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Controlled Anionic Synthesis of Polyisoprene−Poly(2-vinylpyridine) Diblock Copolymers in Hydrocarbon Solution

Roderic P. Quirk* and Sergio Corona-Galvan[†]

The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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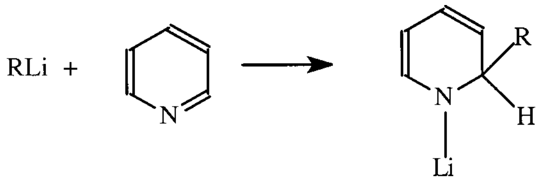
ABSTRACT: Well-defined diblock copolymers of isoprene and 2-vinylpyridine (2VP) were prepared by sequential anionic polymerization at temperatures of 45 and 6−8 °C, respectively, in benzene solution using *sec*-BuLi as initiator in the presence of lithium chloride ([LiCl]/[PLi] = 5−11). Rapid quenching with acidic methanol 4−7 min after 2VP addition was required to obtain controlled polymerization. The polyisoprene-*block*-poly(2-vinylpyridine) diblock copolymers with high 1,4-polyisoprene microstructure exhibited narrow molecular weight distributions [M_w/M_n(SEC) = 1.01−1.06] and molecular weights (light scattering, universal calibration) that were in good agreement with calculated values. Molecular weights (M_n) determined by SEC with polyisoprene standards were much lower than calculated values.

Introduction

Block copolymers possess many interesting and useful properties in solution and in the solid state as a consequence of the incompatibility of the constituent blocks which results in microphase separation into distinct, composition-dependent domains.[1−4] Among the different methods developed to synthesize block copolymers, living anionic polymerization provides one of the best methods for the synthesis of block copolymers with well-defined structures.[2,3,5−8] Because of the living nature of this methodology, block copolymers with low degrees of compositional heterogeneity, predictable molecular weights, and narrow molecular weight distributions can be prepared by sequential monomer addition. Block copolymers of 1,3-dienes and styrene monomers can be prepared anionically without the incursion of termination and chain transfer reactions.[7−9] Although some undesirable reactions can occur with certain polar monomers, even these monomers can be used to prepare the last block in a sequence.[3]

The preparation of well-defined, amphiphilic block copolymers comprised of both polar and nonpolar monomers is of considerable current interest because of the unique properties and applications of this type of polymer. However, the incursion of side reactions for the polymerization of many polar vinyl monomers, especially the acrylates and vinylpyridines, has generally required the use of low temperatures (e.g., −78 °C) and polar solvents [e.g., tetrahydrofuran (THF)] for controlled synthesis.[8] In addition, Teyssie and coworkers[10,11] have demonstrated that the addition of lithium chloride promotes the controlled anionic polymerization of alkyl methacrylates and even *tert*-butyl acrylate under these conditions. Using these optimized conditions and dropwise addition of 2-vinylpyridine, Rempp et al.[12] synthesized block copolymers of 2-vinylpyridine with *tert*-butyl acrylate using 1,1-diphenyl-3-methylpentyllithium as initiator in the presence of lithium chloride in tetrahydrofuran at −60 °C. It was reported that the molecular weight was in fair agreement with the calculated value and that the molecular weight distribution was narrow (M_w/M_n = 1.07). It has been shown that lithium chloride cross-associates with the active ester enolate chain ends and that the resulting cross-associated aggregates are in rapid equilibrium.[13] It is noteworthy that in the absence of lithium chloride controlled polymerization of 2-vinylpyridine required the use of very low temperature (−90 °C) and slow addition of a dilute solution of monomer.[14] It was noted by these authors that the polymerization of 2-vinylpyridine is so fast ($k_p \approx 2100$ L mol^{-1} s^{-1})[15] that the polymerization can be considered to be instantaneous.

An unrealized goal has been to develop methodologies for the preparation of block copolymers of styrenes and 1,3-dienes with 2-vinylpyridine under conditions that are optimum for living anionic syntheses of well-defined polystyrenes and high 1,4-polydienes, i.e., using alkyllithium initiators in hydrocarbon solvents.[7−9] However, in hydrocarbon solutions and when the temperature is not low (<−60 °C), uncontrolled polymerization of 2-vinylpyridine has been reported. For example, Fetters and co-workers[16] reported that star-branched polymers with broad polydispersities were obtained in 29−73% yields by addition of 2-vinylpyridine (2VP) to poly(butadienyl)lithium ([2VP]/[Li] = 1.2−8) in toluene at 25−60 °C. Addition of THF ([THF]/[Li] = 1) did not dramatically affect the amount of star formation. The observed branching reactions were ascribed to the well-known susceptibility of pyridine rings to nucleophilic addition of organolithium compounds (eq 1).[17−19] With respect to the chain-end stability of poly(vinylpyridyl)lithium (P2VPLi) chain ends, Krasnoselskaya and Erussalimsky[20,21] reported a 2-fold increase in viscometric molecular weight of solutions of P2VPLi upon standing at −20 °C in toluene after a period of only minutes; no dimerization was observed upon storage at −50 °C in toluene.



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[†] Present address: Dynasol Elastomeros S. A. de C. V., Carretera Tampico-Mante, Km. 28.5, Altamira, Tamaulipas, 89600 Mexico.

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Biggs and Vincent[22] used sequential anionic polymerization to prepare diblock copolymers of styrene and 2-vinylpyridine (dilute solution of VP added dropwise over a period of 2 h at 0 °C) in benzene. The authors concluded that the relatively broad molecular weight distributions ($M_w/M_n = 1.15-1.25$) were due to the high reactivity of 2-vinylpyridine.

As part of a recent kinetic study by Fontanille and co-workers,[23] it was reported that poly(2-vinylpyridines) with relatively narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) and number-average molecular weights in good agreement with calculated values were obtained by initiation with 1,1-diphenyl-3,3-dimethylbutyllithium in toluene at −20 to 20 °C; these results were obtained using a calorimetric system, and the half-lives for reaction ranged from 2 to 25 s. The ion pair propagation rate constant at 20 °C was reported to be 641 L mol^{-1} s^{-1}.

Watanabe and Tirrell[24] used a complicated method to prepare polyisoprene-*block*-poly(2-vinylpyridine) that involved polymerization of isoprene with *sec*-butyllithium as initiator in *n*-heptane, changing the solvent to tetrahydrofuran/heptane (90/10, vol/vol) and then lowering the temperature (−78 °C) to polymerize 2-vinylpyridine. The resulting diblock copolymers exhibited the desired high 1,4-polyisoprene microstructure; however, even using low temperatures and THF as solvent, the molecular weight distributions of the PI-*b*-P2VP copolymers were somewhat broad ($M_w/M_n = 1.12-1.18$).

The major shortcomings of the previously described methods to prepare well-defined poly(2-vinylpyridine) block copolymers are the requisite use of low reaction temperatures (−60 °C or lower) and the use of polar solvents that will produce polydienes with high vinyl contents. No satisfactory polydiene-*block*-poly(2-vinylpyridine) synthesis has been reported in hydrocarbon media. However, the somewhat controlled polymerizations reported both by Fontanille and co-workers[23] in toluene and by Biggs and Vincent[22] in benzene, the potential ability of lithium chloride to reduce the reactivity of the chain ends,[25] and the limited stability of the poly(vinylpyridinyl)lithium chain ends in hydrocarbon media[20,21] suggested that it might be possible to prepare polyisoprene-*block*-poly(2-vinylpyridines) with well-defined structures in hydrocarbon media in the presence of lithium chloride; however, it would be necessary to terminate the polymerizations rapidly after monomer consumption. Herein are reported the results of an investigation of these procedures for preparation of polyisoprene-*block*-poly(2-vinylpyridine).

Experimental Section

Materials. 2-Vinylpyridine (Aldrich, 97%) was initially stirred over freshly crushed CaH_2 for 48 h. After degassing, it was transferred by vacuum distillation onto fresh CaH_2 (two times), stirred for a few hours, and finally distilled into calibrated ampules that were heat-sealed with a hand torch and stored at −78 °C until used. Isoprene (Kodak) was stirred over freshly crushed CaH_2 for 24 h, transferred by vacuum distillation into a clean flask that contained 1,10-phenanthroline (Aldrich) that had been titrated with dibutylmagnesium[26] under an argon atmosphere, and then distilled into calibrated ampules shortly before use. Benzene was first stirred over H_2SO_4 and washed with water, and after being stored over anhydrous magnesium sulfate the same procedure described for isoprene was applied. From this storage flask containing the 1,10-phenanthroline indicator, the benzene was vacuum-distilled into the polymerization reactor as required. *sec*-Butyllithium (FMC, Lithium Division, 1.46 M) after double titration with 1,2-dibromoethane,[27] lithium chloride (Aldrich, 99.99+%), 2,6-di-*tert*-butyl-4-methylphenol (BHT, Aldrich, 99+%), and dibutylmagnesium (Aldrich, 1.0 M in heptane) were used as supplied.

Table 1. Experimental Parameters and Percentages of Dimer Formation for Synthesis of PI-*b*-P2VP Block Polymers

sample	[LiCl]/[RLi]	reaction time[a] (min)	dimer (wt %)[b]
1	2.07	38	31.9
2	3.59	2	13.0
3	3.36	1	9.1
4	5.48	4	0
5	4.67	4	0
6	10.96	7	0

[a] Reaction time for 2-vinylpyridine polymerization. [b] Dimer formation was calculated by cutting and weighing the peak corresponding to the base polymer and the peak corresponding to dimer in the SEC RI chromatograms.

Procedures. Polymerizations were carried out in all-glass, sealed reactors using standard high-vacuum procedures.[28] After being rigorously cleaned and annealed, a reactor equipped with the monomer and methanol ampules was attached to the vacuum line. The synthesis procedure for sample 4 in Tables 1 and 2 was as follows. Dry lithium chloride (0.0305 g, 0.72 mmol) was introduced by a lateral tube, and the reactor was then subjected to several vacuum-argon-heating (with yellow hand-torch flame) cycles in order to remove moisture from the system. *sec*-Butyllithium (0.131 mmol) was then introduced under an argon atmosphere, and after cooling to −78 °C, the lateral tube was sealed with a hand torch and 250 mL of benzene (10/1 solvent/monomer, vol/vol) was distilled into the reactor. After being detached from the vacuum line by heat-sealing with a hand torch, the reactor was placed in a water bath (40−45 °C), and the isoprene (17.3 mL) was added by smashing the break-seal of the isoprene ampule under efficient stirring. This polymerization was left overnight, after which a small sample was removed via an ampule, deactivated with methanol, and used to characterize the polyisoprene base polymer.

To the remaining poly(isoprenyl)lithium solution, undiluted 2-vinylpyridine (6.8 mL, 6.6 g) was added rapidly under very efficient stirring and controlled temperature (6−8 °C). The solution turned deep red almost instantaneously, indicative of formation of poly(2-vinylpyridinyl)lithium. The reaction was allowed to proceed for only 4 min and then was rapidly deactivated by adding acidic methanol (acetic acid/methanol, 1/10, vol/vol). The base polymer and the block copolymer solutions were treated with BHT (0.2 wt %) filtered to remove the lithium chloride, precipitated into methanol, reprecipitated into methanol, stirred in methanol for several hours, and then vacuum-dried.

Characterization. SEC analyses of the polymers were performed at a flow rate of 0.4 mL/min in THF at 30 °C using a Waters 501 system equipped with RI and UV detectors and Phenogel columns (Phenomenex Co.) (two 500, two 10^3, 10^4, and 10^5 Å) after calibration with polyisoprene standards.

The refractive index increments ($d\tilde{n}/dc$) were calculated at 30 °C using a KMX-16 laser differential refractometer. The light source was a 0.5 mW He−Ne laser operating at 633 nm. Solvent (THF) and polymer solutions were carefully weighed and filtered before each measurement. The values of $d\tilde{n}/dc$ were 0.154, 0.152, and 0.168 cm^3/g for samples 4, 5, and 6, respectively (see Table 2).

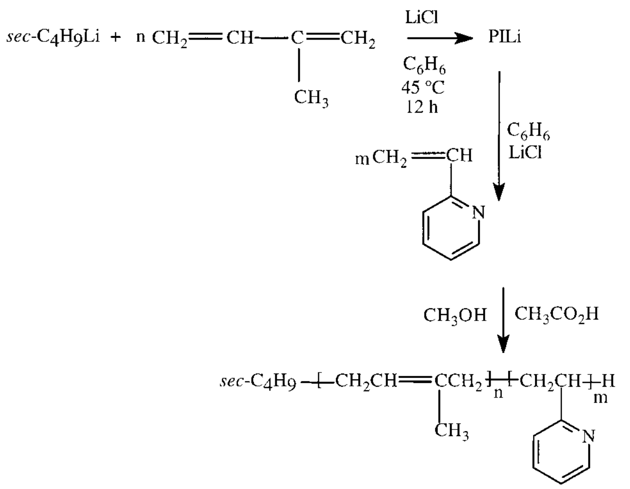
The weight-average molecular weights, M_w, were determined using a SEC (Waters 150 CV/viscometer) equipped with an in-line DAWN-F multiangle laser light scattering (MALLS) detector from Wyatt Technology Co. The SEC was equipped with four Ultrastyragel columns (10^6, 10^5, 10^4, and 10^3 Å). The elution solvent was THF, and all experiments were carried out at 30 °C. Data processing and acquisition were performed on a PC station using DAWN-astra software supplied by Wyatt Technology.

Table 2. Characterization Data for PI-*b*-P2VP Block Polymers[a]

	$M_n \times 10^{-3}$ (g/mol)					
sample	calc[c]	SEC[d]	UC[e]	M_w(LS)[b] × 10^{-3} (g/mol)	M_w/M_n (SEC)	η (dL/g)
1	40.5 (31.1)	− (36.4)			− (1.01)	
2	51.3 (37.3)	− (41.2)		59.5	− (1.02)	
3	90.6 (68.9)	− (78.9)			− (1.01)	
4	140 (90.1)	108 (95.3)	101	139	1.05 (1.05)	0.754
5	224.0 (126)	148 (132)	198 (135)	244 (154)	1.06 (1.04)	1.25 (1.05)
6	206.5 (120.8)	135 (122)	170	221	1.05 (1.05)	1.08

[a] Numbers in parentheses refer to the polyisoprene base polymer. [b] Molecular weight determined using an SEC equipped with MALLS detector. [c] Number-average molecular weight calculated based on the ratio of grams of monomer to moles of initiator. [d] Molecular weight determined by SEC with polyisoprene standards. [e] Molecular weight determined using the universal calibration method.[36]

Scheme 1



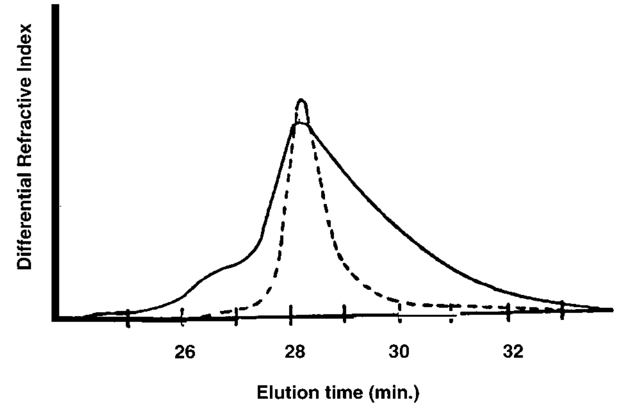


Figure 1. SEC-RI traces of polyisoprene (broken line) and poly[isoprene-*b*-(2-vinylpyridine)] block copolymer obtained in the absence of LiCl at 0 °C. The 2VP polymerization time was 19.8 h.

^{1}H NMR analyses of polymers were made using a Varian Gemini 200 NMR spectrometer at room temperature, using deuterated chloroform (Aldrich, 99.8% D) as solvent.

Intrinsic viscosity measurements were performed in an Ubbelohde viscometer using THF as the solvent. The viscometer was placed in a thermostated water bath at 30 °C. All samples were measured at four different concentrations by the dilution method, and plots of (η_{sp}/c) vs c were extrapolated to zero concentration to obtain the intrinsic viscosity [η].

Results and Discussion

As described in the Introduction, procedures were sought for the block copolymerization of isoprene and 2-vinylpyridine in hydrocarbon solution at reasonable temperatures (≥0 °C) using alkyllithium initiators. On the basis of information available from previous studies,[22,23] it was envisioned that such controlled block copolymerizations could be effected by sequential monomer addition in hydrocarbon solution by optimization of the variables of temperature, amount of added lithium chloride, reaction time for 2VP polymerization, and termination procedure. The general synthetic methodology is outlined in Scheme 1. It is noteworthy that all block copolymerizations were terminated rapidly by addition of a mixture of acetic acid in methanol (1/10, vol/vol).

The reaction of poly(isoprenyl)lithium (M_n = 48 000 g/mol; M_w/M_n = 1.04) with 2-vinylpyridine [M_n(calc) = 8600 g/mol] was first investigated in benzene at 0 °C, and the results of SEC analyses of the block copolymerization are shown in Figure 1. It is noteworthy that the polyisoprene block exhibited the desired high 1,4 microstructure (92.6% 1,4) as expected for diene polymerization in hydrocarbon solution with lithium as counterion.[8,9] The SEC chromatograms in Figure 1 indicate that although the molecular weight distribution of the polyisoprene block was narrow, the chromatogram of the product of the block copolymerization indicates that higher molecular weight products are formed in addition to lower molecular weight fractions, resulting in a very broad, ill-defined product. The formation of higher molecular weight, presumably branched, polymer products is consistent with the observations of Fetters and co-workers[16] as well as Krasnoselskaya and Erussalimsky.[20,21] As discussed in the Introduction, branching reactions are ascribed to the well-known susceptibility of pyridine rings to nucleophilic addition of organolithium compounds (see eq 1).[17−19] The formation of lower molecular weight products can be rationalized in terms of metalation−cleavage (fragmentation) reactions sequences as shown in Scheme 2.[29]

In view of the dramatic effects of added lithium chloride in THF at low temperatures for controlled polymerizations of acrylates, methacrylates,[10,11] and 2-vinylpyridine,[12] it was envisioned that lithium chloride could also help to promote the controlled polymerization of 2-vinylpyridine in hydrocarbon solution. Therefore, the block copolymerization of poly(isoprenyl)lithium [M_n(calc) = 39 300 g/mol)] with 2-vinylpyridine [M_n(calc) = 7400 g/mol)] was effected at 5 °C in benzene in the presence of lithium chloride ([LiCl]/*sec*-BuLi] = 1.4) and quenched after 21.5 h. The SEC chromatograms of the polyisoprene base polymer and the corresponding block copolymer product are shown in Figure 2. A more controlled polymerization resulted from block copolymerization of 2-vinylpyridine in the presence of lithium chloride. Only small amounts of low molecular weight fragmentation products are observed, and the only side reaction appears to be the formation of dimer. In addition, the presence of lithium chloride during the isoprene polymerization did not affect the diene stere-

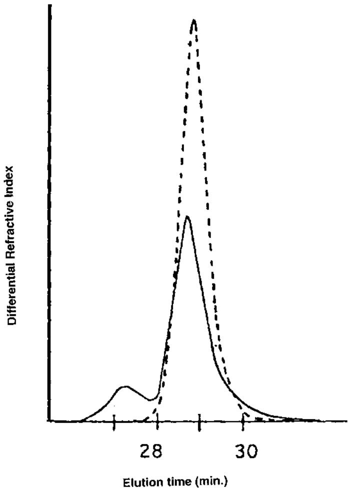
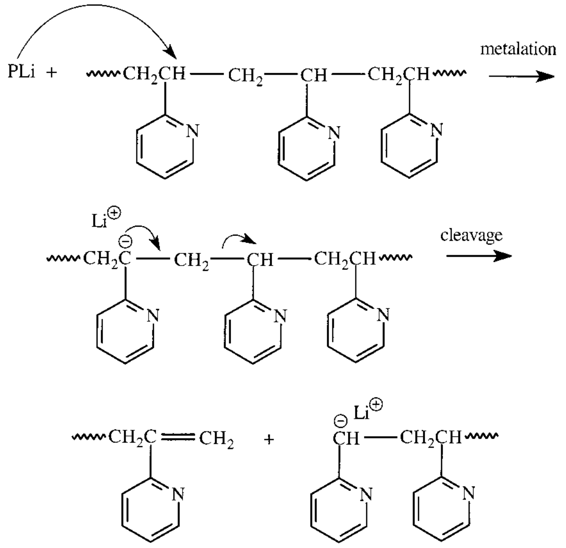


Figure 2. SEC-RI traces of polyisoprene (broken line) and poly[isoprene-*b*-(2-vinylpyridine)] block copolymer [polyisoprene M_n(calc) = 39 300 g/mol; diblock M_n(calc) = 46 700 g/mol] obtained in the presence of LiCl (LiCl/*sec*-BuLi = 1.4). The 2VP polymerization time was 21.5 h.

Scheme 2



ochemistry; 92.6% 1,4-polyisoprene microstructure was obtained.

In an attempt to eliminate dimer formation and side reactions, the effects of the amount of lithium chloride added and the 2-vinylpyridine polymerization time before quenching were investigated as variables. The results are summarized in Table 1 for 2PVP block polymerizations effected at 6−8 °C in the presence of 2−3 equiv of lithium chloride (samples 1−3). The amount of dimer decreased with decreasing 2VP polymerization time. Thus, while 32% dimeric products were observed after 38 min of 2VP polymerization, only 9% dimer was observed when the 2VP polymerization was rapidly quenched with acetic acid/methanol (1/10, vol/vol) after only 1 min.

In view of the difficulty of rapid and effective mixing and quenching on a time scale less than 1 min in conventional polymerization reactors, the effect of increasing amounts of lithium chloride was examined. Quite surprisingly, when 5−11 equiv of lithium chloride was present during the polymerization of 2VP, no dimer was formed even when the reaction was not terminated until 4 min (samples 4 and 5, Table 1) or even 7 min (sample 6, Table 1) after addition of 2VP. The SEC chromatogram for sample 4 (Tables 1 and 2) is shown in Figure 3. In all cases the conversions of monomer to polymer were 97% or higher.

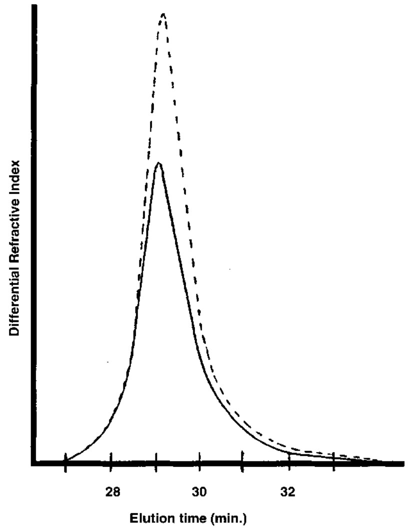


Figure 3. SEC-RI traces of polyisoprene (broken line) and poly(isoprene-*b*-2-vinylpyridine) block copolymer (sample 4, Tables 1 and 2) obtained in the presence of LiCl (LiCl/*sec*-BuLi = 5.5). The 2VP polymerization time was 4 min.

The characterization data for all of the PI-*b*-P2VP block copolymers are listed in Table 2. The block polymer samples that exhibited no dimer formation (samples 4−6) also exhibited apparent narrow molecular weight distributions [M_w/M_n(SEC) = 1.05−1.06]. The SEC chromatogram for sample 4 (Tables 1 and 2) is shown in Figure 3. The number-average molecular weights of the diblock copolymers calculated by SEC using polyisoprene standards (see Table 2) were only slightly higher than those of the corresponding base polyisoprene precursors. This is also apparent from the SEC chromatograms shown in Figures 1−3, where the peaks for the diblocks are only slightly shifted toward lower elution volumes. This phenomenon was observed for all the samples, independent of molecular weight or composition, and was also observed previously when characterizing poly(styrene-*b*-ethylene oxide) samples in this laboratory.[30] In different reports dealing with the synthesis and SEC characterization of poly(2-vinylpyridine), it is mentioned that the addition of TMEDA to the eluting solvent prevented the adsorption of such polymers onto the polystyrene gels of the SEC columns.[22,31−33] However, when TMEDA was added to the eluent solvent (THF/TMEDA = 95/5, vol/vol) for the molecular weight determination of the poly(isoprene-*b*-2-vinylpyridine) diblock copolymers, no improvement was detected. Therefore, it is concluded that no interaction has occurred between the block copolymer samples and the column packing. The SEC behavior of these diblocks might be attributed to the fact that THF is a better solvent for polyisoprene than for poly(2-vinylpyridine), as can be deduced from the solubility parameter (δ) values which are 16.6 × 10^3 and 21.7 × 10^3 $(\text{MPa})^{1/2}$ for polyisoprene[34a] and poly(2-vinylpyridine),[35] respectively, compared to 18.6 × 10^3 $(\text{MPa})^{1/2}$ for THF.[34b] Thus, the chain segments in poly(2-vinylpyridine) may be less expanded than those of polyisoprene with equivalent molecular weights. It is concluded that SEC analyses in THF using polyisoprene standards does not

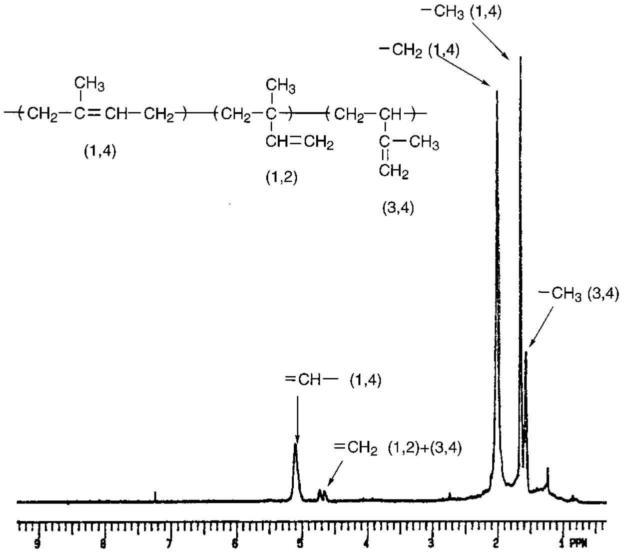


Figure 4. ^{1}H NMR spectrum of polyisoprene precursor synthesized in the presence of LiCl and used for the synthesis of poly[(isoprene-*b*-(2-vinylpyridine)] (sample 4, Tables 1 and 2).

provide reliable estimates of molecular weight for poly-isoprene-*b*-poly(2-vinylpyridine)s.

Further evidence regarding the intrinsic error in the determination of molecular weights of the PI-*b*-P2VP diblock copolymers using only SEC with polyisoprene standards as reported by Watanabe and Tirrell[24] is evident from M_w (light scattering) data in Table 2. The weight-average molecular weights were determined using a MALLS in-line detector after determination of the refractive index increments for each diblock copolymer (see Experimental Section). While the M_w values determined by light scattering are in reasonable agreement with M_n values calculated from the reaction stoichiometry, the M_n values determined by SEC with polyisoprene standards are 24% (sample 4) to 35% (sample 6) lower than the calculated values. In general, observed number-average molecular weights are higher than the calculated molecular weights when side reactions occur that decrease the effective number of growing chains.[8] The molecular weights determined using the universal calibration method[36] were also lower than the calculated values but significantly larger than the values determined by SEC (except for sample 4, Table 2).

The presence of LiCl in the system not only fulfills the requirement for the formation of well-defined diblock copolymers of 2-vinylpyridine but also does not affect the microstructure of the diene block. The ^{1}H NMR spectrum for the PI-*b*-P2VP diblock with a polyisoprene base polymer $M_n = 95.3 \times 10^3$ g/mol is shown in Figure 4 (sample 4, Tables 1 and 2). The resonance peak at δ 5.1 ppm was used to determine the amount of (1,4) content, and the doublet at δ 4.65 and 4.75 ppm was used to calculate [(1,2) + (3,4)] enchainments.[37] The ^{1}H NMR spectrum for the corresponding diblock copolymer [M_n(theoretical) = 140×10^3 g/mol] is shown in Figure 5, where the signals between δ 8.1 and 8.4 ppm were used to calculate the content of 2-vinylpyridine in the block copolymer. The polyisoprene microstructures obtained from Figures 4 and 5 were the same [92.9% (1,4) and 7.1% (1,2) + (3,4)].

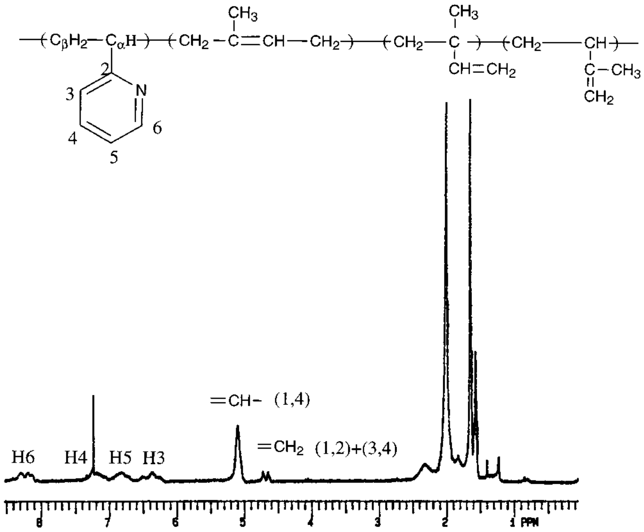


Figure 5. ^{1}H NMR spectrum of poly[(isoprene-*b*-(2-vinylpyridine)] diblock copolymer synthesized in the presence of LiCl (sample 4, Tables 1 and 2).

The dramatic effects of lithium chloride to provide control for the organolithium-initiated block polymerization of 2-vinylpyridine in benzene at readily accessible temperatures (ca. 5 °C) are presumably a result of cross-association of the polymeric organolithium chain ends with lithium chloride. Sigwalt and co-workers[38] examined the ^{7}Li NMR of hexane solutions of α,ω-dilithium-polyisoprene in the presence of lithium chloride and concluded that the addition of LiCl decreases the fraction of the most highly associated species and that mixed aggregates are formed between LiCl and the living poly(isoprenyl)lithium chain. It has been reported that cross-associated aggregates of alkyllithium compounds and lithium halides[39] generally have decreased reactivity compared with the uncomplexed alkyllithium.[40−42] Recent NMR studies by Jerome and co-workers[13,43,44] indicate that 1:1 and 2:1 complexes (LiCl:RLi) with reduced reactivity[45−47] are formed by the addition of lithium chloride to lithium ester enolates in THF. These precedents suggest that lithium chloride can cross-associate with poly(2-vinylpyridyl)lithium chain ends to form aggregates with reduced reactivity and increased selectivity as shown in eq 2.

$$(\mathrm{P2VPLi})_n + (\mathrm{LiCl})_m \rightleftharpoons (\mathrm{P2VPLi})_x(\mathrm{LiCl})_y \qquad (2)$$

Conclusions

Well-defined block copolymers of isoprene and 2-vinylpyridine can be prepared using *sec*-butyllithium as initiator in the presence of at least 5 equiv of lithium chloride at 6−8 °C in benzene using rapid quenching with acetic acid in methanol. In the absence of lithium chloride, PI-*b*-P2VP copolymers with broad, multimodal molecular weight distributions are obtained. The high 1,4-polyisoprene microstructure is not affected by the presence of added lithium chloride.

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