

# Fourier Transform Infrared–Photoacoustic Spectroscopy of Poly (*N*-butyl methacrylate) Adsorbed from Solution on Alumina

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**ABSTRACT:** Fourier transform infrared–photoacoustic spectroscopy (FTIR–PA) has been used to investigate the adsorption of poly(*n*-butyl methacrylate) (PnBMA) from solution on alumina. Qualitative and quantitative analysis of the FTIR–PA spectra of PnBMA adsorbed from cyclohexane, benzene, and carbon tetrachloride on alumina were performed. The efficiency of adsorption was found to increase in the order of  $C_6H_{12} > CCl_4 > C_6H_6$ . Methanol and tetrahydrofuran, on the other hand, showed negative adsorption. The effects of temperature and the amount of adsorbent were also investigated and it was observed that the adsorption of PnBMA has a negative temperature coefficient. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1669–1674, 1998

**Key words:** photoacoustic spectroscopy; adsorption; poly(*n*-butyl methacrylate)

## INTRODUCTION

Infrared (IR) spectroscopy has been one of the most powerful spectroscopic techniques in the analysis of surfaces and surface-related processes. One of the most important and challenging processes in surface science is adsorption. In this context, the adsorption of polymers from their solutions by inorganic and/or organic substrates is of both theoretical and industrial importance. The problems inherent with the sample preparation techniques (pellet spectroscopy) in the classical IR studies were among the major limitations of this powerful tool when working with nontransparent, opaque samples, which are typical of polymer-inorganic systems. Since the discovery of the photoacoustic (PA) effect by Rosencwaig,<sup>1</sup> this drawback has been eliminated and it became possible to study virtually any sam-

ple and even perform surface depth profiling. Especially during the last decade, Fourier transform IR (FTIR)–PA technique has been widely used to study not only qualitatively but also quantitatively the adsorption of polymers by inorganic substrates.<sup>2,3</sup> A recently published review article gives detailed and up-to-date information on the principles and application of PAs to polymers.<sup>4</sup> A comprehensive analysis of the same subject can also be found in a recently published book.<sup>5</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 generally consists of the application of a protective polymer solution. Alkyl methacrylates comprise the group of polymers most widely used for this purpose. The polymer and substrate are selected for better understanding of the adsorption of

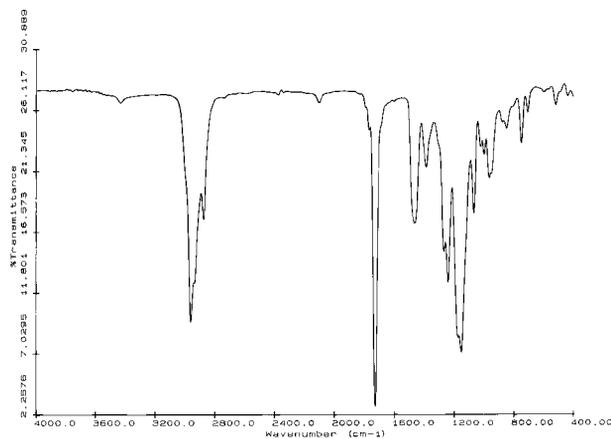
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**Figure 1** FTIR spectrum of PnBMA.

poly(*n*-butyl methacrylate) (PnBMA) on alumina typically encountered in the composition of stone.

It is interesting to note that although there are several studies investigating the adsorption of PnBMA from polymer mixtures PnBMA + polystyrene<sup>6</sup> and PnBMA + rubber,<sup>7</sup> no detailed work on the adsorption of pure PnBMA on silica or alumina has been reported so far.

The aim of this work is, therefore, to examine the effects of solvent, concentration, and temperature on the adsorption of PnBMA from solution by alumina, which is the major constituent of stone. FTIR spectroscopy coupled with a photoacoustic detector has been used to analyze the structure of polymer-adsorbent composites.

## EXPERIMENTAL

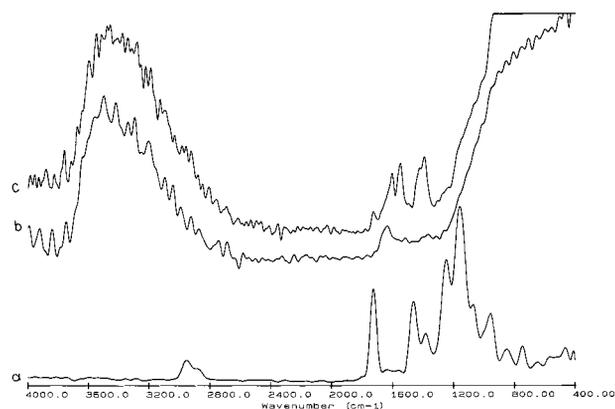
Infrared spectra were recorded with a Nicolet Model 520 FTIR Spectrometer and MTEC Photoacoustic Model 200 PA detector. The PA detector was purged with dried helium (99.99% purity). In most cases, the spectra were collected for 100 scans of 8 cm<sup>-1</sup> resolution in the spectral range of 400 to 4,000 cm<sup>-1</sup>.

The solvents used in the preparation of solutions, namely, cyclohexane, benzene, carbon tetrachloride, methanol, and tetrahydrofuran, were obtained from Merck and used as received. The adsorbent used in this work was neutral  $\chi$ -alumina which was obtained from BDH. The average particle diameter of the alumina used in this work was found to be in the interval of 71 to 125  $\mu$ m. The surface area of the same alumina was determined to be 111 m<sup>2</sup>/g by Brunauer-Emmett-Teller analysis.

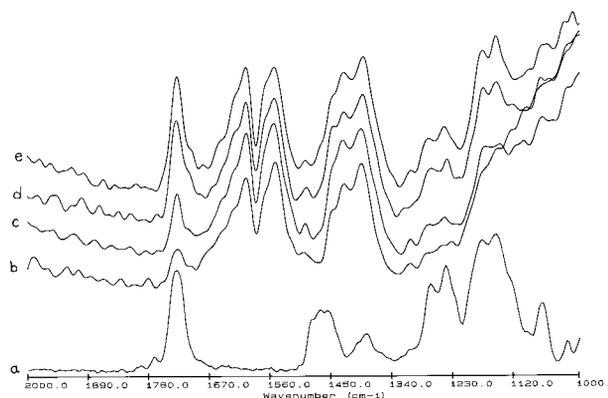
The adsorbate sample used in this study was PnBMA with a viscosity average molecular weight of 400,000. The polymers were weighed into 100-mL volumetric flasks, made up to volume, and left at room temperature overnight. These solutions, 100 mL each, were added into flasks containing previously weighed and dried alumina (0.1–2.0 g). The flasks were then agitated in a water bath thermostatically controlled at 25  $\pm$  1°C until the adsorption equilibrium was attained.<sup>8</sup> The supernatant solution was separated to sediment alumina particles by using a centrifuge. The supernate was decanted, and alumina was washed with solvent and dried at room temperature. For FTIR-PA analysis, the dried solid particles were placed into the aluminum sample cap of the PA cell. The quantitative analysis of the spectra was performed by resolving the peaks through applying a computer program and measuring the respective areas.

## RESULTS AND DISCUSSION

Typical transmission spectra of the PnBMA sample used in this work appear in Figure 1. The primary IR absorbances of this polymer are carbonyl stretch at 1730 cm<sup>-1</sup> and C—O—C stretching bands between 1100 and 1200 cm<sup>-1</sup>. Figure 2 shows the FTIR-PA spectra of PnBMA adsorbed onto the alumina surface. The upper spectrum in this figure is the composite of alumina/PnBMA; the middle spectrum, that of the alumina; and the bottom spectrum is that of the unadsorbed polymer. To analyze the spectra of polymers adsorbed on alumina, it is necessary to compare the spectra of unadsorbed polymers to those after adsorption.



**Figure 2** FTIR/PA spectra of (a) PnBMA; (b) alumina; (c) PnBMA adsorbed on alumina.



**Figure 3** FTIR/PA spectra of (a) PnBMA and PnBMA adsorbed from cyclohexane,  $C_6H_{12}$ , solution with concentrations; (b) 0.1 g/dL; (c) 0.5 g/dL; (d) 0.6 g/dL; (e) 1.0 g/dL.

The adsorption of polymers from their solutions was influenced by various factors, such as solvent, concentration, temperature, etc. All of these factors have been considered in this work and relevant details are presented in the following discussion.

#### Effect of Polymer Concentration

Figure 3 shows the helium-coupled FTIR-PA spectra of alumina treated with cyclohexane solutions of PnBMA in various concentrations. The bottom spectrum is for unadsorbed PnBMA; the upper spectra are those of adsorbed PnBMA. To enhance the spectral information of polymers in their adsorbed states, we subtracted the alumina spectrum from those of the alumina + polymer composite spectra. The traces given in the upper part of this figure and those shown in the following figures are therefore spectra of polymers in their adsorbed states.

The spectra of free and adsorbed polymers are given in the  $1000\text{--}2000\text{ cm}^{-1}$  range because this is the spectral region where most of the interactions between the adsorbate and adsorbent have been observed. The spectra given in Figure 3(b–e) correspond to PnBMA adsorbed on alumina from cyclohexane,  $C_6H_{12}$ , solutions with 0.1, 0.5, 0.6, and 1.0 g/dL concentrations, respectively. In Figure 3(b), a small peak is seen at  $1730\text{ cm}^{-1}$  showing the existence of some free carbonyl groups which are not involved in adsorptive interaction with the alumina surface. The adsorption of a poly(alkyl methacrylate) will take place primarily through the attachment of the carbonyl oxygen

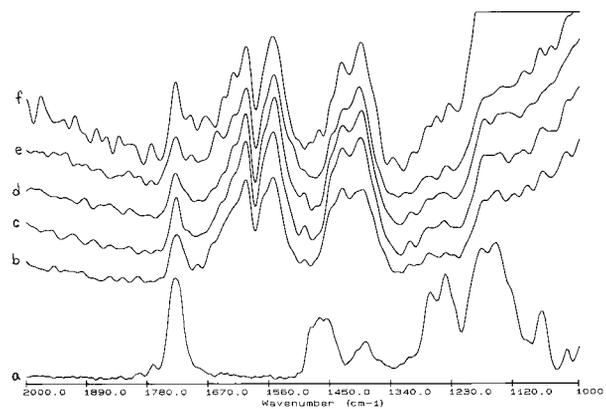
**Table I** Effect of Polymer Concentration on Adsorption of PnBMA on Alumina

Concentration (g/dL)	Area of Free C=O (abs.cm <sup>-1</sup> )	Area of Bonded C=O (abs.cm <sup>-1</sup> )	Bonded C=O (%)
0.1	19.44	0.99	4.82
0.5	30.22	2.91	8.46
0.6	42.25	11.09	20.79
1.0	57.73	4.96	7.71

Solvent:  $C_6H_{12}$ ; temperature:  $25^\circ\text{C}$ ; substrate: 0.25 g alumina.

atoms of the ester with the OH groups available at the solid surface and/or metal ion of the oxide.

The interaction of carbonyl oxygens with the surface will cause a shift in their characteristic stretching frequencies to lower wavelengths. These can arise either from hydrogen bonding between surface hydroxyls and oxygen of C=O, or from interaction between the metal of the oxide and C=O groups, or from both. This typical behavior has been observed in the pioneering work of Fontana and Thomas<sup>9</sup> and in the other studies conducted with  $SiO_2$ <sup>2</sup> and  $Al_2O_3$ .<sup>3–10</sup> In Figure 3(b), two new and relatively strong peaks are easily seen to appear at  $1550$  and  $1610\text{ cm}^{-1}$ . These are assigned to be due to symmetric and asymmetric stretching bands of the adsorbed carbonyl groups. A quite-similar effect has been observed in the cement formation between  $Al_2O_3$  and polyacrylic acid where the original carbonyl stretching band seen at  $1700\text{ cm}^{-1}$  was recorded



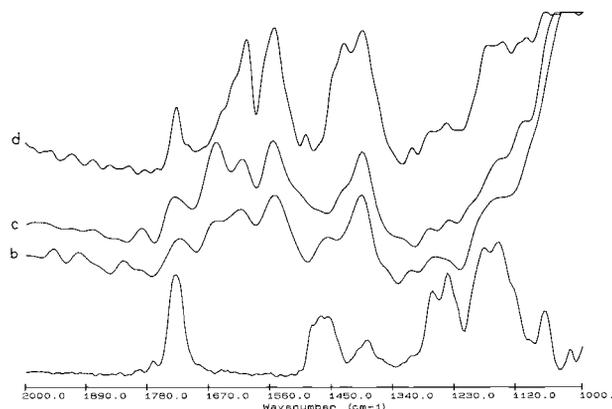
**Figure 4** FTIR/PA spectra of (a) PnBMA and PnBMA adsorbed by (b) 0.05 g, (c) 0.25 g, (d) 0.75 g, (e) 1.0 g, and (f) 2.0 g alumina from  $C_6H_{12}$  solution of 0.5 g/dL concentration.

**Table II** Effect of the Amount of Adsorbent on Adsorption

Adsorbent (g alumina)	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	25.76	1.28	3.54
0.25	30.22	2.91	8.46
0.75	23.58	1.89	6.43
1.00	24.46	3.23	10.96
2.00	17.70	4.18	19.10

Solvent: C<sub>6</sub>H<sub>12</sub>; temperature: 25°C; concentration: 0.5 g/dL.

to shift to even lower frequencies<sup>11</sup> of 1420 cm<sup>-1</sup>. Approximately spectral shifts of 300 cm<sup>-1</sup> have also been observed in the adsorption of poly(dimethyl siloxanes) from solution on silica.<sup>12</sup> With increasing polymer concentration, the intensities of these two peaks first increase then remain unchanged, indicating the full coverage of available sites of the Al<sub>2</sub>O<sub>3</sub> surface. At higher polymer concentrations the intensity of the peak at 1730 cm<sup>-1</sup> also increases, showing the increase in the amount of nonbonded carbonyls. This increase can be attributed either to increasing amounts of free loops of the adsorbed polymer chain or to settlement or entanglement of secondary layers of polymer chains onto the previously adsorbed layer. Detailed investigation of Figure 3 also shows that the C—O—C etheric bands appearing at 1150, 1195, 1240, and 1270 cm<sup>-1</sup> are unaffected by the adsorption process. These bands are observed to appear at these wavenumbers both for nonbonded [Fig. 3(a)] and bonded [Fig. 3(b–e)] polymers, indicating that etheric oxygens are not involved in the adsorption process. As seen from Figure 3, however, there is one more vibration frequency which was affected by the adsorption process. The peak seen at 1460 cm<sup>-1</sup>, which is due to CH<sub>2</sub> deformation mode of the butyl side chain, is shifted to lower frequencies upon adsorption. Out-of-plane-type deformation motion of CH<sub>2</sub> groups in the butyl structure appears at 1390 to 1420 cm<sup>-1</sup> wavenumbers due to interaction of these groups with the metal ion of the adsorbent. The spectra given in Figure 3 were also analyzed quantitatively, and the peak areas due to bonded (1550 and 1610 cm<sup>-1</sup>) and nonbonded (1730 cm<sup>-1</sup>) carbonyl groups were measured and are given in Table I. The fraction of carbonyl groups attached to the surface of alumina does not seem

**Figure 5** FTIR/PA spectra of PnBMA adsorbed from C<sub>6</sub>H<sub>12</sub> solutions at (b) 35°C, (c) 30°C, and (d) 25°C.

to be too much affected by the polymer concentration. The decrease in bonding carbonyls for the concentrated solution (1.0%) is most probably due to the chains entangled with the adsorbed layers.

#### Effect of the Amount of Adsorbent

When the 0.5 g/dL solution of PnBMA in C<sub>6</sub>H<sub>12</sub> was treated with different amounts of adsorbent, the spectra of the adsorbed polymer did not show any significant changes qualitatively (Fig. 4). The ratio of the intensities of carbonyl bands of bonded polymer to nonbonded were analyzed quantitatively and the results are collected in Table II. The increase in bonded C=O with increasing alumina can be explained by an increase in the extended configuration of chains adsorbed on the adsorbent. In other words, the fraction of polymer segments as free loops decreases.

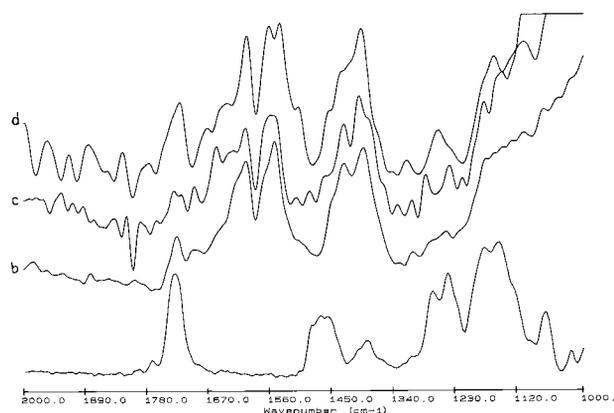
#### Effect of Temperature

The adsorption of a polymer may have a quite-different temperature dependency to be influ-

**Table III** Effect of Temperature on Adsorption

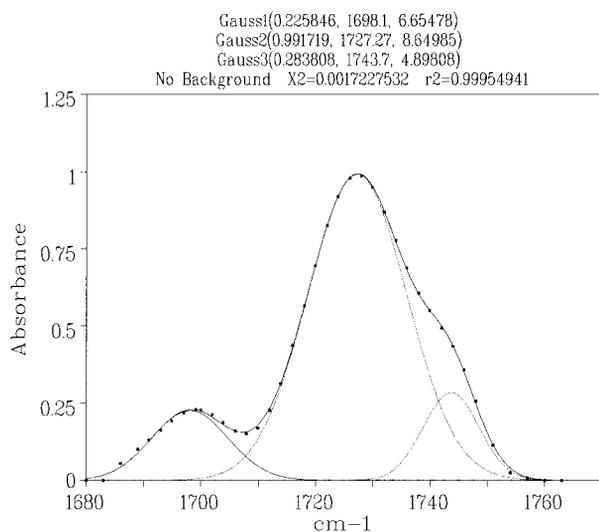
Temperature (°C)	Area of Free C=O (abs.cm <sup>-1</sup> )	Area of Bonded C=O (abs.cm <sup>-1</sup> )	Bonded C=O (%)
25	30.22	2.91	8.46
30	14.77	14.27	49.13
35	18.41	6.76	26.87

Solvent: C<sub>6</sub>H<sub>12</sub>; concentration: 0.5 g/dL; substrate: 0.75 g alumina.



**Figure 6** FTIR/PA spectra of PnBMA adsorbed by alumina from (b)  $C_6H_6$ , (c)  $CCl_4$ , and (d)  $C_6H_{12}$  solutions.

enced by the nature of solvent, adsorbent, or both. The limiting viscosity number of PnBMA, which is a direct measure of polymer coil size in respective solutions, has been found to increase with temperature in cyclohexane.<sup>8</sup> PnBMA, therefore, is a polymer exhibiting upper critical solution temperature in this solvent. As the temperature increases, the polymer coils will expand and every adsorbed polymer chain will occupy more volume at the surface of the adsorbent, causing a decrease in the amount of adsorbate. In the kinetic analysis of the adsorption of PnBMA from solution by alumina we have already determined this behavior gravimetrically.<sup>8</sup> In Figure 5, the upper curves (b–d) are the spectra of PnBMA adsorbed



**Figure 7** Deconvolution of the part of the spectrum from Figure 6 (b) in the region  $1760$  to  $1680\text{ cm}^{-1}$ .

**Table IV** Effect of the Nature of Solvent on Adsorption

Solvent	Area of Free C=O (abs.cm <sup>-1</sup> )	Area of Bonded C=O (abs.cm <sup>-1</sup> )	Bonded C=O (%)
$C_6H_{12}$	27.26	16.04	33.45
$CCl_4$	9.42	2.48	15.74
$C_6H_6$	21.81	3.65	12.69

Temperature:  $25^\circ\text{C}$ ; concentration:  $0.1\text{ g/dL}$ ; substrate:  $0.50\text{ g alumina}$ .

at  $35$ ,  $30$ , and  $25^\circ\text{C}$ , respectively. The intensity of carbonyl bands appearing at  $1550$  and  $1610\text{ cm}^{-1}$ , which correspond to the bonded segments of polymer, increase with decreasing temperature. The adsorption of PnBMA from  $C_6H_{12}$  has, therefore, an inverse temperature coefficient. The results of the quantitative analysis of the curves given in Figure 5 are collected in Table III. Bonding of PnBMA chains decreases with increasing temperature in conformity with the qualitative aspects mentioned above.

#### Effect of Solvent

When the effect of solvent on the adsorption of a polymer has been considered, the interaction between the adsorbent and solvent and the thermodynamic power of the solvent are the two most important factors to be evaluated, the former playing the decisive role. In our preliminary trials we have noticed that no adsorption takes place when PnBMA solutions are prepared from methanol and tetrahydrofuran. Strong adsorption of these polar solvents by the adsorbent reduces the effective sites of adsorbent, which markedly decreases the polymer adsorption. The effect of solvent has been investigated by considering three nonpolar solvents, namely, benzene, carbon tetrachloride, and cyclohexane. The equilibrium values of PnBMA adsorbed from equimolar solutions of these solvents by equal amounts of alumina were found to be  $0.2$ ,  $0.3$ , and  $0.4\text{ g/g}$  of the adsorbent.<sup>8</sup> The same trend was found when the FTIR-PA spectra of these polymer composites were recorded (Fig. 6). A sample figure showing the deconvolution of the part of the spectrum in Figure 6(b) in the region  $1760$ – $1680\text{ cm}^{-1}$  is given in Figure 7. The area of peaks corresponding to carbonyl bands of bonded polymer chains increases in the order of  $C_6H_{12} > CCl_4 > C_6H_6$ . The

same trend has been confirmed quantitatively, as shown in Table IV.

A typical mass balance made for the adsorption study of PnBMA in cyclohexane in the concentration of 0.1 g/dL and at 25°C with an adsorbent amount of 0.05 g was made and it was determined that the sum of the polymer in the supernatant solution and adsorbed on alumina is within the 95% range of polymer present in the stock solution.

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