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Quantitative Anionic Synthesis of Pyrene-End-Labeled Polystyrene and Polybutadiene

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ABSTRACT: ω-Pyrenylpolystyrenes and ω-pyrenylpolybutadienes were synthesized in quantitative yield by reacting polystyryllithium and polybutadienyllithium, respectively, with 1-phenyl-1-(1′-pyrenyl)ethylene in benzene. The addition of tetrahydrofuran (2 vol %) was required for polybutadienyllithium because of the slow rate of addition in benzene. The addition reaction can be monitored by UV-visible spectroscopy at 476 nm, λ_{max} of the 1-phenyl-1-pyrenylalkyllithium anion. The functionalization reaction is not a termination reaction; the addition product is a living carbanion that can initiate polymerization of monomers to produce in-chain, pyrene-labeled polymers. The pyrene-labeled polymers were characterized by size-exclusion chromatography, vapor phase osmometry, ultraviolet-visible spectroscopy, and both ^1H and ^{13}C NMR. No evidence for unlabeled polymer was observed. The ultraviolet-visible spectra for the pyrene-labeled polymers show absorption bands at 330 and 346 nm, which are bathochromically shifted relative to the corresponding bands of pyrene. 1-Phenyl-1-(1′-pyrenyl)ethylene was synthesized in 34% yield starting from 1-pyrenecarboxaldehyde.

Introduction

Fluorescence techniques provide a useful methodology to probe structural, conformational, and dynamic properties of synthetic polymers, their blends, and colloids.[1-3] The scope and uniqueness of this method are defined by the fact that processes with time scales in the nanosecond range and with spatial scales in the range of less than 1-100 Å can be investigated.[1,4] For example, the pyrene label is often used as the fluorescent probe because it exhibits strong monomeric emission in the region of 370-430 nm (λ_{max} = 380 nm) with a fluorescent lifetime of about 200 ns and also forms excimers by reaction of singlet excited pyrene with ground-state pyrene (3-4 Å spatial range), which fluoresces in a broad, structureless band centered at 480 nm.[5-7] Realization of the full potential of fluorescence techniques requires the availability of synthetic methods for incorporating fluorescent labels such as pyrene in structurally well-defined polymers at precise locations, i.e., at the chain end(s) or within the polymer backbone.

Living anionic polymerization is the most versatile and widely used method to synthesize functionalized polymers with well-defined structures.[8] When this methodology is used, polymers can be prepared with control of the major variables affecting polymer properties, e.g., molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity and diene microstructure, chain-end and in-chain functionality, architecture, and morphology.[8-17] Under certain carefully controlled conditions, the living anionic polymerizations of styrene, diene, methacrylate, epoxide, and lactone monomers produce polymers that 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. In practice, however, many of the reported functionalization reactions have not been well-characterized.[10]

Anionically prepared polystyrene has previously been end-labeled with pyrene by reacting α,ω-dipotassium polystyrene with 5-bromobutylpyrene with reported efficiencies of 72-90%.[18] Alternatively, either α,ω-dipotassium polystyrene or polystyryllithium was first functionalized with ethylene oxide, followed by esterification with 4-(1-pyrene)butyryl chloride with reported efficiencies of >90%.[6,19,20] In conjunction with an ongoing effort to develop general methods for the synthesis of functionalized polymers based on the addition reactions of polymeric carbanions to 1,1-diarylethylenes and their derivatives,[21,22] the use of 1-phenyl-1-(1′-pyrenyl)ethylene to introduce the pyrene fluorescent label has been investigated and the results are reported herein. This approach is analogous to previous reports for naphthalene functionalization of polystyrene[21] and poly(methyl methacrylate).[23]

Experimental Procedures

Chemicals and Solvents. 1-Pyrenecarboxaldehyde (Aldrich), phenyllithium [Aldrich; 2.0 M in cyclohexane/diethyl ether (Et_2O) (70/30)], methyllithium (Aldrich; 1.4 M in Et_2O), *p*-toluenesulfonic acid monohydrate (Fisher Scientific Co.), and 1,4-dioxane (Aldrich 99+%) were used as received. Pyridinium chlorochromate was synthesized from CrO_3 (Fisher Scientific) and HCl in pyridine (Fisher Scientific).[24] Styrene, benzene, and tetrahydrofuran (THF; Fisher Scientific) were carefully purified as described previously.[25] Toluene (Fisher Scientific, certified ACS) was purified as described by Perrin and Armarego[26] followed by storage over polystyryllithium. Diethyl ether (EM Science, anhydrous) was stirred over a Na dispersion (Alfa) and then distilled onto sodium benzophenone ketyl. Butadiene (Matheson; CP 99%) was purified by condensation onto *n*-butyllithium at -78 °C and stirring for several hours at -78 °C with periodic warming to -40 °C for 10-min intervals. The purified butadiene was distilled into an ampule followed by dilution with benzene. Solutions of *sec*-butyllithium (Lithium Corp.; 12.0 wt % in cyclohexane) and polystyryllithium were analyzed by using the double titration method with 1,2-dibromoethane.[27] Argon (Linde) was passed through columns of 4-Å molecular sieves and manganese oxide dispersed on vermiculite.[28] 1-Methylpyrene was obtained from Molecular Probes.

Phenyl-(1-pyrenyl) Ketone. To a solution of 1-pyrenecarboxaldehyde (26.70 g, 0.1160 mol) in 600 mL of Et_2O at -78 °C was added 60 mL of 2.0 M phenyllithium [0.120 mol] under argon flushing. After warming to 25 °C and stirring for 18 h, the solution was poured onto 500 mL of ice, followed by washing the organic layer with 150 mL of 15% aqueous HCl, 150 mL of saturated aqueous NaCl, and two 150-mL portions of H_2O. The Et_2O layer was combined with the organic extract from washing the aqueous layers with 250 mL of Et_2O, dried with anhydrous $MgSO_4$, and filtered and the solvent removed using a rotary evaporator to give phenyl-1-pyrenylmethanol as a pale yellow solid. ^1H NMR

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($CDCl_3$): δ 7.9–8.3 (m, 9 H, pyrene), 7.1–7.5 (m, 5 H, phenyl), 6.82 (d, $^3J_{HH}$ = 5.5 Hz, 1 H, C*H*OH), 2.49 (d, $^3J_{HH}$ = 5.7 Hz, 1 H, CHO*H*).

Phenyl-1-pyrenylmethanol was oxidized with pyridinium chlorochromate using the procedure described by Piancatelli, Scettri, and D'Auria.[29] The resulting gold crystals, mp 117.7–118.2 °C, of phenyl-1-pyrenyl ketone exhibiting one HPLC peak were obtained in 40% yield (based on aldehyde) after recrystallization from cyclohexane/EtOH (1/1, v/v). ^{1}H NMR ($CDCl_3$): δ 7.1–8.4 (m, aromatic). IR (film): 3045 (w, aromatic, 1653 (vs, (C=O), 1596 (m,) 1264 (vs), 939 (m), 850 (s), 838 (s), 706 (vs) cm^{-1}.

1-Phenyl-1-(1′-pyrenyl)ethylene (1). To a solution of phenyl-1-pyrenyl ketone (13.7 g, 0.0447 mol) in 300 mL of Et_2O was added 35 mL (0.049 mol) of 1.4 M solution of CH_3Li in Et_2O via syringe under argon flushing. After warming to 25 °C and stirring for 20 h, the solution was poured onto 500 mL of ice, followed by washing the resulting organic layer with two 150-mL portions of saturated aqueous NaCl and 150 mL of H_2O. The Et_2O layer was combined with the organic extracts from washing the aqueous layers with three 100-mL portions of Et_2O, dried with anhydrous $MgSO_4$, and filtered and the solvent removed by using a rotary evaporator to give a white precipitate of 1-phenyl-1-(1′-pyrenyl)ethanol. ^{1}H NMR ($CDCl_3$): δ 7.7–8.4 (m, 9 H, pyrene), 7.1–7.4 (m, 5 H, phenyl), 2.50 (s, 1 H, OH), 2.18 (s, 3 H, CH_3). IR (film): 3560 (w sh, OH), 3460 (w br, OH), 3050 (w, Ar), 2970 (w, CH_3), 1600 (w), 1490 (w), 1440 (w), 1070 (w), 910 (w), 848 (s), 765 (m), 722 (m) cm^{-1}.

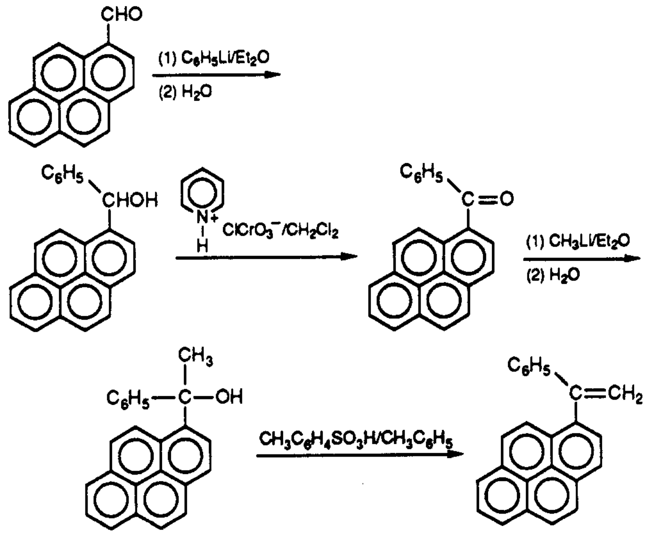
The resulting sample of 1-phenyl-1-(1′-pyrenyl)ethanol in 300 mL of toluene was dehydrated with 0.25 g of toluenesulfonic acid monohydrate by heating under reflux with a Dean-Stark trap for 1.5 h. The resulting solution was washed successively with 150 mL of H_2O, two 150-mL portions of saturated aqueous $NaHCO_3$, two 150-mL portions of saturated aqueous NaCl, and 150 mL of H_2O. The toluene layer was combined with the toluene extract of the combined aqueous layers, dried with anhydrous $MgSO_4$, and filtered and the solvent removed by using a rotary evaporator to give after recrystallization from acetone/toluene (10/1, v/v) 11.5 g of 1 as a light tan solid (85% yield based on ketone). MP: 114.0–114.8 °C, one HPLC peak. ^{1}H NMR ($CDCl_3$): δ 7.9–8.2 (m, 9 H, pyrenyl), 7.2–7.4 (m, 5 H, phenyl), 6.14 (d, $^2J_{HH}$ = 2 Hz, 1 H, =CH_2), 5.49 (d, $^2J_{HH}$ = 2 Hz, 1 H, =CH_2). ^{13}C NMR ($CDCl_3$, decoupled): δ 148.85, 141.83, 137.72, 131.28, 131.20, 129.47, 128.77, 128.13, 127.73, 127.69, 127.22, 126.32, 125.94, 125.45, 125.33, 125.24, 125.14, 124.96, 117.29. IR ($CDCl_3$): 3083 (sh), 3046 (m), 1604 (m), 1491 (m), 1443 (w), 1301 (w), 1181 (w), 1028 (w), 847 (vs), 781 (s), 708 (s), 689 (s), 638 (m) cm^{-1}. Elem anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.63; H, 5.31.

Polymerizations. Styrene and diene polymerizations were carried out at room temperature in all-glass, sealed reactors using standard high-vacuum techniques,[30] except J. Young brand high-vacuum stopcocks, connectors, and O-ring ball joints (Brunfeldt, Bartlesville, OK) were used in place of hand-torch heat-sealing and break-seals. In general, the monomer concentration was 10% by volume and the total solution volume varied from 100 mL to 1 L.

Pyrene Functionalization. Labeling reactions of benzene solutions of polystyryllithium (ca. 0.02 M) were effected by addition of 1.2 molar equiv of 1-phenyl-1-(1′-pyrenyl)ethylene (1) in a recirculating, argon-atmosphere glovebox.[28,31] The rate and extent of the reaction was monitored by using ultraviolet–visible spectroscopy by measuring the increase of the 1-phenyl-1-(1′-pyrenyl)alkyllithium absorbance at 476 nm. After 6 h the reaction was quenched with degassed CH_3OH. The functionalized polystyrenes were isolated by precipitation into excess methanol and dried in vacuo. Labeling reactions of polybutadienyllithium (ca. 0.02 M) were similarly effected after addition of 2 vol % of THF to the benzene solution.

Characterization. Number-average molecular weights were determined using by a vapor pressure osmometer (VPO; Knauer Type 11.00) at 45 °C in toluene. Size-exclusion chromatographic analyses of polymers were performed at a flow rate of 1.0 mL min^{-1} in tetrahydrofuran at 30 °C by using a Waters HPLC component system (RI or Hewlett Packard 1040 diode array detectors) equipped with six ultra-μ-Styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) after calibration with standard polystyrene (Polymer Laboratories) or polybutadiene (American Polymer Standards) samples. HPLC analyses were performed by using a Waters HPLC component system (Hewlett Packard 1040 diode array detector) equipped with a MicroPak CH-10 column (30 × 4 mm) in 70/30 (v/v) CH_3CN/H_2O at 600 psi. UV–vis spectra were recorded on an HP8452A diode array spectrometer. ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra were recorded on a Varian Gemini-200 spectrometer using $(CH_3)_4Si$ as internal standard. IR spectra were recorded on a Beckman FT 2100 spectrometer as thin films on a KCl plate or in $CDCl_3$ between KCl plates. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

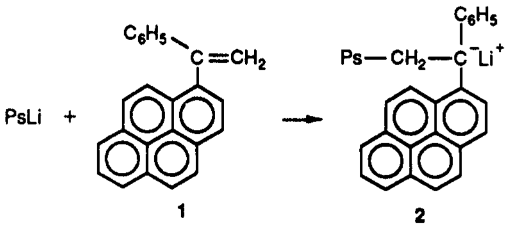
Scheme I



Results

Synthesis. 1-Phenyl-1-(1′-pyrenyl)ethylene (1) was synthesized in approximately 34% overall yield from 1-pyrenecarboxaldehyde as shown in Scheme I. The structure of 1 was confirmed by elemental analysis and by its ^{1}H NMR spectrum, which exhibited two vinyl doublets at δ 5.49 and 6.14 and two groups of aromatic protons in the range of δ 7.9–8.2 and δ 7.2–7.4 for the pyrenyl and phenyl groups, respectively. The UV–vis spectrum of 1 exhibits λ_{max} at 330 and 346 nm.

The reaction of polystyryllithium (PsLi) with 1 (eq 1) was investigated in benzene solution at 25 °C. The crossover reaction from the PsLi to 1-phenyl-1-(1′-pyrenyl)alkyllithium species, 2, was monitored by UV–visible spectroscopy as shown in Figure 1. The polystyryllithium band at 335 nm is easily distinguished from the addition product, 2, with absorptions at 476 and 656 nm. The rate of the crossover reaction of polystyryllithium with 1 (1.2 equiv) was monitored at 476 nm, and the results are shown in Figure 2d. At a concentration of 0.0016 M PsLi, the reaction is completed in approximately 1 h.



(1)

Similarly, the reaction of polybutadienyllithium (PBDLi) with 1 was also monitored by UV–vis spectroscopy (see Figure 2c). The observed rate of addition is exceedingly slow; it was estimated that 1.5 months would be required for complete conversion at 25 °C. These results are consistent with expectations based on the monomer reactivity ratios for the copolymerization of either styrene[32]

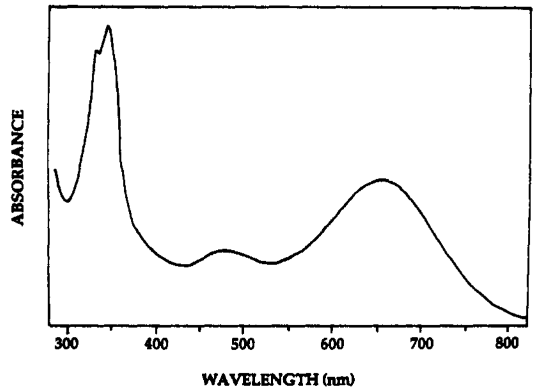


Figure 1. UV-visible absorption spectrum of the addition reaction of polystyryllithium (0.0016 M) with 1.2 equiv of 1-phenyl-1-(1′-pyrenyl)ethylene.

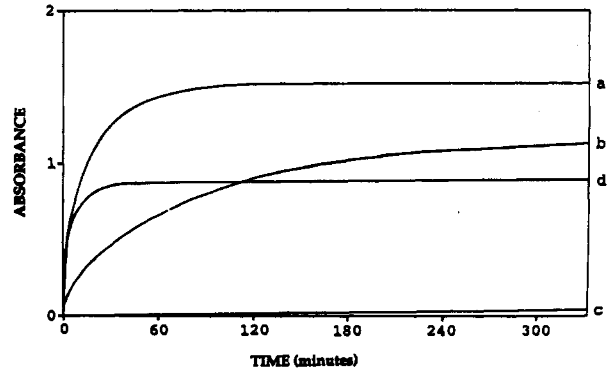


Figure 2. Absorbance at 476 nm versus time for the reaction of 1.2 equiv of 1 in benzene with polybutadienyllithium (0.0021 M, $\bar{M}_n = 2 \times 10^3$ g/mol) in the presence of (a) 120 equiv (2.0 vol %) of THF; (b) 15 equiv (0.26 vol %) of THF; (c) no THF; and (d) with polystyryllithium (0.0016 M, $\bar{M}_n = 3 \times 10^3$ g/mol).

Table I
Reactivity of Ratios, *r*, for the Copolymerization Reactions of Styrene and Butadiene with 1,1-Diphenylethylene (DPE)

M_1	M_2	solvent	r_{12}
styrene[a]	DPE	benzene	0.71
		THF	0.13
butadiene[b]	DPE	benzene	54
		THF	0.13

[a] Reference 32. [b] Reference 33.

or butadiene[33] with 1,1-diphenylethylene as shown in Table I. These data indicate that the addition of polystyryllithium to 1,1-diphenylethylene in benzene is slightly faster than homopolymerization, i.e., addition to styrene. However, the addition of polybutadienyllithium to 1,1-diphenylethylene is 54 times slower than homopolymerization, i.e., addition to butadiene. Since the anionic homopolymerization of butadiene is ca. 5 times slower than the homopolymerization of styrene,[34] it is not surprising that the rate of addition of PBDLi to 1 in benzene, which can be considered as an analogue of 1,1-diphenylethylene, is much slower than addition of PsLi to 1. The results in Table I also show the dramatic effect of tetrahydrofuran (THF) on the anionic copolymerization of butadiene with 1,1-diphenylethylene. In THf the rate of addition of PBDLi to 1,1-diphenylethylene is faster than homopolymerization. This suggested that the addition of PBDLi to 1 could also be accelerated in the presence of THF. Since simple and polymeric organolithium compounds are not stable in THF at room temperature,[35-38] the rate of addition of PBDLi to 1 was investigated in the presence of only 0.26 and 2.0 vol % THF (see Figure 2a,b). Although both systems effected large increases in the addition rate compared to rates in benzene, 2 vol % THF was required to achieve addition rates comparable to the rates for polystyryllithium in benzene; this amount of THF corresponds to [THF]/[Li] = 12.3 for 0.02 M PBDLi. This mode of addition of THF, i.e., after preparation of PBDLi, ensures that pyrene-labeled polybutadiene with high 1,4-enchainment can be prepared. If this amount of THF were added during the polymerization, high 1,2-enchainment would be expected.[39] Thus, the pyrene-labeled polybutadiene prepared by postpolymerization addition of THF and 1 contained only 8% 1,2-enchainment as estimated by ^{1}H NMR analysis.[40]

Characterization. The characterization data for the pyrene-labeled polymers and their corresponding unfunctionalized base polymers are shown in Table II. The UV-vis absorbance spectra in dioxane for the pyrene end-functionalized polymers with $\bar{M}_n$ 2×10^3 g/mol are shown in Figure 3. The UV-visible spectra for polystyrene and pyrene are included in Figure 3 for comparison with the labeled polymers. These polymers exhibit absorbances in dioxane for the pyrene label at 330 and 346 nm, in contrast to pyrene, which has absorbances at 321 nm (log ϵ = 4.40) and 337 nm (log ϵ = 4.61),[41] and 1-methylpyrene, which has absorbances at 325 nm (log ϵ = 4.42) and 342 nm (log ϵ = 4.54). It appears that the absorbances at 320–330 nm are less sensitive to substitution than the absorbances at 337–346 nm; also, the bands for 1-methylpyrene are closer to those observed for the labeled polymers. When this information and the observation that the absorbances of the pyrene labels at 330 and 346 nm do not overlap with the polystyrene absorbance at 262 nm are used, the efficiency of the labeling experiment was calculated by using the 1-methylpyrene extinction coefficient at 325 nm and assuming that it can be used to approximate the expected absorbance for the labeled polymer at 330 nm; similar results were obtained by using the absorbance for pyrene at 321 nm. The number-average molecular weights calculated from the spectral absorbances are in good quantitative agreement with the VPO and SEC molecular weights as shown in Table II.

The size-exclusion chromatograms for the pyrene-labeled polymers give essentially identical curves when the diode array UV-vis detector is set at either 254 or 330 nm as shown in Figure 4. These results are consistent with uniform pyrene labeling for all of the polymer molecules. With regard to the SEC behavior of the pyrene-labeled polystyrenes, it is interesting to note that the calculated value of $\bar{M}_n$ for the labeled polymer is less than expected on the basis of the SEC $\bar{M}_n$ for the unlabeled polymer (see Table II). Apparently the hydrodynamic volume of the pyrene end group is less than the hydrodynamic volume of an equivalent weight of polystyrene. This is perhaps one of the most subtle demonstrations of the limitations of using polystyrene calibration curves to estimate $\bar{M}_n$ values for diverse polymers.

The efficiency of the pyrene labeling can also be estimated by NMR. The ^{13}C NMR spectrum of pyrene-labeled polystyrene with $\bar{M}_n = 2 \times 10^3$ g/mol shows no resonance for the terminal, benzylic carbon [$-CH_2(Ph)$] at δ 33.71, which is observed for the unfunctionalized polystyrene base polymer.[42] The ^{1}H NMR shows a resonance at δ 4.66, which can be assigned to the terminal proton [$-CH(Ph)(pyrenyl)$] in the labeled polymer. The integration of the pyrenyl proton resonances compared to the aliphatic resonances for the ω-pyrenylpolystyrene is also consistent with quantitative end functionalization. The absence of a terminal $-CH_3$ resonance at δ 1.62 in the ^{1}H NMR spectrum of ω-pyrenylpolybutadiene is also

Table II
Molecular Weight Characterization of Base Polymers and Pyrene-Labeled Polymers[a]

polymer	$\bar{M}_n$ SEC	calc[b]	VPO	abs[c]	^{1}H NMR[d]	$\bar{M}_w/\bar{M}_n$
2000PS	1.75×10^3					1.04
2000PSPPE	1.81×10^3	2.05×10^3	1.90×10^3	1.97×10^3	2.00×10^3	1.03
10000PS	10.4×10^3					1.02
10000PSPPE	10.1×10^3	10.7×10^3	10.1×10^3	8.86×10^3	10.1×10^3	1.01
2000BPD	1.79×10^3					1.04
2000PBDPPE	1.88×10^3	2.09×10^3	2.1×10^3	1.92×10^3	2.1×10^3	1.03

[a] PS = polystyrene, PBD = polybutadiene, PPE = pyrene label ($M_w = 304.4$). [b] Calculated from the SEC $\bar{M}_n$ of PS or PBD base polymer plus the molecular weight of PPE. [c] The UV absorbance of a known concentration of PSPPE or PBDPPE in dioxane was measured. $\bar{M}_n$ is equal to the weighed concentration of polymer (g/L) divided by the UV concentration of pyrene (mol/L). The reported value is the average of the values calculated at 330 nm for two different concentrations using the observed absorbance for 1-methylpyrene at 325 nm ($\log \epsilon = 4.42$). [d] Determined from the normalized relative integration of the pyrenyl protons vs PS aliphatic or PBD methine protons.

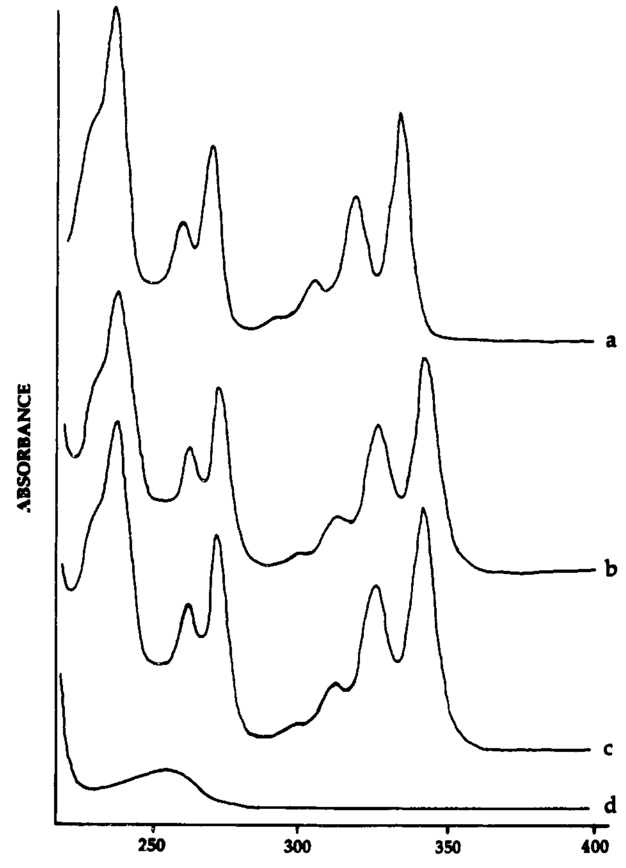


Figure 3. UV–vis spectra of (a) pyrene, (b) ω-pyrenylpolystyrene ($\bar{M}_n = 2 \times 10^3$ g/mol), (c) ω-pyrenylpolybutadiene ($\bar{M}_n = 2 \times 10^3$ g/mol) and (d) base polystyrene ($\bar{M}_n = 2 \times 10^3$ g/mol) in dioxane.

consistent with quantitative end functionalization for polybutadienyllithium. The molecular weight calculated from the integration of the pyrenyl proton resonances compared to the vinyl resonances for the ω-pyrenylpolybutadiene is in good agreement with the other measures of molecular weight listed in Table II.

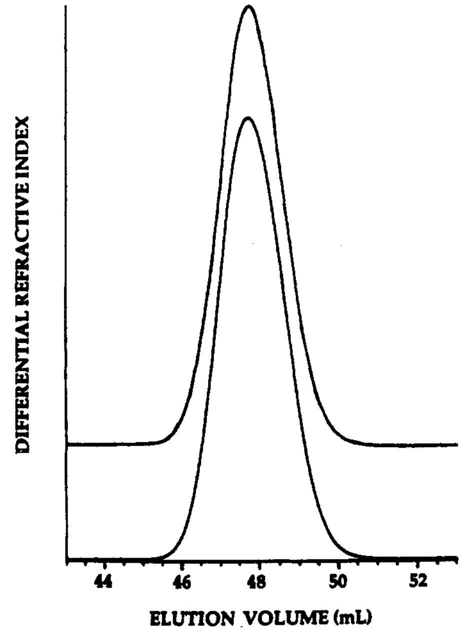


Figure 4. SEC curves for ω-pyrenylpolystyrene ($\bar{M}_n = 2 \times 10^3$ g/mol) using the diode array UV–vis detector monitoring at 254 nm (upper curve) and 330 nm (lower curve).

Discussion

The reaction of polymeric organolithium compounds with 1,1-diarylethylenes and their derivatives is an excellent system for development of general functionalization reactions because these addition reactions are simple and quantitative; only monoaddition, i.e., no oligomerization, has been reported; the rate and efficiency of the crossover reaction can be monitored by ultraviolet–visible spectroscopy; and a variety of 1,1-diarylethylenes can be prepared readily.[11,13,21,22,35,41-46] The application of this methodology for the anionic synthesis of polymers labeled with fluorescent groups has been demonstrated by the results reported herein. All of the available evidence is consistent with quantiative end labeling of both polystyryllithium and polybutadienyllithium with 1-phenyl-1-(1′-pyrenyl)ethylene. These results can be contrasted with the lower efficiencies reported for other anionic labeling methods (see Introduction).[6,18-20] This methodology can be described as a *living functionalization reaction*, since the addition product is a living carbanion (see eq 1) that can initiate the anionic polymerization of additional monomers. Thus, this method can be used to prepare polymers with the pyrene label within a polymer chain. An additional advantage of the present method is the fact that the pyrene label is bound to the polymer by chemically and thermally stable carbon–carbon bonds in contrast to ester bond linkages in other labeling methods.[6,19,20] It is anticipated that these labels will be useful for examining high-temperature processes in the melt and in solution. Work is in progress to further elucidate the scope and limitations of the 1,1-diarylethylene addition reactions with carbanions to form a variety of functionalized and labeled polymers.

Conclusion

The living carbanionic chain ends of polystyryllithium and polybutadienyllithium react quantitatively with 1-phenyl-1-(1′-pyrenyl)ethylene in benzene or benzene/THF (2 vol %), respectively, to cleanly produce ω-pyrenylpolystyrene and ω-pyrenylpolybutadiene. No evidence for unlabeled polymers was apparent from analysis by SEC (UV–vis and RI detectors), VPO, ^{13}C and ^{1}H NMR, and UV–vis absorption spectroscopy. The pyrene is bound to the polymer chain through carbon–carbon bonds; thus, the label should be as chemically and thermally stable as the polymer itself. This living functionalization method can be used to prepare polymers labeled with fluorescent groups within the polymer chain since the labeling reaction is not a termination reaction. The results of fluorescence studies of polymers labeled by using the techniques reported herein will be reported elsewhere.

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Registry No. 1, 64897-63-8; phenyl-(1-pipenyl) ketone, 7376-03-6; 1-pyrenecarboxaldehyde, 3029-19-4; phenyllithium, 591-51-5; phenyl-1-pyrenylmethanol, 95811-57-7; phenyl-1-(1′-pyrenyl)-ethanol, 130797-49-8.