (eq. 6).

Attempts to repeat these results in our laboratories with poly(styryl)lithium failed. The aminated polystyrene was contaminated with 15 — 19% of a dimeric product. In fact, the aminated polystyrene was obtained in only 69% yield for poly(styryl)



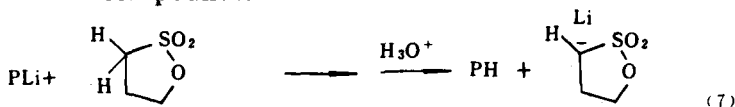
lithium with $M_n = 3 \times 10^3$ g/mol. It is proposed that the dimeric side reaction product results from a Cannizzaro-type reaction (Scheme 1) as previously identified for corresponding benzaldehyde functionalization reactions^[39].

Scheme 1

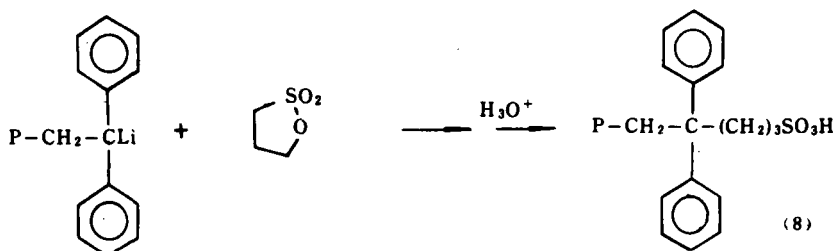


Sulfonation

It has been reported that chain-end sulfonated polymers can be obtained in high yield from polymeric organolithium compounds by functionalization with sultones such as propane sultone^[40]. However, a recent report by Omeis, Muhleisen and Moller^[41] indicates that direct sultone functionalization reactions produce the corresponding sulfonated polymer in only about 70% yield. We have independently examined this functionalization reaction and have found that under optimized experimental conditions the functionalized polymer can only be obtained in about 55% yield. The major side reaction is apparently metalation of the acidic α -methylene hydrogens adjacent to the sulfonate group (eq.7) as documented by Durst and Manoir^[42] for simple organolithium compounds.



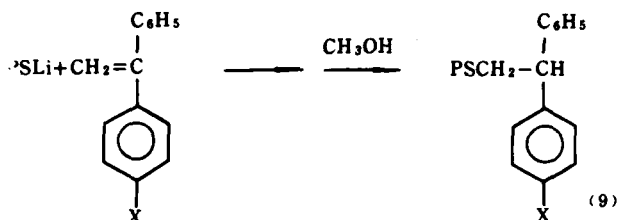
In order to optimize this functionalization reaction we have examined the effect of reducing the reactivity of the chain end by converting it to the corresponding diphenylalkyllithium derivative by reaction of the polymeric organolithium compound with 1, 1-diphenylethylene (eq.2) prior to reaction with the sulfone. Using this procedure, the corresponding pure, sulfonated polymer could be isolated in >95% yield as shown in eq.8.



This overview has described results which are typical of the types of problems which are encountered in developing specific methods for preparation of functionalized polymers with a variety of electrophilic species. Our ability to prepare chain-end functionalized or labelled polymers is not limited by the range of potential and reported functionalization and labelling reactions for living carbanionic chain ends^[7, 43]. However, it is limited by the fact that many of the reported functionalization reactions have not been adequately characterized^[12]. Another limitation is the necessity of developing, optimizing and characterizing new reactions for each different functional group as illustrated by the previous discussion. Because of these limitations, we embarked recently on a search for general, quantitative functionalization reactions. We have explored the use of the addition reactions of polymeric organolithium compounds to 1,1-diphenylethylene derivatives as a general functionalization method, independent of the nature of the functional group.

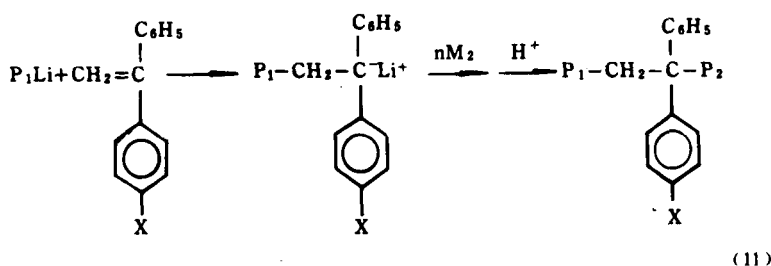
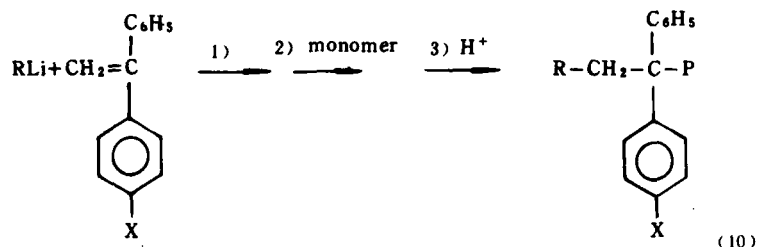
1, 1-Diphenylethylene Functionalization Reactions

The reaction of polymeric organolithium compounds with substituted 1,1-diphenylethylene derivatives is an excellent system for development of a general functionalization reaction (eq.9) because (a) these addition reactions are simple and quantitative; (b) only monoaddition, i. e. no oligomerization, has been reported; (c) the rate and efficiency of the crossover reaction can be monitored by ultraviolet-visible



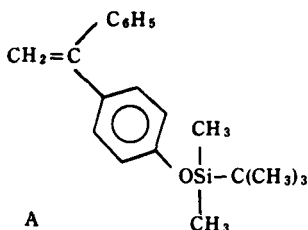
spectroscopy; and (d) a variety of substituted 1, 1-diphenylethylenes with functional groups on the aromatic ring can be prepared readily^[3, 5, 43-47]. The 1, 1-diphenylethylene system offers the added advantage that it can be used to prepare polymers with functional groups at the initiating end of the polymer chain (see eq. 10) or within the polymer chain (see eq.11), in addition to the terminating end of the polymer chain as described in eq.9. Thus, it offers the potential of providing a versatile, general

functionalization procedure. This ability to rationally design and place functional groups at essentially any position in the polymer molecule is a consequence of the fact that, unlike most electrophilic functionalization reactions, this reaction is not in itself a termination reaction. The product of the addition reaction of a simple or polymeric organolithium compound to a substituted 1, 1-diphenylethylene is a carbanionic



(see eq.2) which can initiate anionic polymerization of additional monomer to extend the chain or form a new block^[48]. Thus, this procedure can be described as a *living functionalization reaction*.

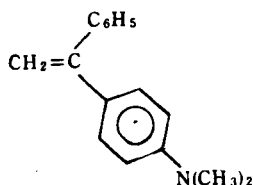
For most of the functional groups of interest such as hydroxyl, carboxyl and primary amine, conversion of the functional group to a protected form is required to prevent side reactions from occurring during the addition reaction to the 1, 1-diphenylethylene unit. Such is the case for the phenol functionality, which was chosen as our initial synthetic target functionality to illustrate the utility of this new functionalization method^[49]. The *tert*-butyldimethylsilyl-protecting group was chosen for the aromatic hydroxyl group based on the results reported by Nakahama and coworkers^[50, 51]. Poly(styryl) lithiums with $M_n = 1.5 \times 10^3$ to 13.1×10^3 g/mol were functionalized with 1-(4-*tert*-butyldimethylsiloxyphenyl)-1-phenylethylene (A) to form



the corresponding phenol-end-functionalized polystyrenes in >99% yield after hydrolysis with 1% HCl in tetrahydrofuran. The efficiency of these functionalization reactions was evaluated by end-group titration, elemental analyses, ¹H NMR and ¹³C NMR analyses, as well as thin-layer chromatography. All of the available evidence suggests that this is an essentially quantitative functionalization reaction. It is noteworthy

that Heitz and Hocker^[52] have carried out similar conversions using 1, 1-(4, 4'-dimethoxyphenyl)ethylene.

We have also investigated the use of 1-(4-dimethylaminophenyl)-1-phenylethylene (**B**) to prepare amine-terminated polymers. This substituted diphenylethylene was readily prepared from the corresponding benzophenone derivative via the Wittig reaction.

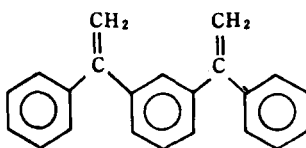
**B**

The reaction of poly(styryl)lithiums ($M_n = 3.1 \times 10^3$ and 4.2×10^3 g/mol) in benzene solution with **B** could be monitored by ultraviolet-visible spectroscopy at 406nm. Analyses of these functionalization reactions indicates that the amine-terminated polymers are obtained in >95% yields.

These results suggest that the addition reaction of polymeric organolithium compounds to substituted 1, 1-diarylethylene derivatives can provide a general method for the synthesis of functionalized and labelled polymers. We are currently investigating the scope and limitations of this functionalization methodology. It is anticipated that with appropriate protecting groups and reaction conditions, a wide variety of well-characterized, quantitatively functionalized and labelled polymers and copolymers can now be systematically prepared.

HETEROARM, STAR-BRANCHED POLYMER SYNTHESSES

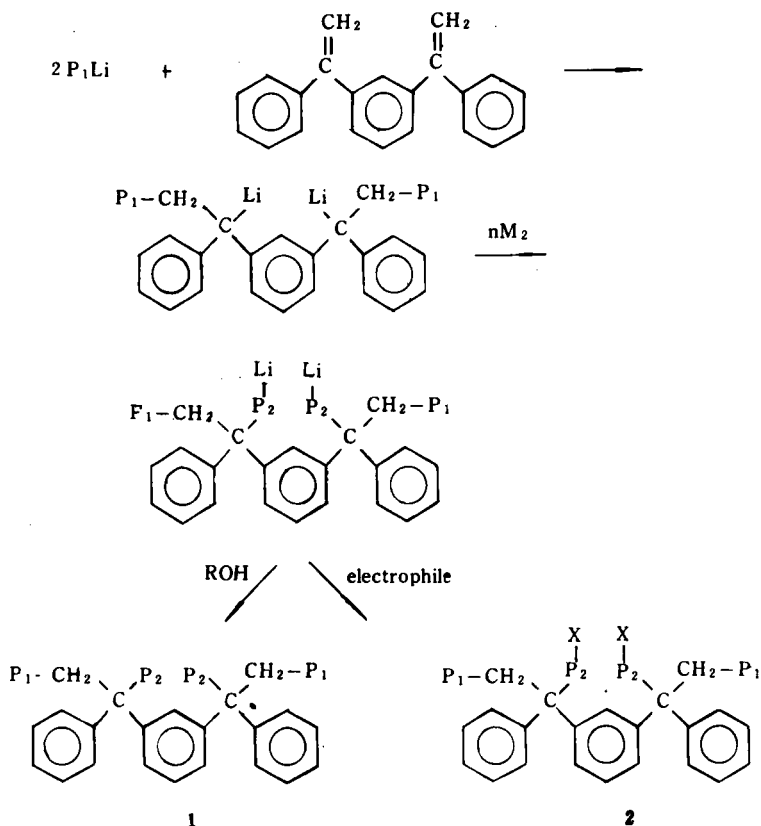
A previous report has described preliminary results from a study of the use of 1,3-bis(1-phenylvinyl)benzene (MDDPE) as a living coupling agent for the synthesis of star-branched copolymers with compositionally heterogeneous arms^[12].

**MDDPE**

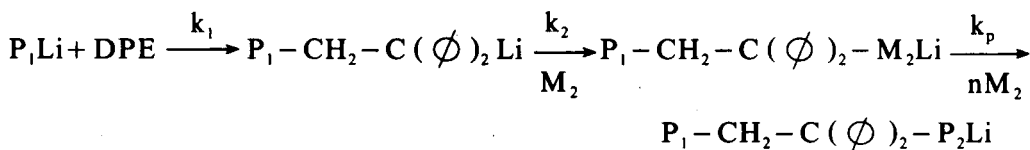
A general scheme for heteroarm, star-branched copolymer (**1**) synthesis is shown in Scheme 2. This scheme also illustrates the versatility of this synthetic methodology, since the product of the reaction retains the active carbanionic centers and can be functionalized with an electrophilic species to form a star-branched copolymer with two functionalized chain ends (**2**).

We have carried out a detailed investigation of the scope and limitations of the use of MDDPE as a carbanionic coupling agent for polymeric organolithium compounds to form heteroarm, star-branched copolymers^[13]. In addition, the reaction of polymeric organolithium compounds with 1, 1-diphenylethylene (DPE) and the crossover reaction of the resulting polymeric diphenylalkyllithium species with monomers has been investigated as shown in Scheme 3. The effects of solvent, temperature, concentration and molecular weight have been studied to find the optimum conditions for these

Scheme 2



Scheme 3



reactions. The addition of poly(styryl)lithium to 1,1-diphenylethylene (or MDDPE) and subsequent crossover reactions with styrene monomer can be followed by UV-visible spectroscopy, since poly(styryl)lithium and diphenylalkyllithiums exhibit absorption maxima in benzene at 335nm ($\epsilon = 1.3 \times 10^3$)^[53] and 440nm ($\epsilon = 1.6 \times 10^4$)^[45], respectively. The visible absorption for the MDDPE living coupled adduct exhibits an absorption maxima at 438nm ($\epsilon = 21,000$) in benzene^[12]. We have measured the rate constants k_1 and k_2 at 25 °C and the results agree with literature values^[45, 54]. Of critical importance for the synthesis of heteroarm star-branched block copolymers was the determination of reaction conditions which would accelerate the rate of crossover (k_2) relative to the rate of propagation (k_p) as described by the relative rate ratio, k_2/k_p (R). The values of R for crossover to styrene monomer in benzene were 0.07 and 0.10 at 25 °C and 5 °C, respectively. The analogous value of R at 25 °C in cyclohexane was 0.12. Using the molecular weight distribution as an experimental criterion for R it was found that the narrowest molecular weight distributions for the polymers obtained by

crossover experiments of polymeric diphenylalkyllithiums with styrene were obtained at 5 °C (versus 25 or 45 °C), in cyclohexane (*versus benzene*), and at higher chain-end concentrations (10^{-2} versus 10^{-3} M).

The coupling of poly(styryl)lithium of various molecular weights with purified, crystalline MDDPE in benzene is a very efficient reaction when the stoichiometry of the reaction is carefully controlled by determining the exact chain end concentration by titration^[13] and by weighing the required amount of MDDPE using an analytical balance in an argon atmosphere dry box^[55]. Essentially complete coupling (>99%) can be effected as monitored by SEC. However, the crossover reaction of the resulting coupled product with styrene monomer to form a heteroarm star-branched polymer of ten produced a polymeric product which was contaminated with a very high molecular weight shoulder^[13]. After extensive investigations, it has been concluded that the high molecular weight contaminant results from inexact stoichiometric control in the coupling reaction, i. e. an excess of MDDPE. Unreacted MDDPE or half-coupled polymer would be expected to react with the growing difunctional, living heteroarm star to produce polymer with functionality greater than two and with molecular weights corresponding to 1.5 or 2 times the molecular weight of the expected 4-armed star. ¹³C-NMR analyses confirms the presence of unreacted double bonds in those coupled polymers which exhibit high molecular weight peak contaminants in the stars. A deficiency of MDDPE results in an unsymmetrical peak since uncoupled poly(styryl)lithium produces a low molecular weight tail compared to the dicarbanionic star^[13]. When the stoichiometry is carefully controlled, a monomodal polymeric product is obtained; however, the molecular weight distribution is often broadened ($M_w/M_n = 1.15$) relative to that of the coupled product before crossover ($M_w/M_n = 1.04$)^[13]. Narrower molecular weight distribution stars were obtained when synthesized in cyclohexane *versus benzene* and also when the arm molecular weights resulting from the crossover reaction are larger^[13]. Preliminary results indicate that polystyrene heteroarm star-branched polymers synthesized in cyclohexane with a small amount of added tetrahydrofuran have even narrower molecular weight distributions ($M_w/M_n = 1.02 - 1.03$).

We are currently characterizing these heteroarm star-branched polymers and examining their properties. In addition we are synthesizing star-branched, block copolymers with polystyrene (PS) and polybutadiene (PBD) arms [(PS)₂MDDPE (PBD)₂] and these results will be reported in a full paper of our studies.

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