Adsorption of a Functionalized Polymer from Dilute Nonaqueous Solutions by Silica

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Synopsis

The adsorption of a functionalized styrene–butadiene (SB) diblock copolymer from toluene solutions at 25°C onto silica of varying particle sizes was studied using thermogravimetric analysis. The copolymer was chemically modified by hydroformylation, and the adsorbate concentration ranged from 0 to 2% by weight. The modified copolymer was adsorbed by the silica particles, but the unmodified copolymer was not. The plateau adsorption was found to increase with silica surface area, and the level of surface coverage ranged from 0.4 to 0.8 mg/m^2.

INTRODUCTION

The adsorption of polymers onto the surface of inorganic fillers has been studied extensively over the years. Reviews on adsorption of macromolecules and polymers on solids have been written by Ash,[1] Takahasi and Kawaguchi,[2] and Howard.[3] Methods used to determine free polymer concentration after adsorption have included gravimetry, infrared and ultraviolet spectroscopy, and chromatography.[4-8]

The purpose of this investigation is to present a systematic study of the adsorption, as determined by thermogravimetric analysis, of a functionalized styrene–butadiene (SB) diblock copolymer from toluene solutions onto particulate silica of three different particle sizes.

EXPERIMENTAL

Materials

The diblock copolymer, FINAPRENE 410, (styrene : butadiene weight ratio = 48 : 52; MW = 70,000 with 10% vinyl unsaturation) was supplied by Petrofina Inc., Deer Park, Texas. The polymer was purified by dissolution in toluene (5% solution by weight) followed by coagulation with methanol, prior to hydroformylation. Toluene was distilled over sodium metal under an argon atmosphere before use. All other solvents used were reagent grade. Carbon monoxide and hydrogen gases (Matheson Gas Products, Canada) had a minimum purity of 99.99%. The catalyst, hydridocarbonyltris(triphenylphosphine)rhodium(1), [RhH(CO)(PPh$_3$)$_3$], was prepared according to published methods.[9] HiSil 233 and HiSil T-600 silica were supplied by PPG Industries Inc., Pittsburgh, Pennsylvania, and Silene 732-D silica was obtained from Harwick Chemical

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TABLE I
Properties of Silicas Used

Silica	Particle size (nm)	Surface area (BET, m^2/g)
Silene 732-D	80	30
HiSil 233	22	140
HiSil T-600	19	165

Corporation, Akron, Ohio. Table I lists some important properties of the silicas used in this study.

Hydroformylation of SB Diblock Copolymer

A Parr bench-top mini reactor (600 cm^3) was charged with an 8% toluene solution of the SB diblock copolymer (350 cm^3). The catalyst, [$RhH(CO)(PPh_3)_3$] (0.14 g, 0.5% loading by weight) was then placed in the catalyst addition system, and the reactor was sealed. The solution was purged with carbon monoxide for 15 min, and then the reactor was brought to operating conditions ($60°C$, 400 psi with $CO : H_2 = 1 : 1$). The catalyst was released from the catalyst addition system, and the ensuing reaction was monitored by the amount of gas consumed. Two control experiments were also performed under the stated conditions. In the first experiment, no catalyst was added, while in the second, no polymer was added. In both cases, no significant uptake of reac-
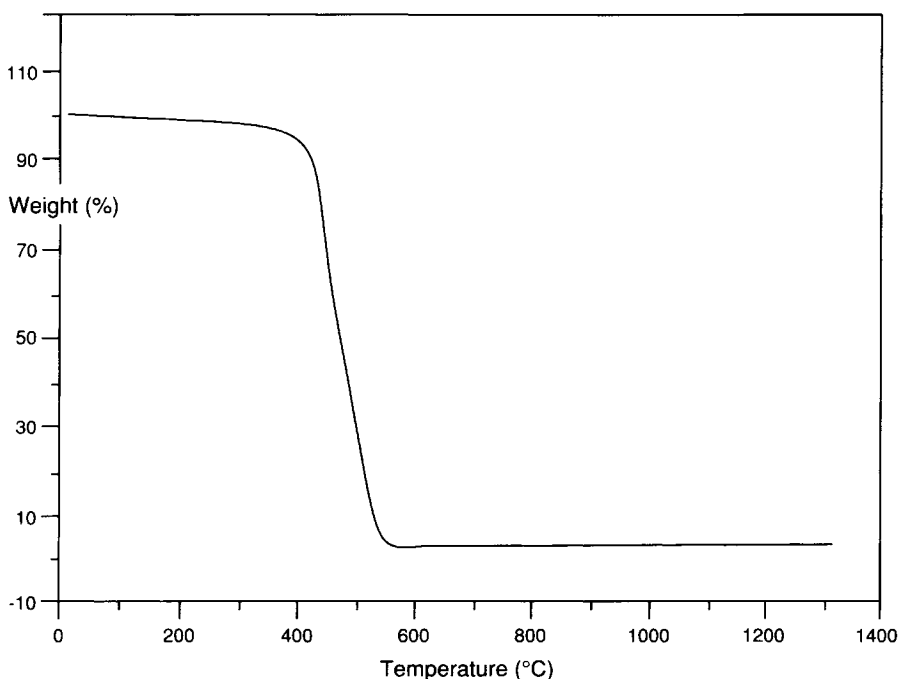

Fig. 1. Thermal degradation of hydroformylated SB diblock copolymer.
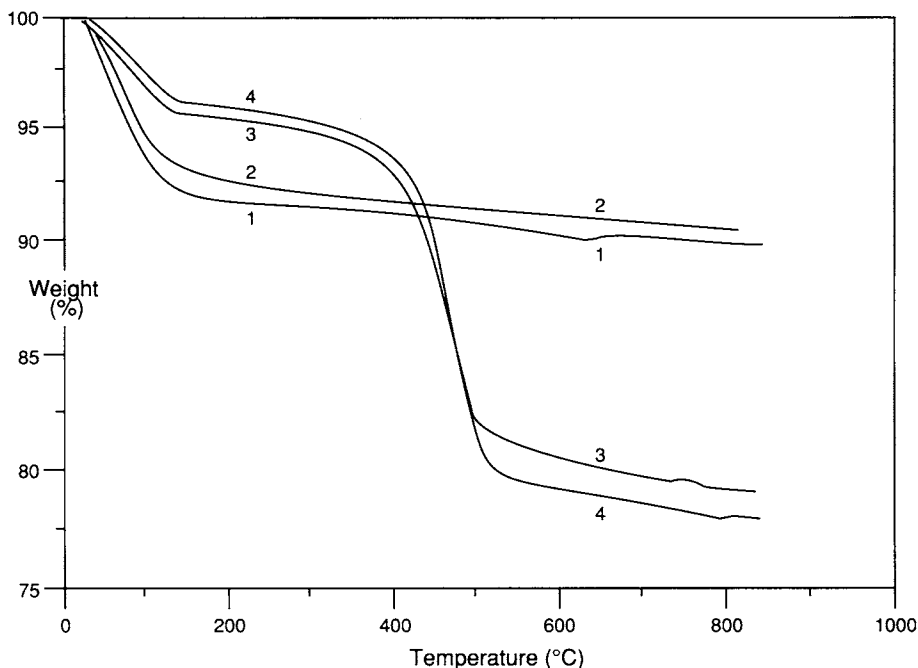
Fig. 2.   Thermal degradation of HiSil T-600 silica (1) untreated, (2) coated with unmodified FINAPRENE 410 copolymer, (3) coated with 15% hydroformylated copolymer, (4) coated with 25% hydroformylated copolymer. Initial concentration of copolymer solution is 1% by weight.

tant gases was observed. The degree of functionalization was therefore determined from the gas consumption through the use of a calibration curve with ^{1}H-NMR data as the primary standard.[10] After the desired degree of hydroformylation was achieved, the reaction was stopped by quickly cooling and venting the reactor. The modified copolymer was coagulated with methanol and dried under vacuum.

Adsorption Measurements

The adsorption of the hydroformylated SB diblock copolymer on the various silicas was determined by thermogravimetric analysis (TGA). A 25-cm^3 solution of the functionalized copolymer in toluene of known concentration was added to 0.500 g silica in a capped serum bottle. The suspensions were shaken in a Fisher Model 224 Versa-Bath S Shaker Bath at 25°C for a required time, usually 0.5 h, after which they were centrifuged for 10 min at 1000 rpm, using an IEC Model CRU-5000 centrifuge. The sedimented silica was consequently washed for 30 min with excess toluene and centrifuged again. Analysis of the dried solids indicated that no significant amount of functionalized copolymer was removed from the silica surface during this extraction process. The solids were dried under vacuum at 70°C for 24 h prior to thermogravimetric analysis. In a selected case, the time dependence of the adsorption process was studied. Polymer solution concentrations are expressed in wt %, i.e., weight of copolymer per 100 g solution.
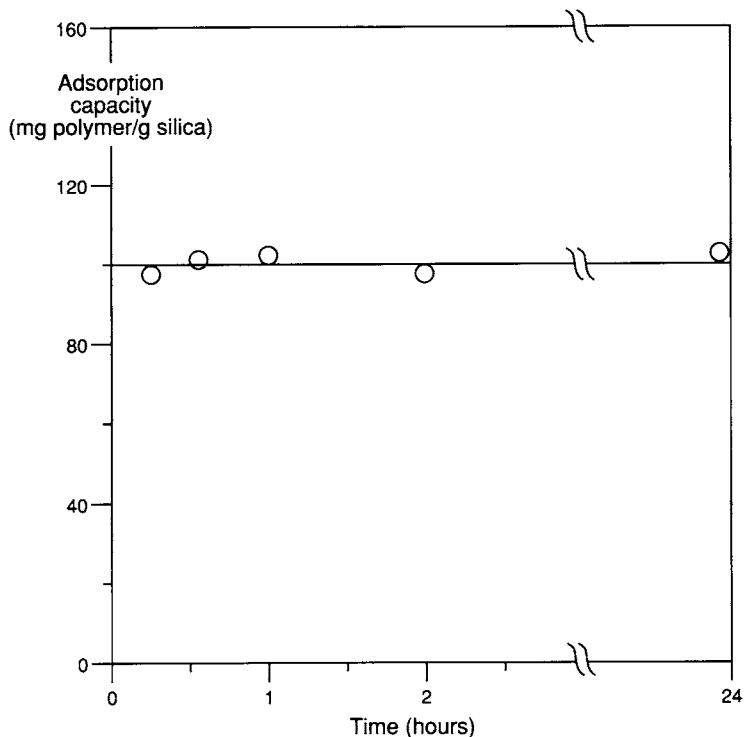
Fig. 3. Time dependence on the adsorption of hydroformylated (25%) copolymer on HiSil T-600 silica. Initial concentration of added copolymer is 2% by weight.

Thermogravimetric Analysis (TGA)

The amount of functionalized polymer adsorbed on the silica surface was determined by TGA using a DuPont 951 Thermogravimetric Analyzer. The dried silica samples were heated in nitrogen (50 cm^3/min) from 30 to 800°C at 20°C/min. The weight loss during the reaction interval 200–800°C was used to determine the amount of copolymer adsorbed, and, from this data, the concentration of free polymer in solution after adsorption was determined.

RESULTS AND DISCUSSION

Figure 1 illustrates that the decomposition of the hydroformylated copolymer occurs in a single step. Figure 2 shows the thermograms, as determined by TGA, of bare silica (curve 1), silica treated with the unmodified diblock copolymer (curve 2), and silica treated with the hydroformylated copolymer (curves 3 and 4). On comparing these thermograms, we can conclude that any weight loss during the reaction interval 200–800°C is due to the thermal decomposition of the copolymer and can be used to determine the amount of copolymer adsorbed on the surface of the silica. From this data and the known initial concentration of added copolymer, the equilibrium concentration of free copolymer can be determined. In this respect, we suggest that TGA is a useful
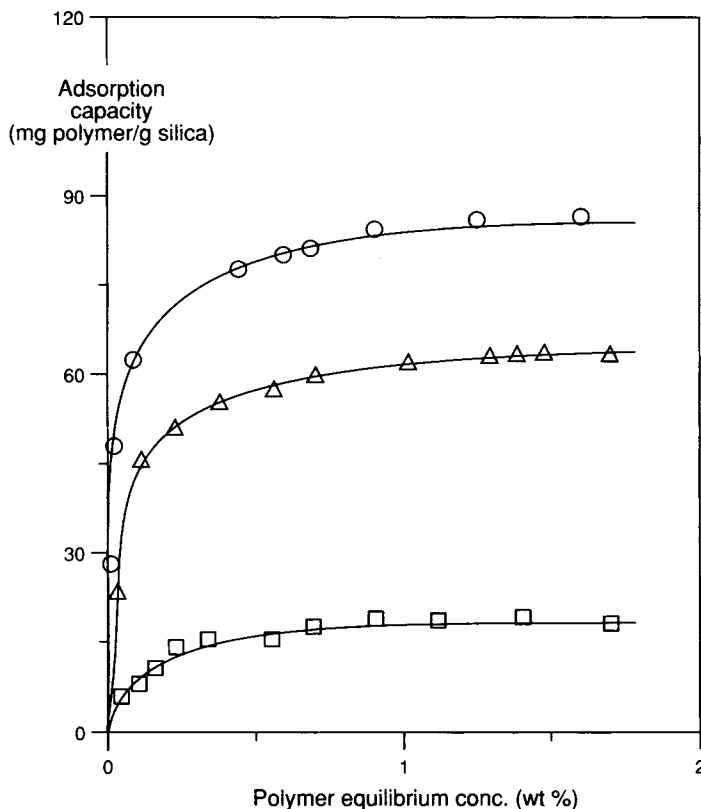
Fig. 4.   Adsorption of hydroformylated copolymer from toluene on silica. ○ HiSil T-600, △ HiSil 233, □ Silene 732-D. Degree of hydroformylation = 15%.

tool to determine adsorption of this copolymer onto silica. From curve 2, we determined that no significant amount of the unmodified copolymer relative to the functionalized copolymer was adsorbed onto the silica particles.

The adsorption kinetics of the hydroformylated copolymer on HiSil T-600 silica are shown in Fig. 3. In this case, as well as for Silene 732-D and HiSil 233 silica, equilibrium is essentially reached well within the equilibrium time of 0.5 h used in this study. This short equilibration time appears to be in agreement with adsorption studies on similar systems reported in the literature.[4,5,11,12]

The adsorption isotherms of 15 and 25% hydroformylated FINAPRENE 410 from toluene solutions on Silene 732-D, HiSil 233 and HiSil T-600 silica are shown in Figs. 4 and 5, respectively. The isotherms all show an initial steep rise in adsorption followed by a plateau where adsorption is almost constant. The free energies of adsorption, ΔG°_{ads}, calculated from linearized Langmuir isotherms, are given in Table II. Error estimates of the ΔG°_{ads} values are also given in order to prevent unrealistically detailed discussions of any small differences in these values. Thus we conclude that the free energies of adsorption appear to be independent of the degree of functionalization of the copolymer. Furthermore, the free energies of adsorption of the hydroformylated copolymer onto Silene 732-D and HiSil 233 silica are essentially similar, while ΔG°_{ads} in the case of HiSil T-600 silica is somewhat lower. These values correspond well
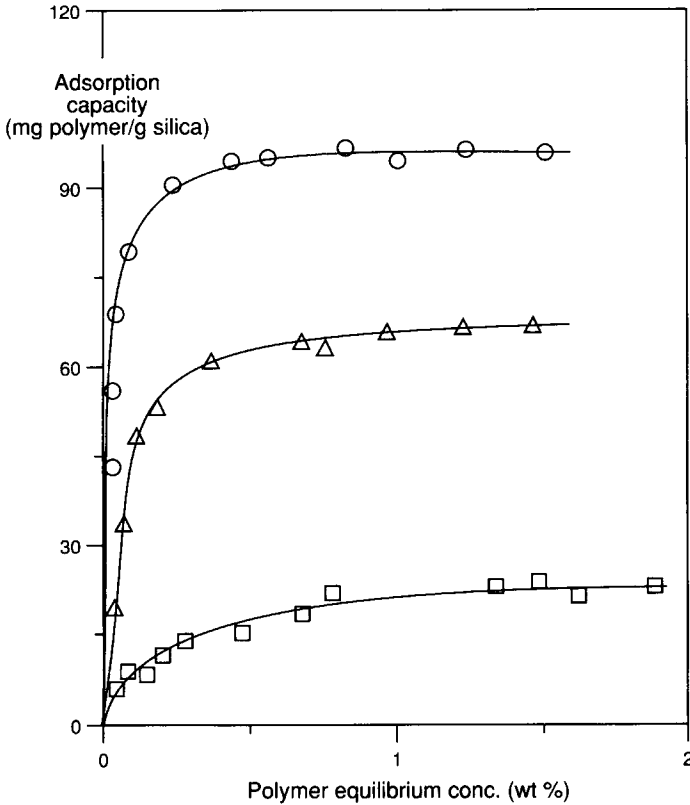
Fig. 5. Adsorption of hydroformylated copolymer from toluene on silica. ○ HiSil T-600, △ HiSil 233, □ Silene 732-D. Degree of hydroformylation = 25%.

with those estimated for the adsorption of other charged block copolymers onto silica.[4,7,13]

The plateau region, in all cases, is reached at an equilibrium solution concentration within 0.5 wt %, indicating that the isotherms are of the high-affinity type.[14] The possibility of multilayer adsorption, in the concentration range studied, is certainly not apparent from the relatively smooth Langmuir ad-

TABLE II
Surface Coverage and Free Energies of Adsorption on Silica

| | Degree of hydroformylation | | | |
| | 15% | | 25% | |
Silica	$-\Delta G^\circ_{ads}$ (kJ/mol)	Surface coverage (mg/m^2)	$-\Delta G^\circ_{ads}$ (kJ/mol)	Surface coverage (mg/m^2)
Silene 732-D	6.0 ± 0.7	0.5	6.8 ± 0.6	0.8
HiSil 233	7.1 ± 0.5	0.4	7.4 ± 0.4	0.5
HiSil T-600	8.9 ± 0.3	0.6	9.8 ± 0.3	0.6

sorption isotherms obtained in each case. The isotherms indicate that, for a fixed degree of copolymer modification, the plateau adsorption increases with silica surface area; for example, for 25% hydroformylation, the plateau adsorption is about 23 mg/g silica for Silene 732-D, 65 mg/g silica for HiSil 233, and 94 mg/g silica for HiSil T-600 silica. However, the plateau adsorption does not seem to depend significantly on the degree of copolymer functionalization. If we assume that the silica particles present effectively flat surfaces for copolymer adsorption, then the specific surface coverage in the plateau region can be estimated. Table II lists the calculated values using the BET surface area of each silica. The estimated surface coverage is in the range 0.4–0.8 mg/m^2. These values appear to be in good agreement with those obtained by Forsman et al.[5] and Thies[15] for the adsorption of poly(methylmethacrylate) from toluene on silica; similar results for the adsorption of polyvinyl chloride from monochlorobenzene on calcium carbonate were reported by Felter and Ray.[16]

CONCLUSION

We have studied the adsorption of a hydroformylated SB diblock copolymer on silica particles using thermogravimetric analysis. We have shown that TGA is a useful technique to determine the amount of adsorbed copolymer. The plateau adsorption increases with silica surface area and the level of copolymer–surface interaction is associated with a surface coverage in the range 0.4–0.8 mg/m^2.

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