Formation and Characterization of Anchored Polymer Coatings on Alumina

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Maleic acid adsorbed on alumina can copolymerize with 1-alkenes to form monolayers of polymer coatings that are tightly anchored on the alumina surface. The structure of the copolymer formed on the alumina surface was characterized by means of solid-state ^{13}C NMR and proton NMR of the extractable polymer fraction. The molecular weight of the extracted polymer was determined using gel permeation chromatography. The conditions for producing a high loading of polymer coating on alumina were optimized. The change of the surface area and pore size of alumina after the formation of the polymer coating was studied by the use of nitrogen adsorption. The morphology of the coated alumina particles was studied by the use of scanning electron microscopy. The stability of polymer-coated alumina was tested against solvent washing, and it was found that poly(maleic acid−1-octadecene) cross-linked with divinylbenzene was stable in many aqueous and nonaqueous solvent systems. Finally, the copolymerization of maleic acid adsorbed on alumina with allyl compounds was explored for possible introduction of other functional groups onto the alumina surface.

Introduction

Inorganic oxides such as alumina and silica have many important applications. In some of these applications, such as fillers for plastics and rubber and the use as packing material in reverse-phase HPLC, it is desirable to modify the inorganic oxide with an organic coating, especially a polymer, to make it more compatible with the organic phase. A common procedure to deposit a polymer coating on an inorganic oxide is to dissolve the polymer in a proper solvent and mix with alumina particles for a period of time, followed by evaporation of the solvent. If the polymer (or sometimes prepolymer) has reactive functionality, it can be cross-linked by using radiation or initiators.[1−7] For example, poly(maleic acid−butadiene), which contains a certain degree of unsaturation, can be first deposited on silica and then immobilized by in situ cross-linking.[8] This material has a high ion-exchange capacity and selectivity as well as excellent chemical stability toward organic modifiers[8] and can be used as a cation-exchange stationary phase for HPLC, but it is difficult to control the homogeneity of the thickness of the polymer layer.

The formation of rather uniform polymeric thin films on an inorganic oxide can be accomplished by admicellar polymerization from a surfactant template.[9−14] The surfactant bilayer functions as a two-dimensional reaction solvent and acts as a template for the polymerization,[13,14] but the polymer film formed is not directly anchored to the surface of the oxide and has limited stability.

It is well-known that carboxylic acids are strongly adsorbed on the surface of alumina.[15] If the acid contains a polymerizable group, it may be possible to carry out in situ polymerization of the adsorbed acid to form polymer films that are tightly anchored on the oxide surface. Acrylic acid, methacrylic acid, and maleic acid are some of the obvious candidates as starting materials. The adsorption of acrylic acid and maleic acid on alumina is dependent on pH and obeys the Langmuir isotherm; the kinetics and equilibrium of the process has been studied in detail.[16] The adsorbed acrylic acid and methacrylic acid can be made to polymerize with other acid molecules or different acrylate derivatives, but the degree of polymerization, and therefore the thickness of the polymer layer, is difficult to control. On the other hand, maleic acid has the potential to undergo 1:1 copolymerization with alkenyl compounds to result in monolayers of anchored polymer films. In fact, the copolymerization of maleic anhydride with vinyl ethers, 1-alkenes, dienes, and allylic com-

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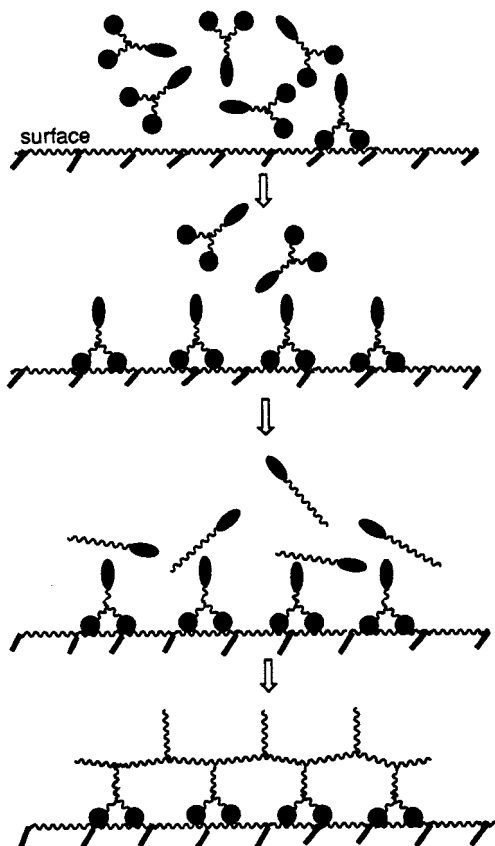
Figure 1. Schematic representation of the APCA process. The circles represent carboxylic groups and the ovals represent =CH₂ groups.

pounds in organic media to form alternating copolymers is a very common industrial process. In particular, a great deal of effort has been made to study the conditions of synthesis and purification for the copolymerization of maleic anhydride with a wide range of 1-alkenes ranging from C_6 to C_{30}.[17-19] The anhydride copolymers also can be hydrolyzed to yield the acid forms,[20] which can act as polyelectrolytes[21,22] and cation exchangers.[23-25] We have found that maleic acid adsorbed on alumina can be copolymerized similarly. Because of the strong interaction of maleic acid with the alumina, the polymer films are tightly anchored on the alumina surface and have better stability compared to conventional polymer coatings.

For the sake of simplicity, we will use the abbreviation APCA for anchored polymer coating on alumina to describe the process and the product. Figure 1 is a schematic representation of the APCA process. In the first step, a solution of maleic acid is mixed with alumina particles to allow the adsorption to reach equilibrium. After adsorption, a well-organized monolayer is formed on the surface. The adsorption of maleic acid on the alumina surface alters its polar nature to make it more hydrophobic. In the second step, the adsorbed maleic acid molecules are allowed to copolymerize with a 1-alkene or an allyl compound with the help of a free-radical initiator such as azobisisobutyronitrile (AIBN). A cross-linking agent such as 1,4-divinylbenzene can be used to enhance the stability of the polymer film. A systematic study on the factors governing the APCA process and a detailed characterization of the polymer coatings formed have been carried

out. The results provide an understanding of the nature of the coatings and lay a foundation to the potential applications of the APCA products.

Experimental Section

Materials. All chemicals are G.R. or A.R. grade and used as received. Alumina was obtained from Aldrich with specification listed as activated, acidic, Brockmann I, specific surface area 155 m²/g, particle size 150 mesh, pore diameter 5.8 nm. 1-Alkenes were gifts from Shell Chemical Co.

Preparation of Alumina with Adsorbed Maleic Acids. Maleic acid solution in water (60.0 mL, 0.1 M) was added to 5.0 g of alumina. The mixture was left in a water-bath shaker at room temperature for 4 days. The alumina particles were then filtered and air-dried. More details of the procedure are described elsewhere.[16]

Polymerization. Alumina particles with adsorbed maleic acid was mixed with a monomer under stirring in a three-neck round-bottom flask. After the system was purged with nitrogen for 3–4 min, AIBN was added, and polymerization was initiated by raising the temperature. The system was maintained at 80 °C for 3 h under nitrogen. Afterward, the mixture was filtered, and the alumina particles were washed with acetone to remove unreacted monomers. The polymer-coated alumina particles were dried in air. Five types of experiments were carried out for different purposes, and the conditions are given below.

(1) Effect of the amount of maleic acid absorbed on alumina on polymer loading. To prepare samples with various amount of adsorbed maleic acid, 4 g of alumina and 50 mL of five feed solutions with concentrations of 0.01, 0.02, 0.03, 0.06, and 0.1 M were used. No adjustment of the solution pHs was needed since the different initial concentrations were sufficient to produce various loading of maleic acid on alumina. The systems were kept in a water-bath shaker at room temperature for 4 days for the adsorption to attain equilibrium. Then, 1.50 g of alumina with adsorbed maleic acid was mixed with 5 mL of 1-octadecene. A fixed molar ratio of AIBN to maleic acid of 0.45 was employed for each system. Surface polymerization was carried out, and the particles were washed and dried.

(2) Effect of the amount of initiator on the polymerization of maleic acid on alumina with 1-octadecene. Alumina (1.00 g) with adsorbed maleic acid was mixed with 10 mL of 1-octadecene in a 50 mL three-neck round-bottom flask. The amount of added AIBN varied from 0.04 to 0.4 g with an increment of 0.02–0.03 g, so that 17 reactions were carried out.

(3) Effect of monomer chain length on polymer loading. The same batch of alumina (1.00 g) with adsorbed maleic acid was mixed with 0.045 g of AIBN and 7 mL of a series of 1-alkenes containing even numbers of carbon ranging from 6 to 18. The polymerization was carried out in the same way.

(4) Preparation of cross-linked poly(maleic acid–1-octadecene) on alumina with divinylbenzene (DVB). To a 50 mL three-neck round-bottom flask, 2.2 g of alumina with adsorbed maleic acid, 0.061 g of AIBN, and 10 mL of 1-octadecene were added. After the reaction proceeded for 1 h at 80 °C under stirring, 0.24 mL of DVB (2 vol % with respect to the total monomer) was added from an addition funnel placed in one of the necks of the flask, and the reaction was allowed to continue for two additional hours.

(5) Polymerization with allyl bromide and allylamine. For polymerization with allyl bromide, 1.4 g of alumina with adsorbed maleic acid, 0.017 g of AIBN, and 6 mL of allyl bromide were added to a 50 mL three-neck round-bottom flask. For polymerization with allylamine, two trials were made with and without a solvent. In the case of using hexane as solvent, the amounts of the components were 5.0 g of alumina with adsorbed maleic acid, 0.12 g of AIBN, 5 mL of allylamine, and 20 mL of hexane. For polymerization without solvent, the mixture contained 3.0 g of alumina with adsorbed maleic acid, 0.07 g of AIBN, and 25 mL of allylamine.

Weight Gain/Loss Determination. All samples were dried under vacuum at 60 °C for 72 h and then kept in a desiccator. Sample (0.4–0.6 g) was weighed out into a crucible and calcinated with a Bunsen burner for 20 min and then cooled to room temperature in a desiccator. After being kept in the desiccator for 25 min, the crucible with sample was quickly removed from the desiccator and weighed again. The data analysis was carried out in the following way. For a dry sample with a weight W and a weight difference DW after calcination, the weight gain or loss per gram of sample is $d = DW/W$. The symbol d_p is used to designate the weight loss for polymer-coated alumina after calcination, d_m for maleic acid adsorbed alumina, and d_a for pure alumina. Then, the net weight gain due to maleic acid adsorption on alumina is $(d_m)_n = d_m - d_a$, and the net weight gain due to the polymerization is $(d_p)_n = d_p - d_m$. To evaluate the validity of the calcination method, the results obtained from calcination with a Bunsen burner were compared with those from thermal gravimetric analysis (TGA).

Bromide Analysis. The content of bromide in the APCA product formed by the reaction of maleic acid adsorbed on alumina with allyl bromide was analyzed by the use of a chemical method. The product (1.10 g) was suspended in 15 mL of isopropyl alcohol, and 0.64 g of sodium was added piece by piece with stirring. The product was gently refluxed for 2 h. Water (10 mL) was added through an additional funnel, and the refluxing was continued for one more hour. The mixture was cooled and neutralized with nitric acid. Then, it was titrated with 0.01 N AgNO₃, using erosin Y as an indicator.

Stability Testing. The stability of the polymer coated on the alumina particles prepared in the APCA process toward various solvents was evaluated in the following way. The polymer-coated alumina (1.1 g) was washed with the solvent under stirring in a 100 mL round-bottom flask for 24 h both at room temperature and under reflux. Then the mixtures were centrifuged, and the solvents were decanted. The remaining solid particles were first dried in an oven at 70 °C for 24 h and then dried under vacuum at 60 °C for 72 h to remove moisture and adsorbed solvents. Finally, the samples were subjected to calcination for the determination of weight loss. Alumina with and without adsorbed maleic acid was treated in the same way to be used as blanks. The solvents tested were H₂O, 0.1 N HCl, 0.1 N NaOH, 1:1 H₂O/CH₃OH, CH₃OH, 1:1 H₂O/CH₃CN, and CH₃CN. The purpose of using these solvents was to evaluate the stability in aqueous media with a wide pH range and the tolerance toward the solvents commonly used in RP (reverse phase) HPLC, because one of the potential applications of the APCA particles could be as the reverse-phase packing material.

Surface Area Measurement. The experiments were carried out on accelerated surface area and porosimetry system ASAP 2010. Sample (0.5 ± 0.0001 g) was loaded into a sample holder which was then connected to the degas port. Degassing was accomplished at 60 °C until the vacuum pressure reached below 1 mmHg. Then the sample holder with the degassed sample was transferred to the analysis port. The nitrogen adsorption and desorption isotherms were performed at 77 K. The analysis and data processing were automated by computer control.

Gel Permeation Chromatography (GPC). The GPC equipment consists of a Scientific Systems Model 520C HPLC system connected with a Showdex RI-71 refractive index detector. The PL gel column (300 mm × 7.5 mm i.d.) was purchased from Polymer Laboratories. All measurements were carried out at room temperature. For preparing a sample, 18 g of alumina coated with poly(maleic acid–1-octadecene) was mixed with 25 mL of dichloromethane into af 100 mL one-neck round-bottom flask at room temperature under stirring for 24 h. Then the mixture was filtered, and the filtrate was kept. The filtrate was evaporated to remove the solvent to dryness using a rotary evaporator. The residue was dried under vacuum for 4 h and then redissolved in chloroform to be ready for GPC. The mobile phase was chloroform at a flow rate of 0.5 mL/min, and 20 µL of sample

Table 1. Net Weight Gain (mg/g) after the Reaction of 1-Octadecene with Maleic Acid Adsorbed on Alumina

	calcination	TGA
batch I (with AIBN)	40	40
batch II (with AIBN)	29	
batch II (without AIBN)	1.7	

in chloroform was injected. The same procedure was applied to extract poly(maleic acid–1-octadecene) cross-linked with DVB from alumina but using toluene to dissolve the residue. Toluene was also used as the mobile phase at a flow rate of 1.0 mL/min, and 20 µL of sample in toluene was injected. In another trial, 20 mL of *N,N*-dimethylformamide (DMF) was mixed with 10 g of alumina coated with poly(maleic acid–1-octadecene) cross-linked with DVB at 80 °C for 24 h. After filtration and evaporation, the residue was dissolved in chloroform, and 20 mL was injected. Chloroform was used as the mobile phase at a flow rate of 0.5 mL/min.

After washing with solvents, the polymer-coated alumina samples were calcinated to determine the amount of polymers remained on alumina. The results were used to evaluate the washing efficiency and to estimate the percentage of polymers extracted and used in the GPC study on the overall molecular weight distribution.

Commercial polystyrenes with narrow molecular weight distribution (MWD) were utilized to construct the calibration curve. Polystyrenes with molecular weight of 4075, 32 660, 184 200, and 1 444 000 daltons, respectively, were dissolved in chloroform with a final concentration of 5.0 mg/mL for the calibration.

UV Spectroscopy. The residue obtained by washing alumina coated with poly(maleic acid–1-octadecene) with dichloromethane was redissolved in chloroform. Then the solution was washed three times with dilute sodium hydroxide aqueous solution (pH = 8.5) which had the same volume as the organic layer to remove any unreacted free maleic acid. The remaining organic layer was dried and redissolved in acetonitrile for UV scanning in the range 200–400 nm against acetonitrile as a reference.

¹³C and ¹H NMR. Solid-state ¹³C NMR with cross-polarization (CP) and magic angle spinning (MAS) was utilized in the study to determine the presence of functional groups to confirm the formation of polymers on alumina surface. The experiments were carried out on a Varian UNITY/INOVA 400 NMR spectrometer, using a Doty MAS probe with 7 mm (o.d.) × 12 mm rotors. The spinning rate was 6 kHz, and the proton decoupler power was 53 kHz. The total data acquisition time varied from 8 to 14 h, depending on the sample. Solution proton NMR was also performed for comparison to provide additional information regarding the formation of polymer on the alumina surface. To prepare samples of the solution NMR experiments, the residue obtained from washing the alumina coated with poly(maleic acid–1-octadecene) was dried under vacuum for 4 h and then dissolved in CDCl₃. The ¹H NMR spectrum of 1-octadecene in CDCl₃ was also obtained.

Scanning Electron Microscopy. The experiments were performed on a JEOL JSM 880 system with LaB6 filament at 15 keV accelerating voltage. The samples were prepared by means of sputter coating with Au–Pd (60–40) using the Technique Hummer VI apparatus.

Results and Discussion

Formation of Poly(maleic acid–1-octadecene) on Alumina. In the first step of our characterization, the solid products were calcinated to determine the change in the net weight compared with the starting material, namely, alumina with adsorbed maleic acid. The data in Table 1 show that the result obtained from the calcination with a Bunsen burner is the same as that from TGA. Therefore, we conclude that the calcination procedure is a reliable method for the weight
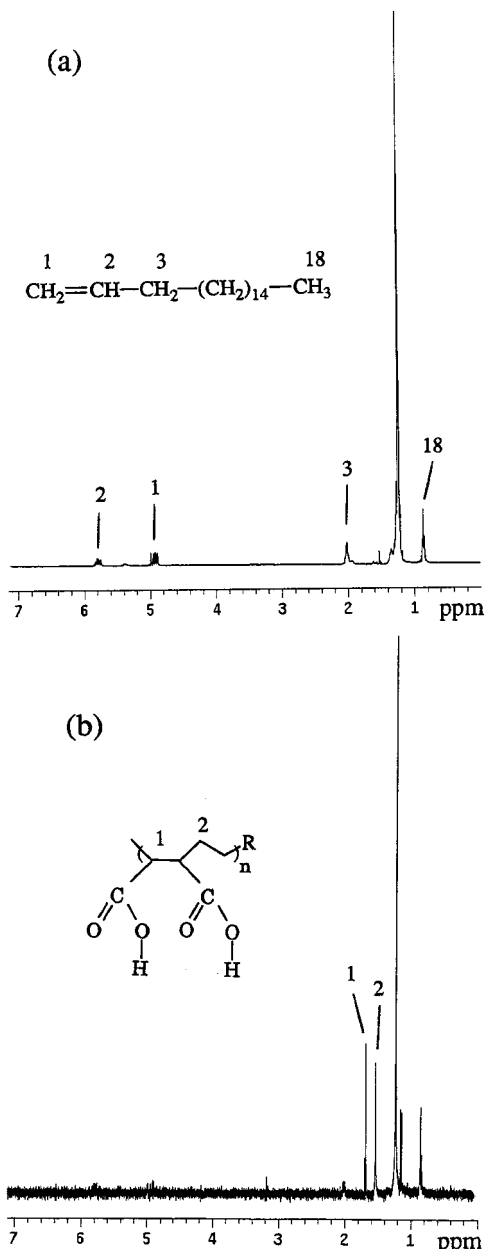
Figure 2. Solid-state ^{13}C NMR spectra at 100.6 MHz with CP-MAS. (a) Alumina coated with poly(maleic acid−1-octadecene); (b) alumina with adsorbed maleic acid; the shoulder at 113 ppm is a spinning sideband of the peak at 173 ppm; (c) alumina. The structures shown in (a) and (b) are for peak identification only; in actuality the two carboxylic groups are likely to be perpendicular to the double bond rather than being on the same plane.[16]

change determination and used it for our routine analysis because of its convenience and simplicity. The results in Table 1 also show that no significant weight gain was obtained when alumina with adsorbed maleic acid was brought into contact with 1-octadecene at 80 °C for 3 h without AIBN, indicating that AIBN is needed to initiate the polymerization process.

Solid-state ^{13}C NMR spectra with CP-MAS give useful information regarding the presence of the species on the surface. The pure alumina samples show two broad peaks of unknown origin (Figure 2c). The spectrum of alumina with adsorbed maleic acid shows two peaks for carbonyl (173.3 ppm) and methylene carbons (134.0 ppm, Figure 2b), respectively. The spectrum of the APCA product showed new peaks with chemical shifts in the range 10−40 ppm (Figure 2a). For copolymers

formed between 1-octadecene and maleic acid adsorbed on alumina, the repeating unit should be

poly(maleic acid-1-octadecene)

The methyl carbon, A, has a typical chemical shift at 12.5 ppm. The major peak at 29.8 ppm and the smaller peak at 22.5 ppm are assigned to the carbons in the main chain (B). The shoulder at 34.2 ppm is likely due to the carbon next to the carbonyl group (C). The carbonyl carbon (D) shows a broad peak at about 180 ppm. The peaks at 173 and 134 ppm are due to unreacted maleic acid molecules adsorbed on alumina. This is reasonable because the polymer formed on the surface would shield part of the unreacted maleic acid molecules to prevent them from coming into contact and reacting with 1-octadecene. For comparison, the ^{13}C chemical shifts of eicosanoic acid are[26] as follows (in ppm): a, 14.0; b, 22.5; c, 24.8; d, 29.1; e, 29.4; f, 31.4; g, 34.1; h, 175.2.

In a separate determination, the APCA product was washed with a strong solvent, dichloromethane, to extract the organic coating. After the solvent was evaporated, the residue was dissolved in $CDCl_3$, and the proton NMR spectrum was obtained. Compared with the spectrum of 1-octadecene (Figure 3), the disappearance of the peaks in the range of 4.5−6 ppm in the spectrum of the residue indicates that the C=C bonds were mostly converted to C−C bonds. In other words, 1-octadecene had reacted with maleic acid by opening up its C=C double bond. However, because the polymerization was carried out in 1-octadecene without solvent, it is possible that a very small amount of unreacted 1-octadecene molecules remained trapped in the polymer film.

The solid-state ^{13}C NMR spectrum demonstrates that a new compound exists on the surface in addition to

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Figure 3. ^{1}H NMR spectra at 400 MHz in CDCl$_3$. (a) 1-Octadecene; (b) extracted poly(maleic acid−1-octadecene).
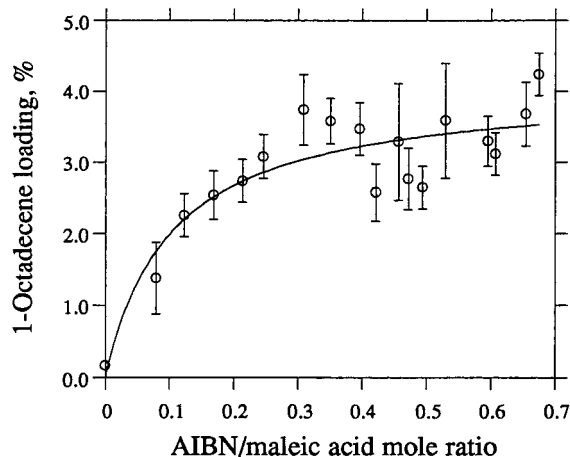

Figure 4. Relationship between monomer loading and the mole ratio of AIBN to maleic acid adsorbed on alumina.

broad distribution is likely due to the heterogeneity of the surface reaction.

After being washed with dichloromethane, the remaining solid was dried, and the weight loss was determined by calcination to evaluate the washing efficiency. By knowing how much of the polymer had been washed off, we were able to evaluate whether the GPC result is representative of the characteristic of the majority of the surface polymer. The result indicates that 68% of polymer was stripped off, demonstrating that dichloromethane was suitable to extract most of the poly(maleic acid−1-octadecene) from the surface, and the molecular weight determination gave the representative MW distribution of two-thirds of the polymer on the surface. The UV spectrum of the residue shows a peak at 225 nm. Because the only group active in the UV range is −COO− from maleic acid of the sample, this observation indicates that maleic acid on alumina did participate in the polymerization and is one of the linking units in the polymer.

In summary, maleic acid adsorbed on the alumina surface does copolymerize with 1-octadecene through a stepwise process as shown in Figure 1. The surface of alumina was altered from being hydrophilic to hydrophobic because of this polymer coating.

Optimization of Polymerization on Alumina. For the copolymerization of maleic acid adsorbed on alumina with 1-octadecene in the presence of the initiator AIBN, the amount of 1-octadecene was in great excess since the polymerization was employed without solvent. It was important to study the effect of the amount of AIBN and maleic acid loading on polymerization in order to control the surface modification. Thus, various amounts of AIBN were used to monitor the weight gain after reaction, while all other conditions were kept the same for each reaction. The net weight gain due to the polymerization of 1-octadecene with maleic acid adsorbed on alumina was plotted against the mole ratio of AIBN to maleic acid in Figure 4. It was stated previously that no polymerization occurred in the absence of initiator; this is substantiated by a least-squares fitting of the data (solid curve). At low mole ratios of AIBN to maleic acid, the 1-octadecene loading gradually increases. When the ratio is larger than about 0.3, the loading reaches a plateau and becomes independent of the ratio, having an average
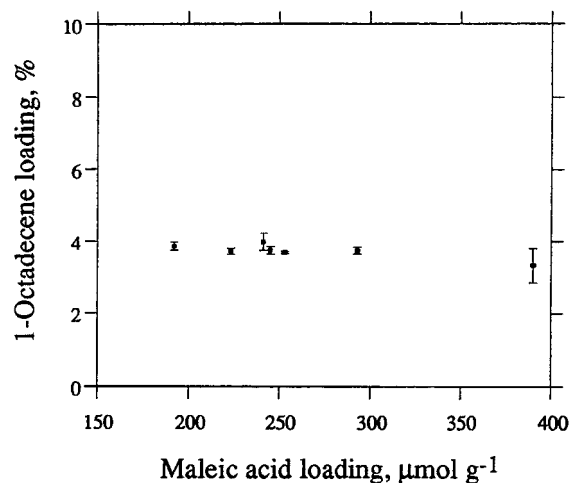
maleic acid. The component has a long CH$_2$ chain, which could come only from 1-octadecene. The solution proton NMR spectrum indicates that the extractable species has a saturated hydrocarbon chain instead of containing a double bond. At this point it can be concluded that poly(maleic acid−1-octadecene) was formed on the alumina surface.

To further confirm the formation of poly(maleic acid−1-octadecene) on alumina surface, the reside was injected into a GPC system to determine the molecular weight and its distribution. A MWD was estimated by using the onset and the ending time of the peaks, and was found to be 500−275 000 daltons. When the results were analyzed, it was found that there was a major fraction with a molecular weight (MW) range 500−43 000, and a minor fraction with a MW range of 43 000−275 000. The results confirm that the organic coating has the characteristic of a polymer, and the

Figure 5. Relationship between monomer loading and the amount of maleic acid adsorbed on alumina.

value of 3.4%. To understand this result, the following consideration can be made.

When an adsorbed maleic acid molecule is activated by a free radical initiator, it can react with the double bond of an approaching alkene molecule, forming another radical. The alkene radical would not be reactive enough to activate another alkene molecule but can seek out a neighboring adsorbed maleic acid to add to its electron-poor double bond. This process would propagate to form an alternating polymer on the surface. However, the adsorbed maleic acid molecules are not mobile, and their distances from one another may not be completely uniform, so that the propagation of the activated molecules after free-radical initiation is much more limited than that in an isotropic solution. As a result, the threshold value of initiator (AIBN/maleic acid mole ratio = 0.30) is quite high compared to solution polymerization. In the case of low initiator concentration, all the maleic acid molecules on the surface are available to be initiated. Therefore, the amount of initiator becomes the factor that determines the yield. As the ratio increases, more sites are initiated and more 1-octadecene was polymerized, resulting in a higher loading in the same reaction period. When a high concentration of initiator is used, the availability of the maleic acid molecules becomes the limiting factor for the initiation. Because the number of initiated sites is the same no matter how much initiator is used, the loading does not increase further. In other words, there is a threshold amount of initiator required for the maximum loading, and it is not necessary to use an amount of initiator higher than this threshold value. Moreover, high concentrations of initiator usually lead to low molecular weights because more chains are initiated.

In a detailed study of the adsorption of maleic acid from aqueous solutions onto alumina, it was found that the adsorption obeys the Langmuir isotherm, with an optimum amount of adsorption of 525 ± 33 μmol g^{-1}.[16] Below this value, one might expect that the alkene loading would increase with maleic acid loading if the amount of maleic acid is the only limiting factor for the polymer formation. However, the result in Figure 5 shows that the polymer loading stayed more or less constant for maleic acid loading from about 180 to 400 μmol g^{-1}. Because the reaction is heterogeneous, the
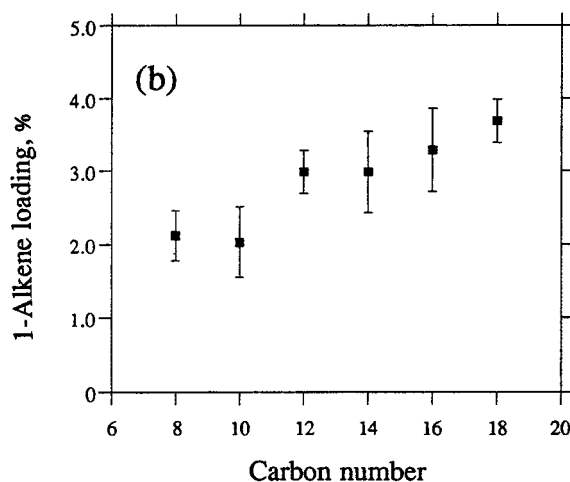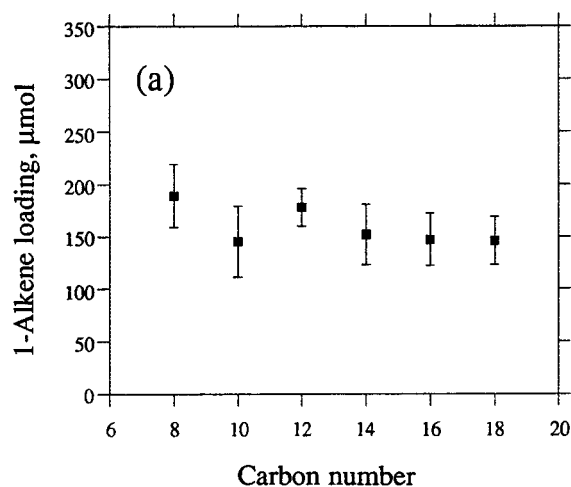

Figure 6. Relationship between monomer loading and the chain length of the monomer: (a) micromole scale; (b) weight percentage scale.

results can be explained by the role of steric hindrance in determining the overall yield of the polymerization: after the surface is partially covered by the copolymers, it would be too crowded for the 1-octadecene monomers to approach the unreacted maleic acid molecules to form more polymers. The results obtained using a series of 1-alkenes with the chain length varying from carbon number 8–18 are given in Figure 6. They are consistent with the interpretation given above: the polymers formed from smaller alkenes allow the surface maleic acid molecules to be more accessible for the formation of more polymers, so that the number of 1-alkene molecules reacted decreases as the chain length increases (Figure 6a). However, the loading in weight increases with the chain length because the larger molecule have higher molecular weights (Figure 6b). Because higher loading is desired for the potential application as reverse-phase packing materials in HPLC, 1-octadecene was chosen for our study.

Effect of Surface Modification on Surface Area and Morphology. The main result of the APCA process is the formation of a monolayer of polymer coating on alumina. The modification of the alumina surface alters its surface property. It could also result in a decrease of the surface area because the coating may block some of the pores, which impart a large

Table 2. Surface Area and Pore Diameter of Alumina Particles before and after Modification

substance	BET surface area (m²/g)	pore diameter (nm)
alumina	150	5.3
	155[a]	5.8[a]
with absorbed maleic acid	150	5.3
polymerized with 1-octene (C8)	129	5.2
polymerized with 1-tetradecene (C14)	122	5.3
polymerized with 1-octadecene (C18)	103	5.4
C18 cross-linked with DVB	130	4.4
polymerized with allyl bromide	126	5.4

[a] Provided by the manufacturer.

internal surface on alumina. From this consideration, the surface area of alumina was measured before and after modification. The results are listed in Table 2.

When maleic acid is adsorbed on alumina, the surface area and pore diameter do not show any change. This can be easily understood because maleic acid is a small molecule, and only a monolayer is formed on the surface. After polymerization with 1-alkenes and allyl bromide, the surface area decreases, but the pore diameter is essentially the same as pure alumina for each case, except for that with DVB cross-linking. When 1-octadecene is used for copolymerization, the resulting product has the smallest surface area. This is probably due to the blocking of some of the pores by the alkyl chains, while the remaining pores still have the same pore diameter as pure alumina. Using DVB as a cross-linking agent, the surface area does not decrease as much as the system of poly(maleic acid−1-octadecene), but the pore diameter becomes smaller. Because of the cross-linking, a more extensive two-dimensional network is distributed on the surface. Some of the pores are probably partially blocked, resulting in a smaller average pore diameter.

The morphology of the alumina particles before and after modification was studied by examining the scanning electron micrographs (SEM; Figures 7 and 8). Figure 7 shows that the alumina particles are aggregates of small crystals. In the process of preparing the polymer-coated alumina, the mechanical stirring broke up some of the larger particles into smaller ones (Figure 7, bottom graph). This kind of mechanical change was also observed for alumina particles with the same mechanical treatment in the absence of maleic acid. At a higher magnification, there is no obvious difference between the uncoated alumina particles and the polymer-coated alumina particles in the SEM (Figure 8). Therefore, the disagglomeration process probably does not contribute significantly to the changes in surface area and porosity as discussed above.

Stability of Polymer Coatings on Alumina. After having established the formation of a monolayer of polymer on alumina and characterized its properties, it is important to test the stability of the polymer coating with respect to different solvents. Since one of the potential applications of the APCA material is as reverse-phase packings in HPLC, the effects of commonly used solvents for mobile phases were studied. These solvents were methanol, methanol/water (1:1), acetonitrile, and acetonitrile/water (1:1). In addition, the tolerance of the material toward aqueous media with extreme pH values was also tested with 0.1 N hydro-
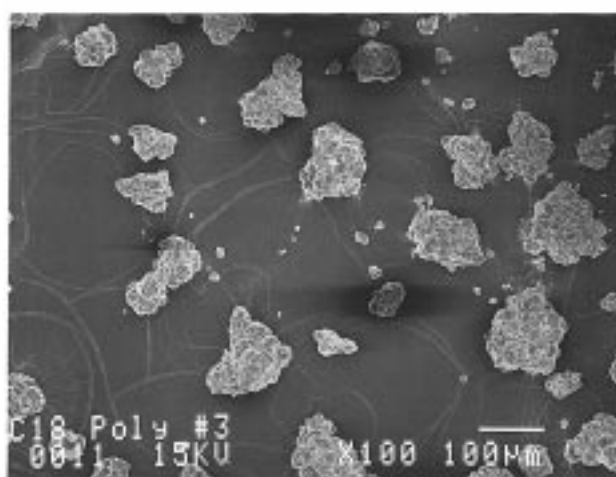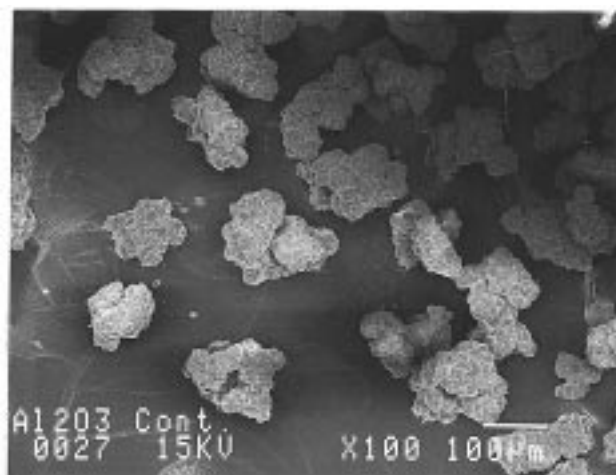

Figure 7. Electron scanning micrographs at ×100 magnification. Top: alumina. Bottom: Alumina coated with poly(maleic acid−1-octadecene).

chloric acid and 0.1 N sodium hydroxide. The stability is evaluated in terms of the relative loading, d', after washing both at ambient temperature and under reflux for 24 h:

$$d' = (d_s)_n/(d_c)_n \qquad (2)$$

where $(d_s)_n$ and $(d_c)_n$ are for the sample after washing and for the control, respectively, as defined in eq 1. Therefore, d' gives a measure of the stability of the sample for a given solvent. The value of d' ranges from 0 to 1; 0 is the least stable and 1 is the most stable. The results are plotted in Figures 9a−c, the error bars in which represent standard deviations.

When alumina with adsorbed maleic acid was washed with the solvents, the adsorbed maleic acid was unstable in aqueous media. In water and 0.1 N HCl, only about half remained, and it was completely washed off from the surface in 0.1 N NaOH. The stability increased slightly in methanol/water (1:1) and acetonitrile/water (1:1). In methanol the majority of maleic acid was retained. In acetonitrile maleic acid was stable and remained on the surface (Figure 9a). This can be explained by the following consideration. Although the exact nature of the interaction between the adsorbed maleic acid and alumina is not fully understood, the
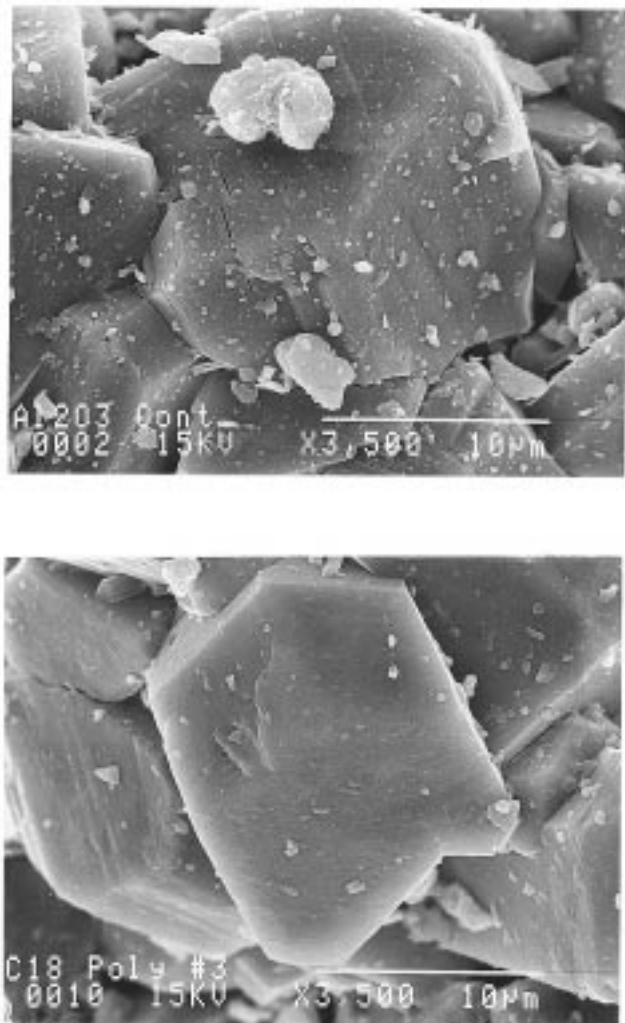
Figure 8. Electron scanning micrographs at ×500 magnification. Top: alumina. Bottom: alumina coated with poly(maleic acid−1-octadecene).

major interaction probably involves hydrogen bonding between the maleic acid molecules and the surface hydroxyl groups of alumina. These linkages cannot withstand the attack of water molecules through prolonged washing, and the maleic acid molecules would desorb from the surface in an aqueous environment. On the other hand, the adsorption of maleic acid on alumina is so strong compared with that of other organic molecules[15] that it does not desorb easily from the surface when it is washed with organic solvent.

After the adsorbed maleic acid is polymerized, the stability of the adsorbed organic layers changes drastically (Figure 9b). The poly(maleic acid−1-octadecene)-coated alumina show results opposite to maleic acid itself. In general, the polymer coating is stable in the aqueous media but not in organic media. The stability drops sharply as the polarity of the solvent decreases, as indicated by the results in methanol and acetonitrile. Even in a mixture of acetonitrile and water, the polymer coating was washed off to some extent. The reason for the reversal in the stability is the following: When a polymer coating is formed, the surface becomes hydrophobic, which prevents water from getting close to the surface. Therefore, the polymer-coated alumina withstands washing in the aqueous media very well. In a
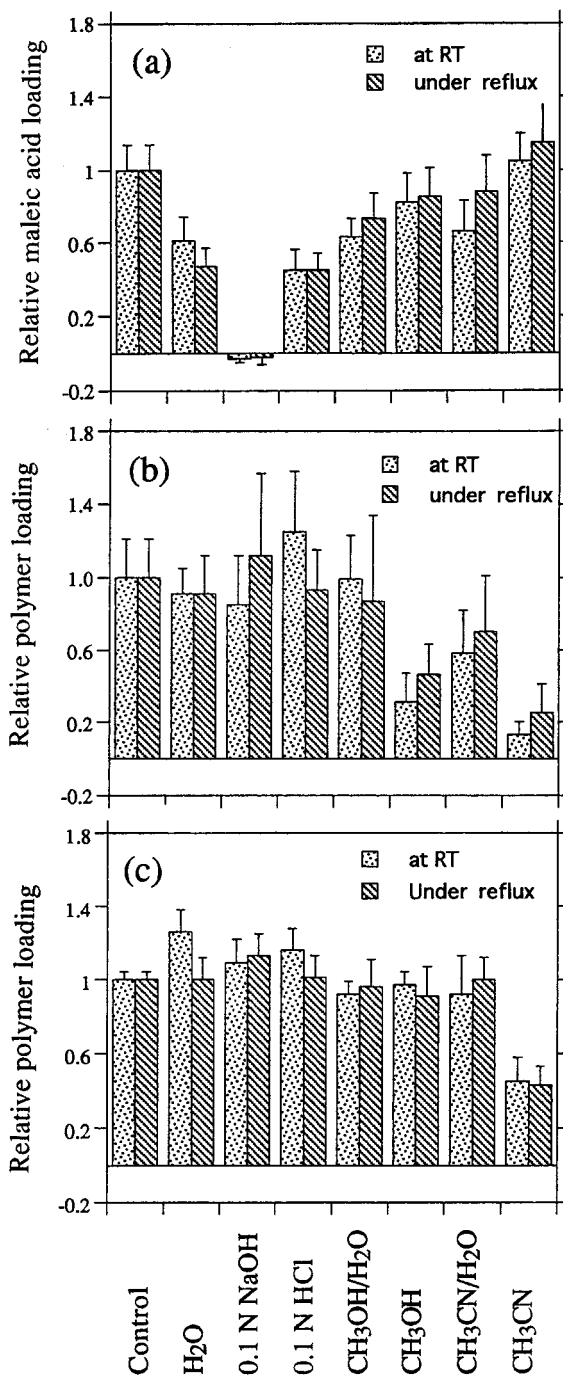

Figure 9. (a) Stability of maleic acid adsorbed alumina after washing with various solvents for 24 h; (b) stability of alumina coated with poly(maleic acid−1-octadecene) after washing with various solvents for 24 h; (c) stability of DVB-cross-linked poly-(maleic acid−1-octadecene) coated alumina after washing with various solvents for 24 h.

polar organic solvent such as acetonitrile, the low MW fragments of the polymer coating can be dissolved and stripped off the surface.

To increase the stability of the polymer coating, the MW should be increased. Therefore, divinylbenzene (DVB) was selected as a cross-linking agent. Indeed, the stability of the organic coating after cross-linking with DVB was greatly enhanced (Figure 9c). It is very stable in all tested solvents, except in acetonitrile. Although it is not completely stable in acetonitrile, the stability increases by about 25% compared with the

Table 3. Weight Loss and Molecular Weight Distribution (MWD) for Alumina Coated with DVB-Cross-Linked Poly(maleic acid−1-octadecene)

	weight loss relative to control	MWD
washed with CH_2Cl_2	26%	640−6600 6600−135000
washed with DMF	<1%	620−2400 2400−23000

simple poly(maleic acid−1-octadecene) coating without cross-linking. To confirm the effect of cross-linking on the MW of the polymer, a batch of alumina coated with DVB cross-linked polymer was washed with dichloromethane and DMF at 80 °C, respectively. The MWD of the extracted polymer coatings was determined for each case using GPC. Meanwhile, the weight loss was also determined after washing. The results are summarized in Table 3. Again, for each solvent, there were two fractions with different ranges of MWD. The results show that alumina coated with DVB cross-linked poly(maleic acid−1-octadecene) has a better stability than those without cross-linking. Only 26% of the cross-linked polymer coating was washed off with CH_2Cl_2, whereas 68% of the non-cross-linked polymer was washed off under the same conditions. The small portion that was washed off has a higher MW, up to about 135 000 daltons. The portion that remains on the alumina surface should have an even higher MW. The cross-linked polymer coating was very stable toward DMF, and almost all of it remained on the surface with DMF washing; only a small amount with very low MW was washed into the solvent. To summarize, DVB is an effective cross-linking agent and suitable to be used in the system of maleic acid and 1-octadecene. The stability of the cross-linked polymer is greatly enhanced, so that the material has a very good tolerance toward the solvents.

Polymerization of Maleic Acid Adsorbed on Alumina with Allyl Compounds. If there are active functional groups available on the polymer coating, the surface can be further derivatized. Allyl bromide and allylamine are suitable for this purpose, since after polymerization either a free bromine atom or a free amine group is present on the polymer monolayer for further reaction. The reaction products were evaluated by calcination, elemental analysis (carried out by Midwest Microlab, Indianapolis), and titration of the bromide content produced from hydrolysis. All results

showed that there were significant weight gains (16−25 mg/g) after the adsorbed maleic acid was reacted with allyl bromide or allylamine in the presence of AIBN, indicating the formation of polymers on the surface. Detailed characterization of the polymers and test of their stability need to be performed.

The APCA products with different coatings may have various applications. For example, alumina coated with DVB-cross-linked poly(maleic acid−1-octadecene) may find its application as packing material in reverse phase (RP) HPLC[27] if the mobile phase is water/methanol or water/acetonitrile rather than a pure polar organic solvent such as acetonitrile (Figure 9). The APCA materials may also be used as fillers for plastics and rubber, components of specialty paints, in the production of sintered aluminum oxide through calcination of the polymer, and for the formation of protective coatings on aluminum metal or its alloys. When the functional group of the APCA materials are properly derivatized, the products may also find applications in heterogeneous catalysis and water purification.

Conclusion

Through a two-step process, anchored polymer coatings can be produced on the surface of alumina. This process utilizes inexpensive chemicals, such as maleic acid, 1-alkenes, and allyl compounds as starting materials. Because each maleic acid molecule in the backbone of the polymer has two carboxylic groups which are hydrogen-bonded to alumina,[16] the coating can be tightly anchored onto the surface. On the contrary, direct deposition of a polymer onto the surface does not produce a uniform thin film; furthermore, due to the steric hindrance of both surface and the polymer itself, few functional groups in the polymer can be brought into direct contact with the surface hydroxyl groups to have extensive polymer-alumina interaction.

CM970451R

(27) Mao, Y.; Fung, B. M. *J. Chromatogr. A* **1997**, *790*, 9.