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Notes

Deactivation of Epoxide-Derivatized Surfaces

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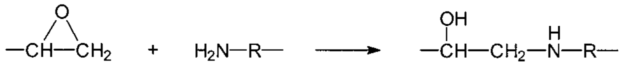
Introduction

One of the ongoing research efforts in our laboratory involves the tethering of functional-ended polymer chains to the surfaces of impenetrable solids, such as silica and alumina. In our approach, a solution of the functional-ended polymer of interest is placed in contact with the solid, previously treated so its surface contains reactive groups, and the process of tethering is followed quantitatively. Tethering itself occurs by means of a heterogeneous phase chemical reaction between the functional end group of the polymer chain and the reactive group on the surface of the solid.

A useful functional end for the polymer is the primary amine group, and a useful reactive site for the surface of the solid is the epoxide group. The latter can be attached by treatment of the solid with the appropriate organofunctional silane, such as 3-glycidoxypropyltrimethoxysilane. The chemical reaction between the epoxide group and the primary amine group is well-known in the lexicon of organic chemistry:[1]



Once tethered to the surface, the polymer cannot be removed even by exhaustive extraction at elevated temperature with a good solvent. In our systems, no segmental adsorption is involved, and each chain is attached to the surface only by the single chemical bond formed in the chemical reaction above. Reactions at a surface are expected to be completely analogous to their counterparts in the homogeneous phase, but slower due to steric hindrance from the impenetrable surface.

In the course of studying tethering, we have conducted various types of control experiments. For example, to verify the absence of segmental adsorption, we exposed solutions of inert-ended polystyrenes of various molecular weights to epoxide-derivatized surfaces and found that, as expected, the solution concentration remained at its original value indefinitely.[2,3] The subject of the present note is another control experiment, in which tertiary amine-ended polystyrene was exposed to an epoxide-derivatized surface. Since a tertiary amine group has no labile hydrogens, we expected no actual tethering and, correspondingly, expected the amount of polymer in solution to remain at its initial level at all times during the tethering run. Much to our surprise, we observed that a significant portion of the polymer disappeared from solution for a time and subsequently returned to solution.

Experimental Section

For a tethering run, a dilute solution of monodisperse, tertiary amine-ended polystyrene ($M_n = 4100$) in tetrahydrofuran was exposed at 60 °C under inert atmosphere to the epoxide-derivatized surface of finely divided silica. The total number of epoxide groups in the initial mixture exceeded the number of tertiary amine groups by 16%. At the conclusion of the run, the finely divided silica was isolated by filtration, extracted with a good solvent (toluene), and exposed to monodisperse, primary amine-ended polystyrene ($M_n = 4000$) under the same conditions used for exposure to tertiary amine. The progress of all tethering runs was followed with a quantitative, real-time method based on size exclusion chromatography.[4] In this method the amount of polymer in solution at any time is measured by comparison with an internal standard; if measurements are taken at frequent intervals, the disappearance of polymer from solution can be followed over time. Use of finely divided solid in the tethering runs ensures that the surface area available for tethering is ample and that the amount of polymer that disappears from solution is large enough to be detected easily.

Results and Discussion

Figure 1 presents the data for the tertiary amine-ended polystyrene, plotted as relative amount of polymer in solution vs time. The decrease and subsequent increase, instead of the expected “no change”, can be seen easily. For an explanation of this behavior, we drew on epoxy resin chemistry, where it is well-known that the tertiary amine group does not form a chemical cross-link with the epoxide group but does initiate homopolymerization.[5−7]

In the case of tethering from solution, we suggest that the reaction scheme shown in Figure 2 occurs on the surface of the solid. The scheme is analogous to the homopolymerization that occurs in epoxy resins.[8,9] In Figure 2a,b, the tertiary amine group initiates the process by attacking the most electrophilic of the epoxide carbons, opening the ring and generating a negatively charged oxygen atom. (Tetrahydrofuran is sufficiently polar to support separation of charge.) This negatively charged oxygen atom then attacks the most electrophilic carbon of a neighboring epoxide group, forming an ether linkage and generating a new negatively charged oxygen (Figure 2b,c). In reality, multiple local chain reactions like this will be occurring. Termination (Figure 2d,e) occurs when a negatively charged oxygen atom happens to attack a carbon atom bearing a tertiary amine; as usual, an ether linkage is formed,

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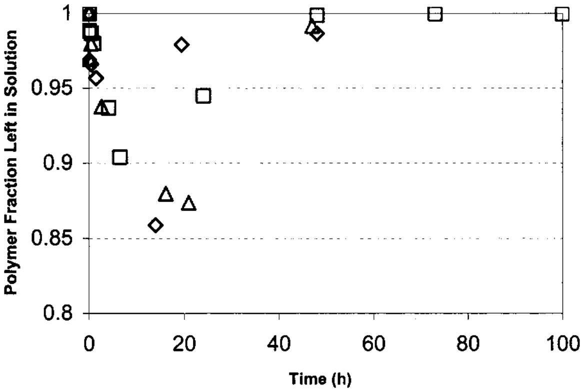

Figure 1. Fraction of tertiary amine-ended polystyrene (M_n = 4100) in solution vs time of exposure to epoxide-derivatized surface. Polymer disappears from solution and then returns to solution. Data from three replicate runs are indicated by open diamonds, squares, and triangles.

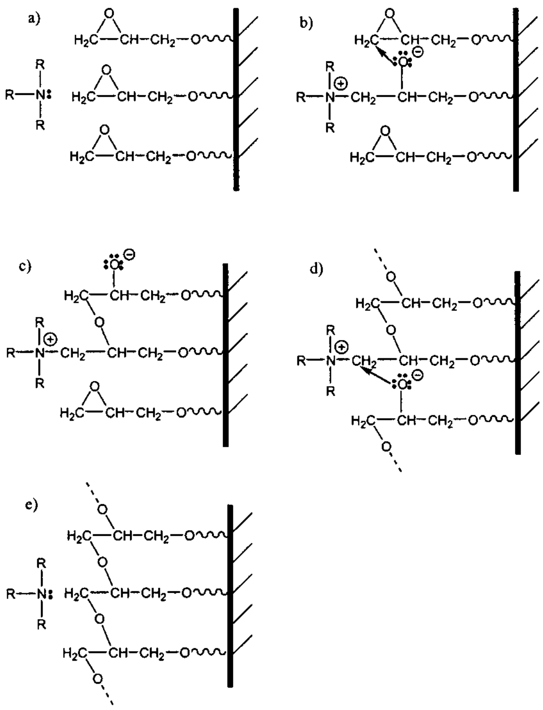

Figure 2. Proposed reaction scheme. A single tertiary amine causes formation of many ether linkages and is ultimately displaced.

but the tertiary amine is displaced back into solution without the generation of a negatively charged oxygen atom. (An alternative to the last step could be a Hofmann-type elimination, in which an alkene is formed, as a negatively charged oxygen removes a proton from one carbon and the positively charged nitrogen acts as a leaving group from the adjacent carbon.) This scheme explains both the initial disappearance from—and the subsequent return to—solution of the tertiary amine. It also indicates that the surface of the solid would be deactivated by conversion of the epoxide groups to ether linkages.

To verify the deactivation of the epoxide groups, we isolated the solid from tethering runs with tertiary amine and subjected it to follow-up tethering runs with primary amine-ended polystyrene.[10] Results of these follow-up runs are shown in Figure 3, which shows that less than 10% of the polymer in solution was tethered to the deactivated surface, even after 80 h. This is in sharp contrast to the 40% of the same primary amine-ended polystyrene (M_n = 4000) tethered to an epoxide-derivatized surface *not* previously exposed to tertiary amine (closed diamonds[11] in Figure 3). Taken together, these results are consistent with our hypothesis that exposure to tertiary amine groups results in deactivation of the epoxide groups on the surface of the solid.

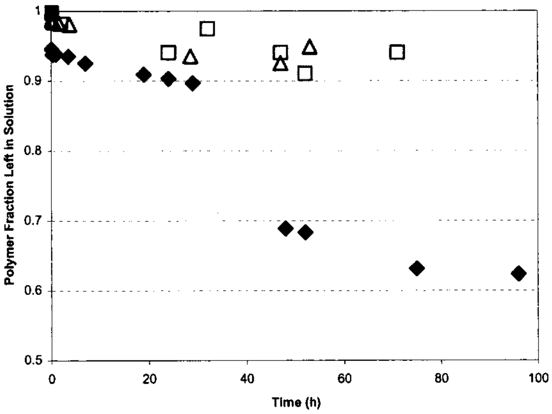

Figure 3. Fraction of primary amine-ended polystyrene (M_n = 4000) in solution vs time of exposure to epoxide-derivatized surfaces. Open triangles and squares represent two replicate runs using epoxide-derivatized surfaces already exposed to tertiary amine. Closed diamonds represent a run using epoxide-derivatized surface *not* previously exposed to tertiary amine.

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(10) Spectral methods, such as reflectance infrared, are not sufficiently surface-sensitive for direct evaluation of the decrease in epoxide groups.
(11) The interesting features of this curve are discussed in detail in ref 2.

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