qualitative features—a relatively low barrier to open the second bond and a minimum with both bonds open—in the triplet state along the second reaction coordinate as well. An example of such a double window structure with a 13-membered ring hole, for which the barrier to open the second bond (measured from the minimum with the bond open) is ~4 eV, is shown in Fig. 4. Some atoms or molecules may require such large windows for insertion.

Our theoretical predictions suggest an improved method of making endohedral fullerene compounds through this triplet window mechanism. We propose using a laser to irradiate C_{60} clusters in the gas phase and create a large population of the triplet state. By first producing an excited singlet state that intersystem crosses to the triplet, this process occurs with near quantitative yield (*30*), and it has the additional advantage of generating hot molecules, because the crossing releases energy. Heating this system to the sublimation point would ensure excellent thermal excitation and also keep unfilled cages cycling through an atmosphere of atoms to be inserted. With a large excess of such atoms, much of the material should react to X@C_{60}. Such a setup might allow the insertion of many different atoms and perhaps even small molecules. Furthermore, the *sp* carbons of the window minimum structure should be very reactive. Similar experiments under reactive atmospheres (such as H_2, F_2, or Li) might create compounds such as $C_{60}H_2$ or $C_{60}Li_2$, with addition across a 5–6 bond, in macroscale quantities. Thus, the existence of a C_{60} window mechanism described herein may open new avenues for the generation of both known and undiscovered endohedral and exohedral fullerene compounds.

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Suppression of Rupture in Thin, Nonwetting Liquid Films

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Stabilization against the rupture and breakup of thin, nonwetting liquid films spread on surfaces is generally sought by modification of equilibrium interfacial properties. A mechanism for suppressing rupture in such films that uses surface-attached polymers together with free chains in the bulk of the film is reported. Films of an oligostyrene liquid, which rupture within several minutes when spread on a silicon wafer, may be stabilized for many months by a polystyrene brush attached to the substrate, together with some free polystyrene in the liquid. The effect may arise from entanglements of the free chains with the immobilized brush.

A liquid spread thinly on a surface that it does not wet will spontaneously rupture and break up into droplets. This everyday observation has practical importance in areas as diverse as detergency, greenhouse efficiency, and resist-lithography in microelectronic applications. Where nonretarded van der Waals interactions are dominant, the free energy *U* per unit area of a film of thickness *h* is given by

$$U(h) = -A/(12\pi h^2) \qquad (1)$$

Here, *A* is the difference between the liquid-liquid and solid-liquid Hamaker constants (*1*). If *A* is positive, the van der Waals interactions thin the film, enhancing surface fluctuations, and after a characteristic time, the film ruptures (*2–5*). Dewetting of the surface takes place as the resulting holes grow. The rupture and breakup of such films have been extensively studied and are reasonably well understood (*2–10*).

An outstanding issue concerns the prevention of film rupture. Methods to stabilize nonwetting films have invariably focused on modification of the interactions at the liquid interfaces. This can be done with surface-active agents or with treatments that modify the substrate chemistry and thereby change the wettability (*4, 11*). Our strategy relies on a very different mechanism for suppressing the breakup of thin fluid layers. Liquid films can be stabilized by formation of a polymer "brush" together with small amounts of free polymer in the liquid. This effect does not result from changes in the surface tension, as in usual surfactant action. It may result from long-ranged entanglement coupling of the surface-attached brush with

Table 1. Molecular characteristics of oligostyrene and polystyrenes.

Sample	Weight-averaged molecular weight	M_w/M_n*
PS(580)†‡	580	1.02
PS(7 × 10^5)†	710,000	1.05
dPS(5 × 10^5)†	500,000	1.04
PS-X(2.6 × 10^4)§	26,500	1.02
dPS-X(3.8 × 10^5)§	380,000	1.05

*The ratio of weight-averaged molecular weight to number-averaged molecular weight is a measure of sample polydispersity. †Purchased from Polymer Laboratories (Church Stretton, United Kingdom) and used as received. Manufacturer's molecular weight data, based on size exclusion chromatography and light scattering. ‡Glass transition temperature, T_g = −18°C. §Synthesized as described in (*16*). Molecular weight data based on size exclusion chromatography and light scattering.

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free chains in the bulk of the film itself.

The films were created with an oligostyrene, PS(580), which is a nonvolatile liquid at room temperature (glass transition temperature, −18°C). It was spin cast from toluene solution onto polished silicon wafers to create films of mean thicknesses between 250 and 350 nm, uniform to within a few nanometers. Polystyrene (PS) chains of molecular weight M end-functionalized with the zwitterionic group $-[N^+(CH_3)_2(CH_2)_3SO_3^-]$ at one end, designated PS-X(M), were used as the polymeric amphiphiles. These were added to the toluene solution of the oligomer to the desired concentration, as were unfunctionalized PS chains where required. The polymer chains could be deuterated (d), so that we could determine their composition-depth profiles within the films by nuclear reaction analysis (NRA) (*12, 13*). Molecular characteristics of the materials are given in Table 1.

When the pure liquid is first spin cast, it forms an unbroken and uniform film (Fig. 1A), but within about 10 min, holes begin to form. These holes grow and eventually expose the underlying surface of the wafer. Over several hours, the film breaks up into droplets, which form a characteristic polygon pattern (*10*) on the exposed silicon surface (Fig. 1B).

We stabilized the liquid film against such breakup by adding small amounts of a long polymeric amphiphile. Figure 1C shows a spin cast film of the PS(580) liquid to which the zwitterion-terminated, deuterated polystyrene dPS-X(3.8 × 10^5) had been added, to a concentration of 4.6%. This picture, which shows that the film remains coherent and uniform, was taken 6 months after it was first cast; it shows the striking effect that the addition of the polymeric amphiphile to a concentration of a few percent has on the stability of the liquid film.

Experiments in which nonfunctionalized PS molecules, rather than the PS-X chains, were added to the liquid to comparable concentrations shed light on the mechanism by which stability is achieved. The PS chains by themselves impart no long-term stability to the film: PS(580) films containing PS(M) with M as high as 7 × 10^5, at bulk concentrations up to 8% polymer, break up into the polygonal droplet pattern (Fig. 1B) within a day or so.

The origin of the different behavior is indicated by NRA depth profiles of the polymer segment distribution for PS and for PS-X chains incorporated in oligostyrene films on silicon (Fig. 2). The unfunctionalized chains are uniformly distributed throughout the film, whereas the zwitterion-terminated ones have a clear peak at the silicon-liquid interface (Fig. 2A). This reveals unambiguously the formation of a layer of end-attached (but otherwise nonadsorbing) PS-X chains at the silicon surface, whose height, at 100 ± 20 nm, is between one-half and one-third of the overall film thickness. The absence of any surface excess of either the amphiphiles or the unfunctionalized chains at the liquid-air interface (Fig. 2) indicates that changes in the surface tension at this interface must be slight and independent of the polymers added. We note that the oligomer is a moderately good solvent for polystyrene (*14, 15*). Similar brush formation by PS-X chains on a mica surface immersed in the good solvent toluene has been extensively documented (*16*).

The polymeric brush thus plays an important role in the stabilization of the liquid film. But stabilization is not achieved simply by modification of the interfacial tensions, as in the case of surfactants or surface treatments that induce wetting (*4, 11, 17*): For dPS-X(3.8 × 10^5) chains added to the liquid, long-term stability of the film (Fig. 1C) is only attained at amphiphile concentrations higher than ~4%. At lower concentrations, the brush still forms at a similar surface density (*18*) (Fig. 2B), but the smooth film surface becomes rapidly pocked (Fig. 1D). Although the holes in this case do not reach all the way to the silicon substrate (*19*) (as they do in Fig. 1A, where no brush is present), it is clear that the brush alone cannot maintain the long-term integrity of the smooth film. The difference between the conditions leading to Fig. 1C and those leading to Fig. 1D is not in the brush itself, which is similar for both films (*18*), but in the amount of excess unattached polymer in the bulk of the film above the brush; this excess is appreciably greater for the film of Fig. 1C compared with the film in Fig. 1D. This implies that a certain concentration of free polymer chains (not attached to the substrate) within the bulk of the liquid is necessary, in addition to the brush, to suppress rupture of the film. We demonstrated this directly by incorporating in the liquid an even lower concentration (~1%) of dPS-X(3.8 × 10^5) together with a low (3 to 4%) concentration of PS(7 × 10^5). Even though neither of these by itself imparts stability at these concentrations, a brush of the zwitterion-terminated chains readily formed within the spin-cast film (Fig. 2C), which remained unbroken and uniform for

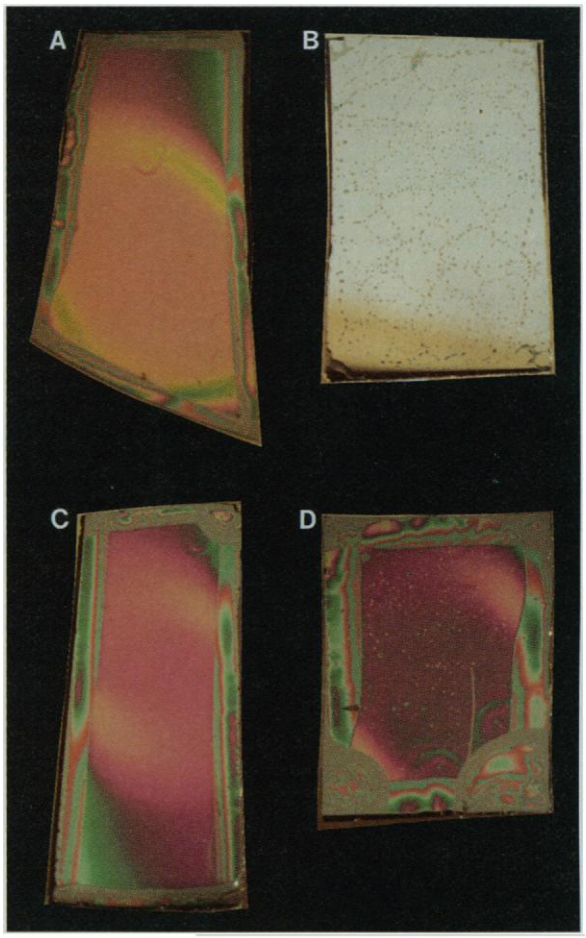

Fig. 1. (**A**) A layer of oligostyrene PS(580) spin cast (1800 to 2000 rpm) from a toluene [Frutarom (Haifa, Israel) analytical grade] solution (70 mg/ml) onto a silicon wafer [P100, 0.5 to 1 ohm·cm, purchased from Aurel Ltd. (Landsberg, Germany) and sonicated in toluene before use]. The film is ~400 nm thick. Such films of pure PS(580) retained their uniform, unbroken appearance for the first 10 min or so after casting, after which holes began to form and grow. (**B**) A film of pure PS(580) on a silicon wafer 24 hours after spin casting. Similar droplet patterns were obtained within 24 hours of casting films of PS(580) containing up to 8% of unfunctionalized PS(*M*) (*M* up to 7 × 10^5). (**C**) A film of PS(580) containing 4.6% dPS-X(3.8 × 10^5), spin cast onto a silicon wafer from a toluene solution containing the oligomer and the polymer in the appropriate ratio. The picture was taken 175 days after the film was cast. Similar uniform, unbroken films were observed at comparably long periods after spin casting films of the oligomer in which 1.0 to 1.5% dPS-X(3.8 × 10^5) together with 3 to 4% PS(7 × 10^5) were incorporated. (**D**) A film of PS(580) containing 2.2% dPS-X(3.8 × 10^5) 5 hours after spin casting. The holes in such films evolved somewhat at longer times, but even after many weeks, the appearance was still that of holes in an otherwise continuous film and not the droplet pattern in (A). The holes did not appear to penetrate to the underlying silicon surface, as in (A) (*19*). Similar patchy appearances were observed when PS-X(2.6 × 10^4) chains were added to the oligomer film to concentrations up to 8%, with or without added unfunctionalized PS.

extended periods, as in Fig. 1C.

We examined independently the role of the adhering zwitterions in modifying the chemistry of the silicon surface by incorporating PS-X(2.6×10^4) chains in the oligomer film. These much shorter amphiphiles form shorter and denser brushes, and the surface concentration of zwitterions tethering them to the silicon is over an order of magnitude greater than that for PS-X(3.8×10^5) layers (*16*). Instead of a stronger stabilizing action, as might be expected from an effect controlled purely by changes in the surface chemistry (*4, 11*), these shorter brushes both on their own (at concentrations up to 8% of the bulk film) and with added PS chains with M up to 7×10^5 (and concentrations up to an additional 8%) did not impart long-term stability to the film. The smooth films become pocked within hours, reaching a state similar to that of Fig. 1D. Clearly, it is not the extent of zwitterion coverage, which modifies the surface tension at the film-substrate interface, that is important for suppression of the rupture of the smooth films, but the nature of the brush and its interactions with the free polymer in the bulk of the film. It is these interactions that must be responsible for stabilizing the film-air interface against fluctuations and hole formation, resulting (for the longer brushes) in the long-term integrity of the film.

The stabilization is not related to changes in interfacial tensions or bulk liquid viscosity alone, effects that control the characteristic time (*20*) for rupture by surface fluctuations. Rather, the responsible mechanism appears to be an entanglement coupling of the free (unattached) chains in the bulk of the film with the immobilized chains incorporated in the brush. We believe this coupling results in a transient, surface-attached network with some effective finite-frequency shear modulus E: Recent calculations (*21*) suggest that even extremely small values of E in a thin, nonwetting supported film can lead to suppression of rupture for very long times. This mechanism is also qualitatively consistent with our observation that shorter brushes, composed of chains too short to exhibit entanglement effects with the free polymers (*22*), do not lead to suppression of rupture under otherwise similar conditions.

The precise mechanism of the stabilization process remains to be determined. Together with the known robustness and self-healing nature of polymer brushes (*16, 23*), these observations indicate a conceptually new approach to control of the integrity of thin liquid films in a broad spectrum of applications.

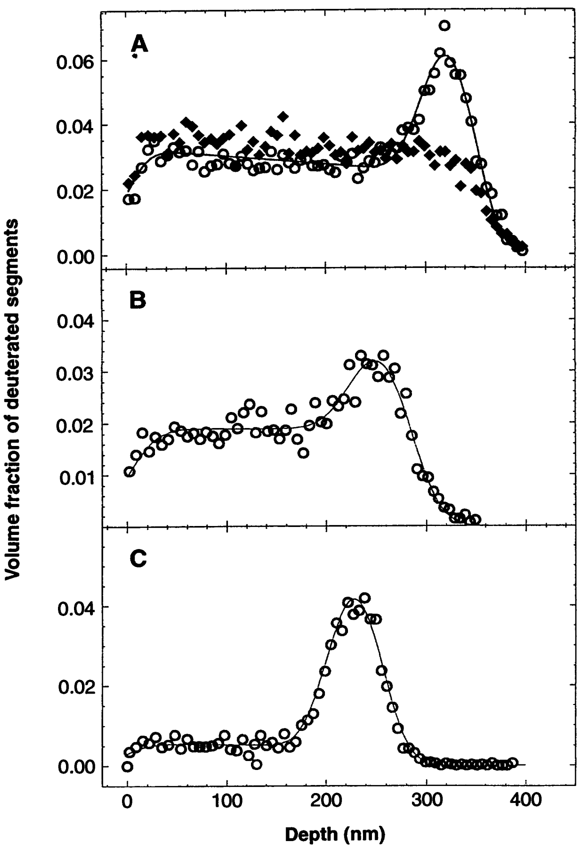

Fig. 2. Concentration-depth profiles of deuterated polymer segments within oligostyrene films determined by NRA (*12, 13*). The zero depth of each profile is the liquid-air interface, and the cutoff around 250 to 350 nm (which is the range of our film thicknesses) is the liquid-solid interface. (**A**) Superposed profiles of dPS-X(3.8×10^5) (○) and dPS(5×10^5) (◆) in oligostyrene films incorporating 3.4% of the polymers, spin cast onto silicon wafers. The excess of dPS-X at the oligomer-silicon interface is attributable to formation of the end-attached layer (brush). The oligomer used in these films, PS(1700), was microstructurally identical to PS(580) but had a slightly higher molecular weight; its higher viscosity resulted in longer coherence times of the layers, enabling NRA measurements to be made on unbroken films. Both samples were annealed for 19 ± 2 hours at 90°C, appreciably higher than the glass transition temperature for PS(1700) of 66°C. (**B**) Profile of dPS-X(3.8×10^5) incorporated in a PS(580) film to a mean concentration of 2.2%, showing the excess due to brush formation at the silicon surface. The film was spin cast onto silicon as described in Fig. 1A. This sample at later times partially dewetted as in Fig. 1D. (**C**) Profile of dPS-X(3.8×10^5) incorporated to a mean concentration of 1.4% in a PS(580) film containing 3.9% PS(7×10^5), showing the clear excess of the deuterated amphiphile due to brush formation at the silicon surface. This sample remained uniform and unbroken after many months, as in Fig. 1C. The surface density of the zwitterion-anchored dPS-X chains may be evaluated directly from these profiles to yield a mean interanchor spacing of 17 ± 2 nm, similar to that reported earlier for the same amphiphiles end-attached to mica from toluene (*16*). The solid lines in all profiles are a guide to the eye.

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