

# Fourier Transform Infrared Photoacoustic Studies of the Adsorption Behavior of Poly(2-hydroxypropyl methacrylate) at Solid–Liquid Interface

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**ABSTRACT:** Adsorption of poly(2-hydroxypropyl methacrylate) on alumina from dimethylformamide was studied by ultraviolet (UV) and Fourier transform infrared (FT-IR) photoacoustic spectroscopy (FTIR PA) techniques. Adsorbent amount and concentration effects were investigated. The adsorption results are in conformity with Langmuir's isotherm. The differences observed in Langmuir parameters were explained by polymer–polymer, polymer–solvent, polymer–adsorbent, and solvent–adsorbent interactions. The fraction of carbonyl groups attached to the surface of alumina was calculated with a curve-fitting computer program. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2750–2756, 2002

**Key words:** adsorption; poly(2-hydroxypropyl methacrylate); alumina; FTIR photoacoustic spectroscopy

## INTRODUCTION

The adsorption of polymers at solid–liquid interfaces has been studied extensively.<sup>1–3</sup> In the studies concerned with polymer adsorption onto solid surfaces, conclusions about polymer surface binding were first arrived at by Jenkel and Rumbach<sup>4</sup>; but they are not yet well understood because of the conformational changes and the complexity of the adsorption process itself. The adsorption behavior of polymers at the solution–solid interface is of considerable technological importance in various chromatographic applications,<sup>5</sup> material and food sciences,<sup>6</sup> medical science,<sup>7</sup> and also in some unique applications, such as stone conservation.<sup>8</sup> For chromatographic applications, Nguyen and Berek<sup>9</sup> have studied the separation of six-compo-

nent blends of chemically similar homopolymers, such as poly(methyl methacrylate), polystyrene, poly(lauryl methacrylate), and poly(ethyl methacrylate), using the full adsorption–desorption process. They carried out the separation of these homopolymer blends with successive and independent size-exclusion chromatography. In another study, for the purpose of water clarification, the adsorption of rhodamine-B-labeled cationic polyelectrolyte, as flocculants of negatively charged contaminants onto colloidal silica, were investigated.<sup>10</sup>

Although there are a number of scientific and industrial reasons that lead researchers in the fields of polymer and spectroscopy to devote their attention to a better understanding of adsorption of polymers from solution by inorganic substrates, our interest in this context is related to the use of such solutions for the preservation of stones and stone structures. Preservation of stone surfaces against environmental deteriorating agents gen-

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erally consists of the application of a protective polymer solution. Alkyl methacrylates comprise the group of polymers most widely used for this purpose. In previous studies, we examined the adsorption of poly(*n*-butyl methacrylate) on alumina from solutions for the purpose of stone conservation.<sup>11,12</sup>

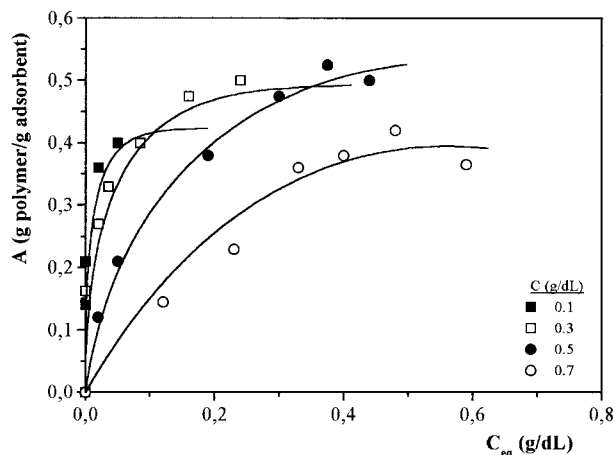
The adsorption behavior of polymers from solutions can be explained with five pairwise energetic interactions: polymer–polymer, polymer–adsorbent, polymer–solvent, solvent–solvent, and solvent–adsorbent. In this study about the conservation of ancient stones, the adsorption of poly(2-hydroxypropyl methacrylate) (PHPMA) from dimethylformamide (DMF) on an alumina surface at 25°C was studied. Adsorption amount and concentration effects on the adsorption were investigated. Adsorption results were applied to various equations (Langmuir, Brunauer–Emmett–Teller [BET], etc.) and observed to be in conformity with Langmuir’s isotherm. The structure of the polymer adsorbed on alumina was quantitatively determined by a Fourier transform infrared (FTIR) photoacoustic (PA) technique.

## MATERIALS AND METHODS

PHPMA was synthesized by solution polymerization of 2-hydroxypropyl methacrylate with benzoyl peroxide as initiator in methanol at 65°C. Purified polymers were weighed into 100-mL volumetric flasks, made up to volume, and kept at room temperature for 1 day. Then, 100 mL of solutions were added on alumina powder (neutral  $\chi$ -alumina; 0.01–2 g) in a flask. The stoppered flasks were then placed in a thermostatically controlled water bath at  $25 \pm 1^\circ\text{C}$  and continuously agitated. Aliquots were taken at various time intervals, and the supernatant solution was separated from alumina particles by centrifugation. The equilibrium concentration,  $C_{\text{eq}}$ , in the supernatant solution was determined with a Philips PU 8715 ultraviolet–visible (UV–vis spectrophotometer).

The amount of adsorbed polymer ( $A$  in g polymer/g alumina) was calculated from the following equation:

$$A = \frac{V}{m} (C_0 - C_{\text{eq}}) \quad (1)$$



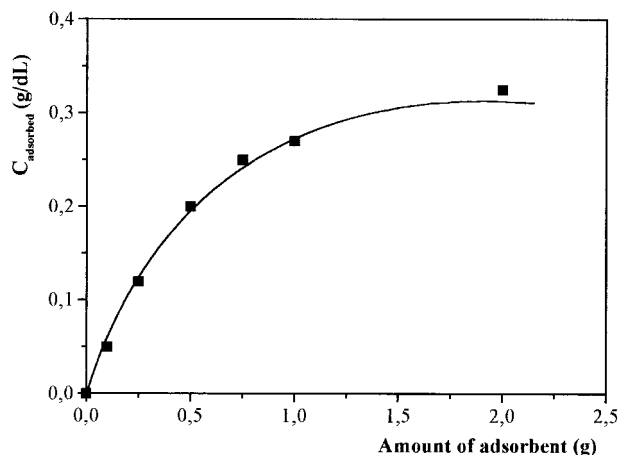
**Figure 1** Adsorption isotherms of PHPMA from various polymer concentrations.

where  $V$  is the volume (mL) of polymer solution used,  $m$  is the weight of the alumina (g), and  $C_0$  and  $C_{\text{eq}}$  are the initial and equilibrium concentrations of polymer solution (g/100 mL), respectively. The  $A$  values were then plotted against their corresponding  $C_{\text{eq}}$  values to construct the adsorption isotherms.

To explain polymer–alumina interactions, IR spectra of the adsorbed polymer on alumina samples were recorded with a Nicolet model 520 FTIR spectrometer and MTEC photoacoustic model 200 PA detector. The PA detector was purged with dried helium (99.99% purity). In most cases, the spectra were collected for 100 scans of  $8 \text{ cm}^{-1}$  resolution in the spectral range of 400 to  $4000 \text{ cm}^{-1}$ . A curve-fitting program was used for the band analysis.

## RESULTS AND DISCUSSION

Adsorption isotherms are shown in Figure 1. Initially, all isotherms rose steeply, with an increase in the equilibrium concentration,  $C_{\text{eq}}$ , in the supernatant solution that thereafter reached a plateau region. The adsorption isotherms are of the usual high-affinity type, which is characteristic for the adsorption of polymers. As shown in Figure 1, as the concentration of adsorbate increases, the initial rate of adsorption decreases and the plateau values are reached at higher equilibrium concentrations. At higher concentrations, polymer–adsorbent interactions slow down because of the increasing polymer–polymer interactions

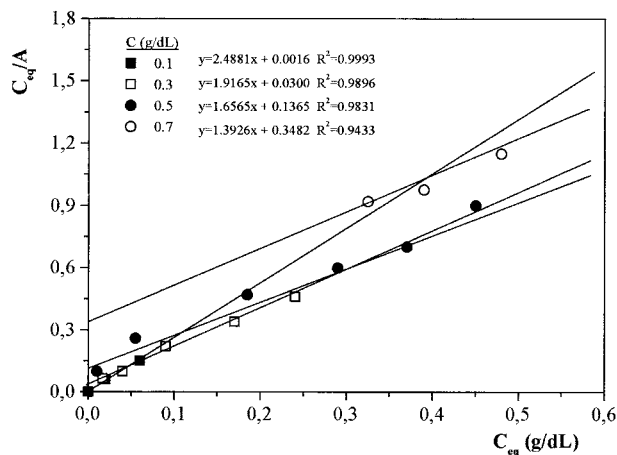


**Figure 2** The change of adsorption with adsorbent amount in the same concentration.

(polymer entanglement reaches a higher value at high concentrations).

The effect of adsorbent amount on the adsorption was also investigated (see Figure 2). Equilibrium adsorption values increase with an increasing adsorbent amount for the same bulk polymer concentrations. At higher adsorbent amount, adsorption reaches a constant value. The specific surface area of adsorbent is a very important factor in adsorption processes. The specific surface area of alumina used in this study was found  $111 \text{ m}^2/\text{g}$ , as determined by BET analysis.<sup>11,12</sup> For the same concentration, polymer coils interact more with a smaller amount of adsorbent than with a larger amount of adsorbent. Therefore, adsorption speeds up in small amounts. At higher amounts, polymer coils do not completely interact with alumina surface, and adsorption does not change beyond a certain extent.

In the adsorption studies, the solvent effect on adsorption is another important factor. In this work, adsorption was investigated in polar solvents, 2-propanol, methanol, and tetrahydrofuran (THF) in addition to from DMF. However, no adsorbance was observed in these solvents because these polar solvents have stronger affinity for the alumina surface. Therefore, solvent-adsorbent interactions blocked polymer-adsorbent interactions. On the other hand, adsorption was observed in only the DMF-PPMA solution. DMF is a good solvent for PHPMA, and the polarity of this solvent is smaller than other solvents already given. Analysis of the adsorption behavior showed that adsorption took place in monolayer because



**Figure 3** Langmuir plot of  $C_{eq}/A$  versus  $C_{eq}$ .

of the highly expanded coil structure of PHPMA in this solvent.

Various adsorption equations were applied to the adsorption isotherms. The results are in good conformity with Langmuir's isotherm. The  $C_{eq}/A$  values are plotted against  $C_{eq}$  (Figure 3) by using following equation:

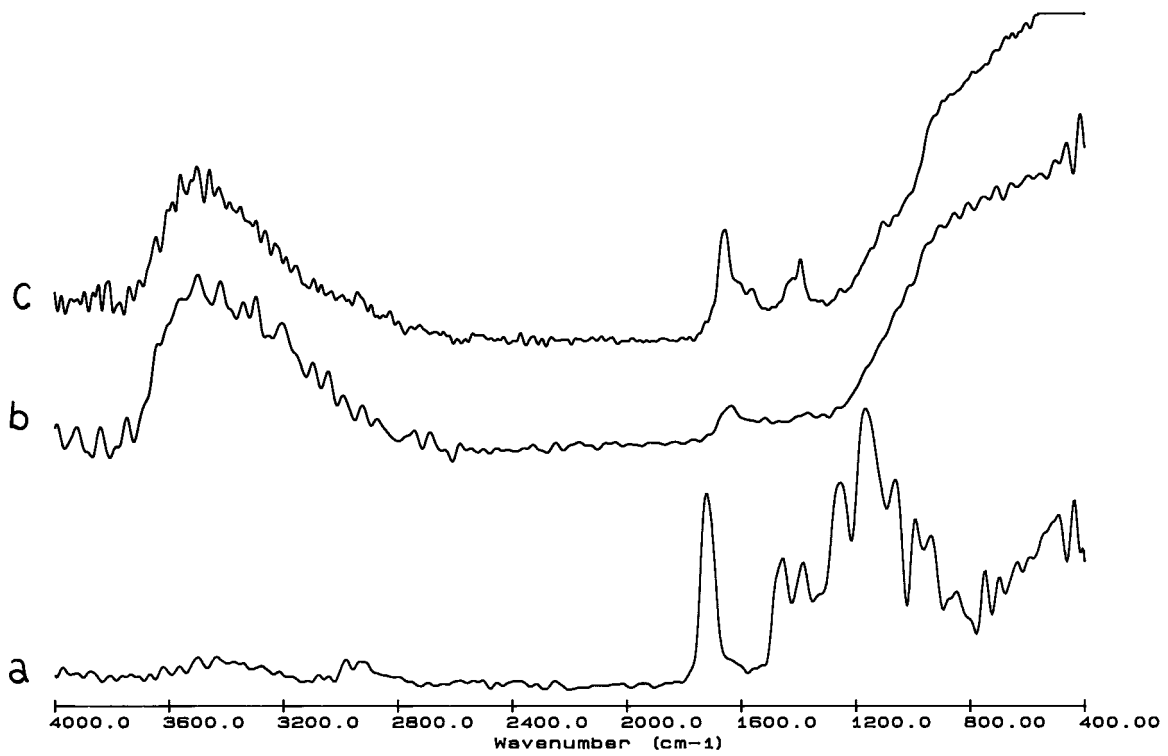
$$\frac{C_{eq}}{A} = \frac{1}{\lambda \cdot A_{mon}} + \frac{C_{eq}}{A_{mon}} \quad (2)$$

where  $C_{eq}$  is the equilibrium concentration in the supernatant solution (g/dL),  $A$  is the amount (g) of adsorbed polymer per amount (g) of alumina,  $A_{mon}$  is the amount (g) of adsorbed polymer per the amount (g) of alumina if monolayer adsorption occurs, and  $\lambda$  is the constant term involving energetic interactions between polymer and alumina.

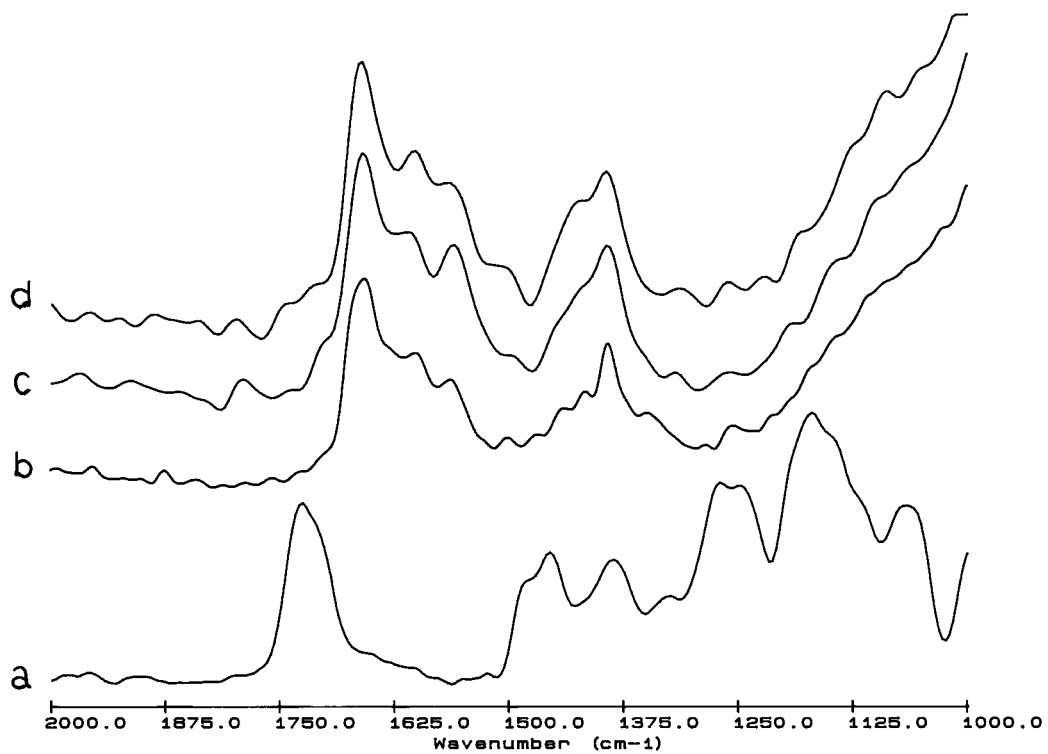
The values of  $A_{mon}$  and  $\lambda$  are calculated from the slope and intercept values obtained from Figure 3 and are listed in Table I. The conclusions presented in the discussion of the adsorption iso-

**Table I**  $A_{mon}$  and  $\lambda$  Values Obtained from Figure 3

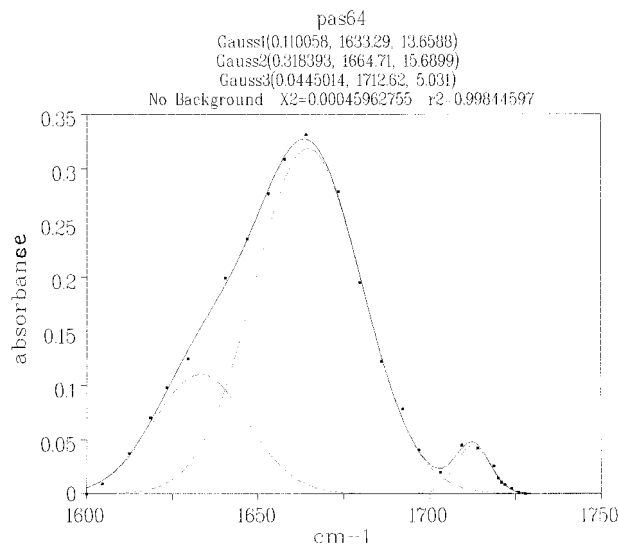
Concentration (g/dL)	$\lambda$	$A$ (g/g)	$A_{mon}$ (g/g)	$\theta = A/A_{mon}$
0.1	1655	0.40	0.40	1.00
0.3	64	0.50	0.52	0.96
0.5	12	0.50	0.60	0.83
0.7	4	0.39	0.72	0.54



**Figure 4** FTIR PA spectra of (a) PHPMA, (b) alumina, and (c) PHPMA adsorbed on alumina.



**Figure 5** FTIR PA spectra of (a) PHPMA and PHPMA adsorbed from DMF solution with concentrations of (b) 0.1 g/dL, (c) 0.3 g/dL, and (d) 0.5 g/dL.



**Figure 6** Deconvolution of the part of the spectrum from Figure 5(d) in the region 1760–1680  $\text{cm}^{-1}$ .

therms are also valid and substantiated by these  $A_{\text{mon}}$  and  $\lambda$  values: Adsorptivity increases with increasing polymer–adsorbent interactions. At low concentrations, polymer–surface binding is strongly and  $\lambda$  has a higher value. When the concentration is increased,  $\lambda$  decreases considerably. At the same time, the fraction of the surface sites occupied,  $\theta$  (calculated from  $A/A_{\text{mon}}$  ratio), decreases with increasing bulk equilibrium concentration, as seen in Table I. For the same amount of adsorbent considered, in spite of increasing bulk polymer concentration, equilibrium adsorption of polymer decreases. The reason for this decrease is that at higher concentrations, polymer–polymer interactions, or polymer aggregations, become dominant. Therefore, polymer–adsorbent bindings diminish and  $\theta$  values shift to small values. A similar result was observed in Kawaguchi et al.’s<sup>13</sup> work. They studied the adsorption of polystyrene onto silica and observed

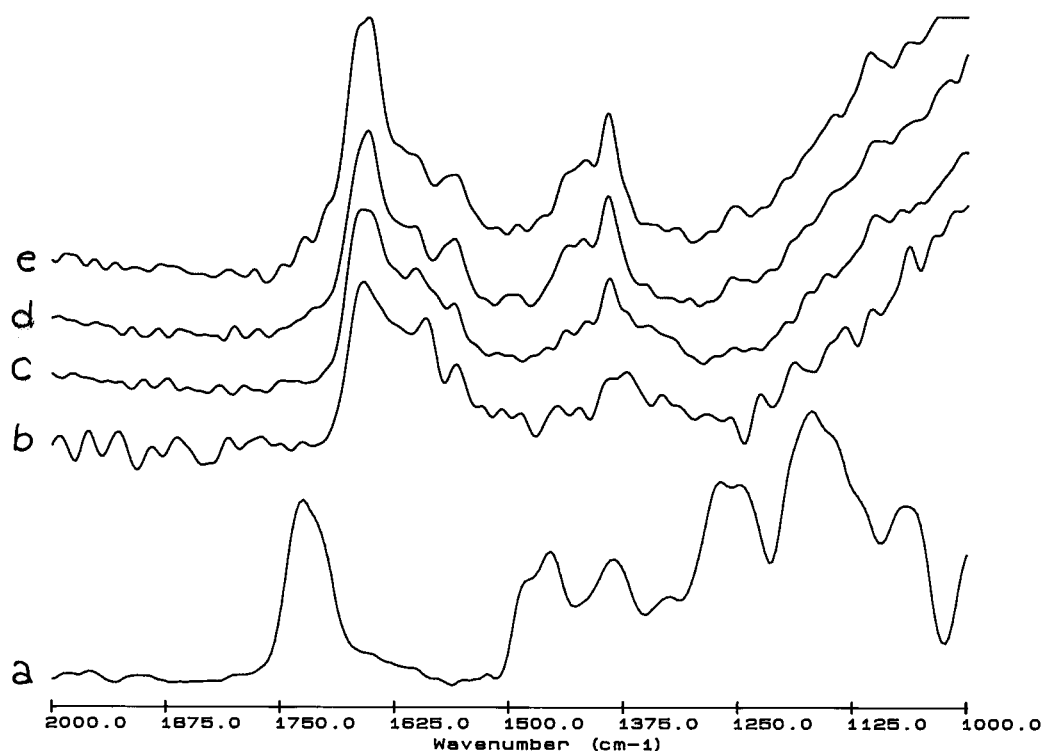
that  $\theta$  decreases with increasing bulk polymer concentration.

To explain polymer–surface interactions, FTIR PA spectra of PHPMA adsorbed on alumina were taken. In Figure 4, FTIR PA spectra of alumina, PHPMA, and polymer-adsorbed alumina are shown. The surface of alumina presumably consists to a large extent of hydroxyl groups bound by covalent links to alumina. These hydroxyl groups appearing in the 4000–2500  $\text{cm}^{-1}$  spectral range, dominate this part of the spectrum and prevent any evaluation. Therefore, spectra were investigated in the 2000–1000  $\text{cm}^{-1}$  range in more detail. FTIR PA spectra of PHPMA adsorbed from solutions with different concentrations are shown in Figure 5. The normal carbonyl peak of PHPMA observed at 1730  $\text{cm}^{-1}$  on H-bonding to the alumina surface shifts to lower frequency values ( $\sim 1650 \text{ cm}^{-1}$ ). Hydrogen bonding should cause both a changes in intensity and frequency of the normal carbonyl IR absorption. Similar results were obtained in the adsorption of poly(*n*-butyl methacrylate) onto alumina surface from various organic solvents.<sup>11,12</sup>

In accordance with the H-bonding mechanism of carbonyl groups to the surface of alumina presumed to be functioning here, it is observed that the free carbonyl peak of the polymer virtually disappears, and the intensity of the bound carbonyl peak is markedly increased with the extent of adsorption. The spectra given in Figure 5 were also analyzed quantitatively, and the peak areas due to bonded ( $\sim 1650 \text{ cm}^{-1}$ ) and nonbonded ( $1730 \text{ cm}^{-1}$ ) carbonyl groups of PHPMA were calculated with a curve-fitting computer program. A sample figure showing the deconvolution of the part of the spectrum in Figure 5(d) in the region 1760–1680  $\text{cm}^{-1}$  is given in Figure 6 and results are collected in Table II. The fraction of carbonyl groups attached to the surface of alumina increases with increasing polymer concentration

**Table II** Concentration Effect on PHPMA Adsorption on Alumina (0.025 g alumina, 25°C)

Concentration (g/dL)	Area of Free C=O (abs · $\text{cm}^{-1}$ )	Area of Bonded C=O (abs · $\text{cm}^{-1}$ )	% Bonded C=O
0.1	0.375	5.93	37
0.3	1.043	15.42	94
0.5	1.330	15.60	92



**Figure 7** FTIR PA spectra of (a) PHPMA and PHPMA adsorbed by (b) 0.05 g, (c) 0.10 g, (d) 1.00 g, and (e) 2.00 g of alumina from DMF of 0.1 g/dL concentration.

and reaches a constant value. In other words, at higher concentrations, the fraction of bonded carbonyl groups is not affected by polymer concentration.

At constant polymer concentration, to investigate the effect of adsorbent amount on adsorption, FTIR PA spectra recorded for four different alumina amounts, and the results are shown in Figure 7. Bound carbonyl peak intensity at  $\sim 1650 \text{ cm}^{-1}$  increase with increasing adsorbent amount. The same quantitative approaches were applied to the spectra in Figure 7, and the results are collected in Table III.

**Table III Adsorbent Amount Effect on PHPMA Adsorption (Concentration: 0.1 g/dL, 25°C)**

Adsorbent Amount (g)	Area of Free C=O (abs · cm <sup>-1</sup> )	Area of Bonded C=O (abs · cm <sup>-1</sup> )	% Bonded C=O
0.05	1.200	13.35	63
0.10	0.620	16.64	93
2.00	0.560	16.26	96

## CONCLUSIONS

PHPMA is synthesized by solution polymerization in methanol at 65°C. The amount of PHPMA adsorbed onto alumina increases with increasing alumina amount and PHPMA concentration and tends to plateau at steady values because of the saturation of the surface. Adsorption is investigated in various solvents such as DMF, 2-propanol, methanol, and THF. No adsorbance was observed in the latter three solvents because these polar solvents have stronger affinity for the alumina surface. This study shows that the adsorption of PHPMA on alumina surfaces, like other methacrylate-type polymers, can be achieved very efficiently for the purpose of conservation of ancient stones.

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