Polymerization of Styrene in Supercritical CO2-Swollen Poly(chlorotrifluoroethylene)

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ABSTRACT: The heterogeneous (solid/supercritical fluid solution) free-radical polymerization of styrene in supercritical carbon dioxide-swollen poly(chlorotrifluoroethylene) (PCTFE) polymer film (63 mil) has been studied as an approach to polymer blend preparation. Decompression followed by thermal initiation using AIBN or *tert*-butyl perbenzoate yields polymer blends with the polystyrene trapped inside the matrix polymer. Polymerization prior to decompression yields more extensively modified products. Polystyrene content and the distribution of polystyrene in the blend can be controlled by adjusting the concentration of styrene in the supercritical fluid or by controlling the time that the PCTFE film is in contact with the fluid. The control imparted is consistent with the phase behavior and absorption kinetics of the styrene–CO2–PCTFE system. Transmission electron microscopy and energy dispersive X-ray analysis (EDX) indicate that the polystyrene exists as discrete phase-segregated regions throughout the thickness of the PCTFE film. Thermal analysis of blends and infrared data from extraction experiments indicate that radical grafting reactions do not occur to any significant extent. EDX data indicate that blends with composition gradients of adjustable degrees of severity can be produced by using soaking periods of shorter duration than is required to achieve equilibrium solubility of the monomer in the substrate.

Introduction

We recently reported[1] the supercritical fluid (SCF)-assisted infusion of vinyl monomers into and subsequent free-radical polymerization within several organic polymer substrates. This new route to composite polymer materials is summarized in eq 1. A solid polymer sample is soaked with a SCF CO2 solution of monomer and thermal initiator (I) at a temperature at which the initiator decomposes very slowly. The reactor is then either vented, removing the solution, and heated to promote polymerization or heated in the presence of the monomer/initiator/SCF solution and subsequently vented. The synthesis of polystyrene/substrate blends was demonstrated for six semicrystalline and glassy polymer substrates: polyethylene, Bisphenol A polycarbonate, poly(oxymethylene), nylon 66, poly(4-methyl-1-pentene), and poly(chlorotrifluoroethylene) (PCTFE). This method was found to be generally applicable, and it was demonstrated that blend composition (polystyrene content) was a function of the reaction conditions. This approach may prove uniquely successful for the preparation of certain types of polymer blends, for example, if one or both polymer components are insoluble, infusible, and/or solvent resistant or if one component has already been processed to a desired shape. Extension of this method to the preparation of interpenetrating and semiinterpenetrating networks using multifunctional monomers and/or network substrates is straightforward.

This paper addresses several issues regarding the synthesis of polymer blends via SCF-swollen substrates. First, can experimental variables including temperature, pressure, monomer concentration, and absorption/polymerization conditions be manipulated to control the composition of the blends and the distribution of the components? Second, can the results of the experiments be explained via the underlying phase behavior and the absorption and polymerization kinetics of the system?

Third, does the nascent polystyrene exist as a discrete phase or is there extensive grafting reactions to the substrate polymer? To answer these and other questions, we examined the PCTFE/polystyrene system in detail and report on control of blend composition by manipulation of the variables mentioned above. In addition, the morphology and distribution of polystyrene throughout the blend have been briefly investigated.

PCTFE was chosen as the substrate for this study for several reasons. It is chemically and spectroscopically dissimilar to polystyrene which facilitates analysis of the blends. It exhibits excellent solvent resistance, chemical stability, and barrier properties, making it both a difficult substrate to chemically modify[2-5] and a rigorous test for the SCF modification scheme.

This work is the first step in a larger effort directed at the modification of solid organic polymers by carrying out chemical reactions in supercritical fluid-swollen polymer substrates. Background information is provided in the preliminary communication,[1] and reviews of supercritical fluids are available;[6] only several important advantages of SCFs are summarized here: First, the degree of polymer swelling[7-11] and partitioning of penetrants[12,13] between SCF solvents and swollen polymers can be manipulated by adjusting the solvent strength of the SCF via changes in temperature and pressure. Second, diffusion rates in SCF-swollen (plasticized) polymer substrates can be orders of magnitude greater than those in the unswollen polymer,[9,10] which significantly enhances the kinetics of absorption of penetrants. Third, common SCF solvents are gases at ambient conditions, and, therefore, the solvent rapidly dissipates (and can be easily recovered) upon release of pressure. Fourth, SCF solutions exhibit no surface tension and are thus useful in situations where wettability of the polymer substrate is an issue. Finally, SCFs, especially carbon dioxide, have obvious environmental advantages compared to organic solvents. Recently, both homogeneous and heterogeneous polymerizations in SCF CO2 have received attention.[14-16]

(1)

solid polymer
substrate

SCF/styrene/initiator
swollen substrate

substrate/polystyrene
blend
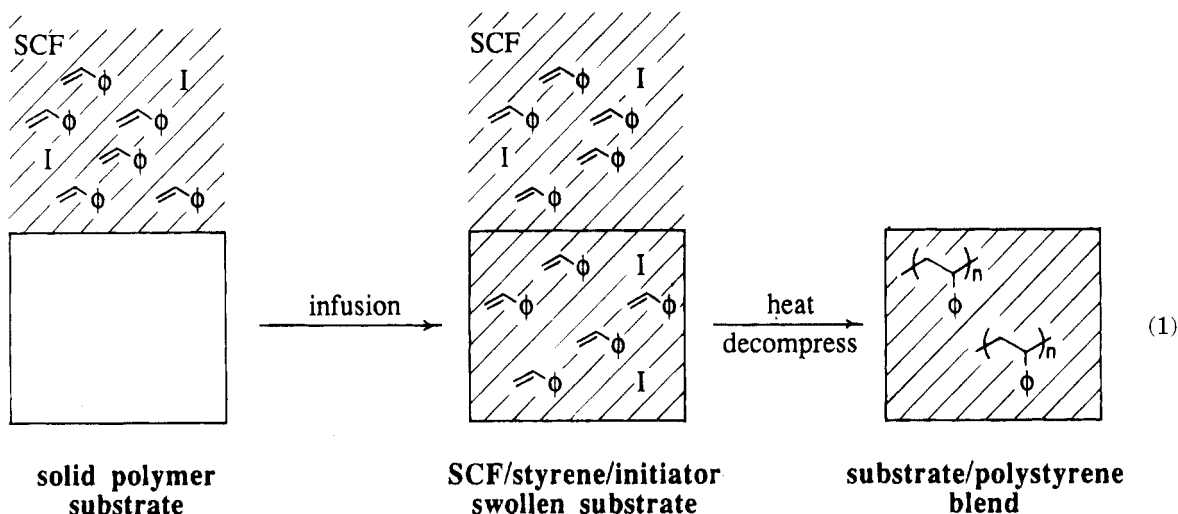
Experimental Section

General Procedures. Poly(chlorotrifluoroethylene) (Kel-F, 3M Co.) in the form of 63-mil-thick sheets was obtained from Modern Plastics Inc. (Springfield, MA). The actual thickness of the film was about 0.164 cm, with thickness variations of approximately 0.004 cm. The T_g of PCTFE is reported to be 52 °C;[17] no distinct transition was observed by us using DSC. The percent crystallinity of the PCTFE was determined by DSC to be approximately 30% using 10.3 cal/g for the heat of fusion of the perfect crystal.[18] Carbon dioxide (99.99% purity) was obtained from Merriam Graves and used as received. Styrene (Aldrich) was distilled from calcium hydride under reduced pressure. AIBN (Polysciences) was recrystallized twice from methanol. *tert*-Butyl perbenzoate (Aldrich), ethylbenzene (Fisher), and ruthenium tetroxide (0.5% in water; Polysciences) were used as received.

Attenuated total reflectance infrared spectroscopy (ATR-IR) was performed using a Nicolet 44 FTIR with a 45° KRS-5 internal reflection element. Spectra were recorded at 2 cm^{-1} resolution, and a minimum of 128 scans were accumulated. Differential scanning calorimetry (DSC) measurements were conducted on a DuPont 2000 DSC under flowing, dry nitrogen at a heating rate of 10 °C/min. After the first heating run, the samples were quenched with liquid nitrogen and the measurements were repeated. Molecular weight determinations were made by gel permeation chromatography using a series of Polymer Laboratories PL gel columns (10^4, 10^3, and 10^2 Å), a Rainin Rabbit pump, an IBM UV detector, and THF as the mobile phase. Data were collected and analyzed using Polymer Laboratories software. Calibration was performed using narrow molecular weight distribution polystyrene standards. Transmission electron microscopy (TEM) was performed using a JEOL 100 CX. Sections of PCTFE and PCTFE/polystyrene blends were microtomed at room temperature using a diamond knife and stained with ruthenium tetroxide in a glass desiccator. Energy-dispersive X-ray analysis (EDX) was performed using a Fisons Mark VI Super Quantum detector on a JEOL JSM-820 scanning electron microscope. Prior to analysis by EDX, the samples were microtomed in cross section and a light carbon coating was applied.

Reactions were run in 316 stainless steel reaction vessels fabricated from 1.2 cm i.d. × 10 cm sections of ½-in. schedule 160 stainless steel pipe threaded to accept ¼-in. NPT fittings. One end of the vessel was plugged and the other attached to a ⅛-in high-pressure valve (High Pressure Equipment, Erie, PA) via a coupling and high-pressure tubing. The reaction vessels were filled with CO$_2$ from a high-pressure manifold described previously.[1] A variable-volume view cell similar to that described by McHugh[6] was used to verify phase behavior.

Determination of CO$_2$ solubility in PCTFE was performed in a manner similar to that described by Berens for other polymers.[9,10] Sections of PCTFE weighing approximately 1 g were sealed individually in the reaction vessels. The vessels were purged with CO$_2$ three times, preheated in a

circulating temperature bath, and filled with CO$_2$ to the desired pressure from the manifold. After the appropriate time, the vessels were vented and the PCTFE samples were quickly transferred to a Cahn 29 electrobalance. Mass loss (CO$_2$ desorption) as a function of time was recorded beginning approximately 45 s after depressurization.

Synthesis of PCTFE/Polystyrene Blends. All of the reactions involved variants of this general procedure: A single tared sample (~1 × 4 cm) of PCTFE was placed in a reaction vessel which was sealed, purged with CO$_2$, weighed, and immersed in a circulating controlled-temperature bath equilibrated at 80 °C. *tert*-Butyl perbenzoate (0.3 mol % based on styrene) was dissolved in styrene (~3 mL), and the solution was transferred to the vessel via syringe. The vessel was filled with CO$_2$ to 240 atm using the high-pressure manifold. The contents of the reactor were mixed using a vortex mixer, reequilibrated to 80 °C, and repressurized to 240 atm (the pressure drops due to the dissolution of styrene); the mass of CO$_2$ transferred was determined gravimetrically. The PCTFE sample was allowed to soak for a period of 4 h at these conditions, and then the vessel was drained, pressurized with N$_2$ (100 atm), and heated at 120 °C for 4 h. The reactor was cooled and opened, and the PCTFE sample was isolated and weighed. Variations of this procedure involved changing the soaking time over a range of 1–24 h, the styrene concentration from 15 to 60 wt %, and the pressure from 50 to 300 atm. Reactions were also run at a soaking temperature of 40 °C and a heating temperature of 80 °C (with AIBN as the initiator and CO$_2$ pressure of 103 atm). Another variation involved heating the reactor after the soaking period prior to draining to promote polymerization in the presence of the SCF/monomer solution, draining, and reheating under N$_2$.

Results and Discussion

In the preliminary account of this work[1] we reported three PCTFE/polystyrene blend syntheses based on the strategy in eq 1 using 63 mil PCTFE sheet samples, styrene as the monomer, CO$_2$ as the SCF, and either AIBN or *tert*-butyl perbenzoate as the initiator. In each synthesis the concentration of styrene in carbon dioxide was ~37 wt % and 0.3 mol % initiator was used. The reaction conditions chosen for these syntheses gave mass uptake values of 4.8, 13.4, and 75.7 wt % based on the original mass of the PCTFE film. These mass increases correspond to blends of ~5, 12, and 43 wt % polystyrene. The 5% blend was prepared by soaking the PCTFE sample in the supercritical solution at 40 °C and 103 atm of CO$_2$ for 4 h, draining and pressurizing the reactor with N$_2$ (100 atm), and then heating at 80 °C for 4 h. AIBN was used as the initiator. The 12% blend was prepared similarly, except that the soaking and heating periods were at 80 °C, 240 atm of CO$_2$, and 120
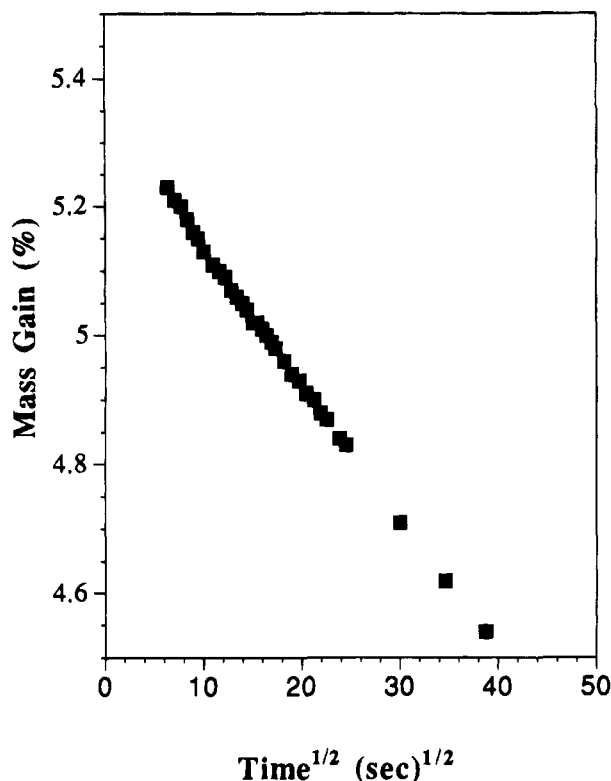
Figure 1. Representative CO_2 desorption data used to determine CO_2 solubility in PCTFE. The example shown is for a PCTFE film sample treated for 8 h at 80 °C and 240 atm of CO_2.

Figure 2. Absorption kinetics for CO_2 in PCTFE at 40 °C, 103 atm (◆) and 80 °C, 240 atm (■).

°C, 100 atm of N_2, respectively, and *tert*-butyl perbenzoate was the initiator. The soaking and heating temperatures were chosen based on the thermal stability of the initiators; the half-lives are hundreds of hours at the soaking temperatures and ~2 h at the heating temperatures.[19] The 43% blend was prepared using *tert*-butyl perbenzoate by soaking at 80 °C, 150 atm of CO_2, for 4 h, heating (8 h, 120 °C), draining, and then reheating (12 h, 120 °C, 100 atm of N_2).

It is clear from the results of these three experiments that blend composition is controlled by the reaction conditions, but these conditions were chosen somewhat arbitrarily for the purpose of demonstrating substrate modifications of increasing severity. Below we discuss experiments that address the phase behavior and absorption kinetics of the system and the effects of important experimental parameters on blend composition. These experiments were designed to help establish rational guidelines for predicting blend composition and structure.

Phase Behavior and Absorption Kinetics. Suppes and McHugh[20] have published the phase behavior of the CO_2–styrene system. Except as noted, all experiments in this study were run under conditions at which CO_2 and styrene are a single phase. The solubilities of CO_2 in PCTFE at two conditions of approximately equal CO_2 density (40 °C, 103 atm, and 80 °C, 240 atm) were determined using a method similar to that described by Berens.[9] PCTFE samples were exposed to CO_2 in pressure vessels under these conditions for various extents of time. The vessels were depressurized, and sample mass was measured over ~30 min beginning ~45 s after depressurization. Plots of mass vs time$^{1/2}$ are linear (r^2 values are ~0.99), indicating Fickian kinetics for desorption of CO_2 from PCTFE. Figure 1 shows a typical desorption curve; the example shown
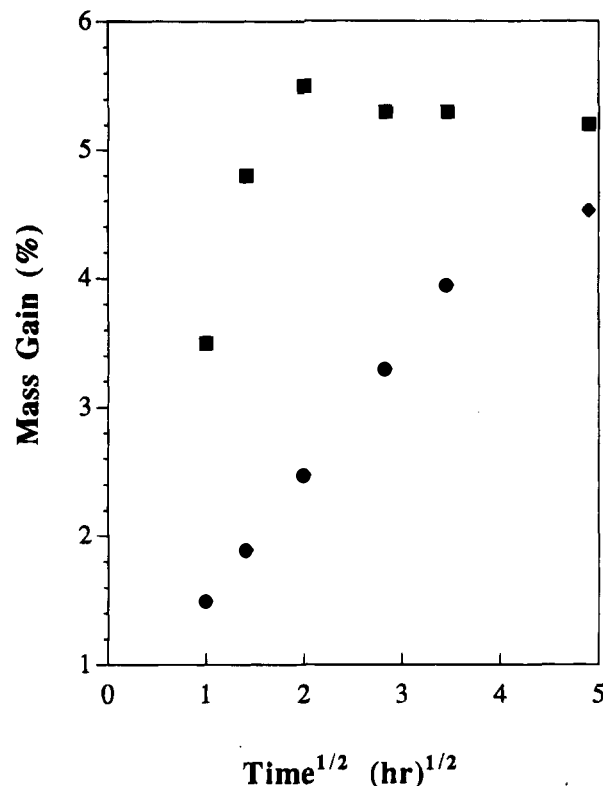
in the figure is for desorption from a PCTFE sample exposed to CO_2 for 8 h at 80 °C and 240 atm. The mass of CO_2 absorbed during exposure was estimated by linear extrapolation to zero desorption time. Absorption kinetics plots were compiled from absorption measurements made at each time interval. Figure 2 shows plots of absorption vs time for exposure of PCTFE to CO_2 at 40 °C, 103 atm, and 80 °C, 240 atm. The plot of the 80 °C data indicates an equilibrium solubility of ~5.3 wt % and that this concentration is reached in ~4 h. The plot of the 40 °C data indicates that equilibrium absorption has not been reached after 24 h. The apparent maximum in the 80 °C curve is consistent with data from other systems in which a semicrystalline polymer is annealed by plasticization with CO_2. For example, Lambert and Paulaitis[21] and Baldwin and Suh[22] observed maxima in time-dependent sorption studies of CO_2 in poly(ethylene terephthalate) (PET). The decrease in CO_2 solubility at long times is attributed to an increase in crystallinity of the PET. While this method for measuring CO_2 solubility and absorption rates is sufficiently accurate for our purposes, it is also possible to determine gas solubility in polymers using a quartz spring balance.[8,21]

The diffusivity of CO_2 (during sorption) can be estimated[23] by determining the initial slope of plots of M_t/M_{inf} vs $t^{1/2}/\lambda$ where M_t is the mass of CO_2 absorbed by the sample at time t, M_{inf} is the equilibrium mass absorbed, and λ is the thickness of the sample. The diffusion coefficient for CO_2 at 40 °C and 103 atm is estimated to be 7.1×10^{-8} cm^2/s by this method. There is an insufficient number of points prior to reaching equilibrium to accurately determine the diffusivity of CO_2 at 80 °C; however, a crude estimate of 4.8×10^{-7} cm^2/s can be made from the data. It is obvious that equilibrium is achieved much more rapidly at 80 °C than at 40 °C; below we discuss absorption kinetics effects on blend morphology.
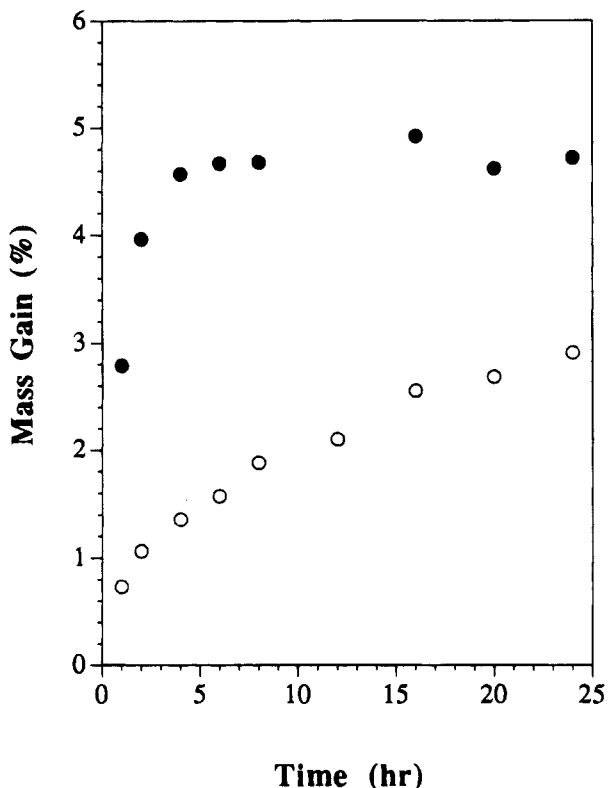
Figure 3. Absorption kinetics for neat ethylbenzene in PCTFE at 80 °C (O) and ethylbenzene (40 wt %)/CO$_2$ in PCTFE at 80 °C, 240 atm (●).

Figure 4. Mass uptake (polystyrene incorporation) of PCTFE as a function of soaking time (80 °C, 240 atm of CO$_2$, 37 wt % styrene).

The kinetics for absorption of ethylbenzene (a model for styrene) into PCTFE both from ethylbenzene/CO$_2$ solution at 80 °C, 240 atm and from neat ethylbenzene at 80 °C were determined (Figure 3). Ethylbenzene was used as a model for styrene because styrene polymerizes under these conditions (see below). We have also measured the kinetics of absorption of styrene containing a radical inhibitor,[1] and these data attest to the validity of using ethylbenzene as a model. An equilibrium solubility of ~4.7% ethylbenzene in PCTFE (CO$_2$-free basis) is attained after 4 h from a 40 wt % solution of ethylbenzene in CO$_2$ (Figure 3). In comparison, equilibrium absorption from neat ethylbenzene at 80 °C is ~5.3% and requires over 100 h to achieve. The diffusion coefficient of ethylbenzene in PCTFE at these conditions (neat ethylbenzene) was determined to be ~1.6 × 10^{-8} cm^2/s. Absorption of ethylbenzene from ethylbenzene/CO$_2$ solution at 80 °C reaches equilibrium at essentially the same rate as neat CO$_2$. Using the limited kinetic data from Figure 3, a crude estimate of the diffusion coefficient of ethylbenzene in CO$_2$-swollen PCTFE is ~5 × 10^{-7} cm^2/s, a ~30-fold increase over the neat solution. Hydrostatic pressure has been shown to decrease diffusion rates of penetrants in solid polymers.[24-26] The observed increase in diffusion rates in the presence of CO$_2$ at elevated pressures is further evidence that CO$_2$ plasticizes the PCTFE matrix.

These absorption data serve as a consistent explanation for the composition difference between the 5% and 12% blends discussed above. These were prepared using 4 h soaking periods at 40 and 80 °C, respectively. Figure 2 indicates that equilibrium CO$_2$ absorption was reached after 4 h at 80 °C, but not at 40 °C. Temperature is a complicated variable in this synthetic system and cannot be easily isolated and controlled independently. Temperature changes affect absorption kinetics, phase equilibria, initiation and propagation kinetics,
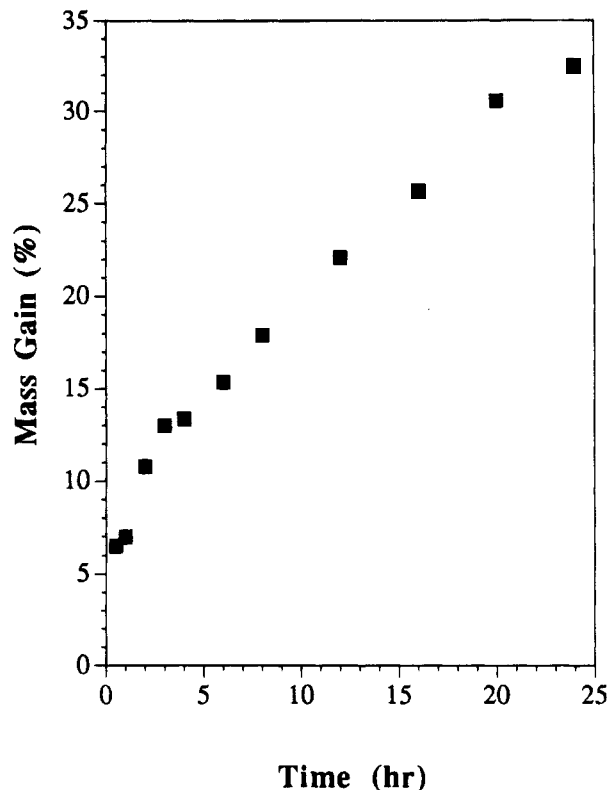
SCF density at constant pressure, and the physical state of the substrate. Manipulation of experimental parameters can be used to partially compensate for some of these differences: Initiators can be chosen such that half-lives are approximately equal during the soaking and heating periods at different temperatures and system pressure can be adjusted to maintain approximately equivalent fluid density. Temperature effects, however, remain sufficiently complicated that we have not studied temperature as a variable beyond the comparison of the 40 and 80 °C soaking conditions and the structures of the blends produced (see below). In the case of semicrystalline polymers, synthesis of the blends at temperatures which exceed the crystalline melting point of the polymer can have a profound effect on the resulting morphology. Highly expanded composite foams have been produced by the synthesis of poly(4-methyl-1-pentene)/polystyrene blends at temperatures in excess of the depressed (by the styrene/SCF solution) melting point of poly(4-methyl-1-pentene).[27] All experiments described in this paper were carried out at a temperature below the melting point of PCTFE.

Effects of Soaking Time, Monomer Concentration, and Pressure. The conditions used to prepare the 12% blend described above were used as the basis for a series of experiments to determine the extent to which the blend synthesis can be controlled by experimental variables. This choice of conditions was made for several reasons: First, a soaking period of 4 h at 80 °C and 240 atm is sufficient to reach equilibrium solubility of both CO$_2$ and styrene (by inference from the ethylbenzene data). Second, 80 °C is well above the T_g of PCTFE (52 °C). Sorption of CO$_2$ has been shown to depress the glass transition temperature of polymers.[28-32] Operation well above T_g obviates concerns regarding the solvent-dependent location of the transition. Third, a pressure of 240 atm is sufficiently high
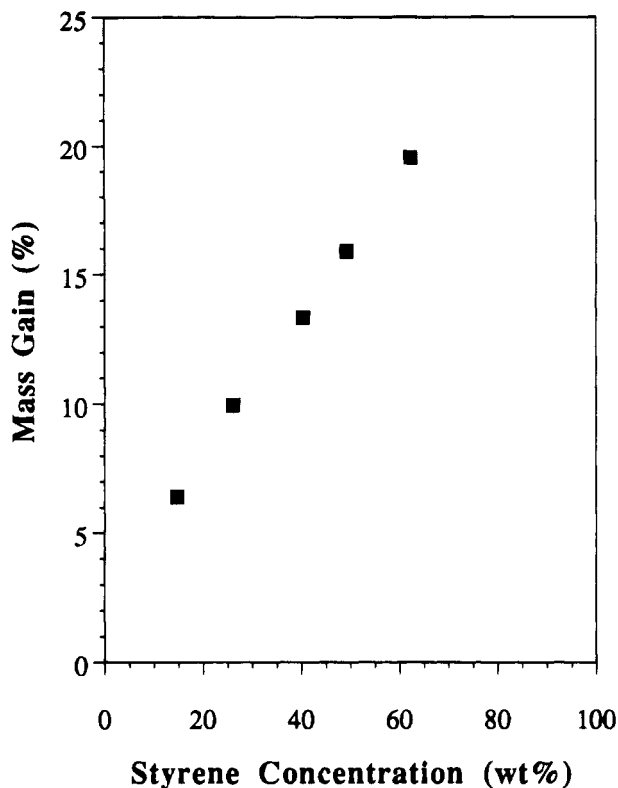
Figure 5. Mass uptake (polystyrene incorporation) of PCTFE as a function of styrene concentration (80 °C, 240 atm of CO_2, 4 h).

Figure 6. Mass uptake (polystyrene incorporation) of PCTFE as a function of pressure at constant styrene mass (■, variable concentration) and at constant styrene concentration (□) (80 °C, 4 h).

to be above the highly compressible region for CO_2 at 80 °C. Operating in the highly compressible region would amplify the effect of slight variations in pressure from experiment to experiment. This point is illustrated in the pressure profiling data that follows. Finally, operation in this regime results in mass gains on the order of 15%. This level of polystyrene incorporation is low enough to minimize changes in absorption kinetics and phase behavior but high enough to facilitate the characterization of the blends.

Soaking time was varied from 1 to 24 h prior to venting and heating the infused PCTFE samples under nitrogen. Figure 4 shows mass uptake results as a function of soaking time. The data indicate that the mass of polystyrene incorporated in the PCTFE matrix is far in excess of that predicted from equilibrium solubility (4.7%; see Figure 3) of the styrene in the SCF-swollen matrix (based on the ethylbenzene model). This indicates that styrene must polymerize within the PCTFE matrix during the soaking period. As polystyrene is neither soluble in CO_2 nor miscible with PCTFE, it must precipitate as a discrete phase in the PCTFE matrix. As styrene in the substrate is consumed by polymerization, styrene in the fluid phase repartitions between the solid and fluid phases, swelling both PCTFE and the nascent polystyrene. The polymerization reaction thus induces a continuing absorption of styrene during the soaking period, producing the high polystyrene content blends indicated by the data in Figure 4.

A series of experiments using these soaking and heating conditions was run with varying styrene concentration (15–60 wt %) in the SCF. The initiator concentration was maintained at 0.3 mol % based on monomer; the overall initiator concentration in the fluid phase, therefore, varied with styrene concentration. Figure 5 shows a plot of mass gain vs styrene concen-
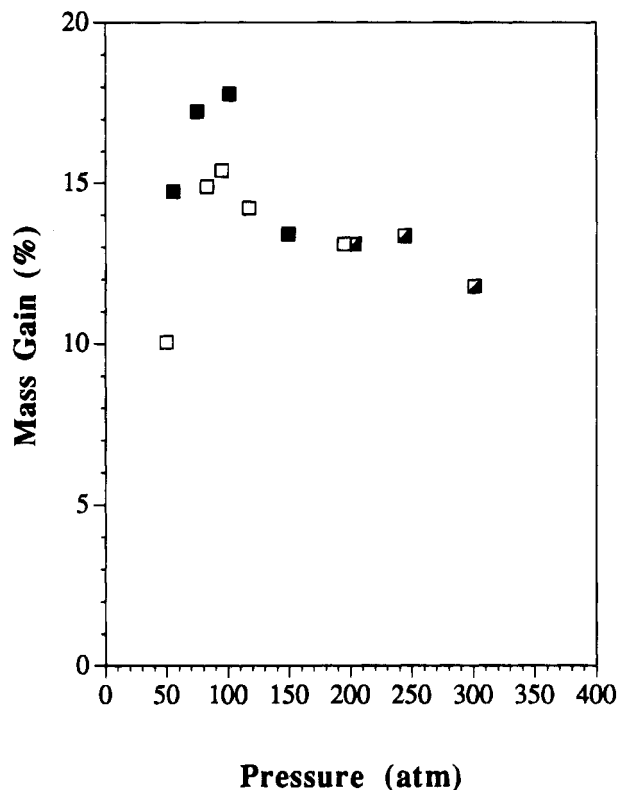
tration that indicates a linear increase in polystyrene content with styrene concentration. The linearity is likely fortuitous, because a number of system properties change with this one variable change (as is the case with temperature, discussed above). Both absorption and polymerization kinetics change with concentration. Increases in styrene concentration also result in increases in the solvent quality of the fluid phase which affect the equilibrium partitioning of CO_2, styrene, and initiator as well as initiator decomposition rates. We have run a control experiment using a neat styrene/ initiator solution at ambient pressure and found the mass uptake to be 7 wt % and the modification to be confined to the surface. In contrast, all blends prepared using CO_2 contain polystyrene throughout the thickness of the samples. A discussion of the morphologies of the samples is provided below. Comparing the data in Figure 5 with the result of the control experiment (at ambient pressure) provides estimates of the mass gains attributable to the presence of CO_2. These estimates are conservative for two reasons: First, as discussed earlier, increasing hydrostatic pressure decreases the diffusion rates of diluents in solid polymers. Second, the surface modification observed in the absence of CO_2 produces a laminate structure rather than a blend. The actual incorporation of polystyrene in the PCTFE matrix is significantly less than 7 wt %.

Two series of experiments were run to determine the effect of pressure on polystyrene incorporation. In the first, the soaking period pressure was varied but the total mass of styrene was held constant. Since the reactions were run in constant-volume vessels, less CO_2 was used at lower pressures, resulting in the superposition of a concentration gradient on the pressure profile. In the second set of experiments, the quantity of styrene used was adjusted so that the fluid composition at each
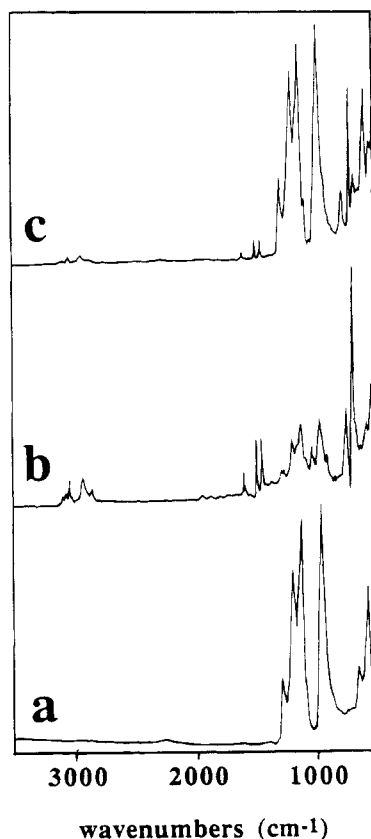
Figure 7. ATR-IR spectra of PCTFE (a), a 12% PCTFE/polystyrene blend (b), and a 12% blend sample extracted with THF for 3 min at room temperature (c).

Figure 8. DSC endotherms for virgin PCTFE (a) and a 43% PCTFE/polystyrene blend (b).

pressure was the same. In both experiments data were taken at pressures above and below the cloud-point pressure of the styrene/CO_2 system.[20] The results of the experiments, with both soaking periods of 4 h at 80 °C and heating periods of 4 h at 120 °C, are shown in Figure 6. Both profiles exhibit maxima in polystyrene content; the maxima are readily explained: at low pressures CO_2 is too poor a solvent to swell PCTFE sufficiently to permit rapid infusion of styrene. At high pressures CO_2 readily swells PCTFE; however, it is also a much better solvent for styrene, and the partitioning of styrene in the fluid phase is enhanced. At intermediate pressures, these competing effects balance and maxima are observed. We note that the maxima occur in the vicinity of the cloud-point pressure for the system. Similar pressure effects have been noted in studies of the partitioning of organic penetrants between CO_2 solutions and a polymer-coated stationary phase at infinite dilution using SCF chromatography.[13]

Blend Characterization. We have described the PCTFE/polystyrene composite samples discussed above as blends, implying that discrete regions of polystyrene exist throughout the bulk of the PCTFE matrix and that the samples are not graft copolymers. We have characterized these samples in regards to these issues.

Figure 7 shows ATR-IR spectra of virgin PCTFE, a PCTFE/polystyrene blend (~12 wt % polystyrene), and the same blend sample subsequent to extraction with THF at room temperature for 3 min. The spectrum of the blend indicates significant polystyrene incorporation by the presence of the spectral features of polystyrene (aromatic and aliphatic C—H stretching at 3100—2850 cm^{-1}, aromatic C—C stretching at 1601, 1493, and 1452 cm^{-1}, and aromatic C—H out-of-plane bending at 698 cm^{-1}) and the reduced intensity of the C—F stretching
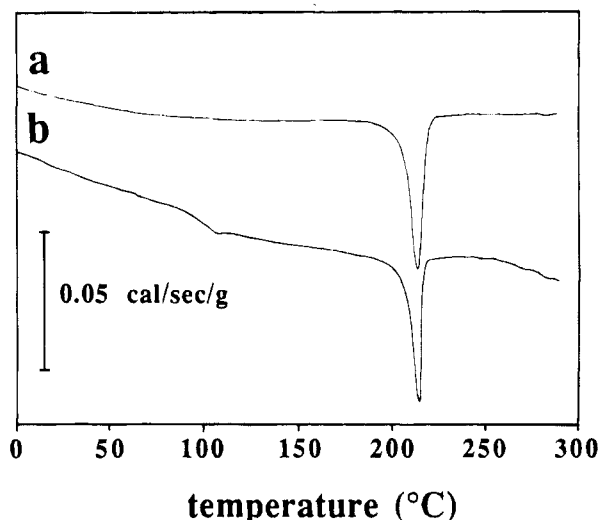
vibrations at 1286, 1192, and 1122 cm^{-1}. The spectrum of the blend after extraction with THF indicates that nearly all of the PS has been removed from the ATR-IR sampling region (the sampling depth using a KRS-5 internal reflection element for the wavenumber range of the peaks discussed above is ~1—3 μm). Transmission IR analysis of the extract indicates that pure polystyrene and no graft copolymer were extracted. We conclude from these analyses that radical grafting of styrene to PCTFE either does not occur or does not contribute significantly to the mass gain observed in the blends. The solvent resistance of PCTFE impedes the polystyrene extraction from the bulk of the blend,[2] however, 70 wt % of the styrene present in the blend could be extracted using refluxing THF. Additional evidence of the absence of grafting was obtained from blends of polystyrene and poly(4-methyl-1-pentene) (PMP) prepared using the same SCF strategy. All of the polystyrene could be extracted from a 50 wt % polystyrene/PMP blend. The hydrocarbon backbone of PMP is likely more susceptible to radical grafting than PCTFE.

Polystyrene was extracted from thin cross sections of the ~43 wt % blend using THF and analyzed using gel permeation chromatography. The analysis indicates that high polymer is formed within the matrix (M_n = 85 000, M_w = 235 000, M_w/M_n = 2.7). Extraction and analysis of polystyrene from the 12 wt % blend indicated a M_n of 140 000 and a M_w of 380 000 (M_w/M_n = 2.7). We have not extensively studied polymerization in the fluid phase; however, we present the following observations: In most cases the addition of methanol or isopropyl alcohol to the styrene solutions recovered after expansion resulted in little or no precipitation of polystyrene. Exceptional cases were those in which long soaking periods were used (>12 h) and those in which the vessels were heated to induce polymerization in the presence of the SCF/monomer solution. It is evident from visual inspection, TEM, and IR analysis that little if any mass gain in the blends is attributable to precipitation of polystyrene on the surface of the substrate. For example, IR absorption peaks due to PCTFE are clearly visible in Figure 7b. The sampling depth for 45° KRS-5 internal reflection elements at 1200 cm^{-1} is ~1 μm.

DSC analysis (Figure 8) was performed on samples of virgin PCTFE and a PCTFE/polystyrene blend with
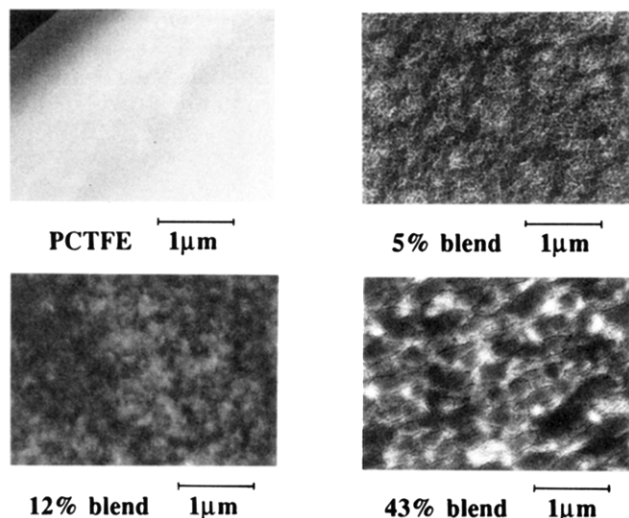
Figure 9. TEM micrographs of virgin PCTFE and 5%, 12%, and 43% PCTFE/polystyrene blends.

~43 wt % polystyrene (the swollen PCTFE sample was heated at 120 °C in the presence of the SCF solution). A polystyrene glass transition for the blend at ~100 °C and a strong PCTFE melting endotherm with a peak melting point equivalent to that of the virgin sample (212 °C) were observed. The heat of fusion for PCTFE in the blend was found to be slightly in excess of that of the virgin sample (after normalization to account for the polystyrene content of the blend). These results support the conclusion that polystyrene and PCTFE are present in the blends as discrete phases. The increase in the heat of fusion may be the result of an increase in crystallinity, as discussed above.

Transmission electron microscopy was performed on several blends. The samples were microtomed in cross section so that the distribution of polystyrene from the surface to the center of the samples could be examined. In all cases SCF-produced blends exhibited phase separation throughout the entire sample. Figure 9 shows TEM micrographs of the centers of a virgin PCTFE sample and blends containing ~5%, ~12%, and ~43% polystyrene. The ruthenium tetroxide-stained polystyrene is the dark phase. We note that the apparent domain size of the polystyrene increases with polystyrene concentration. A more complete morphology evaluation of these blends will be the subject of a future study.

The distribution of polystyrene in the samples as a function of depth in the substrate was qualitatively determined using energy-dispersive X-ray analysis (EDX). Direct quantitative analysis was precluded by the carbon coating; however, the relative concentration of carbon as a function of depth could be determined by conducting spot analysis at various distances from the edge of the sample. Plots of relative carbon concentration vs depth are shown in Figure 10 for ~5 and ~12 wt % blends. The carbon content data are relative to a virgin PCTFE sample coated with carbon at the same time (assigned a carbon content of 1.0). Values above 1.0 indicate the presence of polystyrene. The analysis suggests that the 5% blend has a pronounced polystyrene concentration gradient and that there is no appreciable concentration gradient in the 12% blend. The difference can be rationalized by comparing the conditions of the syntheses. The 5% and 12% blends were prepared using 4 h soaking periods at 40 and 80 °C, respectively, and as discussed above and demonstrated in Figure 2, equilibrium absorption was reached after 4 h at 80 °C, but not at 40 °C.

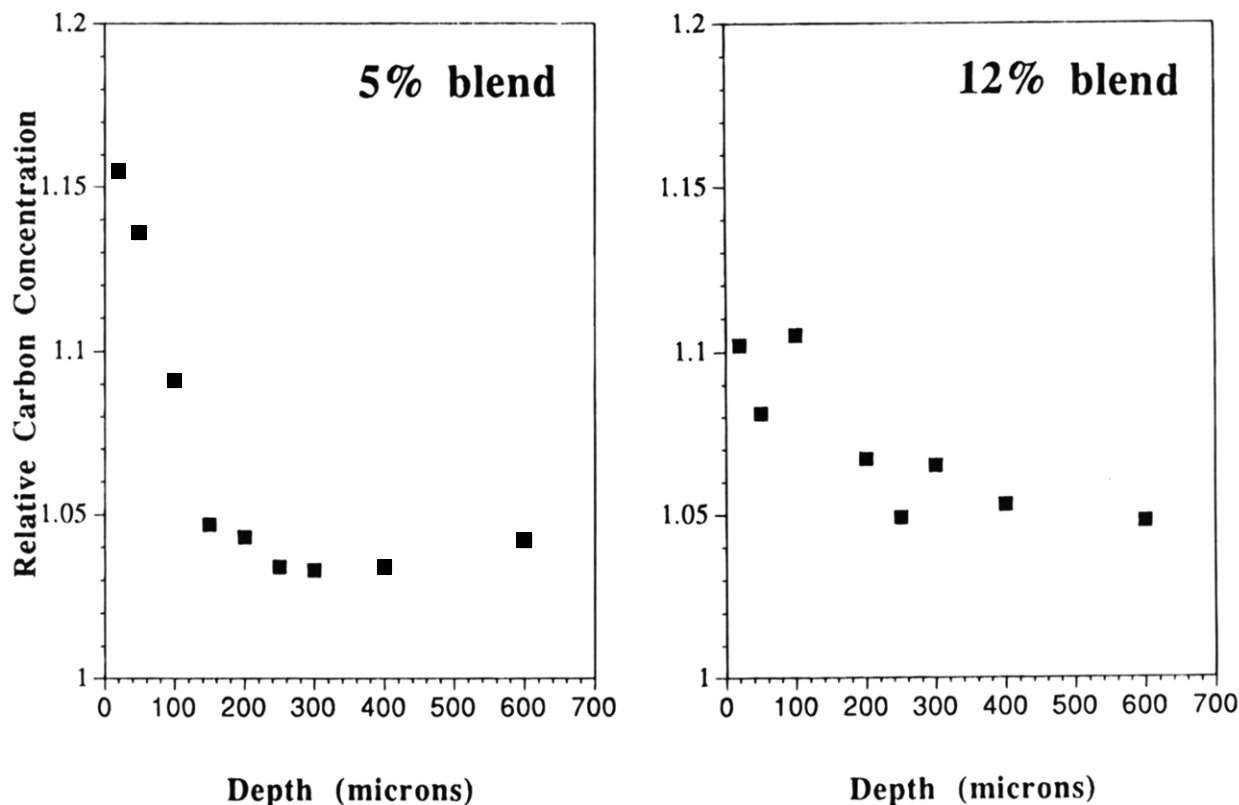Two PCTFE−polystyrene samples were prepared in control experiments without SCF CO₂ as a solvent.

Figure 10. Relative carbon concentration vs depth for a 5% blend prepared with soaking conditions of 37 wt % styrene, 4 h, 40 °C, and 103 atm of CO₂ and a 12% blend prepared with soaking conditions of 37 wt % styrene, 4 h, 80 °C, and 240 atm of CO₂.

PCTFE samples were soaked in styrene/initiator solutions, isolated, and heated at the same temperatures for the same time periods at ambient pressure. The solubility of ethylbenzene in PCTFE (Figure 3) suggests that, in principle, blends containing low levels of polystyrene could be prepared by this method. A mass increase of about ~2% was found for soaking at 40 °C and heating at 80 °C, and an increase of 7 wt % was observed for soaking at 80 °C and heating at 120 °C. The polystyrene was confined to the surface region of these samples. The sample containing 7 wt % polystyrene exhibited a surface layer of polystyrene that easily delaminated. TEM analysis of these samples indicated phase separation near the edges of the sample but interiors identical to virgin PCTFE. The interface between the phase-separated region and the unmodified interior of these samples was very sharp. PCTFE is sensitive to etching by the electron beam while polystyrene is not, and the samples were selectively etched along this interface, ablating the interiors during TEM analysis. EDX analysis confirmed that the interiors of these samples were entirely PCTFE.

Summary and Conclusions

Blends of polystyrene and poly(chlorotrifluoroethylene) can be prepared by infusion of styrene into and radical polymerization within solid PCTFE using supercritical CO_2 as a solvent. GPC analysis of polystyrene extracted from the blends indicates that diffusion rates in swollen PCTFE matrices are sufficiently high such that polymer of high molecular weight ($>100\,000$) can be produced. The PCTFE matrix retains its basic geometry, and the crystalline regions of the sample are unaffected. The polystyrene exists as discrete phase-segregated regions throughout the thickness of the PCTFE sample, and little if any grafting reactions occur. Absorption kinetics indicate that plasticization of PCTFE with CO_2 significantly enhances the diffusion rate of styrene in the matrix. Under the conditions studied, polymerization occurs competitively with the absorption of CO_2 and styrene. When CO_2 is not present, the absorption of styrene is slow and only surface modifications are observed. Polystyrene content can be controlled by adjusting the concentration of styrene in the supercritical fluid or by controlling the time the PCTFE film is in contact with the fluid (soaking time) prior to venting. The results indicate that composition gradients in the blends can be produced by using soaking periods shorter than the time required to achieve equilibrium. It should be possible to control the slope and depth of the gradients by manipulating soaking time, temperature, and monomer composition in the fluid phase. As a result it may be possible to rationally design interfaces between modified and unmodified regions in polymer substrates. Gradient interfaces of this type may offer advantages for minimizing physical property mismatches between dissimilar materials.

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