New Method for Quantitative Functionalization of the Terminus in Poly(styrene). Naphthalene Functionalization

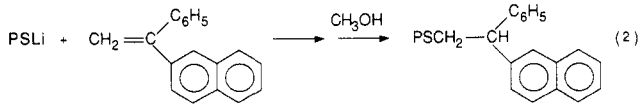
Advances in understanding structure–property relationships require the availability of polymers with well-defined and predictable structures. For selected monomers, living anionic polymerization provides an ideal method for the preparation of polymers with control of the major variables affecting polymer properties.[1-3] However, the ability to prepare chain-end functionalized or labeled polymers via this method has been limited, not by the range of available functionalization and labeling reactions for living carbanionic chain ends, but by the necessity of developing, optimizing, and characterizing new reactions for each, different functional group. Herein is reported a general functionalization method to prepare polymers labeled with fluorescent groups based on the addition reactions of polymeric carbanions to diphenylethylene derivatives.

Polymeric and simple organolithium compounds react quantitatively and relatively rapidly with diphenylethylene to produce the corresponding diphenylalkyllithium species, without homopolymerization, as shown in eq 1.[3-9] This

$$PLi + Ph_2C{=}CH_2 \rightarrow PCH_2CPh_2^-Li^+ \qquad (1)$$

reaction has been utilized to attenuate the reactivity of the chain end and minimize side reactions for the crossover reaction from carbanionic chain ends to methyl methacrylate monomer for the preparation of the corresponding block copolymers[10,11] and to prepare heteroarm star–block copolymers as reported in a preliminary paper.[12]

We have utilized this efficient coupling reaction to synthesize polymers labeled with fluorescent aromatic groups, as illustrated in eq 2 for the functionalization of



(2)

poly(styryl)lithium (PSLi) with a naphthalene (N) derivative to yield an end-labeled poly(styrene) (PS-N). A similar approach has been reported recently for poly(methyl methacrylate).[13] Poly(styryl)lithium was prepared by using *sec*-butyllithium as initiator in benzene at 30 °C in all-glass, sealed reactors, using break-seals and standard high-vacuum techniques.[14] After methanol termination of PSLi two independent measurements of M_n for the poly(styrene) (PS) sample gave results of 1.9×10^3 (by vapor-phase osmometry) and 2.0×10^3 (by size-exclusion chromatography). The latter technique gave M_w/M_n = 1.04. Quantitative covalent attachment of the naphthalene label has been effected by end-capping poly(styryl)lithium with 2-(1-phenylethenyl)naphthalene.[15,16] The crossover reaction was monitored by ultraviolet–visible spectroscopy at 334 nm ($\epsilon = 1.3 \times 10^4$)[17] for poly(styryl)lithium and at 440 nm ($\epsilon = 2.0 \times 10^4$) for the substituted 1-naphthyl-1-phenylalkyl carbanion. The crossover reaction required 8 h for completion, using a 10% excess of 2-(1-phenylethenyl)naphthalene. The number-average molecular weight and molecular weight distribution of the naphthalene end-labeled polystyrene were characterized by size-exclusion chromatography ($M_n = 1.9 \times 10^3$, M_w/M_n = 1.05) and vapor-phase osmometry ($M_n = 2.14 \times 10^3$). These results show that there has been no major change either in M_n or M_w/M_n. They do not, however, provide an accurate assessment of the extent of the covalent incorporation of naphthalene into the polymer.

Determination of the Incorporation of Naphthalene. The number-average molecular weights determined for the unmodified PS by vapor-phase osmometry and size-exclusion chromatography yield an average of 18 and 19 styrene units per chain, respectively. The extent of naphthalene incorporation is conveniently assessed by the comparison of these values with the average number of styrene units per naphthalene unit in the labeled sample.

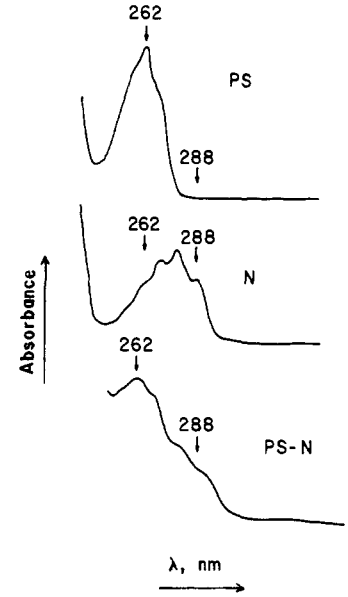


Figure 1. Illustrative absorption spectra in dichloroethane, traced directly from the chart paper, for unlabeled poly(styrene) (top), naphthalene (middle), and labeled poly(styrene) (bottom). Arrows denote 262 and 288 nm on each spectrum.

The ultraviolet absorption spectrum of PS in dichloroethane shows the expected maximum at 262 nm. There is very little absorbance above 280 nm. In the same solvent, naphthalene (N) exhibits an absorption maximum at 278 nm and shoulders at 270 and 288 nm. The PS-N exhibits two shoulders near 280 and 290 nm, in addition to the stronger absorption at 262 nm due to the more abundant benzene rings. Illustrative raw spectra for PS, N, and PS-N are traced in Figure 1.

The weight fraction of naphthalene, W_N, in the labeled sample can be evaluated from

$$\epsilon_{PS\text{-}N,\lambda} = \epsilon_{N,\lambda} W_N + \epsilon_{PS,\lambda} W_{PS} \qquad (3)$$

where W_{PS} is the weight fraction of styrene and $W_N + W_{PS} = 1$. The extinction coefficients, ϵ, are in units of centimeters squared per milligram and are determined as the initial slope of absorbance versus concentration, where the concentration is expressed as milligrams per milliliter. Quantitation of the naphthalene content is performed most easily if λ is selected as 288 nm because ϵ_N (24.8) is 3 orders of magnitude larger than ϵ_{PS} (0.02) at this wavelength. The observed value of $\epsilon_{PS\text{-}N}$ (1.58) yields $W_N = 0.0634$, or one naphthalene unit for every 18.2 styrene units. This number, which is calculated from the absorption spectra, is nearly identical with the average number of styrene units per molecule in the starting polymer. That number is 18 when calculated from the M_n measured for PS by vapor phase osmometry and 19 when calculated from the M_n measured by size-exclusion chromatography. The identity of these two results shows that an average of one naphthalene unit has been attached to each poly(styrene) chain by the reaction depicted in eq 2.

Excitation at 254 nm in dichloroethane produces fluorescence emission from PS-N that has components from poly(styrene) and from naphthalene. Naphthalene dominates the emission at the lower energies. The fluorescence quantum yield for PS-N is slightly higher than

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that expected for the separate components, perhaps due to energy migration from PS to N via the antenna effect.[18]

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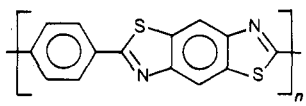
Conductive Polymers Based upon Rigid-Rod Ultrahigh-Modulus Macromolecules. Electrochemical Doping of Poly(*p*-phenylenebenzobisthiazole-2,6-diyl) (PBT)

Rigid-rod benzobisazole-based macromolecules, as exemplified by poly(*p*-phenylenebenzobisthiazole-2,6-diyl) (PBT, I), constitute some of the mechanically strongest



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and most robust polymeric substances known.[1,2] Especially when processed into a highly ordered and crystalline microstructure, PBT exhibits impressive thermal and environmental stability as well as extremely high tensile strength and modulus.[1,2] In addition to these characteristics, the architecture of the PBT π-electron system suggests a possible pathway for delocalization and charge transport. We address here this latter issue and provide the first evidence that PBT can be electrochemically doped and undoped, either as thin coatings or as extruded, highly oriented free-standing films and fibers, to yield an electrically conductive polymer.[3]

Films containing known quantities of PBT were cast onto 0.5-cm^2 Pt flag electrodes from fresh 0.1% (w/w) isotropic solutions of PBT[4a] in trifluoromethanesulfonic acid. Films were coagulated with distilled water, soaked overnight in a large excess of distilled water to remove residual acid, and dried in vacuo. Typical dry film thicknesses were on the order of 0.5 μm.[4b] Electrochemical studies were performed under inert atmosphere using rigorously purified THF and tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) as the supporting electrolyte. The measurements were made in the three-electrode configuration with a Ag wire quasi-reference electrode and a large-area Pt gauze counter electrode. Potential values were referenced back to the SCE potential by using the ferrocene/ferrocenium couple as an internal standard. As can be seen in Figure 1, the electrochemical reduction of thin PBT films on Pt is chemically reversible.[5] Indeed, repetitive cycling of the films evidences no degradation in current response. The reduction of PBT is accompanied by a change in color from yellow to black, which is completely reversed upon reoxidation.

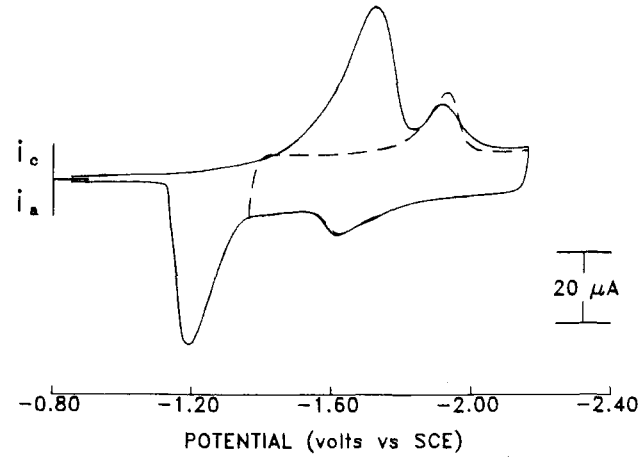

Figure 1. Cyclic voltammetry of a PBT (I) film on Pt in THF/0.1 M tetra-*n*-butylammonium tetrafluoroborate. Solid line: typical CV. Dashed line: CV when potential sweep direction for reoxidation is reversed at −1.35 V. The scan rate is 10 mV/s.

Table I
Electrochemical Data for Films of PBT (I) on a Platinum Electrode and for Dicapped Fragment Compound II in Solution (Volts versus SCE)

	wave	$E_{1/2}$	E_{pc}	E_{pa}
PBT (I)[a]	1	−1.47	−1.70	−1.23
	2	−1.78	−1.92	−1.64
fragment (II)[b]	1	−1.62	−1.66	−1.58
	2	−2.01	−2.06	−1.98

[a] Supporting electrolyte: 0.1 M tetra-*n*-butylammonium tetrafluoroborate in THF. [b] Supporting electrolyte: 0.5 M tetra-*n*-butylammonium tetrafluoroborate in THF.

Two readily identifiable and chemically reversible redox processes are evident in the PBT cyclic voltammogram of Figure 1. Peak potential and half-wave values versus SCE are compiled in Table I. The data exhibit a prominent cathodic peak at −1.70 V and a corresponding anodic peak at −1.23 V, with the difference in peak potentials (ΔE_p) thus being 470 ± 30 mV. This separation is virtually insensitive to IR compensation. Large ΔE_p values are commonly observed in the electrochemistry of conductive polymer films and are usually attributable to redox-related structural reorganization processes within the film.[6,7] This ΔE_p for PBT is one of the largest observed to date for a π-electron conductive polymer. Studies of peak current as a function of scan rate were also carried out and reveal direct proportionality between i_p and v for scan rates between 1.0 and 10 mV/s, as expected for a surface-anchored

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