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Adsorption/Migration of a Perfluorohexylated Fullerene from the Bulk to the Polymer/Air Interface

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ABSTRACT: Adsorption/migration of a perfluorohexylated-C_{60} ($C_{60}(C_6F_{13})_5$) from the bulk of a polymer matrix (polystyrene) to the polymer/air interface is reported here as a tool for surface modification as well as the demonstration of a method to increase the efficiency of polymer additives. Surface activity of $C_{60}(C_6F_{13})_5$ was evaluated as a function of bulk concentration, annealing temperature, and annealing time. $C_{60}(C_6F_{13})_5$ is extremely surface-active in the polystyrene matrix, occupies ~90% of the outermost ~40 Å (XPS sampling depth), and renders a surface that is similar in wettability to a monolayer containing CF_3 groups (hexadecane contact angle data). Surface reconstruction studies were carried out by either spin-casting or the transfer of a free-standing (solid) polystyrene film onto the composite materials (the surface-active agent and polystyrene) and subsequent thermal annealing. Both approaches show similar results: migration of perfluorohexylated-C_{60} from the bulk to the surface is driven by surface free energy minimization and is a function of annealing temperature, annealing time, and molecular weight of the polymer matrix. Peel tests indicate that the composite materials have good mechanical integrity.

Introduction

The interfacial properties of a solid material depend primarily on the surface structure and chemical composition of the outermost surface layer. Research in our group has concentrated on the preparation of specifically functionalized and well-characterized polymer surfaces with the objective of controlling macroscopic properties by manipulating microscopic surface structures. Among the approaches to polymer surface modification are polymer adsorption from solution,[1] chemical modification,[2] layer-by-layer deposition,[3−6] and surface reconstruction.[7]

Solid polymers have nonequilibrium structures with chains rotating and reptating and exhibit a range of relaxations and transitions in response to time, temperature, and other environmental changes.[8] Surface reconstruction has been reported in the literature extensively from both theoretical[9−15] and experimental[7,16−37] point of views. In general, reconstruction tends to concentrate at the surface the component that is the most similar to the phase above it. Reconstructed surface structure and composition depend on bulk concentration,[27,30,31,35] polymer molecular weight,[33,34] incompatibility of the components,[28−31,35] casting solvent,[22,27,31,35] annealing time,[7] annealing temperature,[7,22] temperature of measurement,[33] and the nature of the surface-migrating species.[37] Systems with surface-modified polymers,[7,36] surface-active small molecules,[16,17] block copolymers,[18−30] and polymer blends[31−35] all demonstrate that polymer surfaces are dynamic and reconstruct to lower surface free energy.

Several groups have recently shown that perfluoroalkyl groups which are incorporated into polymers are surface-active[38−45] and adsorb at free polymer interfaces due to surface free energy minimization. The objective of the research reported here was to test the incorporation of perfluoroalkyl groups as a general approach to enhance the efficiency of additives in polymer materials that function at the polymer−environment interface. Flame retardants are additives that function at the polymer−air interface and in the vapor phase above the interface; thus, ignition and combustion are controlled by interfacial structure and properties.[46,47] Making flame retardants surface-active, so that they concentrate at the surface and can migrate to the surface when depleted, should enhance their efficiency. We chose the fullerene, C_{60}, as a model flame retardant to study for several reasons: the chemistry to incorporate perfluoroalkyl groups has been reported,[48] it should inhibit ignition and combustion by hydrogen starvation, and as a radical trap, it should function as a model "char layer" on the surface. We have prepared a perfluoroalkylated-C_{60} sample and studied its mobility and surface activity in a polymer matrix (polystyrene). Surface activity of the perfluoroalkylated-C_{60} was studied as a function of bulk concentration, molecular weight of the polymer matrix, annealing temperature, and annealing time.

Experimental Section

Materials and Handling. Fullerenes were purchased from Materials & Electrochemical Research (MER) Corp. All other materials were obtained from Aldrich unless otherwise specified. Styrene was distilled from calcium hydride (bp = 52 °C/20 mm) and refrigerated in darkness. Immediately prior to use, it was stirred over dibutylmagnesium until yellow and then degassed using freeze−pump−thaw cycles and trap-to-trap distilled. Benzene was distilled from calcium hydride. Immediately prior to use, it was stirred over polystyryllithium until orange and then distilled. Toluene was distilled from calcium hydride; tetrahydrofuran was distilled from sodium benzophenone dianion; hexadecane was distilled from calcium hydride at reduced pressure; house purified water (reverse osmosis) was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps (10^{18} ohm/cm). Polystyrene (498K, PDI < 1.2, Pressure Chemical Co.), calcium hydride, dibutylmagnesium, *sec*-butyllithium (1.3 M in cyclohexane), 30% hydrogen peroxide, concentrated sulfuric acid (Fisher, HPLC grade), perfluorohexyl iodide, 1,2,4-trichlorobenzene, Freon-113 (1,1,2-trichlorotrifluoroethane), and methylene chloride (Fisher, HPLC grade) were all used as received. Methanol (Fisher, HPLC grade) was degassed by sparging with nitrogen prior to use.

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All solvents and reagents were either used immediately after purification or stored under nitrogen in Schlenk flasks. Reagents and solvents were transferred via either cannula or syringes under nitrogen; all distillations and reactions were performed under nitrogen.

Methods. Spin-casting was performed with a Headway Research spin coater. X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer−Physical Electronics 5100 with Mg Kα excitation (400 W). Spectra were obtained at two different takeoff angles, 15° and 75° (between the plane of the surface and the entrance lens of the detector optics). Contact angle measurements were made with a Ramè-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. The probe fluids used were water, purified as described above, and hexadecane, purified by vacuum distillation. Dynamic advancing (θ_A) and receding (θ_R) angles were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The values reported are averages of 5−10 measurements made on different areas of the sample surface. The surfaces reported here showed very homogeneous surfaces as evidenced by contact angle measurements which were within ±2° of the average. Elemental analysis was performed by Galbraith Laboratories. Molecular weights and polydispersities of polymer samples were determined by gel permeation chromatography (GPC) relative to calibration with polystyrene using a system equipped with Polymer Laboratories PL gel columns (10^4, 10^3, and 10^2 Å), a Rainin Rabbit pump with THF as the mobile phase, and an IBM LC9563 variable UV detector. Thermogravimetric analysis was performed with a DuPont TGA 2950.

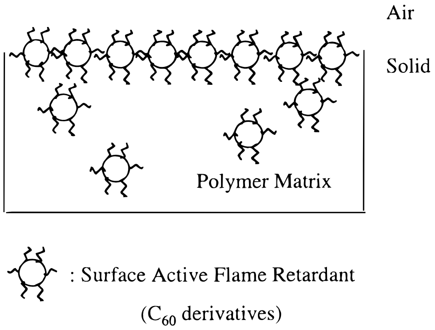
Polymer Matrix. Polystyrene (PS) samples were prepared in benzene at room temperature overnight, using *sec*-butyllithium as initiator. After quenching the living polymer with a few drops of degassed methanol, the solution was transferred via cannula into methanol. The polymer was isolated by filtration, dried at reduced pressure, and stored under nitrogen. Three different molecular weight samples were prepared: $M_n = 6560$ (PDI = 1.037), $M_n = 62\,107$ (PDI = 1.033), and $M_n = 147\,533$ (PDI = 1.034); a fourth was purchased: $M_n = 498\,000$ (PDI < 1.2).

Surface-Active Fullerenes: $C_{60}(C_6F_{13})_5$.[48] A mixture of C_{60} (350 mg), perfluoro-*n*-hexyl iodide (6 mL), and 1,2,4-trichlorobenzene (15 mL) was added to a thick-walled ampule (2.5 cm × 15 cm). The ampule was degassed using freeze−pump−thaw cycles, sealed with a torch, and heated in a sand bath for 24 h at 200 °C. Volatiles were removed at reduced pressure, yielding a brown solid. The solid was purified by two precipitations from Freon-113 solutions into methylene chloride and dried at reduced pressure overnight (0.8 g). Elemental analysis: C, 44.37%; F, 52.01%; Cl, 0.13%; H, <0.5%.

Film Sample Preparation. Supported film samples of composites of C_{60} or $C_{60}(C_6F_{13})_5$ and polystyrene were prepared on Si wafers (1.5 cm × 1.5 cm). The wafers were cleaned by immersion in 30% H_2O_2 and concentrated H_2SO_4 (1:9, v/v) for 30 min, rinsed with distilled water (six times), and then dried in a clean oven (100 °C, 2 h). Polystyrene (100 mg) and 10 mg of C_{60} were dissolved in 10 mL of toluene. Polystyrene (10 mg) and 10 mg of $C_{60}(C_6F_{13})_5$ were dissolved in 1 mL of toluene and 10 mL of Freon-113, respectively. A prescribed amount of Freon solution (for the desired concentration) was added to the toluene solution via a syringe. The toluene solution containing polystyrene and C_{60} or the toluene/Freon solution containing polystyrene and $C_{60}(C_6F_{13})_5$ was added dropwise to a clean Si wafer surface until the sample had rounded edges (~8 drops). The film samples were dried in air (1 h) and then dried at reduced pressure (0.02 mm, room temperature, 24 h) before annealing studies were carried out (either at room temperature at reduced pressure or at 110 °C under N_2).

Surface Reconstruction Experiments. Composite film samples consisting of 1% w/w $C_{60}(C_6F_{13})_5$ and 6.5K polystyrene were prepared on Si wafers as described above. The film samples were then dried at reduced pressure (0.02 mm, room temperature, 24 h) before annealing (110 °C under N_2, 24 h). A thin polystyrene film was constructed over the composite material by either spin-casting or the transfer of a free-standing solid thin film. The film samples were air-dried (1 h) and then dried at reduced pressure (0.02 mm, room temperature, 24 h) before annealing (110 °C under N_2).

Scheme 1. Reconstructed Film Sample Containing Surface-Active Perfluoroalkylated-C_{60} ($C_{60}(C_6F_{13})_5$) in a Polystyrene Matrix



Spin-Casting. A 2.5% w/v polystyrene toluene solution was prepared. A composite film sample was overflowed with the toluene solution and immediately spun at 2000 rpm for 10−15 s on a spin coater. The spin-casting process was repeated three times. The film samples were air-dried (1 h) and then dried at reduced pressure (0.02 mm, room temperature, 24 h) before annealing (110 °C under N_2).

Transfer of a Free-Standing Film. A 2.5% w/v 498K polystyrene toluene solution was prepared. A precleaned microscope slide was overflowed with the toluene solution and spun at 2000 rpm for 10−15 s. The slide was marked ~3 mm from the edges with a razor blade and immersed slowly at ~45° in a bucket of water to detach the polystyrene film. A Si wafer covered with the composite film was placed underneath the floating polystyrene film and lifted gently. The film samples were air-dried (2 h) and then dried at reduced pressure (0.02 mm, room temperature, 24 h) before annealing (110 °C under N_2).

Results and Discussion

XPS and contact angle measurements were used to monitor surface reconstruction in film samples containing specific concentrations of a surface-active agent in a polystyrene matrix. The surface-active agent studied is perfluorohexylated-C_{60}, $C_{60}(C_6F_{13})_5$. Several variables were chosen for manipulation: time and temperature of heating to allow reconstruction, molecular weight of polystyrene, and concentration of the surface-active agent in the film samples. Experiments utilizing these variables were designed to elucidate how certain molecular and environmental parameters influence the rate and extent of surface reconstruction in films of this type.

Surface reconstruction of the film samples containing $C_{60}(C_6F_{13})_5$ in polystyrene was studied at both room temperature and 110 °C. The purpose of heat treatment of these samples at this temperature was to maximize surface reconstruction while minimizing surface oxidation. Previous studies in our group showed that polystyrene samples containing perfluoroalkyl groups that were heated at 110 °C exhibited significant fluorine surface enrichment with minimal oxidation; higher temperatures promoted oxidation.[45]

Due to the different solubility characteristics of $C_{60}(C_6F_{13})_5$ and polystyrene, film samples were prepared from a mixed solvent system, toluene/1,1,2-trichlorotrifluoroethane. The films were supported on Si wafers cut to an appropriate size for XPS analyses. Scheme 1 is a depiction of a reconstructed film sample. A control system containing C_{60} in polystyrene was also studied.

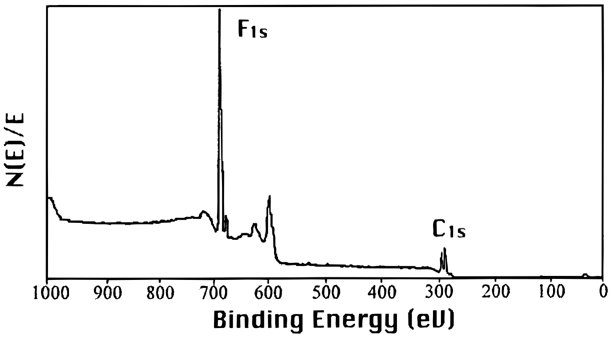


Figure 1. XPS survey spectrum (75° takeoff angle) of a composite film sample containing 1% w/w $C_{60}(C_6F_{13})_5$ in polystyrene matrix ($M_n = 6.5K$).

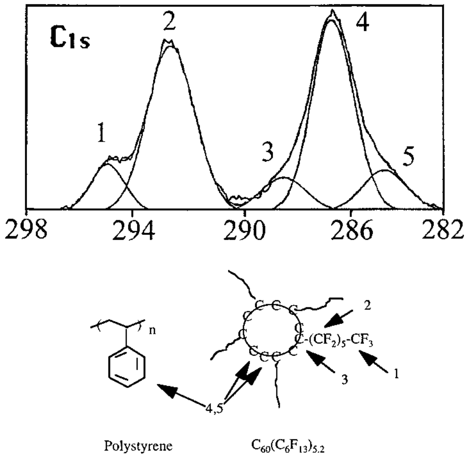


Figure 2. C_{1s} region spectrum (75° takeoff angle) of a composite film sample containing 1% w/w $C_{60}(C_6F_{13})_5$ in a polystyrene matrix ($M_n = 6.5K$).

Table 1. Peak Areas (%) for the $C_{60}(C_6F_{13})_5$ Spectrum Shown in Figure 2

XPS takeoff angle (deg)	peak 1	peak 2	peak 3	peak 4	peak 5
15	10.0	37.5	7.1	38.7	6.7
75	7.8	31.9	7.2	45.9	7.2

Surface Activity of C_{60} in a Polystyrene Matrix. The surface activity of C_{60} (unmodified) in a polystyrene matrix was examined as a control study. A composite containing 10% w/w of C_{60} in 6.5K polystyrene was prepared by solution casting onto a Si wafer from toluene solution. Water and hexadecane contact angle measurements were performed on the composite film samples annealed at both room temperature and 110 °C. Contact angles of the composite materials did not change over time under the annealing conditions studied. (Data were taken daily over 8 days.) Values remained at $\theta_A/\theta_R = 94°/78°$ (water) and $\theta_A/\theta_R = 12°/9°$ (hexadecane)—identical to those of neat polystyrene. This indicates that, in the C_{60} and polystyrene system, polystyrene is the component that has lower surface energy.

Synthesis of Perfluoroalkylated-C_{60}. Although neat C_{60} does not exhibit surface activity in polystyrene, attaching low surface energy moieties such as perfluoroalkyl groups induces surface activity (we demonstrate this below). We tested three different protocols[48] for the preparation of perfluorohexylated-C_{60} and chose the synthesis that gave the highest yield: the reaction of perfluorohexyl iodide and C_{60} in 1,2,4-trichlorobenzene yielded a purified isolated yield of ~70%. Elemental analysis indicates that the average chemical composition of the products is $C_{60}(CF_2CF_2CF_2CF_2CF_2CF_3)_{5.2}$—we abbreviate the structure $C_{60}(C_6F_{13})_5$.

TGA indicates that sharp mass losses (almost 100%) occur at ~750 °C for C_{60} and at ~400 °C for $C_{60}(C_6F_{13})_5$ that are due to sublimation.[48] The low sublimation temperature of $C_{60}(C_6F_{13})_5$ may not be a disadvantage for the objective of flame retardancy. That it vaporizes readily may make it a more effective flame retardant, since fire takes place in the gas phase. We were cautious in the annealing studies described below in choosing heat treatment conditions since severe conditions (high temperature, high vacuum, and long time) will result in the loss of $C_{60}(C_6F_{13})_5$. Surface reconstruction of the film samples containing $C_{60}(C_6F_{13})_5$ in polystyrene was studied at room temperature under reduced pressure and at 110 °C under nitrogen.

Figure 1 shows an XPS survey spectrum (75° takeoff angle) of a composite film sample containing 1% w/w $C_{60}(C_6F_{13})_5$ in a polystyrene matrix ($M_n = 6.5K$). XPS atomic composition of the sample determined at a 75° takeoff angle is C, 54.0%; F, 46.0%. At a 15° takeoff angle the composition is C, 48.9%; F, 51.1%. The 15° takeoff angle data indicate the composition of the outermost ~10 Å of the samples, and the 75° takeoff angle spectra assess the outer ~40 Å.[49] Comparing the atomic composition obtained from XPS to the chemical composition of $C_{60}(C_6F_{13})_5$ (C, 44.37%; F, 52.01%) indicates that there is ~95% $C_{60}(C_6F_{13})_5$ and ~5% polystyrene in the outer 10 Å and ~85% $C_{60}(C_6F_{13})_5$ and ~15% polystyrene in the outer 40 Å. These calculations are biased high in favor of $C_{60}(C_6F_{13})_5$ but nevertheless indicate very high surface affinity. Reasons for the high bias include the following: (1) The perfluoroalkyl groups are located closer to the surface on average than polystyrene repeat units (due to their surface affinity and demonstrated by contact angle analysis—below), and the sensitivity of XPS decreases exponentially with depth. (2) $C_{60}(C_6F_{13})_5$ contains an average of 5.2 perfluorohexyl groups per fullerene, but some fullerenes have a higher number. These may be more surface-active. (3) The perfluorohexyl groups on $C_{60}(C_6F_{13})_5$ may not be distributed evenly around C_{60} core and may adsorb with a dense region of perfluorohexyl groups pointing toward the surface.

Figure 2 shows the curve-fitted C_{1s} spectrum (75°) of this sample (1% $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene) along with assignments of the five peaks used to fit the spectrum. Table 1 gives the percentages of each type of carbon atom (assigned in Figure 2) at both 15° and 75° takeoff angles. Peaks 1 and 2 are due to the carbons of the perfluorohexyl groups and are baseline resolved from peaks 3, 4, and 5 that are due to the fullerene carbons and polystyrene. The ratios of the areas of peaks 1 and 2 to peaks 3, 4, and 5 (ratios of fluorinated carbons to nonfluorinated carbons) are 47.5:52.5 (15° takeoff angle) and 39.7:60.3 (15° takeoff angle). This curve fitting is a qualitative analysis of the data; peak 5 and portions of other peaks may be due to differential charging of the sample. The ratio of fluorinated carbons to nonfluorinated carbons in $C_{60}(C_6F_{13})_5$ (with 5.2 perfluorohexyl groups) is 34.2:65.8, less than either of the ratios determined by XPS. This indicates that these data is biased, likely for all three of the reasons mentioned above, but also that $C_{60}(C_6F_{13})_5$ is extremely surface-active. We point out that these ratios should be higher than the F:C ratios as they compare fluorinated carbons to nonfluorinated carbons (that are stratified), and the F:C ratios compare fluorine to all carbons, including

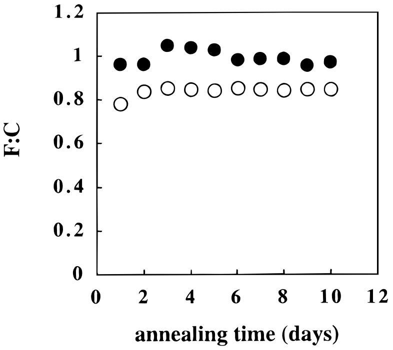


Figure 3. Adsorbed amount (F:C) of 1% w/w $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene matrix as a function of time at room temperature: 15° (●) and 75° (○) takeoff angle data.

fluorinated carbon. The theoretical ratio of areas of peak 1:peak 2:peak 3 should be 1:5:1, which should be observed only if perfluorohexyl groups lie parallel to the surface or have a completely random orientation. At a 15° takeoff angle, the observed ratio is 1.0:3.8:0.7. The difference between these ratios is due to the orientation of the perfluorohexyl groups; trifluoromethyl groups are, on average, closer to the surface than are difluoromethylene groups. The 75° takeoff angle data deviate less from the theoretical prediction because they are less surface-selective than 15° takeoff angle data.

Adsorption Kinetics. Figure 3 shows how surface composition (F:C ratio determined by XPS) changes with annealing time for a film sample containing 1% $C_{60}(C_6F_{13})_5$ in polystyrene ($M_n = 6.5K$) at room temperature. Annealing at 110 °C gave similar results. Very little increase in fluorine concentration is observed—the sample reconstructs to minimize surface energy during solution casting and/or drying. An important feature in Figure 3 is the takeoff angle dependence of the data. The ratios obtained at a 75° takeoff angle (F:C = ~0.8) are about 80% of that observed at 15° (F:C = ~1). This indicates that there is a fluorine-enriched layer at the surface and a somewhat fluorine-depleted layer beneath and that this stratification is in the outermost ~40 Å. This thickness is on the same scale as the $C_{60}(C_6F_{13})_5$ molecules, indicating that they orient upon adsorption. The takeoff angle dependence is much more pronounced in the case of surface-active polymers, where fluorine is concentrated in the outer few angstroms, and a layer that is completely depleted of fluorine exists below this region at the film surface.[44,45] The fluorine-depleted layer is not so obvious in the case of $C_{60}(C_6F_{13})_5$; it is a much more rigid molecule than flexible polymers and perfluorohexyl groups are distributed about its surface—all cannot concentrate in the outer few angstroms.

The water and hexadecane contact angles in the plateau regions of the adsorption plot are $\theta_A/\theta_R = 116°/83°$ and $\theta_A/\theta_R = 68°/22°$, respectively. Comparing the hexadecane contact angles with literature θ_A values[50] of 45° for poly(tetrafluoroethylene) and 72° for a monolayer containing $-CF_3$ groups at the surface indicates that the surface of the composite material is close to that of CF_3, with perfluorohexyl chains lying at some angle to the surface exposing primarily CF_3 end groups. The observed hysteresis is presumably due to surface roughness.

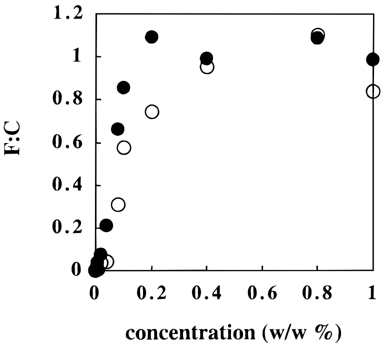


Figure 4. Adsorption isotherm (F:C) of $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene matrix: 15° (●) and 75° (○) takeoff angle data.

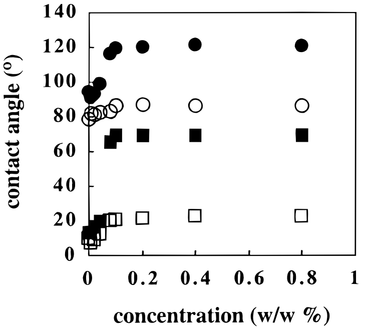


Figure 5. Adsorption isotherm (contact angles) of $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene matrix: advancing water contact angles (●); receding water contact angles (○); advancing hexadecane contact angles (■); receding hexadecane contact angles (□).

Concentration Isotherms. The surface activity of $C_{60}(C_6F_{13})_5$ was also assessed by determining a concentration isotherm. Figures 4 and 5 show how F:C ratios and contact angles change as a function of the concentration of $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene. Both F:C ratios and contact angles increase as a function of surface-active agent concentration before they reach plateau regions. The F:C ratios reach a maximum at ~0.2% w/w $C_{60}(C_6F_{13})_5$. The maximum surface excess (over bulk concentration) is ~500. Contact angle is a more surface-sensitive technique than XPS, and both water and hexadecane contact angles reach plateau values at lower concentration (~0.1%), indicating that the contact angle sampling depth is saturated with $C_{60}(C_6F_{13})_5$ at this concentration.

Mechanical Integrity of the Composite Films. As discussed above, XPS data of the composite material containing 1% w/w $C_{60}(C_6F_{13})_5$ in a 6.5K polystyrene matrix indicate that the surface consists primarily of $C_{60}(C_6F_{13})_5$. Peel tests (180°) were performed using pressure-sensitive adhesive tape (3M #810) to determine how strongly the $C_{60}(C_6F_{13})_5$ is incorporated into the polystyrene matrix. Essentially no fluorine-containing species were detached from the surface of the film sample onto the tape surface after peeling (fluorine content of the tape was less than 0.1%), indicating that no failure occurred within the composite material.

Reconstruction Studies. Due to the high surface affinity of $C_{60}(C_6F_{13})_5$ in the liquid phase during solution casting, its migration from the bulk of polystyrene to the polymer/air interface could not be demonstrated by the adsorption kinetics studied at room temperature or 110 °C. To study the surface reconstruction of the composite film samples, a thin polystyrene film was constructed over the composite material containing 1% w/w $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene via either spin-casting or transferring of a free-standing film. The migration of $C_{60}(C_6F_{13})_5$ through the spin-cast and transferred polystyrene films to the new surfaces was monitored by XPS and contact angle measurements.

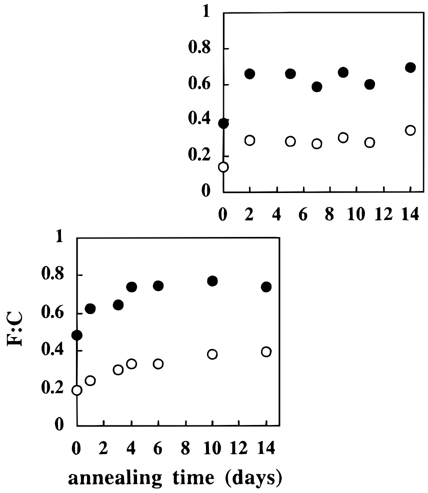


Figure 6. Surface reconstruction (F:C) monitored as a function of annealing time at 110 °C after 6.5K (lower plot) and 62K (upper plot) polystyrene (toluene solution) were spun-cast once onto the composite film samples: 15° (●) and 75° (○) takeoff angle data.

In initial experiments, either 6.5K or 62K polystyrene was spin-cast once onto the composite film containing 1% w/w $C_{60}(C_6F_{13})_5$ in 6.5K polystyrene. In Figure 6, F:C ratios calculated from XPS atomic composition data are plotted as a function of annealing time at 110 °C. (No surface reconstruction was observed at room temperature.) There are some interesting features in this figure. First of all, the F:C plateau values, 0.8/0.4 (15°/75°) for 6.5K and 0.7/0.3 (15°/75°) for 62K, are lower than those for the composite film discussed above, 1.0/0.8 (15°/75°). The polystyrene film cast on top of the composite acts as a barrier for the migration of the surface-active agent from the bulk to the surface. The thickness of the polystyrene film obtained under the experimental condition (2.5% polystyrene toluene solution and 2000 rpm spin rate) is ~1000 Å.[51] The actual barrier layer thickness, however, may vary since the dissolution of the surface-active agent in the polystyrene/toluene solution and mixing with the polystyrene cast on the top are evident from the nonzero starting point of the curve. The thickness was not measured by mass difference because of this issue. The migration is slower when the molecular weight of polystyrene is increased from 6.5K to 62K. Both of the plots start from nonzero values and increase as a function of annealing time until plateau values are reached. This implies that migration of $C_{60}(C_6F_{13})_5$ occurs during spin-casting and that the rate of migration is lower than the rate of drying. This information should enable us cover the surface-active agent completely, i.e., to move the starting point of the curve to zero, by spin-casting more than once. We also note that there is a pronounced takeoff angle dependence of the F:C ratio. This indicates that the $C_{60}(C_6F_{13})_5$ molecules present are concentrated in the outermost region of the outer ~40 Å of the film samples and that they are present in lower concentration than in the solution cast composites. Contact angles are comparable to those obtained on the solution cast films (Figure 5). Plateau contact angles for annealed 6.5K polystyrene-coated samples were θ_A/θ_R = 117°/83° (water) and θ_A/θ_R = 64°/17° (hexadecane). Identically prepared and treated 62K polystyrene-coated samples exhibited θ_A/θ_R = 117°/86° (water) and θ_A/θ_R = 59°/15° (hexadecane).

Figure 7 shows the results of spin-casting various molecular weight samples of polystyrene three times onto the composite film. By spin-casting three times, the initial F:C ratios become very close to zero. The plateau F:C ratios, however, are lower than those of samples spin-cast only once (6.5K and 62K) and lower than those of the composite samples. Spin-casting three times compared to only once creates a thicker barrier layer for the migration of the surface-active agent from the bulk to the surface. Another important feature is that the plateau values of F:C ratios decrease as a function of molecular weight of polystyrene. There is not much difference between 6.5K and 62K samples, but the 148K sample shows a significantly lower F:C ratio and the 498K sample is lower still. Presumably increased entanglement density in the polystyrene matrix at higher molecular weight slows down the migration of the surface-active agent. These polystyrene samples oxidize slowly under these annealing conditions, and experiments longer than 14 days were not carried out. Water and hexadecane contact angles of spin-coated samples that have been annealed are consistent with the XPS analysis. Contact angles increase upon annealing but are not as high as those for solution-cast composites or for those with one spin-cast polystyrene layer.

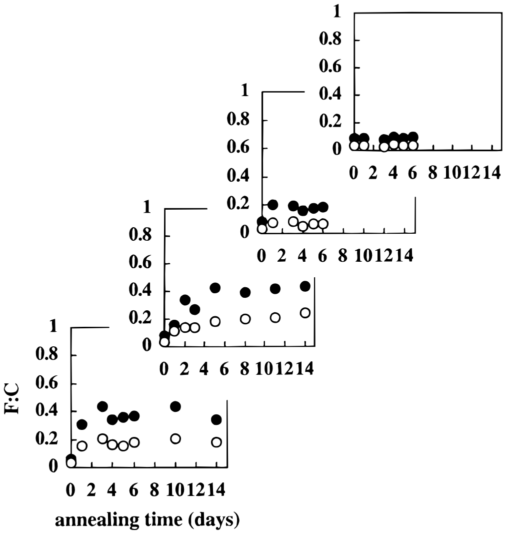


Figure 7. Surface reconstruction (F:C) monitored as a function of annealing time at 110 °C after various molecular weight (6.5K, 62K, 148K and 498K—from bottom to top) polystyrene solutions were spun-cast three times onto the composite film samples: 15° (●) and 75° (○) takeoff angle data.

To avoid mixing of the polystyrene cast on the top with the surface-active agent in the composite sample underneath, a free-standing polystyrene film was precast on a glass slide and transferred over the composite sample. The limitation of this approach is that only high molecular weight polystyrene films are mechanically strong enough to be transferred. Of the four different molecular weight samples, the highest molecular weight polystyrene, 498K, was chosen. The thickness of the polystyrene film obtained under the experimental conditions (2.5% polystyrene toluene solution and 2000 rpm spin rate) is ~1000 Å.[51] F:C ratios were monitored as a function of annealing time at 110 °C (Figure 8). Figure 8 is almost identical to the 498K data in Figure 7, except that the starting point of the spin-cast samples was higher due to the migration of the surface-active agent during casting. That the plateau value is almost the same as that of 498K polystyrene spin-cast three times onto the composite samples suggests that no loss of C_{60}-

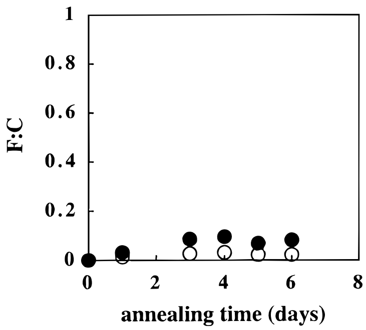


Figure 8. Surface reconstruction (F:C) monitored as a function of annealing time at 110 °C after a ~1000 Å thick 498K polystyrene film was transferred onto the composite film samples: 15° (●) and 75° (○) takeoff angle data.

$(C_6F_{13})_5$ occurred during spin-casting even though its dissolution in the polystyrene/toluene solution and mixing with the polystyrene cast on the top are evident (Figure 6).

Summary and Conclusions

We have prepared a perfluorohexylated-C_{60} (C_{60}-$(C_6F_{13})_5$) and studied its surface activity and mobility in a polymer matrix (polystyrene). Adsorption/migration of the perfluorohexylated-C_{60} from the bulk to the polymer/air interface was studied as a function of bulk concentration, annealing temperature, and annealing time. $C_{60}(C_6F_{13})_5$ is extremely surface-active in the polystyrene matrix and occupies the majority of the outermost ~40 Å of solution-cast samples (XPS results) and renders a surface that is similar to a monolayer containing CF_3 groups (hexadecane contact angle data). Surface reconstruction studies were carried out after either spin-casting or the transfer of a free-standing polystyrene film over the composite materials. Migration of $C_{60}(C_6F_{13})_5$ from the bulk to the surface is a function of annealing temperature, annealing time, and molecular weight of the polymer matrix. Peel tests indicate that the composite materials show good mechanical integrity; no failure occurred within the polystyrene/perfluorohexylated-C_{60} composite film.

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