

The Adsorption of Polystyrene-Poly(methyl methacrylate) Mixtures at a Solid-Liquid Interface¹

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The adsorption of polystyrene (PS) and poly(methyl methacrylate) (PMMA) mixtures on finely divided silica from dilute trichloroethylene solutions at 25° has been studied in order to establish the competitive adsorption behavior of these polymers. It has been shown that under equilibrium conditions, reached within 2–4 hr, PS is not adsorbed unless the available PMMA is unable to saturate the adsorbent surface. If PS is first equilibrated on the silica surface and excess PMMA is added later in a second step, complete PS displacement occurs within 2–4 hr. Within limits of the experimental technique used, the rate and extent of displacement are essentially independent of the time the PS is equilibrated on the surface and the PS surface coverage. Polymer-polymer incompatibility was found to have little effect on the adsorbance and/or adsorbed structure of either polymer. Infrared bound fraction data establish that simultaneous adsorption of PS and PMMA on silica induces relatively small changes in the average number of segments of either polymer that are attached to the adsorbing surface. However, these results may be uniquely applicable to dynamic systems involving small adsorbent particles such as employed in this study.

Introduction

The absorption of polymers at solid-liquid interfaces has been studied extensively and is the subject of several recent reviews.^{2–4} Past studies have led to the conclusion that polymers adsorbed at such interfaces have a looped or coiled structure in which only a fraction of their segments are attached directly to the interface. Many such structures are possible, ranging from ones which yield a relatively flat and compressed adsorbed polymer layer to ones which give adsorbed layers highly extended away from the interface. Thus, efforts have been made to measure directly the structure of adsorbed polymers.^{5–7} Of particular interest is an infrared method first reported by Fontana and Thomas.⁸ This utilizes the fact that various molecular groups possess a characteristic infrared band which appears at a certain frequency when the group is unadsorbed and then shifts slightly to a new frequency when the group is bound or attached to an interface. If only a fraction of a polymer's segments are attached, this fraction can be determined by resolving the infrared peaks due to the adsorbed and unadsorbed segments. From these

peaks, the concentrations of free and bound segments can be determined, and the infrared bound fraction, p , can be calculated. Hence, p represents the average fraction of groups that are bound directly to the interface.

By combining bound fraction data with isotherm data, considerable insight into polymer adsorption phenomena can be gained. The purpose of this study is to utilize these tools to explore the competitive ad-

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