Communications to the Editor

Grafting Rates of Amine-Functionalized Polystyrenes onto Epoxidized Silica Surfaces

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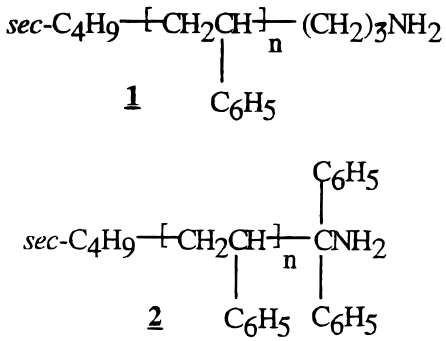
Oligomer or polymer chains that are irreversibly attached, i.e., by polymer grafting rather than segmental adsorption, to a solid surface are important because they impart permanent performance characteristics to the surface without altering the bulk properties. Such grafted layers have potential applications in areas as diverse as adhesive bonding, bioengineering, and friction and wear. Although fully formed grafted layers[1] have received considerable attention from both theorists and experimentalists, relatively little work has been conducted on the kinetics of layer formation, starting with the attachment of the first chain and following through to saturation, where no further grafting occurs. Obviously, for the development of useful, practical models from kinetic or statistical theories,[2,3] data are needed that describe the grafting process of well-defined polymers under well-controlled conditions.

In this communication, we report results of a comparative study of the grafting of two well-defined, end-functionalized polystyrene samples to the epoxidized surface of a silica substrate. The two polystyrene samples were identical except for the steric environment of their functional amine end groups. Both were monodisperse and had the same molecular weight ($M_n = 4 \times 10^3$ g/mol). The functional end group of one sample was an unhindered primary amine (**1**), while that of the other was a severely hindered primary amine (**2**). The reactivity difference in these functional end groups was expected to have a profound effect on the kinetics of grafting.

ω-Amine-functionalized polystyrenes (PS-NH_2) were prepared by termination of poly(styryl)lithium (PSLi) (base polymer: M_n = 4100 g/mol; M_w/M_n = 1.09) in benzene with either *N*-3-chloropropyl-2,2,5,5-tetramethyl-2,5-disila-1-azopentane,[4] to form PS-$(CH_2)_3NH_2$, **1**, or with *N*-trimethylsilyldiphenylcarbimide,[5] to form PS-$C(C_6H_5)NH_2$, **2**. Poly(styryl)lithium was prepared by *sec*-butyllithium-initiated polymerization of styrene[6] in benzene in all-glass reactors sealed with break-seals, under standard high-vacuum conditions.[7] Both amine-functionalized polystyrenes were obtained in quantitative yields; no unfunctionalized polystyrene base polymer was detected by thin-layer chromatography.[5] Both polymers were shown to be monomodal, with narrow molecular weight distributions, by size exclusion chromatography (SEC).



The silica substrate was in the form of glass beads (Potters Industries, Carlstadt, NJ), diameter = 11 μm and specific surface area = 0.24 m^2/g. In preparation for polymer grafting, epoxide reactive sites were created on the surface of the beads by reaction of approximately 100 g of glass beads, previously washed and dried, with 0.2714 g of 3-glycidoxypropyltrimethoxysilane (Aldrich, Minneapolis, MN) in 75 mL of anhydrous toluene under reflux for 16 h. Unreacted material was removed by thorough rinsing in solvent, leaving epoxide reactive sites attached to the underlying glass surface by a six-atom flexible spacer arm. The density of reactive sites achieved was 2.71 ± 0.24/nm^2, determined by dye-coupling analysis.[8]

Grafting reactions were conducted in tetrahydrofuran at reflux (66 °C) under anhydrous conditions and inert (N_2) atmosphere. For this, 6.0 g of glass beads, their surfaces epoxidized as described above, was placed in a solution of 0.0073 g of amine-functionalized polystyrene ($M_n = 4 \times 10^3$ g/mol) in 6.30 mL of tetrahydrofuran. This represented approximately a 2-fold excess of polymer chains over the total number of epoxide sites present on the surface of the glass beads. A small amount of very low molecular weight, inert-ended polystyrene (M_n = 285 g/mol) was added to the mixture to serve as an internal standard.

The kinetics of grafting was monitored with a recently developed, quantitative method described in detail elsewhere.[9] Briefly, small aliquots of the reaction mixture were taken frequently and analyzed off-line by SEC. Each chromatogram was adjusted to quantitative accuracy by reference to the internal standard. Subtraction of each chromatogram obtained during the reaction from the zero-time chromatogram yielded, by difference, the amount of polymer grafted to the surface of the solid substrate at each time. The mass of grafted polymer and corresponding number of chains per unit surface area were computed from the known values of initial mass of polymer, molecular weight, and surface area of the

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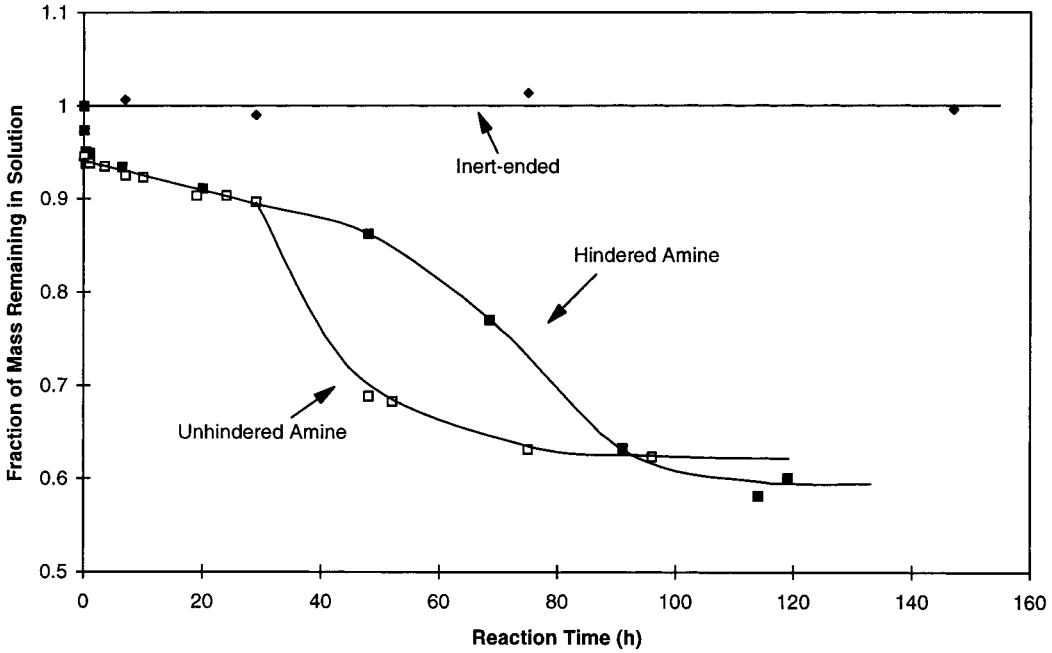

Figure 1. Relative mass in solution versus time.

solid substrate. Coefficient of variation (standard deviation/mean × 100) for experimental values of mass grafted was 5−6%, typical for this method. The chromatograph used for SEC was equipped with a Waters Styragel HR 5E column (1 mL/min flow rate of mobile phase tetrahydrofuran) and a UV absorbance detector.

For this study, systems were selected so that polymer chains would attach to the substrate by end-grafting only and not by segmental adsorption. We wanted to avoid effects such as overshoot, relaxation, loop formation, and desorption that are observed in segmental adsorption[10−14] but are not possible for polymers attaching by irreversible end-grafting in the absence of segmental adsorption. Absence of segmental adsorption for our systems was verified by means of control experiments in which inert-ended, monodisperse polystyrenes (M_n = 285, 2300, and 45 730 g/mol studied separately) were exposed to glass beads with epoxidized surfaces under the same conditions used for grafting reactions. The results are shown in Figure 1, where the relative mass of polymer in solution is plotted against time. The constant value of the inert-ended polystyrene in solution verifies the total absence of segmental adsorption to the epoxidized substrate.[15]

The results for separately conducted grafting reactions are shown together in Figure 1. In this figure, the decrease of polymer in solution corresponds exactly to polymer being grafted to the glass surface, since grafting was the only avenue by which chains could leave solution. (Grafting to the walls of the reaction vessel was not a concern, since the vessel wall surface area was negligible compared with that of the glass beads.) Figure 1 shows that the two polymer samples behaved the same at first, grafting rapidly for the first 0.5 h. Then an abrupt slowdown occurred at 0.5 h, suggesting the development of an energy barrier made by overlap of the grafted chains themselves and through which subsequent chains were required to diffuse.[16] The surface attachment density at 0.5 h, computed from mass grafted (0.070 × 0.0073 g = 0.000 51 g), molecular weight, and substrate surface area (1.44 m^2), is 0.053 chains/nm^2. The surface attachment density at which the polystyrene chains used here should begin to overlap can be estimated from $1/(\pi R^2)$, where[17] $R = 0.186N^{0.595}$ with $N = 40$. The resultant estimate is 0.11 chains/nm^2, which is within a factor of 2 of the value computed from our experimental data. This good agreement supports the notion that the observed slowdown in grafting rate is associated with onset of chain overlap. Slowdowns in rate similar to that in Figure 1 have been observed in studies of diblock copolymers attaching to a solid surface by means of strong adsorption of the anchor block; in these studies, the slowdowns were identified with the surface attachment density at which the buoy blocks began to overlap.[10,18] In our experiments, both samples continued to behave identically up to 30 h, suggesting that, up to that time, transport of the polymer chains to the glass surface was the rate-limiting step, slower than the chemical reaction between the functional end groups of the chains and the epoxide sites on the surface.

Only after 30 h did the behavior of the two polymers diverge, the grafting rate of the unhindered amine becoming much faster than that of the hindered amine. This difference is what would be expected for a process whose rate is controlled by the chemical reaction between the end-functional groups of the chains and the reactive sites on the substrate surface. The surprising aspect of this divergent behavior of the two samples is that it appears to have been achieved by an acceleration of the grafting rate, with the acceleration being greater for the unhindered amine than for the hindered amine. This acceleration, which occurred at different times for the two samples, has been dubbed by us "layer-assisted grafting". This interesting effect cannot be explained by physisorption or layer relaxation of the sort observed in studies of polymer adsorption, because, first, our control experiments showed absence of segmental adsorption to the solid surface and, second, the polymer chains added to the solid surface during the acceleration stage were truly end-grafted, and not physisorbed, as shown by independent determinations of surface attachment density reported below. (Furthermore, we have observed an acceleration in the later stages of end-

grafting of polysulfone, which will be reported in the future.) A possible explanation for the observed acceleration is that, when the grafted layer is dense enough to approximate a concentrated solution, the incoming free chains and/or the grafted chains contract to the theta condition dimensions, a situation that allows easier diffusion of the free chains through the grafted layer to the solid surface. Interestingly, recent neutron scattering data of Fetters et al.[19] have shown that polymer chain dimensions correspond to theta-condition dimensions at high concentrations (>overlap) in solution, in accord with the prediction of the Flory–Edwards mean field theory approach.[20,21]

At saturation (no further grafting), both polymers reached the same value of mass grafted. In terms of chains per unit area, this is $0.29 \pm 0.017/nm^2$. (This value was independently verified by thermogravimetric analysis after extensive extraction, which yielded a value of 0.30 chains/nm^2.) The achievement of identical saturation values for both polymers is reasonable and expected, because saturation is a natural maximum in surface attachment density that is set by thermodynamic factors such as chain length, chain–chain interaction, and conformational entropy loss.[1] Hence, the saturation attachment density is independent of, and not limited by, the areal density of reactive sites on the substrate, as long as this density is high, as it was in our case ($2.71/nm^2$).

In conclusion, this study of grafted layer formation by two monodisperse polystyrene samples, identical except for the steric environment of their functional end groups, has revealed that the kinetics of layer formation changes throughout the process as the grafted layer becomes more densely packed. A surprising acceleration was observed after the surface attachment density reached a value associated with chain overlap and stretching. This study also illustrates that grafting rate can be manipulated by the detailed nature of the functional end group and that more work is needed to fully understand the grafting process. Work is in progress with well-defined polymers of various molecular weights, architectures, and end-functional groups to further probe the acceleration phenomenon.

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