Missouri University of Science and Technology

Scholars' Mine

Chemistry Faculty Research & Creative Works

Chemistry

01 Jan 2005

Estimation of Bound Carbonyls in PMMA-r-PS Copolymers Adsorbed on Silica

Pavan K. Challa

Bing Zhang

Frank D. Blum
Missouri University of Science and Technology

Recommended Citation

ESTIMATION OF BOUND CARBONYLS IN PMMA-r-PS COPOLYMERS ADSORBED ON SILICA

Pavan K. Challa[**], Bing Zhang[*] and Frank D. Blum[**]

[**]Department of Chemistry and Materials Research Center,
University of Missouri-Rolla,
Rolla, MO 65409-0010.

[*]Current address: Global Research-Shanghai GE China Technology

Center, 1800, Cai Lun Road, Shanghai-201203, P.R.China.

Introduction

The adsorption of random copolymers on solid surfaces is essential for developing good properties in composite materials. A good control and understanding of interfaces allows tuning of the properties of the individual components. Interfacial polymers are important in many industrial applications such as photoresists, protective coatings, metal insulator and semi-conductor insulator junctions, metal-filled polymer composites and polymer-lined metal containers for protective food packaging. The effect of the drying process,[1] configuration and tacticity,[2] molecular mass, density of surface hydroxyls,[3] and adsorbed amounts[4] have already been studied for interfacial polymers.

The thermal characterization for polystyrene,[5] PMMA[11] and PMMA-r-PS[6] copolymers adsorbed on silica have been studied recently by our research group. One of the important considerations for adsorbed copolymer composites was the composition of the copolymer and the individual surface affinities of monomer units on the substrate. The dependence of chain length, blockiness and self-association of the chain was also a consideration for these composites.[7]

Bound carbonyls are the ones which hydrogen bond directly with surface hydroxyls that, in our case, are the hydroxyls on silica. Transmission FTIR is one of the simplest techniques used to estimate the number of bound carbonyls. It was shown that the bound fractions decreased with increased adsorbed amounts while molecular weights[8] indicated a flattened configuration for lower adsorbed amounts and shorter chains. However, the dependence of bound fractions on molecular mass[9] was dramatically less.

Experimental

PMMA-r-PS copolymers with different compositions were prepared and have been previously reported.[6] A brief outline is given here. Solution polymerization was done to synthesize the copolymers in toluene at 60 °C with 33% monomer concentration. The compositions of the copolymers were controlled by following the kinetics and adding appropriate amounts of the more quickly consumed monomer. The polymers were precipitated from the reaction mixture by adding methanol, purified by reprecipitation from toluene several times and drying overnight in a vacuum oven at 100 °C. Molecular masses were determined by light scattering. The details of the bulk copolymer samples are given Table 1:

Table 1. Composition of copolymers.

Sample name	Composition, (%MMA)	M_w	Polydispersity
PS-MA-11	11.6	38.6k	2.04
PS-MA-14	14.9	44.3k	2.17
PS-MA-25	25	40k	1.14
PS-MA-30	30.6	36k	2.01
PS-MA-50	50.4	44.9k	2.06

Toluene was used as the solvent in making copolymer solutions of different concentrations. A 10 ml aliquot of each polymer solution was transferred into centrifuge tubes containing ca. 0.3 g of fumed silica (CAB-O-SIL, M-P5, untreated silica with surface area 200 m^2/g from Cabot. Corp, Tuscola, IL). The mixtures were shaken for 48 h at room temperature, 24 °C. The tubes were centrifuged (2800 rpm for 1 h) after adsorption and supernatant liquid was discarded. The residues were washed three times with pure toluene (ca. 10 ml, each wash). A sample was taken from the residue and cast directly onto the KBr windows and dried for 3 hours at 80 °C. The adsorbed amount was estimated from thermogravimetric analysis results (TA Instruments. Hi-Res-TGA 2950 Thermogravimetric analyzer). The equilibrium adsorbed amount is shown in Figure 1 and Table 2.

Table 2. Equilibrium Adsorbed Amount from the Langmuir Adsorption Isotherm.

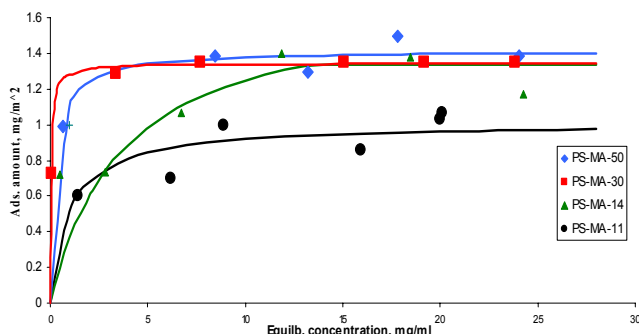| Sample name	Adsorbed Amount(mg/m^2)
PS-MA-11	0.97
PS-MA-14	1.33
PS-MA-30	1.34
PS-MA-50	1.40

Figure 1. Partial adsorption isotherm of PMMA-r-PS copolymers adsorbed on silica. The curves are drawn to a Langmuir isotherm.

FTIR spectra (Nicolet Nexus 470 FTIR E.S.P[TM]) were recorded for the samples after drying them on KBr windows at a resolution of 4 cm^{-1}. 1024 scans were taken for each sample. Curve fitting was done for the spectra using the GRAMS/AI software (Thermogalactic, Salem, NH). The free carbonyl peak was fitted with a single Gaussian line-shape and a hydrogen-bonded carbonyl peak with a Gaussian-Lorentzian mixture.

Results and Discussion

The equilibrium adsorbed amounts that were calculated from the adsorption isotherms are shown in Table 2. These amounts were found to increase in accordance with the percentage of MMA units in the adsorbed copolymers.

A frequency shift in the carbonyl stretch, observed for the hydrogen bonded carbonyl, was due to the electron donation from the surface hydroxyls to the antibonding orbitals of the carbonyl, weakening the C=O bond. The adsorbed copolymer spectra were curve fitted with one free carbonyl peak (A_f) centered at 1730 cm^{-1} and another one with a hydrogen bonded peak (A_b) centered at 1710 cm^{-1}, as shown in the Figure 2. Some difficulty was experienced in fitting the shoulder of the hydrogen bonded carbonyl for the lower adsorbed amounts and for copolymers with low percentage of MMA units. This may be caused by the interaction of two hydroxyls with one carbonyl. We did not quantify these resonances separately.
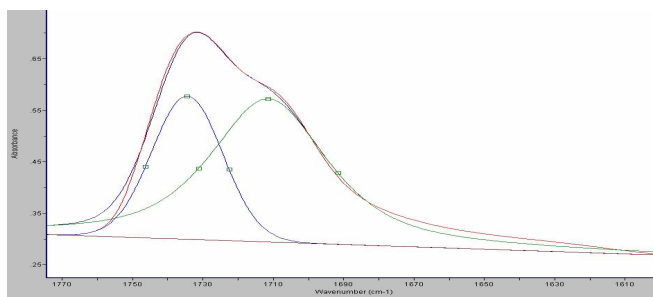

Figure.2. Curve fitting for adsorbed copolymer (PS-MA-30, 1.1mg/m^2) showing the free carbonyl centered at 1730 cm^{-1} and hydrogen bonded carbonyl at 1710 cm^{-1}.

The model used to interpret the IR spectra is based on distinguishing between polymers which are tightly bound and those which are more bulk-like.[10] It is assumed that beyond a certain minimum adsorbed amount of tightly bound polymer, M_b, any additional polymer contains only free carbonyls. The bound fraction, p, based on mass, can be given as:

$$p = M_b/(M_f + M_b) = M_b/M_t. \qquad [1]$$

where M_f and M_t are the free and total adsorbed amounts, respectively. The number of carbonyls is proportional to the integrated absorption intensity divided by the absorption coefficient (A_b/α_b). Based on the ratio of bound and free carbonyl intensities from FTIR spectra, the bound fraction can also be written as

$$p = (A_b/\alpha_b)/(A_b/\alpha_b + A_f/\alpha_f) = A_b/(A_f X + A_b) \qquad [2]$$

where $X = (\alpha_b/\alpha_f)$. Rearranging equations [1] and [2],

$$M_t = M_b + (A_f/A_b)X M_b. \qquad [3]$$

Equation [3] suggests the linearity of M_t with the ratio of the measured intensities, A_f/A_b. The plot (Figure 3) of the adsorbed amount and the ratio of free and bound carbonyl intensities yielded a fairly straight line with an intercept value of 0.19. Based on these calculations, a ratio of molar absorptivities of bound to free carbonyls is found to be 10.14. It is possible that such a high value is due to the absence of solvent and interaction with the dry silica surface. The bound fractions of carbonyl groups in the PMMA-r-PS copolymers adsorbed on silica are calculated by equation [2] using the $X = 10.14$ and $M_b = 0.19$.
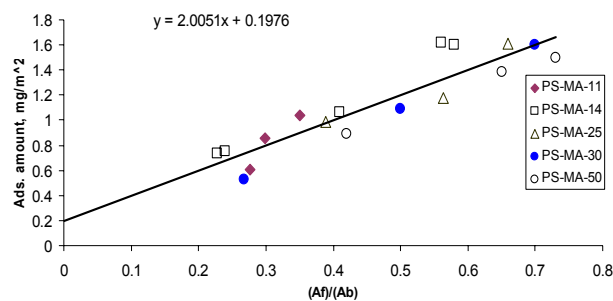

Figure 3. The total adsorbed amount of copolymer, M_t as a function of (A_f/A_b) carbonyl peak intensities.
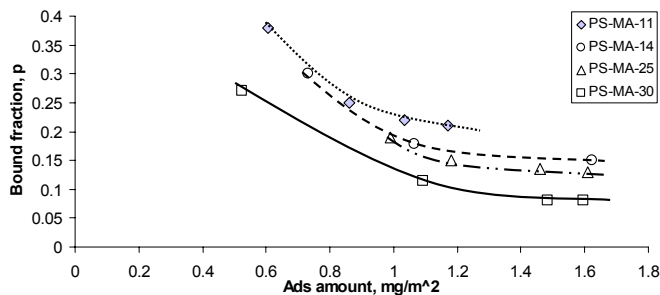

Figure 4. Bound fraction, p, of MMA carbonyls on silica for PMMA-r-PS as a function of adsorbed amount and copolymer composition.

We observe from the plot that for the same adsorbed amounts, as the percentage of MMA content decreases, the fraction of bound fraction of carbonyls increases. As the MMA content decreases, fewer carbonyls are available for hydrogen bonding. The limited number of carbonyl groups available seems to find its way (on a fractional basis) to hydrogen bond to the surface silanols. Also, the remaining surface silanols will have more affinity towards the carbonyls, accounting in part for intensities of the two hydroxyl single carbonyl complex at 1690 cm^{-1}. This is also the reason for the lower adsorbed amounts having greater bound fractions.

Conclusions

The bound fractions of carbonyls in copolymers adsorbed on silica were calculated based on the ratio of intensity of free carbonyl to the bound carbonyl stretch and the adsorbed amount. The bound fractions increased with a decrease in the MMA units, due to the decrease in the density of the total

number of carbonyls, which resulted in a strong affinity of the silanol group on the silica substrate.

References
(1) Zhang, B; Kulkeratiyut, S; Kulkeratiyut, S; Blum, F. D. *Polymer Preprints*. **2003**, *44(1)*, 1195.
(2) a) Brogly,M.; Grohens. Y; Labbe, C; Schultz, *Int. J Adhesion Adhesives* **1997**, *17,* 257. b) Brogly,M.; Grohens Y; Labbe, C; Schultz. J. *European Polymer J.* **1997**, *33,* 691. c) Grohens, Y; Auger, M; Prud'homme,R.E ; Schultz, J. *J. Polym Sci;B; Polym Phys.* **1999**, *37*, 2968.
(3) Frantz, P; Granick, S. *Macromolecules,* **1994**, *27*, 2553.
(4) Kobayashi, K; Araki, K; Imamura,Y. *Bull. Chem. Soc.Jpn,* **1989**, *62*, 3421.
(5) Porter C. E.; Blum, F D. *Macromolecules*, **2000**, *33*, 7016.
(6) Zhang, B.; Blum F. D. *Macromolecules,* **2003**, *36*; 8522.
(7) Fleer, G. J; Cohen Stuart, M. A; Scheutjens, J. M. H. M. *Polymers at Interfaces, Chapman and Hall,* London, U.K. **1993.**
(8) Sakai, H; Imamura, Y. *Bull.Chem. Soc. Japan,* **1987**, *60*, 1261.
(9) Soga, I; Granick, Steve. *Coll. Surf. A:Physico Chem. Eng Aspects;* **2000,** *170*, 113.
(10) Kulkeratiyut. S, Kulkeratiyut. S, Blum, F. D. Submitted
(11) a) M. T. Kabomo, F. D. Blum, *Polymer Preprints*, **2001,** *42(2)*, 67. b) B. Zhang and F.D. Blum, *Thermochimica Acta*, **2003,** *396*, 211.