366 *Macromolecules* **1990,** *23,* 366-374

Reactions of Polystyryl Anions with Poly(chlorotrifluoroethylene) Film at the Solution–Solid Interface[1]

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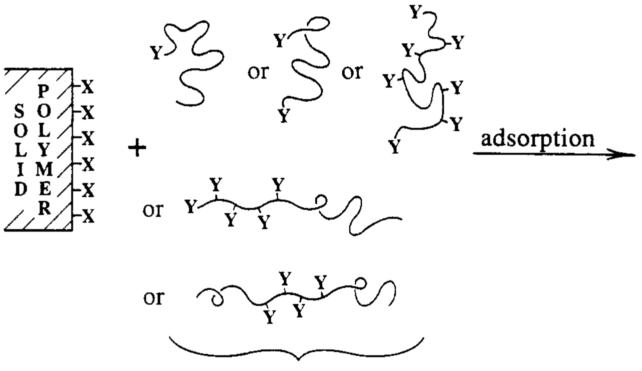
ABSTRACT: Reaction of poly(chlorotrifluoroethylene) (PCTFE) film with polystyryllithium, (polystyrylbutadienyl)lithium, and (polystyrylthio)lithium in solutions in contact with the PCTFE film produces modified polymer surfaces containing polystyrene covalently attached to the PCTFE film surface. The structure of the polystyrene-grafted product depends on the identity of the terminal lithium reagent, the reaction solvent, and the reaction temperature. Polystyryllithium in THF solution reacts with PCTFE predominantly by reduction to render an extensively reduced carbonaceous product containing C=C and C≡C; very little polystyrene is incorporated. Polystyryllithium in benzene solution reacts with PCTFE predominantly by addition of polystyrene; no reduction product was observed. (Polystyrylbutadienyl)lithium reacts with PCTFE to yield a range of modified structures that depend on the reaction solvent. Reactions in benzene, benzene/hexane, THF/benzene, and hexane/THF yield thin films of attached polystyrene, the thickness of which depends on solvent composition and reaction temperature. Reaction in THF yields a soluble graft copolymer that dissolves in the reaction solution. (Polystyrylthio)lithium in THF reacts with PCTFE to yield modified surfaces containing polystyrene, the thickness of which depends on reaction time and temperature. Very thick modified layers (>3000 Å) can be prepared, and there is no evidence of graft copolymer dissolution. No reaction occurs when benzene is used as the solvent.

Introduction

We have begun a research program to study the adsorption, from solution, of polymers containing functional groups (indicated by Y in eq 1) to polymer surfaces that have been specifically functionalized (X, eq 1) to interact with groups on the dissolved polymer. By controlling the density and location of functional groups, the molecular weight, and the solution properties (adjusting temperature and solvent composition) of the dissolved polymer, we hope to develop the means to manipulate the structure of the adsorbed layer and the properties of the solid polymer surface. Our first experiments in this regard do not involve interactions between discrete functional groups as indicated in eq 1 but rather the attachment of polymer chains by reaction of one end with the solid polymer to form covalent bonds. These experiments are extensions of our work on poly(chlorotrifluoroethylene) (PCTFE) surface modification[3,4] and at the time of their conception were thought to be simplified cases of the experiments described in eq 1.



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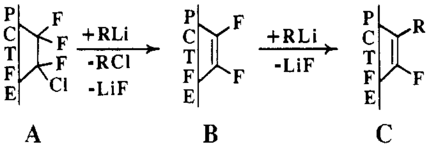
Alkyllithium reagents react with PCTFE film to incorporate alkyl groups on the polymer chains near the film surface (eq 2). Lithium reagents 1–3 were used to introduce alcohol, aldehyde, and carboxylic acid functionalities, respectively, onto the PCTFE surface,[4] and several aspects of these reactions impact on the work reported here: The product surfaces are a mixture of structures B and C (eq 2); for example, quantitative X-ray photoelectron spectroscopy (XPS) indicates that, for lithium reagent 1, the product surface consists of 80% C and 20% B.[5,6] In general, the depth of the reaction (thickness of the resulting modified layer) depends on (at least) three factors: the structure of the lithium reagent, the reaction temperature, and the reaction solvent.[4] Lithium reagents 2 and 3 in heptane/THF mixtures react surface selectively (the outermost 10–60 Å of the film reacts completely within the first 5 min of reaction, and little further reaction occurs subsequently), and the thicknesses of the modified layers can be controlled with reaction temperature. Lithium reagent 1 in heptane/THF does not react with PCTFE surface selectively at any temperature, and the depth of reaction can be controlled from ~50 Å to 1500 Å by varying reaction time and temperature. The depth of reaction of PCTFE with 2 is strongly dependent on the solvent composition (proceeds deeper with a higher THF content), but the reaction of 3 is only weakly solvent-dependent. These observations suggest that the extent to which the solvent interacts with the product is a major feature of the reaction that determines the thickness of the modified layer.



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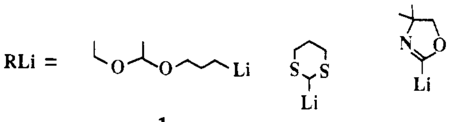

1 2 3

This paper describes studies of the reactions of PCTFE film with polymeric lithium reagents (end functional polystyryl anions) in solutions in contact with the polymer film samples. This polymer grafting reaction, in princi-

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ple, offers certain advantages over the usual methods for grafting a thin polymer film on a solid polymer substrate. The usual methods are centered around the creation of radical species at and near the solid surface in the presence of or before being exposed to free radically polymerizable monomers.[7-15] UV or higher energy radiation is the most common means for surface radical generation, but thermal, mechanical, photochemical, plasma, and wet chemical methods have also been used. The structure of these "grafted from" polymer films is difficult to control and characterize. The molecular weight, molecular weight distribution, attachment site, and cross-link density of the grafted film as well as the structure (covalent bond density, diffuseness) of the interface are generally unknowns. In contrast, if end functional polystyryl anions of known molecular weight and molecular weight distribution were "grafted to" the surface of PCTFE by using the chemistry detailed in eq 2, the above-mentioned factors would not be unknown and could be controlled. These were the objectives of this research.

There are no reports of grafting polystyryl anions to synthetic polymer surfaces; however, a range of surfaces including wood,[16] glass,[17] carbon black,[18] and salt crystals[19] have been modified by this method. Polystyryl anions have been grafted to halogen- or carbonyl-containing synthetic polymers in solution.[20-24]

Experimental Section

Materials. PCTFE film (5-mil Aclar 33C) was obtained from Allied. Film samples (typically 1 × 2 cm) were extracted with refluxing dichloromethane (30 min) and dried (<0.05 mm) until constant mass (±1 μg) was achieved on two gravimetric analyses 24 h apart. This procedure renders film samples that are free from contaminants detectable by any of the analytical techniques used. Film samples were stored in Schlenk tubes under nitrogen or attached to a vacuum manifold. Styrene (Aldrich) was dried with calcium hydride and distilled from calcium hydride just prior to use. Butadiene (Matheson) was dried over calcium hydride at −23 °C, distilled trap-to-trap, dissolved in THF or benzene (0.10–0.35 M butadiene), and stored in Schlenk tubes in the freezer. Ethylene sulfide (Aldrich) was dried over and distilled from calcium hydride. THF was distilled from sodium benzophenone dianion; benzene was distilled from sodium benzophenone dianion or calcium hydride; hexane and toluene were distilled from calcium hydride. *sec*-Butyllithium (Aldrich) was used as received and titrated periodically with 4-biphenylmethanol.[25] 12-Crown-4 (Aldrich) was used as received and stored in a dessicator.

Methods. Dynamic contact angles were measured with a Ramé-Hart telescopic goniometer and doubly distilled water as the probe fluid. Advancing (θ_A) and receding (θ_R) angles were determined as water was added and removed, respectively, from the drop with a Gilmont syringe. The data reported are averages of at least six measurements made on different positions of the film samples. Attenuated total reflectance infrared (ATR IR) spectra were obtained by using an IBM 38 FTIR at 4 cm^{-1} resolution and a germanium 45° internal reflection element. The spectra were ratioed against a spectrum of the internal reflection element. UV-vis spectra were recorded by using a Perkin-Elmer Lambda 3A spectrophotometer; transmission spectra were obtained by using a film-holding attachment. X-ray photoelectron spectra were obtained by using a Perkin-Elmer Physical Electronics 5100 spectrometer with Mg $K\alpha$ excitation (300 W). The pressure in the analysis chamber was 10^{-8}–10^{-9} mm during data acquisition. The chemical shifts reported are approximate as the samples charged variably and were not charge neutralized. Survey spectra were recorded with a pass energy of 89.45 eV; spectra of the C_{1s} region were recorded with a pass energy of 71.55 eV. Gravimetric analyses were performed in air by using a Cahn 29 electrobalance stabilized with a polonium source. The balance is accurate to ±0.2 μg; we estimate that our results are accurate to ±1 μg. Gas chromatography (GC) was performed with a Hewlett-Packard 5790A gas chromatograph at 80–160 °C using an Analabs 10 ft × $^1/_8$ in. 15% AN 600 column. Molecular weight determinations were made by gel permeation chromatography (GPC) using Polymer Laboratories PL gel columns (10^4, 10^3, and 10^2 Å), a Rainin Rabbit pump, a Knauer 98 refractive index detector, and toluene as the mobile phase. GPC data accumulation and analyses were performed by using Interactive Microware GPC software, an Apple IIe computer, and calibration with polystyrene standards.

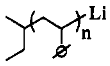
Polystyryl Anion Syntheses. Styrene (1.0–2.0 mL, 8.7–17.4 mmol) and THF or benzene (25–75 mL) were introduced to a dry, nitrogen-purged Schlenk tube and equilibrated to the temperature used for polymerization (−78 °C for THF, 4 °C to room temperature for benzene). The appropriate amount, for the desired molecular weight, of *sec*-butyllithium was added, and the polymerization was allowed to proceed to completion. After 30 min GC indicated that no styrene remained; in practice, the living polystyrene was used for subsequent reactions 30 min to 8 h after initiation. End capping with butadiene or ethylene sulfide was accomplished by titrating to disperse the bright orange living polystyryl anion color with butadiene or ethylene sulfide solution.

Reactions of PCTFE with Polystyryl Anions. A tared PCTFE film sample was placed in a Schlenk tube that was then purged with nitrogen for 15 min and equilibrated to the desired reaction temperature.[26] Polystyryl anion solution (which was also equilibrated to the reaction temperature (~20 mL) was added to the reaction vessel. After the desired reaction time, one of two workup procedures was followed: For butadiene-terminated polystyryllithium reactions, a few drops of ethanol were added, the solution was removed from the flask via cannula, and the film sample was washed with toluene (5 × 20 mL), methanol (5 × 20 mL), and then hexane (5 × 20 mL) and dried (<0.05 mm) to constant mass. For other reactions, the reaction solution was removed and the film sample was washed with reaction solvent (3 × 20 mL), water (3 × 20 mL), and then hexane (2 × 20 mL) and dried (<0.05 mm) to constant mass.

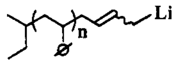
Solvent Swelling of PCTFE Film. PCTFE film samples (1 × 2 cm) were tared, soaked in solvent for 1 h, removed from the solvent, dried under a stream of nitrogen for 5 min, and reweighed. Results were determined as a percent mass gain. Experiments were performed in triplicate, and the reported values are averages; reproducibility was within 0.002% mass gain.

Results

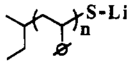
Each of the results that follows pertains to a reaction of PCTFE film with one of three polystyryl anions: polystyryllithium (PS-Li), butadiene-end-capped polystyryllithium (PS-B-Li), sulfur-end-capped polystyryllithium (PS-S-Li). Each is prepared by anionic polymerization



PS-Li



PS-B-Li



PS-S-Li

of styrene using *sec*-butyllithium as the initiator in THF or benzene. PS-B-Li and PS-S-Li[27] were prepared by titrating the colored living PS-Li with butadiene and ethylene sulfide, respectively. We chose film as the PCTFE substrate form for convenience. It is commercially available free of additives and amenable to our characterization techniques.

Reactions with film samples were carried out in ~50-mL Schlenk tubes with a large opening sealed with an O-ring joint (which facilitated introduction and removal of film samples) and a Teflon stopcock connected to a ground-glass joint. The joint was fitted with a rubber septum to allow introduction and removal of reagents and solvents via syringe or cannula or connected directly to a vacuum manifold to dry film samples.

Solvent Swelling Experiments. To assess the relative solvent affinity of PCTFE for the solvents used in

Table I
Solvent Swelling Experiments

solvent	% mass gain
THF	0.27
hexane/THF (67:33	0.19
THF/benzene (75:25)	0.10
THF/benzene (50:50)	0.06
benzene	0.01
benzene/hexane (35:65)	0.00

this study, crude, but practical swelling tests were performed. Tared film samples were treated with solvent for 1 h, dried in a stream of nitrogen for 5 min, and reweighed. The results, reported as percent mass gain, are in Table I.

Reactions of PCTFE with PS-Li. At the outset of this research effort, we foresaw that the reaction of PS-Li with PCTFE film would be an example of the chemistry in eq 2 and that polystyrene would be terminally attached to the PCTFE surface in the product. We anticipated the formation of a thin film of polystyrene (~10–1000 Å) on the PCTFE film surface and planned experiments to control the diffuseness of the PS–PCTFE interface and the PS film thickness by adjusting solvent composition and PS molecular weight.

This simple scenario was not realized. In THF (a solvent in which the reaction in eq 2 is unexceptional for 1–3) at room temperature, PS-Li ($n = 50$;[28] 0.02 M) reacts rapidly with PCTFE film to yield dark colored film samples that continue to darken to pitch black with further reaction. Decreasing the concentration of PS-Li to 0.004 M or the reaction temperature to −78 °C slows the reaction, but the same color changes (as well as all other measured changes) occur, however the rate is diminished. This observation is in sharp contrast to reactions of PCTFE with all other lithium reagents that we have investigated: no visible color change is observed when PCTFE film is reacted with 1–3, methyllithium, or phenyllithium under essentially identical conditions. Figure 1 shows a plot of the absorbance at 310 nm vs reaction time for PCTFE film samples treated with PS-Li ($n = 50$; 0.004 M) at room temperature for different time periods. These data establish that the reduction reaction is not surface-selective and proceeds with little retardation into the bulk of the film. The UV–vis spectrum is broad with no fine structure and tails through the visible region, indicating an extended conjugated π-system. The wavelength value of 310 nm was chosen to obtain the plot in Figure 1; this was an arbitrary choice except for its indication of extent of reactions other than polystyrene addition.[29–31] Gravimetric analysis indicates a gradual and steady mass loss with reaction time. An extensively reacted sample lost ~33% of its initial mass. Quantitative determinations of reaction extents cannot be made with these gravimetric data due to competing mass losses (due to reductive dehalogenation and perhaps graft copolymer dissolution—see below) and mass gains (due to polystyrene addition); however, taken together with the spectroscopic information, these data qualitatively indicate extensive dehalogenation and very deep reactions. XPS indicates that fluorine is absent (<1% atomic composition) from the outer 40 Å. Contact angles ($\theta_A/\theta_R = 97°/15°$) exhibit large hysteresis, indicating a rough surface. Figure 2 exhibits an ATR IR spectrum of a PCTFE film sample that had been (extensively—17 h) reacted with PS-Li ($n = 50$; 0.35 M) in THF at room temperature. The spectrum shows the presence of a small amount (relative to other features) of polystyrene indicated by aromatic C–H stretching at 3100–3000 cm^{-1} but also aliphatic C–H at 3000–2850 cm^{-1} (more than is expected from the polystyrene), conjugated C≡C at 2200–2000 cm^{-1}, conjugated C=C at 1650–1500 cm^{-1}, hydroxyl groups at 3420 cm^{-1}, and carbonyls at 1710 cm^{-1}. The hydroxyl and carbonyl groups can be ascribed to reactions occurring in the aqueous workup.[32] The C=C and C≡C indicate an extensively reduced carbonaceous product similar, in terms of structural features, to benzoin dianion reduced poly(tetrafluoroethylene)[33] and sodium naphthalide reduced poly(tetrafluoroethylene-*co*-hexafluoropropylene).[32]

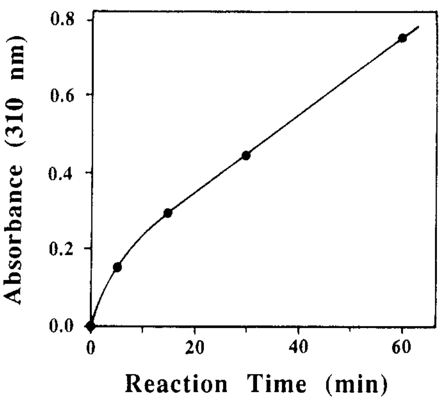


Figure 1. Plot of absorbance (310 nm) vs reaction time for the reaction of PCTFE film with PS-Li ($n = 50$; 0.004 M) in THF at room temperature.

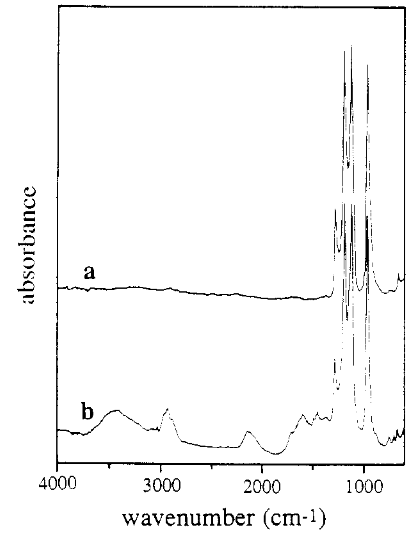


Figure 2. ATR IR spectra of (a) virgin PCTFE film and (b) PCTFE film which had been reacted with PS-Li ($n = 50$; 0.35 M) in THF at room temperature for 17 h.

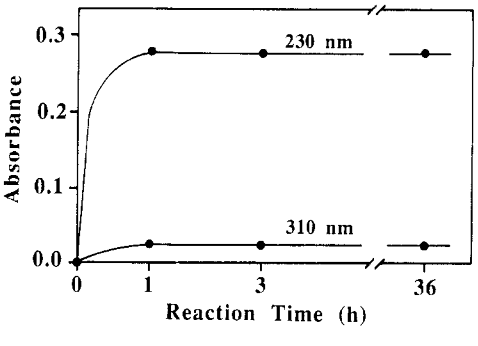
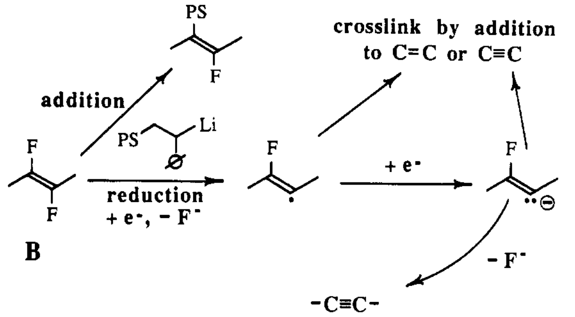


Figure 3. Plots of absorbance (310 and 230 nm) vs reaction time for the reaction of PS-Li ($n = 50$; 0.022 M) in benzene at room temperature.

We offer, as an explanation for the anomalous reactivity of PS-Li, the competitive (with PS-Li addition) reduction of the difluoroolefin intermediate (B in eq 2) by PS-Li via essentially the same mechanism proposed for poly(tetrafluoroethylene) reduction.[33] This mechanism leads to a cross-linked structure containing double and triple bonds; eq 3 gives an abbreviated mechanism. The steric requirements for addition of the secondary benzylic polymeric lithium reagent allow reduction to compete effectively.



(3)

When benzene is used as the solvent for the reaction of PCTFE with PS-Li, the reaction course is very different than with THF as the solvent and occurs in a fashion similar to that of the lithium reagents depicted in eq 2. No visible color change occurs upon reaction. Figure 3 shows plots of absorbance (at 310 and 230 nm) vs reaction time for PCTFE samples reacted with PS-Li (n = 50; 0.022 M) in benzene at room temperature. Very little increase in absorbance was observed at 310 nm (these data are included to compare with the results in THF); the data at 230 nm indicate a surface-selective and autoinhibiting reaction in which the surface reacts completely within 1 h and no subsequent reaction occurs. This type of kinetics is the same as that observed for reaction of **2** or **3** (eq 2) with PCTFE. Gravimetric analysis shows no measurable mass change upon reaction. Contact angles for all reacted samples were indistinguishable, and θ_A/θ_R = 96°/71°. PCTFE exhibits contact angles of θ_A/θ_R = 104°/80°. ATR IR spectra for samples reacted for 1, 3, and 36 h were likewise indistinguishable and show no indication of the reductive dehalogenation that was observed in the reactions carried out in THF. Figure 4 displays a representative ATR IR spectrum. Features expected for polystyrene (3061, 3027, 2924, 1601, 1493, 1452, 760, 701 cm^{-1}) and PCTFE (1286, 1192, 1122, 964 cm^{-1}) are present as well as a broad absorbance (3600–3200 cm^{-1}), indicating the presence of hydroxyl groups. XPS spectra of all reacted samples were also indistinguishable, and a representative spectrum along with a spectrum of PCTFE is shown in Figure 5. Upon reaction, the F_{1s} (692 eV), Cl_{2s} (274 eV), and Cl_{2p} (204 eV) photoelectron lines dramatically decrease in intensity. A small amount of oxygen is introduced (534 eV), and the C_{1s} intensity increases and shifts from 297 to 287 eV. The small peak at 293 eV in the reacted sample spectrum (b inset) is a $\pi \rightarrow \pi^*$ shape-up satellite due to the aromatic carbons in polystyrene. These spectra were recorded at a takeoff angle of 75° (from the sample surface) and indicate the atomic composition of the outer ~40 Å of the surface. The C:F ratio in this region is 18:1, implying that this region is predominantly polystyrene. The C:F ratio measured at a takeoff angle of 15° (measures composition of outer ~10 Å) is 50:1, and the difference between these two ratios demonstrates a composition gradient across the outer 40 Å with increasing fluorine concentration and decreasing polystyrene concentration at greater depths.

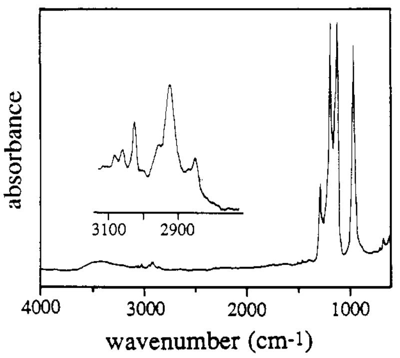


Figure 4. ATR IR spectrum of PCTFE film that had been reacted with PS-Li (n = 50, 0.27 M) in benzene at room temperature for 1 h.

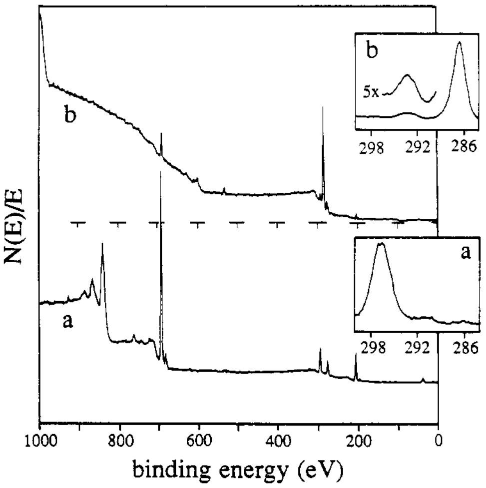


Figure 5. XPS spectrum of (a) PCTFE film and (b) PCTFE film which had been reacted with PS-Li (n = 50; 0.22 M) in benzene at room temperature for 36 h.

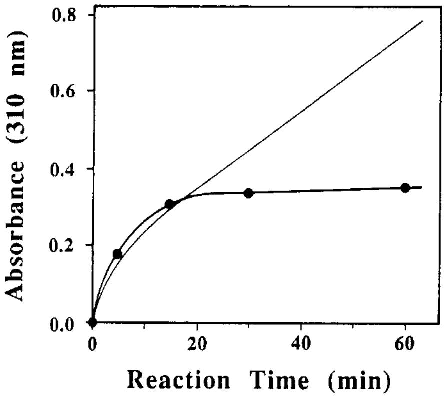


Figure 6. Plot of absorbance (310 nm) vs reaction time for the reaction of PCTFE film with PS-B-Li (n = 50, 0.004 M) in THF at room temperature. The plot without data points is for PS-Li, reproduced from Figure 1.

Reactions of PCTFE with PS-B-Li. In order to increase the relative rate of polystyrene addition over reductive dehalogenation (eq 3) and permit a greater latitude of solvent choice, PS-Li was end-capped with butadiene to form a primary allylic carbanion (PS-B-Li) that has less steric congestion. The experiment described in Figure 1 was repeated by using PS-B-Li instead of PS-Li. The results are shown in Figure 6. No visible color change occurs upon reaction, and the absorbance increase at 310 nm levels after an initial burst. This behavior is typical of most lithium reagents and suggests a surface-selective and autoinhibiting reaction.

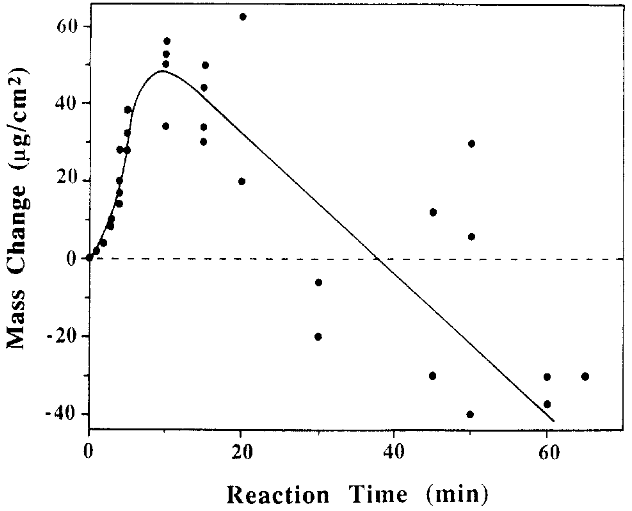


Figure 7. Change in mass vs reaction time for PCTFE film samples reacted with PS-B-Li (n = 50; 0.004 M) in THF at room temperature.

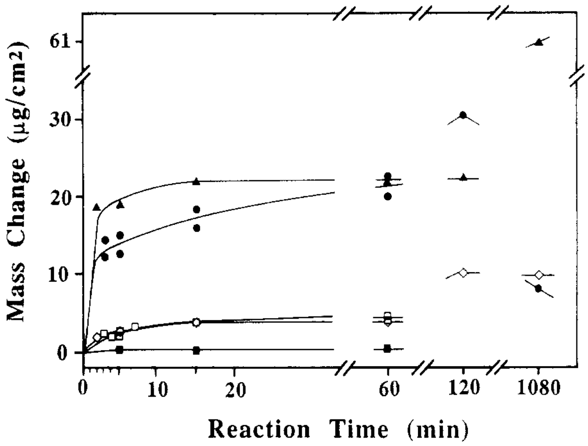


Figure 8. Change in mass vs reaction time for PCTFE film samples reacted with PS-B-Li (n = 50; 0.004 M) at room temperature in hexane/THF (67:33) (▲), THF/benzene (75:25) (●), THF/benzene (50:50) (□), benzene (◇), and benzene/hexane (35:65) (■).

Gravimetric analysis, however, demonstrates that the reaction is not surface-selective. Figure 7 shows the change in mass upon reaction of PCTFE film samples treated with PS-B-Li (n = 50; 0.004 M) at room temperature for various extents of time. Film samples that were allowed to react for times less than 20 min increased in mass, but at longer reaction times mass loss was observed. A sample that was allowed to react for 96 h lost 67% of its initial mass. No indication of extensive reductive dehalogenation was observed by visible inspection, UV–vis, or ATR IR, and we surmised that dissolution of the product graft copolymer was responsible for the mass loss. UV–vis, ATR IR, and XPS spectra of film samples reacted for various times showed no indication of this material loss: all were consistent with a thin film of polystyrene being incorporated in a surface-selective reaction. Contact angle values were θ_A/θ_R = 97°/70°.

The dissolution of the product (polystyrene-grafted PCTFE) in THF is not unreasonable and, in retrospect, should have been anticipated. THF is a good solvent for polystyrene, and though it is a nonsolvent for PCTFE, PCTFE grafted with enough polystyrene should be soluble. Isolation of this graft copolymer from the reaction mixture (which contains a huge excess of PS-B-Li) would be difficult or impossible, so to accomplish this isolation the reaction was carried out in a Θ solvent for polystyrene (and, as well, as nonsolvent for PCTFE) and the graft copolymer was isolated by extracting the isolated film with THF. A PCTFE film sample was allowed to react with PS-B-Li (n = 50; 0.005 M) in hexane/THF (67:33) at room temperature for 48 h. The film sample was then extracted with hexane/THF (67:33) to remove unreacted PS-B-Li and then extracted with THF. A residue was isolated from the THF extract and analyzed by XPS and GPC. XPS of a film cast on a glass slide indicated that fluorine (>2% atomic composition) was present[34] in the residue. GPC analysis showed this material to elute with a retention volume characteristic of polystyrene with a molecular weight of 390 000 (n = 3750). These analyses are consistent with a THF-soluble graft copolymer, and its presence strongly suggests that its dissolution is responsible for the mass losses described above.

The effects of reaction temperature, PS-B-Li concentration, and PS-B-Li molecular weight were investigated in some detail, but none of these variables significantly altered the reaction course. Varying the PS-B-Li concentration over 2 orders of magnitude (n = 50; 0.0004–0.04 M) showed that the reaction is roughly first-order in [PS-B-Li], but the same maximum mass gains were observed at each concentration and mass losses were observed at long reaction times in each case. Reaction temperature likewise affects the kinetics of the reaction but not the outcome. Reactions were carried out at room temperature, −23 °C, −63 °C, and −78 °C (n = 50; 0.004 M PS-B-Li). Lower temperatures are expected to decrease PCTFE chain mobility and PCTFE–THF interactions and thus reduce reaction depths and mass gains.[4] On the other hand, lower temperatures may decrease graft copolymer solubility and increase modified layer thicknesses and mass gains. What is observed is that lower temperatures decrease the rate of mass gain (initially) and the rate of mass loss (at longer times). A film sample reacted for 90 h at −78 °C had lost 14 μg/cm², which corresponds to a sample reacted at room temperature for ~30 min. The maximum mass gain for a film sample reacted at −78 °C was 41 μg/cm², after 21-h reaction; this is a similar maximum value to that obtained for reaction at room temperature. Varying molecular weight of PS-B-Li over 3 orders of magnitude (n = 5, 50, 500, 5000[35]) does not grossly affect the rate of mass change or the ultimate mass gain. These results suggest that solubilization of PCTFE requires a limiting weight percent of polystyrene grafted to it and that graft copolymer swelling and dissolution control the rate of the reaction.

The reaction solvent plays a more important role in determining the product structure than the variables discussed above. Figure 8 shows plots of the mass change vs reaction time for PCTFE film samples reacted with PS-B-Li (n = 50; 0.004 M) at room temperature in various solvents and solvent mixtures. Each plot demonstrates a marked difference in reaction course from the reaction in THF. In hexane/THF (67:33) (▲), the reaction proceeds rapidly for a short initial period (less than 2 min) and then slows dramatically. The reaction continues (mass increases) for at least 18 h. In THF/benzene (75:25) (●) the reaction begins at high rate and gradually slows over the first hour of reaction. After 18 h, gravimetric data indicates that some product graft copolymer has dissolved. Reactions in benzene (◇) and THF/benzene (50:50) (□) showed small initial mass gains over the first 15 min of reaction and little subsequent change. Reactions in benzene/hexane (35:65) (■) were very slow.

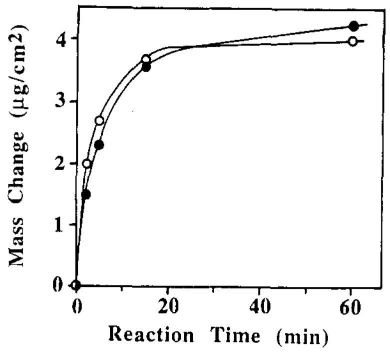


Figure 9. Effect of 12-crown-4 on the rate of mass change of PCTFE films allowed to react with PS-B-Li (n = 50; 0.004 M) in benzene at room temperature (●, with 12-crown-4; ○, without 12-crown-4).

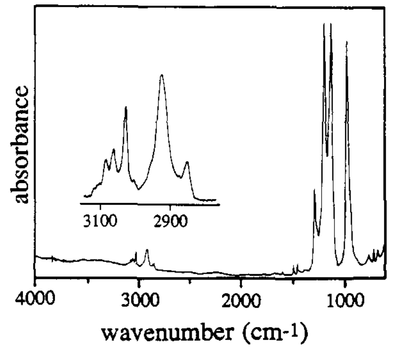


Figure 10. ATR IR spectrum of PCTFE film that had been reacted with PS-B-Li (n = 50, 0.024 M) in refluxing benzene for 3 h.

To determine whether or not differences in solution structure of PS-B-Li due to aggregation are responsible for the different rates of reaction, reaction kinetics of the reaction of PCTFE with PS-B-Li (n = 50; 0.004 M) at room temperature in benzene with and without 1 equiv of 12-crown-4 were measured and compared. Figure 9 shows these data. The rates of mass gain by the film samples in the two reactions are essentially identical, indicating that aggregation effects are not important.

The products of the reactions of PCTFE with PS-B-Li in benzene were studied in some detail: Film samples that were allowed to react at room temperature for 1 h showed changes in contact angles (θ_A/θ_R = 94°/68°), an increase in the C:F ratio indicated by XPS, but essentially no changes by ATR IR. The reaction temperature was increased to refluxing benzene temperature in an attempt to incorporate more (enough to be visible by ATR IR) polystyrene on the surface: PCTFE samples were allowed to react with PS-B-Li (n = 50; 0.024 M) for 2, 3, 4.5, and 14 h. The product film samples showed appreciable and indistinguishable amounts of polystyrene by ATR IR. Figure 10 shows the ATR IR spectrum of a sample allowed to react for 3 h. The absorbances at 3061, 3027, 2924, 1601, 1493, 1452, 760, and 701 cm^{-1} are those expected for polystyrene. This spectrum indicates a clean addition reaction and little or no competitive reduction (Figure 2, eq 3). XPS spectra of reacted samples are likewise indistinguishable and indicate complete reaction within the outer 40 Å of the film sample and that most of this region is polystyrene. Figure 11 shows both a survey spectrum, indicating a C:F ratio of 60:1 and a high resolution spectrum of the C_{1s} region exhibiting the $\pi \rightarrow \pi^*$ shake-up satellite of polystyrene.

These reaction conditions were used to test whether or not the amount of polystyrene incorporated (thickness of the polystyrene thin film) could be controlled by the PS-B-Li chain length. PCTFE film samples were reacted with PS-B-Li (n = 50; 0.024 M) and PS-B-Li (n = 5; 0.024 M) in refluxing benzene in side-by-side experiments. Reaction sets were run for both 2 and 6 h, and XPS and ATR IR spectra of each set were indistinguishable. There was, however, a pronounced difference between the XPS and ATR spectra for the n = 5 and n = 50 reactions. Figure 12 indicates that the longer chain PS-B-Li reacts to incorporate a thicker polystyrene layer.

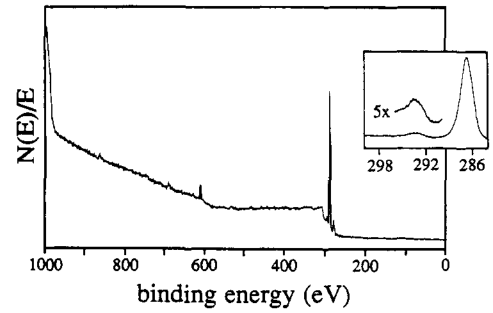


Figure 11. XPS spectrum of PCTFE film that had been reacted with PS-B-Li (n = 50; 0.024 M) in refluxing benzene for 14 h.

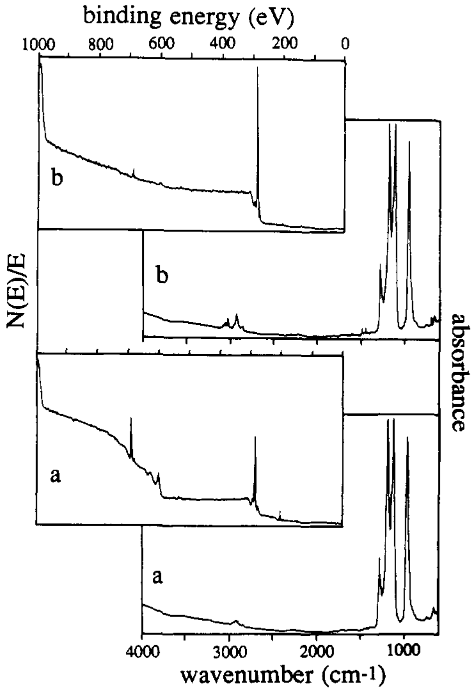


Figure 12. XPS and ATR IR spectra of PCTFE film samples that had been reacted with PS-B-Li (0.024 M) in refluxing benzene for 2 h: a, PS-B-Li, n = 5; b, PS-B-Li, n = 50.

Reactions of PCTFE with PS-S-Li. Reactions of PCTFE with thiolates have been reported,[36,37] and a mechanism for this reaction has been proposed.[37] In this work PCTFE was reacted with PS-S-Li in both benzene and THF solution under a range of conditions.

PCTFE film samples were allowed to react with PS-S-Li (n = 50–80) in THF solution at concentrations varying from 0.004 M to 0.05 M at −78 °C, −20 °C, room temperature, and refluxing THF temperature for various periods of time. ATR IR and XPS indicate that polystyrene is incorporated in the product surface under all conditions. Temperature and concentration appear by these analyses to affect only the reaction kinetics and not the product structure. Reaction is faster at higher temperatures and higher concentrations. The product film samples varied in color, depending on the extent of reaction,

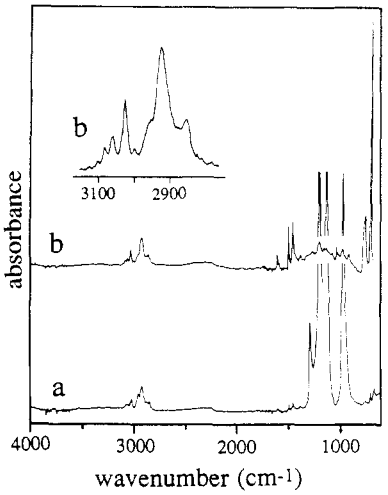


Figure 13. ATR IR spectra of PCTFE film samples that had been reacted with PS-S-Li (n = 50) in THF with the following conditions: a, room temperature, 0.04 M, 37 min; b, refluxing THF, 0.2 M, 3 h.

over a spectrum ranging from clear to "tinted" (brown) to metallic copper-colored. Film samples that were lightly modified exhibit contact angles of θ_A/θ_R = 95°/70°. More extensively modified samples showed pronounced contact angle hysteresis, indicating roughened surfaces: a sample reacted for 3 h at room temperature exhibited θ_A/θ_R = 130°/10°; a sample reacted for 3 h at reflux exhibited θ_A/θ_R = 129°/25°. Gravimetric analysis was performed on samples reacted in THF at room temperature for 48 h (n = 80; 0.05 M). The film samples gained an average mass of 100 $\mu g/cm^2$ upon reaction. This is in sharp contrast to the reaction of PCTFE with PS-B-Li in THF, which under these conditions exhibits mass loss and product dissolution. Figure 13 shows representative ATR IR spectra of PCTFE films that had been reacted with PS-S-Li under different conditions. Both spectra show the expected absorbances due to polystyrene. It is noteworthy that the sample prepared in refluxing THF (Figure 13b) shows that there is little PCTFE in the ATR IR sampling region (outer ~3000 Å); this indicates that an extensive modification has occurred and also that the product graft copolymer is not appreciably soluble (and not comparably soluble to the graft copolymer prepared with PS-B-Li) in refluxing THF; this is consistent with the gravimetric data.

Reactions of PCTFE with PS-S-Li using benzene as a solvent were carried out with conditions varying from 10 min to 60 h, room temperature to refluxing temperature, and 0.004–0.04 M PS-S-Li. No appreciable reaction was observed under any conditions. (Some small changes in XPS spectra that could be ascribed to no more than sample contamination were seen sporadically.)

General Discussion

We noted in the Introduction that at the outset of this research we predicted that the experiments described above would be simplified cases of polymer adsorptions, and, in fact, we thought of these reactions as routes to idealized models for terminally adsorbed polymer chains. In retrospect, our naiveté is obvious.

In carrying out a surface modification reaction (this is a general discussion at this point and not specific to surface-grafting polymer chains) of a solid polymer at a solid polymer–solution interface, several factors should be considered in anticipating the outcome of the reaction, especially with regard to the surface selectivity of the reaction and the ultimate interface structure of the product:

(1) **The Unreacted Polymer–Solvent Interface.** A solid polymer in contact with a solvent may interact with the solvent to varying extents along a continuum ranging from not being wet by the solvent to (ultimately) being dissolved by the solvent. The nonmolecularly lucid terms *wetting* and *swelling* are used to describe points on this continuum, and polymers (or polymer surfaces) can be wet to varying extents or swollen to varying degrees. The interface can thus vary from sharp to diffuse, and because solvent facilitates reaction, the depth (into the solid polymer) of the modification reaction and therefore the thickness of the modified layer in the product will be affected by the nature of this interface. The diffuseness of this interface can be temperature dependent.[4] Solvent mixtures add a complexity to this situation as the solid polymer may have an affinity for one solvent and not the other, giving rise to a partitioning of one solvent between the solid polymer and the solution.

(2) **The Product Polymer–Solvent Interface.** As a reaction proceeds at a solid polymer–solvent interface, the structure of the interface changes. Two simplified general scenarios are as follows: (a) *The product (modified polymer surface) interacts with the solvent to a greater extent than does the unreacted polymer surface.* This can lead to a continuum of processes, an extreme of which involves an unreacted polymer that is barely wet by the solvent converting to a modified polymer that is soluble; the sample reactively dissolves. The oxidation of polypropylene with CrO_3 in acetic acid/acetic anhydride is an example of this.[38] The thickness of the modified layer in the product depends on the disparity between the solvent-unreacted polymer and the solvent–product interfaces. In the case of polypropylene oxidation this disparity is large and a thin modified layer is produced by a relatively deep reaction and product dissolution. (b) *The product interacts with the solvent to a lesser extent than does the unreacted polymer.* Again, a range of processes can occur depending on the extents of and disparity between the interactions. If the unreacted polymer is not extensively swollen by solvent and reagents, autoinhibition will occur: the product will act as a barrier layer and protect the underlying material from reaction. The phase transfer catalyzed dehydrofluorination of poly(vinylidene fluoride)[39] exhibits a pronounced autoinhibition; the poly(fluoroacetylene) product serves as a barrier layer. The reaction of PCTFE with lithium reagents **2** and **3** are other examples.[4]

(3) **Reagent Solubility.** The solubility and relative solubility of the reagent(s) in the unreacted polymer, the modified polymer, the interphase region (wet or swollen unreacted and modified polymer)—which changes throughout the reaction—and solvent have to be considered. The same factors that have been discussed for solvents are equally important for reagents. The reagent will partition among the regions of the system, and the dynamic partition coefficients (changing throughout the reaction) will affect product structure.

(4) **Interface Chemistry.** In addition to how the modification reaction affects the solvent and reagent affinities of the solid polymer, the chemistry can effect other properties. If the solution interacts strongly with the product but cross-linking occurs in the modification reaction, the product will not dissolve and a thick modified layer will result. If the modification cleaves polymer chains, low molecular weight material will ablate and chain ends will be important chemical features. The oxidation of

polyethylene with chromic acid[40,41] to form a surface rich in carboxylic acids is an example of this. The nature of the interphase region as the reaction site needs to be considered as well in predicting the reaction course. We have reported several examples[5,6] of reactions that do not proceed to the products predicted by the analogous solution chemistry.

(5) Isolated Product Structure. The structure of the modified solid polymer in contact with the reaction solution may vary significantly from the structure of the isolated product that is free of solvent and reagents. The compatibility (or lack of compatibility) of the unreacted and modified polymer and the disparity between surface free energies may induce reorganizations during rinsing procedures and solvent removal that segregate components and concentrate either modified or unreacted polymer at the surface.

An individual polymer surface modification can thus be a complex process, and there is a great deal of latitude in processes system-to-system. The differences in the product structures resulting from the very similar reactions of PCTFE with reagents **1**–**3** (described in the Introduction) point out the difficulties in making generalizations.

Discussion and Conclusions

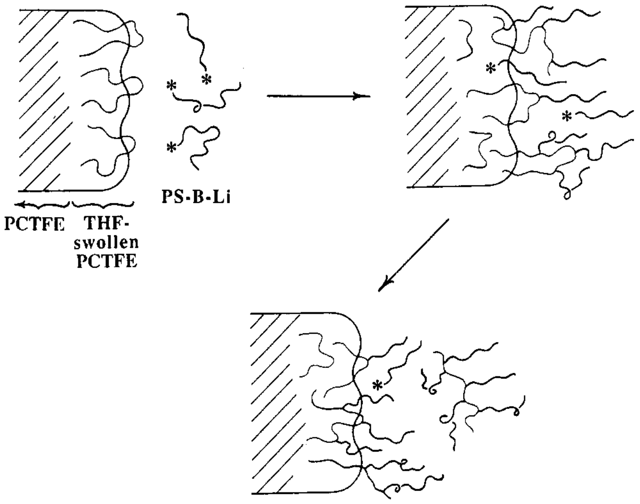
We report in this paper the reactions of polystyryl anions with PCTFE film samples. The reaction course and the modified surface structure vary greatly with end functional group identity, and we discuss each in turn.

Polystyryllithium (PS-Li) in THF reacts with PCTFE primarily as a reducing agent (eq 3) to form a complex carbonaceous product containing conjugated $C{=}C$ and $C{\equiv}C$ (Figure 2). A small amount of polystyrene is incorporated as well. The modification is not surface-selective (Figure 1) and proceeds deep into the bulk of the film. The initial PCFTE–THF interface is rather diffuse (THF swells PCTFE—Table I), and a large number of reactive sites on PCTFE chains are solvated. We propose that many of these sites can react with PS-Li by one-electron reduction steps which do not require close (bond length) encounter, but comparatively few sites can react via addition of PS-Li. The carbonaceous product is most certainly less swollen by THF (and PS-Li), but its formation does not inhibit reduction. We propose (as we did for PTFE reduction with benzoin dianion[33,42]) that the reaction continues because the product conducts electrons from solution down to the virgin PCTFE. We envision a complex interfacial process occurring in which an outer layer of swollen PCTFE reacts either by reduction or by addition of PS-Li (eq 3) and a sublayer that cannot be accessed by PS-Li reacts only by reduction.

When benzene is used as the solvent for reaction of PS-Li with PCTFE, the deep reduction observed with THF as solvent does not occur. A surface-selective addition reaction occurs that is complete within 1 h, and no further changes result after longer reaction times. Benzene forms a much sharper interface with PCTFE (Table I) than does THF, and we propose that all PCTFE reaction sites are accessible to addition by PS-Li and addition competes favorably with reduction thus no conducting carbonaceous layer forms. An additional factor could be that the relative rates of addition and reduction are different in THF and benzene-swollen PCTFE.

PCTFE film reacts with butadiene-terminated polystyryllithium (PS-B-Li) in THF to yield surface-modified PCTFE derived from only the addition reaction sequence described in eq 2. There was no evidence of the reduction that was observed with PS-Li in THF. The reactivity differences between PS-Li and PS-B-Li can be explained by their steric differences. Addition of the primary allylic lithium alkyl is more facile. Gravimetric analysis of the product film samples of this reaction indicated that the reaction is not surface selective and that the graft copolymer product dissolves in the reaction medium. Scheme I pictorially represents the progression of events in this reaction. The diffuse PCTFE–THF interface becomes more diffuse as polystyrene is grafted (the solvent interacts to a greater extent with the product). This increases the mobility of PCTFE chains and exposes more reaction sites. When a sufficient weight percent polystyrene is grafted to a PCTFE chain, it becomes soluble in the reaction medium. The PCTFE film is progressively etched leaving a surface of graft copolymer.

Scheme I



The reactions of PCTFE with PS-B-Li in several different solvent systems were studied (Figure 8), and several points warrant discussion. In most solvents the mass gain was rapid in the first several minutes of reaction and subsequently slower. The relative magnitude of these initial mass gains correlates well with the PCTFE film's affinity for each solvent (Table I). The initial reaction is thus controlled by the structure of the PCTFE–solvent interface. After this initial period, the solvent affinity of the product copolymer contributes to the reaction course. Comparing the results of the reactions in hexane/THF (67:33) and THF/benzene (75:25), we note: The PCTFE film has a greater affinity by a factor of $\sim$2 for hexane/THF than for THF/benzene (hexane is a nonsolvent for PCTFE; THF must partition into PCTFE from hexane to a greater extent than it does from benzene), and the reaction is about twice as fast in hexane/THF than it is in THF/benzene in the first 5 min. Over the next 55 min the reaction in THF/benzene continues and at a higher rate than the reaction in hexane/THF proceeds. This indicates that the product interacts to a greater extent with THF/benzene than with hexane/THF. After 18 h of reaction mass loss is observed in THF/benzene; the reaction continues in hexane/THF and there is no indication of product dissolution. Reactions in benzene are much less extensive than in THF/hexane or THF/benzene, indicating the sharp interface between PCTFE and benzene. No dissolution is observed. We anticipate that PCTFE heavily grafted with polystyrene to be benzene-soluble and propose that sufficient PCTFE sites are not available at the benzene–polymer interface to form a heavily grafted copolymer. Increasing the reaction temperature to refluxing benzene temperature causes more extensive reaction and incorporates a sufficient amount of polystyrene to be visible in the infrared spectrum (none was visible in room-temperature reaction products). The experiments described in Figure 12 indicate that some control of the amount of polystyrene incorporated under these conditions can be exercised by adjusting the molecular weight of PS-B-Li.

Reactions of PCTFE with PS-S-Li were carried out under a variety of conditions using benzene and THF as solvents. No reactions were observed under any conditions using benzene. The PCTFE–benzene interface may be too sharp to allow the reactive end of PS-S-Li to come into intimate contact with a reactive PCTFE site. Reaction occurred under all conditions at the comparatively diffuse PCTFE–THF interface, and the product graft copolymer interacted with the reagent solution enough to allow very deep modification. Unlike the reaction with PS-B-Li, the graft copolymer is not soluble and very thick modified layers result on the film surface. Figure 13b shows an extensively modified sample with a graft copolymer layer >3000 Å thick. The sharply contrasting solubilities of the graft copolymers prepared by using PS-S-Li and PS-B-Li is surprising and indicates that the reaction with PS-S-Li is more complex than the reaction described in eq 2. We propose that some cross-linking must occur in the reaction with PS-S-Li with PCTFE that renders the product insoluble.

Acknowledgment. We are grateful to the Office of Naval Research and the University of Massachusetts National Science Foundation sponsored Materials Research Laboratory for financial support. T.J.M. acknowledges the support of the National Science Foundation in the form of a Presidential Young Investigator Award.

References and Notes

(1) A preliminary account of some of this work has been reported: Kolb, B. U.; Patton, P. A.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(2), 248.
(2) Present address: A. E. Staley Manufacturing Co., P.O. Box 151, Decatur, IL, 62525.
(3) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 1826.
(4) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068.
(5) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 1437.
(6) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 2318.
(7) Cohn, D.; Hoffman, A. S.; Ratner, B. D. *J. Appl. Polym. Sci.* **1987**, *33*, 1.
(8) Yamakowa, S.; Yamamoto, F.; Kato, Y. *Macromolecules* **1976**, *9*, 754.
(9) Rao, M. H.; Rao, K. N.; Lokhande, H. T.; Teli, M. D. *J. Appl. Polym. Sci.* **1987**, *33*, 2345.
(10) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.
(11) Lai, J. Y.; Chang, T. C.; Wu, Z. J.; Hsieh, T. S. *J. Appl. Polym. Sci.* **1986**, *32*, 4709.
(12) Omichi, H.; Chundury, D.; Stannett, V. T. *J. Appl. Polym. Sci.* **1986**, *32*, 4827.
(13) Misra, B. N.; Sood, D. S.; Mehta, I. K. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1749.
(14) Yamakawa, S. *Macromolecules* **1979**, *12*, 1222.
(15) Feng, X. D.; Sun, Y. H.; Qin, K. Y. *Macromolecules* **1985**, *18*, 2105.
(16) Narayan, R.; Krauss, M.; Tsao, G. T. *Polym. Mater. Sci. Eng. (Am. Chem. Soc., Div. Polym. Mater.)* **1985**, *52*, 112.
(17) Fery, N.; Hoene, R.; Haman, K. *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 337.
(18) Donnet, J. B.; Riess, G.; Majowski, G. *Eur. Polym. J.* **1971**, *7*, 1065.
(19) Yanova, L. P.; Kuznetsov, V. A.; Taubman, A. B. *Kolloid-Z.* **1975**, *37*, 614.
(20) Takaki, M.; Asami, R.; Kuwata, Y. *Macromolecules* **1979**, *12*, 378.
(21) Takaki, M.; Asami, R.; Inukai, H.; Inenaga, T. *Macromolecules* **1979**, *12*, 383.
(22) Lechermeier, G.; Revillon, A.; Pillot, C. *J. Macromol. Sci., Chem.* **1978**, *A-12*, 285.
(23) Cameron, G. G.; Qureshi, M. Y. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 287.
(24) Ceausecu, E.; Bordeianu, R.; Buzdugen, E.; Cerchez, I.; Ghioca, P.; Stancu, R. *J. Macromol. Sci., Chem.* **1985**, *A-22*, 803.
(25) Juaristi, E.; Martinez-Richa, A.; Garcia-Rivera, A.; Cruz-Sanchez, J. S. *J. Org. Chem.* **1983**, *48*, 2603.
(26) No temperature equilibration was performed on reactions at or above room temperature.
(27) Morton, M.; Kammerick, P. F. *J. Am. Chem. Soc.* **1970**, *92*, 3217.
(28) Values given for *n* are approximate and are based on the degree of polymerization predicted from styrene: *sec*-butyllithium ratios. Actual values (determined by GPC) are very close.
(29) Garcia-Rubio, L. H. *Macromolecules* **1987**, *20*, 3070.
(30) Partridge, R. H. *J. Chem. Phys.* **1967**, *47*, 4223.
(31) Klöpffer, W. *Eur. Polym. J.* **1975**, *11*, 203.
(32) Bening, R. C.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*(2), 356.
(33) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2819.
(34) No quantitative information can be derived from this analysis; it indicates only that the sample is not entirely polystyrene. The structure of the cast (from THF) film likely may be perturbed to concentrate polystyrene at the surface. No chlorine was observed, but unreacted PCTFE repeat units may be present beneath the XPS sampling depth of the cast film.
(35) The concentration of PS-B-Li ($n = 5000$) was 0.001 M for these experiments. The concentration was reduced to lower the solution viscosity.
(36) Taylor, R. T.; Pelter, M. W. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 215.
(37) Taylor, R. T.; Pelter, M. W. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2651.
(38) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 309.
(39) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2529.
(40) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736.
(41) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4746.
(42) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1985**, *18*, 2087.

Registry No. PCTEE, 9002-83-9; PS-Li, 36345-04-7; PS-B-Li, 9060-29-1; PS-S-Li, 124153-22-6.