Polymer-Coated Alumina Particles: Correlation of Structure and Chromatographic Performance

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A study combining structural characterization by solid-state ^{13}C NMR and measurement of chromatographic performance is reported for a series of polymer-coated Unisphere alumina particles. The alumina particles, coated with cross-linked polybutadiene (PBD) or polybutadiene oxide (PBO) or derivatives thereof, can function as the stationary phase in reversed-phase liquid chromatography (RPLC). Cross-polarization magic-angle spinning ^{13}C NMR spectroscopy allowed detailed characterization of the polymer-coated samples, including comparison of polymer loading levels, measurement of olefinic vs aliphatic carbon, and determination of 1,2- and 1,4-olefinic units in the PBD portions of the polymers. In situ chemistry, including hydrogenation and reactions of the cross-linked polymers with C_{10} and C_{18} aliphatic chains, was also monitored by solid-state NMR. The ability of each of the polymer-coated alumina samples to separate a standard mixture of five organic compounds was evaluated. Correlations between the NMR results and RPLC performance provide insights into those structural features of polymer coatings which are most important in determining their suitability for use in chromatographic separations. In particular, hydrophobicity is found to be a key parameter in determining a polymer coating's chromatographic performance.

Introduction

Reversed-phase liquid chromatography (RPLC) has traditionally used surface-modified silica as a stationary phase. Silica has a number of advantageous properties which makes it well-suited for chromatographic media.[1,2] Microparticulate silica materials having well-controlled size, shape, pore size, and pore-size distribution are readily available. Silica surface modification, necessary for RPLC, is usually accomplished via silanization of surface silanol groups[2-5] to yield a molecularly bound lipophilic coating. In recent years, a number of reports[6-11] have demonstrated that coating the inorganic particle with a cross-linked organic polymer film is an alternate route to produce a chromatographically acceptable lipophilic surface. Examples of this approach include polymers which are structurally similar to alkyl-silanized silica, such as octadecyl-substituted polysiloxane,[6] and polymers such as polybutadiene (PBD)[7,8] which bear little structural resemblance to any well-known RPLC surface.

In recent years, there has been growing interest in developing chromatographic media based on other inorganic particulates such as alumina and zirconia.[12-14] This interest is driven largely by the limited pH range over which silica is stable. In particular, the inability of silica media to survive prolonged exposure to environments of pH 10 or greater limits its usefulness for RPLC. For inorganic species such as alumina, however, there is no straightforward route to a stable lipophilic surface which is comparable to silanization.[15] In these cases, polymer coating appears to be the only feasible route to a lipophilic surface suitable for RPLC. Indeed, at least one RPLC stationary phase has recently been commercialized which is based on PBD-coated alumina.[16] However, little information has been published relating the structure of the polymer coating to chromatographic performance. Such information is critical in order to optimize performance and to lay the groundwork for understanding chromatographic retention mechanisms. In fact, the use of PBD-coated inorganic particulate fillers or pigments to impart improved impact strength to thermoplastic materials[17] suggests that the development of in situ methods of structure/property analysis will be of general interest.

NMR spectroscopy has been used extensively to study the structure and dynamics of a wide variety of polymers. Solution NMR studies of soluble polymer systems provide

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chemical identification and are a source of information about polymer tacticity.[18,19] Modern two-dimensional solution NMR techniques[20] can afford detailed microstructural characterization of polymers.[21-24] Solid-state NMR spectroscopy[25,26] provides compositional information in polymers whose molecular weight and/or degree of cross-linking preclude analysis in solution.[27,28] Solid-state NMR is especially appropriate for evaluating polymer-coated, porous chromatographic media because the analysis can be conducted on the polymer in situ. The majority of the surface area in a typical porous chromatography support is contained in the interior portion of the particle. This effectively precludes the use of analytical techniques that require a line of sight to the polymer film.

Experimental Section

Materials. Seven different polymer-modified alumina samples were examined in this study. The alumina is a proprietary material developed at Alcoa[29] (Unisphere particles) which is composed of θ-alumina plates fused around an α-alumina core to form a spherical particle. The particle size is approximately 8 μm. The surface area is 46.6 m^2/g, the pore volume is 0.280 cm^3/g, and the average pore size diameter is 240 Å, as determined by BET analysis. The material is available commercially from Biotage Inc. (Charlottesville, VA). Three of these alumina samples were coated with cross-linked polybutadiene (PBD) or a modified-PBD polymer: (1) PBD; (2) partially hydrogenated PBD; and (3) C_{18}-modified PBD. The other four samples were Unisphere particles coated with cross-linked poly(butadiene oxide) (PBO), a polybutadiene-based polymer in which a fraction of the double bonds have been epoxidized, or modified PBO: (4) PBO; (5) PBO that was subsequently fully hydrolyzed to produce polybutadiene dihydroxide; (6) PBO that was subsequently reacted with decylamine; and (7) PBO that was subsequently reacted with undecyl alcohol. The partially-hydrogenated PBD-coated alumina (no. 2, above) and C_{18}-modified PBD-coated alumina (no. 3, above), are proprietary products of Monsanto Co.[13]

Polymer loading levels for the PBD and modified-PBD-coated alumina samples were determined by elemental carbon analysis and were consistent with those measured from absolute solid-state ^{13}C NMR signal intensities (vide infra). If the polymers were distributed uniformly on the surface area of the alumina, coating thicknesses would be $\leq$100 Å for all of the samples described above. Desorption isotherm data of coated alumina showed slightly diminished pore volumes across the complete range of pore sizes, consistent with thin, uniform coatings. Extensive SEM/TEM analysis of PBD-coated alumina stained with osmium tetroxide showed no polymer accumulations of greater than 100-Å thickness.

Synthesis. *Polybutadiene (PBD)-Coated Alumina.* A mixture of 10.00 g of Unisphere alumina, 1.00 g of polybutadiene [Aldrich; MW = 3400; 99% unsaturation (25% *trans*-1,2, 40% *trans*-1,4, 35% *cis*-1,4)], and 150 mL of toluene (Fisher, reagent grade) were added sequentially to a 500-mL single-neck round-bottom flask. The flask was swirled in a 60 °C water bath for 30 min and then allowed to cool to room temperature. Dicumyl peroxide (0.050 g, Aldrich) was dissolved in a small amount of reagent grade toluene and added directly to the slurry. The flask was then placed on a rotary evaporator and reduced to dryness in vacuo. A dust screen was attached to the flask neck and the entire vessel was placed in a vacuum oven. Cross-linking and immobilization of polymer on the alumina surface was accomplished by heating the flask to 160 °C for 3 h in vacuo. Following this thermal curing, the alumina powder was washed with approximately 300 mL of hot hexane and then 300 mL of hot methanol. The final product was dried in vacuo at 80 °C for 1 h.

Partially Hydrogenated PBD-Coated Alumina. The above procedure was repeated with partially hydrogenated PBD (prepared from the native PBD (MW 3400; 99% unsaturation) by the method of Harwood[30] and Lenz.[31] The partially hydrogenated PBD was characterized by solution ^1H and ^{13}C NMR and the observed NMR spectra were consistent with those reported previously for this material.[30,31] Partially hydrogenated PBD (1.50 g) and 0.15 g of dicumyl peroxide were applied to 10.00 g of Unisphere alumina.

Olefin-Modified PBD-Coated Alumina. To prepare olefin-modified PBD, the above procedure was repeated with 1.00 g of native PBD (MW = 3400; 99% unsaturation). 1-Octadecene (2.00 g, Aldrich) and 0.10 g of dicumyl peroxide were applied to 10.00 g of Unisphere alumina. Following the thermal curing, the polymer-coated alumina was washed with 150 mL of 10% acetic acid in hexane, 300 mL of hot hexane, and then 300 mL of hot methanol. The final product was dried in vacuo at 80 °C for 8 h.

Polybutadiene Oxide (PBO)-Coated Alumina. Polybutadiene oxide (PBO) was purchased from Polysciences, Inc. (Warrington, PA) and was used as received. High-resolution solution ^1H and ^{13}C NMR characterization of the PBO is reported below. A solution of 0.150 g of benzoyl peroxide in 100 mL of methylene chloride was placed in a round-bottom flask containing 50 g of Unisphere alumina particles. A solution of 7.50 g of PBO in 100 mL of methylene chloride was added to the flask. The mixture was stirred for 15 min after which the solvent was removed under reduced pressure on a rotary evaporator. The flask, after the removal of solvent, was placed in a vacuum oven at room temperature, and under reduced pressure, the temperature was raised to 160 °C. Curing was carried out for 3 h at 160 °C, after which the pressure was increased back to atmospheric by bleeding in nitrogen.

Polybutadiene Dihydroxide-Coated Alumina. Polybutadiene dihydroxide coating was obtained by hydrolyzing the PBO-coated particles. PBO-coated alumina particles (10 g) were added to a flask containing 25 mL of 31.5% perchloric acid. The contents of the flask were stirred overnight under a nitrogen purge. The solid was filtered and then washed extensively with water. Particles were then dried in vacuo at 80 °C for 1 h.

Decylamine-Modified PBO-Coated Alumina. Decylamine was reacted with the PBO-coated alumina described above. Under a nitrogen atmosphere, 10.00 g of PBO-coated alumina particles was placed in a flask containing 25 mL of THF. Decylamine (3 mL) was then added to the flask dropwise. The reaction was carried out overnight at room temperature. Solid was filtered, washed with THF, and dried in vacuo at 80 °C for 1 h.

Undecyl Alcohol-Modified PBO-Coated Alumina. Undecyl alcohol was reacted with the PBO-coated alumina described above. Under a nitrogen atmosphere, 10.00 g of PBO-coated alumina particles was placed in a flask containing 5.0 mL of undecyl alcohol dissolved in 25 mL of THF. The mixture was refluxed at 80 °C for approximately 2 h. After cooling to room temperature, the solid was filtered, thoroughly washed with THF, and then dried in vacuo at 80 °C overnight.

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Solution NMR Characterization of Polybutadiene Oxide. The starting PBO polymer was characterized in solution by 1-D ^{1}H and ^{13}C NMR and by 2-D ^{1}H-^{13}C heteronuclear shift-correlation (HETCOR) spectroscopy. The PBO was dissolved in $CDCl_3$ and all spectra were collected at 25 °C. ^{1}H and ^{13}C NMR spectra were collected on a Varian VXR-400 spectrometer, while the HETCOR experiments were performed on a Varian XLA-200 instrument. The 1-D proton and carbon NMR spectra were consistent with those expected for PBO and the 2-D shift-correlation spectrum helped to confirm both the ^{1}H and ^{13}C line assignments. From integration of the ^{1}H signals due to olefinic and epoxide protons, we estimate that 40% of the double bonds in the original PBD polymer were epoxidized to produce the PBO polymer. The 1-D ^{13}C NMR spectrum indicates that only internal 1,4 PBD olefinic units were epoxidized; no spectroscopic evidence for the epoxidation of 1,2 units was found.

Solid-State NMR Spectroscopy. Solid-state ^{13}C NMR spectra were collected on a home-built spectrometer operating at a proton Larmor frequency of 127.0 MHz. Samples were spun at the magic angle (54.7°) with respect to the static magnetic field in a double-bearing rotor system[32] at a rate of 3 kHz. Cross-polarization magic-angle spinning (CPMAS) ^{13}C NMR spectra were obtained at 31.9 MHz following 2-ms matched, 50-kHz ^{1}H–^{13}C cross-polarization contacts. High-power proton dipolar decoupling (H_1(H) = 65 kHz) was used during data acquisition. Under these conditions, the relative intensities of the peaks observed in each of the spectra are correct.[33,34] Additional experimental details are provided in the figure captions.

Chromatography. The polymer-coated alumina particulate samples were packed into 316 stainless-steel HPLC columns (4.6 mm × 25 cm) using standard techniques by Phenomenex Inc. (Torrance, CA). Reversed-phase chromatographic performance was evaluated with a standard Waters HPLC system consisting of a Model 501 solvent delivery system, Model 481 UV/vis detector, and a Model R-401 refractive index detector. Retention data were collected from an eluant compound test mixture comprised of theophyllin, *p*-nitroaniline, methyl benzoate, phenetole, and *o*-xylene. All RPLC runs were conducted under ambient conditions with a 50/50 (v/v) aqueous/acetonitrile mobile phase.

Results and Discussion

PBD-Coated Alumina. *NMR Characterization.* Figure 1 shows the CPMAS ^{13}C NMR spectrum of native PBD-coated alumina particles. Resonances between 10 and 65 ppm are due to aliphatic carbons, while those in the range 110–150 ppm are due to olefinic carbons. In addition, there is a small, broad signal near 170 ppm at a chemical shift characteristic of carbonyl carbons. On the basis of previous solution-state ^{13}C NMR work on PBD,[35,36] the major signal at 129 ppm can be assigned to olefinic 1,4-PBD units and the peaks at 115 and 145 ppm to olefinic 1,2-PBD units. Because the relative intensities of signals in this spectrum are correct, the different spectral regions can be deconvoluted and integrated to determine both the aliphatic/olefinic carbon ratio and 1,4-PBD to 1,2-PBD composition. Results of these integrations are reported in Table I and indicate that the alumina-bound PBD in this sample is 69% aliphatic carbon/31% olefinic carbon and 83% 1,4 PBD/17% 1,2-PBD (Table I, line 1).

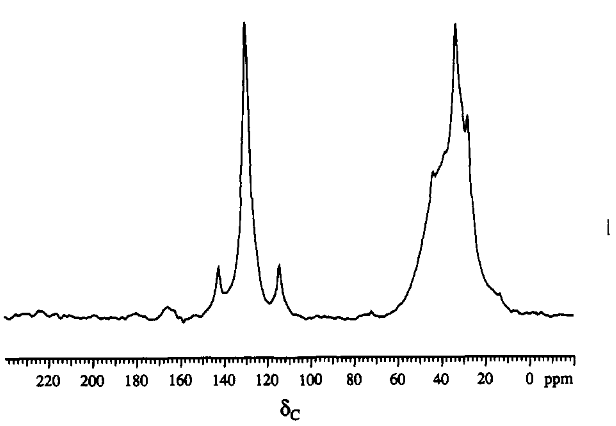

Figure 1. Cross-polarization magic-angle spinning (CPMAS) ^{13}C NMR spectrum of Unisphere alumina particles coated with cross-linked polybutadiene (PBD), sample weight = 468 mg, 135 000 transients. Line assignments are olefinic carbons (1,4-PBD units, δ_c = 129 ppm; 1,2-PBD units, δ_c = 115, 145 ppm); aliphatic carbons (δ_c = 10–65 ppm). This spectrum was obtained at 31.94 MHz, following a 2-ms, matched 50-kHz ^{1}H–^{13}C cross-polarization contact. The sample was spun at the magic-angle at a rate of 3 kHz. High-power proton dipolar decoupling (H_1(H) = 65 kHz) was used during data acquisition.

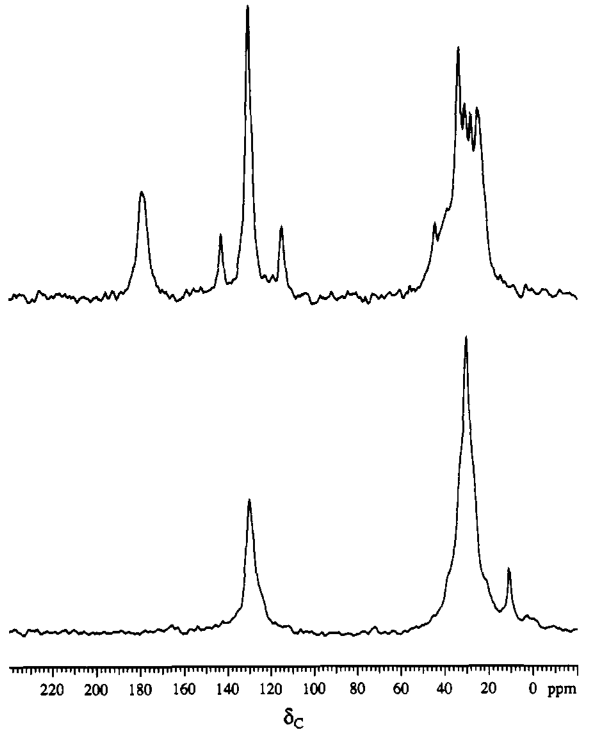

Figure 2. CPMAS ^{13}C NMR spectra of Unisphere alumina particles coated with modified-PBD polymers: (bottom) partially-hydrogenated PBD, sample weight = 455 mg, 150 000 transients; (top) C_{18}-modified PBD, 406 mg, 50 000 transients. All experimental conditions are as described in the caption to Figure 1.

Table I. Carbon Composition of PBD-Coated Aluminas

sample	carbon composition olefinic	carbon composition aliphatic	olefinic carbon 1,4-units	olefinic carbon 1,2-units	relative ^{13}C signal
native PBD	0.31	0.69	0.83	0.17	1.00
partially hydrogenatedPBD	0.25	0.75	1.00	0.00	0.32
C_{18}-modified PBD	0.38	0.62	0.75	0.25	0.33

Figure 2 (bottom) shows the CPMAS ^{13}C NMR spectrum of alumina particles coated with partially-hydrogenated PBD. When compared to the spectrum of native PBD (Figure 1), a number of differences are apparent. As would be expected for a hydrogenated polymer, the aliphatic/olefinic carbon ratio in this sample has increased (75%

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Table II. Chromatographic Performance of PBD-Coated Aluminas

	PBD					PBD (hydrogenated)					C_{18}-PBD				
component	T_r	V_r	N/M	k'	α	T_r	V_r	N/M	k'	α	T_r	V_r	N/M	k'	α
theophylline	5.40	1.08	51 900	0	0	4.95	0.99	54 500	0	0	5.37	1.07	47 900	0	0
p-nitroaniline	6.96	1.39	55 900	0.29	0	6.60	1.32	66 400	0.34	0	6.73	0.25	53 400	0.25	0
methyl benzoate	7.53	1.51	51 600	0.40	1.36	7.85	1.57	63 800	0.59	1.76	7.90	1.58	50 300	0.47	1.85
phenetole	8.43	1.69	53 000	0.56	1.42	10.35	2.07	66 700	1.09	1.86	9.77	1.95	52 200	0.82	1.74
o-xylene	10.27	2.05	50 800	0.90	1.61	15.45	3.10	64 900	2.13	1.94	13.19	2.64	50 700	1.46	1.78

Table III. Chromatographic Performance of PBO-Coated Aluminas

	PBO (hydrolyzed)					PBO (C_{11} alcohol)					PBO (C_{10} amine)				
component	T_r	V_r	N/M	k'	α	T_r	V_r	N/M	k'	α	T_r	V_r	N/M	k'	α
theophylline	5.64	1.13	18 100	0	0	5.08	1.02	28 500	0	0	5.43	1.09	46 400	0	0
p-nitroaniline	8.27	1.65	15 200	0.47	0	7.47	1.49	17 400	0.47	0	8.29	1.66	56 600	0.53	0
methyl benzoate	9.62	1.92	15 800	0.71	1.51	8.70	1.74	19 800	0.71	1.51	9.26	1.85	55 600	0.71	1.34
phenetole	11.89	2.38	14 000	1.11	1.57	10.73	2.15	17 300	1.11	1.56	11.42	2.28	56 900	1.10	1.57
o-xylene	15.64	3.13	13 800	1.77	1.60	14.17	2.83	13 500	1.79	1.68	14.27	2.85	59 900	1.63	1.48

aliphatic/25% olefinic, Table I, line 2). The more active 1,2-PBD sites have been completely hydrogenated, producing the methyl-carbon signal at 11 ppm and leaving only 1,4-PBD signals in the olefinic-carbon region. Also, the aliphatic region of the spectrum has been shifted upfield slightly (~2 ppm) and narrowed considerably compared with that of the native PBD sample. This narrowing is particularly evident on the low-field side of the aliphatic-carbon envelope and suggests that the partially hydrogenated PBD is a less heterogeneous polymer than the starting PBD. Since aliphatic-carbon signals in PBD are sensitive to neighboring olefinic carbons, part of this narrowing may result from the elimination of 1,2-PBD olefinics. Normalized on a per mg of sample basis, this sample produces only 0.32 times as much ^{13}C signal as the native-PBD/alumina sample. This finding is consistent with polymer loading levels as determined by elemental carbon analysis. It may be that in the process of deposition and cross-linking, a fractionation of the PBD polymer has occurred, with only one-third of the available polymer actually being held in place on the alumina particles. This fractionation could also contribute to the narrowing of the aliphatic region of the spectrum.

The spectrum of alumina particles in which the native PBD was simultaneously cross-linked and reacted with 1-octadecene is shown in Figure 2 (top). The pattern of resonances is similar to that of Figure 1, though several new spectral features are apparent. We observe a new aliphatic-carbon resonance at 30 ppm, due to C_{18} hydrocarbon chains that have been incorporated into the PBD. Also, new signals at 180 and 24 ppm are seen that are due to the carboxyl and methyl carbons, respectively, of acetic acid that was present during sample preparation and that has become immobilized on the alumina particles. Excluding these acetic acid resonances, the bound polymer is found to be 62% aliphatic carbon/38% olefinic carbon and 75% 1,4-PBD/25% 1,2-PBD (Table I, line 3). Again excluding the acetic acid signals, the relative amount of carbon signal on a per mg sample basis is 0.33 times that of the native-PBD/alumina sample. Fractionation during the cross-linking process is again the most likely explanation of this observation.

Chromatographic Performance. The chromatographic performance of the aluminas coated with PBD, PBO, and their derivatives was evaluated by measuring their ability to resolve the five components of the standard eluant test mixture. This mixture of species represents a good test of a variety of potential substrate/eluant interactions with broad implications for the RPLC selectivity properties. Results of the chromatographic performance are reported in Tables II and III and in Figures 3, 4, and 7.

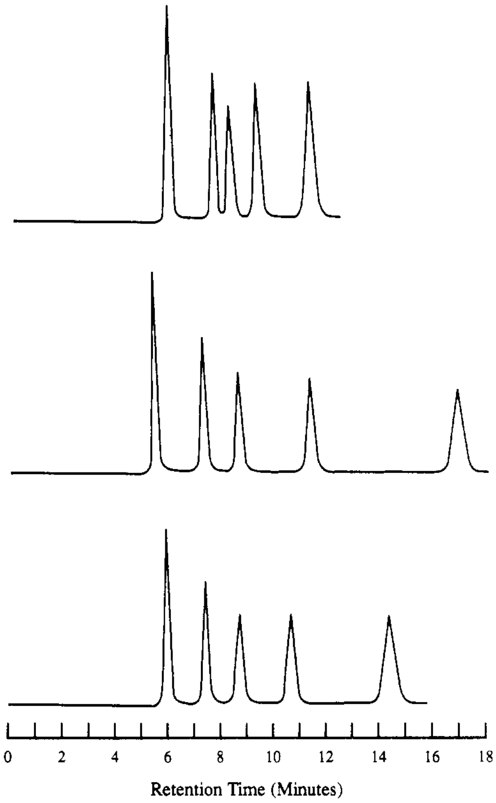

Figure 3. Reversed-phase liquid chromatography (RPLC) plot of theophylline, *p*-nitroaniline, methyl benzoate, phenetole, and *o*-xylene vs retention time in 50/50 (v/v) aqueous acetonitrile for Unisphere alumina particulate stationary phases coated with cross-linked PBD (top) or modified PBD: (middle) partially hydrogenated; (bottom) C_{18}-modified.

The relative retention of any pair of compounds, α, may be obtained from their respective retention times (t_r):

$$\alpha = \frac{t_{r2} - t_0}{t_{r1} - t_0} = \frac{t'_{r2}}{t'_{r1}}$$

where t_0 is the retention time of some inert solute. In this equation $t' \equiv t - t_0$ is referred to as the *adjusted* retention time. α may also be expressed in terms of the relative capacity factors, k':

$$\alpha = k'_2/k'_1$$

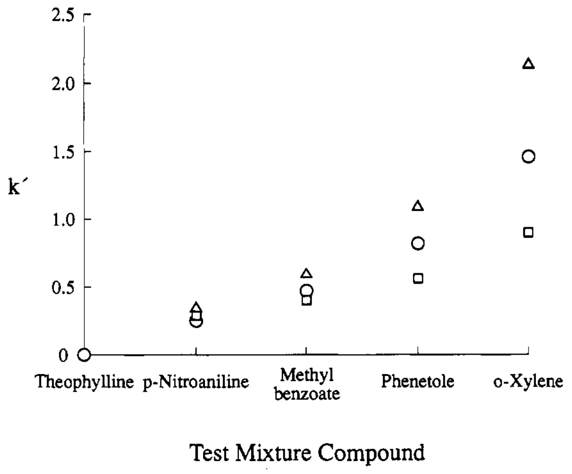

Figure 4. Comparison of RPLC capacity factors (k') of theophylline, p-nitroaniline, methyl benzoate, phenetole, and o-xylene for Unisphere alumina particulate stationary phases coated with cross-linked PBD (□) or modified PBD (partially hydrogenated (△); C_{18}-modified (○)).

The capacity factor k' may be determined directly from the chromatogram by dividing the *adjusted* retention time by t_0:

$$k' = \frac{t_r - t_0}{t_0} = \frac{t'_r}{t_0}$$

The value of the k' is particularly useful for evaluating polymer modified supports since it is proportional to the overall equilibrium constant for the phase distribution underlying the retention process.

The primary mechanism of solute retention in RPLC is a matter of ongoing debate (vide infra). Solute association with the lipophilic stationary phase may consist of partitioning, surface adsorption, or some combination of the two. The solvophobic theory proposed by Melander and Horváth[37] suggests that the retentive binding of solute to the stationary phase is an adsorption phenomenon[38] which is dependent on the free energy of solvation and the solute surface area. Partition models of retention[39] focus on the characteristics of the stationary phase, such as the surface density of bonded alkyl chains, average carbon number, and total carbon loading level. The majority of the experimental data is derived from monomeric-bonded silica and its relevance to polymer-coated media is not clear. Schomburg[8] has reported a strong dependence of retention time on polymer loading level, which he attributes to increased screening of surface silanol groups from the solution. We have found similar behavior for the polymer-coated alumina materials showing that comparisons of chromatographic performance should ideally be normalized relative to carbon content.

A key measure of the extent of lipophilization of the alumina surface may be found in the relative retention properties of o-xylene. For the PBD series (Table II), maximum hydrophobicity is observed for the partially hydrogenated material, which is devoid of 1,2 unsaturation. The significant increase in k' value with either 1,2 hydrogenation or C_{18} olefin grafting is particularly impressive in light of the significantly lower loading levels of these modified PBD materials compared with the native PBD/alumina sample (vide supra). The markedly higher reactivity of 1,2 unsaturation relative to 1,4 in PBD is well-known and, in most instances, is attributed to greater steric accessibility of the vinyl carbons. Intuitively, reactivity differences based on chemical accessibility should translate into differences in surface dependent physical processes such as the chemical partitioning effects present in RPLC. However, to our knowledge, no report of this particular structure/property relationship vis-à-vis RPLC has previously appeared.

The PBD-coated alumina which is modified by C_{18} olefin grafting during the cross-linking step exhibits an intermediate level of enhanced hydrophobicity ($k' = 1.46$; compared with 0.90 for PBD and 2.13 for partially hydrogenated PBD). The C_{18} olefin-grafted PBD has an enriched olefin content, particularly in the form of 1,2 isomer, relative to the parent PBD material. This is strong evidence that the grafting occurs primarily through the allylic carbon on the olefin. In fact, the allyl radical is expected to be the most abundant reactive species for this type of olefin. Given that the *total* polymer loading levels in the partially hydrogenated PBD and C_{18} grafted PBD-coated aluminas are comparable, the net hydrophobicity must reflect the balance of chromatographically active functional groups. Thus, the additional olefin, especially in the form of the 1,2 isomer, probably cancels some of the hydrophobic benefit arising from the C_{18} side chains. The overall linear chromatographic performance of the C_{18} PBD alumina (Figure 4) reflects a balance of properties ideally suited for many RPLC separations.

PBO-Coated Alumina. Another route to functionalized lipophilic surfaces on alumina utilizes coatings based on epoxidized polybutadiene (PBO). The unsaturation that is present in the PBO backbone allows immobilization and cross-linking on the alumina surface using standard radical initiators. The epoxy moiety provides a convenient site for the addition of pendant groups. The approach we have pursued has been to coat the inorganic support with the parent PBO, cross-link and immobilize, and then treat with a modifying reagent. The rationale for adding side chains to the PBO on the last step is to insure that polymer modification is concentrated at chromatographically accessible surfaces.

Three different chromatographic surfaces were generated via the in situ reaction of immobilized PBO on alumina. Acidic hydrolysis produced a coating with geminal glycol groups. Side chains comprising C_{10} and C_{11} hydrocarbons were prepared by the reactive addition of decylamine and undecyl alcohol, respectively. The epoxide ring-opening chemistry yields C_{10} and C_{11} graft attachment to the base coating through secondary amine or ether linkages with an equimolar amount of free α-hydroxy functionality.

NMR Characterization. Figure 5 shows the CPMAS ^{13}C NMR spectrum of PBO-coated alumina particles. As in the PBD-coated samples, resonances between 10 and 50 ppm are due to aliphatic carbons, and those in the range 110–150 ppm are assigned to olefinic carbons, with the major olefinic-carbon signal at 129 ppm due to 1,4-PBD units in the PBO polymer and the peaks at 115 and 145 ppm to 1,2-PBD units. In addition, there are two broad signals centered at 58 and 77 ppm that are due to aliphatic carbons bonded to oxygen. From solution NMR work on PBO (data not shown), and the spectrum of alumina particles coated with PBO that has been fully

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[37] Horváth, C.; Melander, W. *J. Chromatogr. Sci.* **1977**, *15*, 393.
[38] Colin, H.; Guiochon, G. *J. Chromatogr.* **1978**, *158*, 183.
[39] Scott, R. P.; Kucera, P. *J. Chromatogr.* **1977**, *142*, 213.

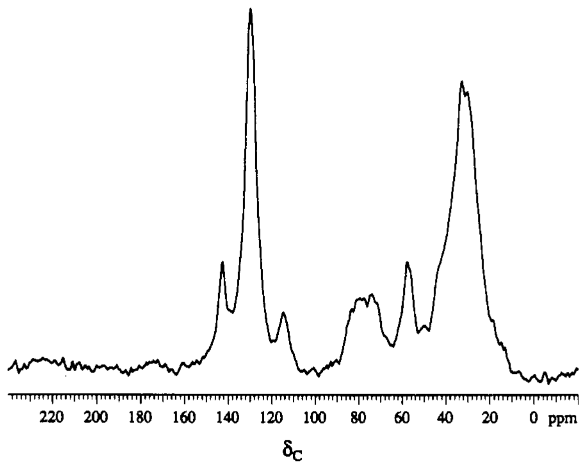

Figure 5. CPMAS ^{13}C NMR spectra of Unisphere alumina particles coated with cross-linked polybutadiene oxide (PBO), sample weight = 448 mg, 60 000 transients. Line assignments are: olefinic carbons (1,4-PBD units, δ_c = 129 ppm; 1,2 PBD units, δ_c = 115, 145 ppm); hydroxide carbons (δ_c = 75 ppm), epoxide carbons (δ_c = 57 ppm), other aliphatic carbons (δ_c = 10–65 ppm). All experimental conditions are as described in the caption to Figure 1.

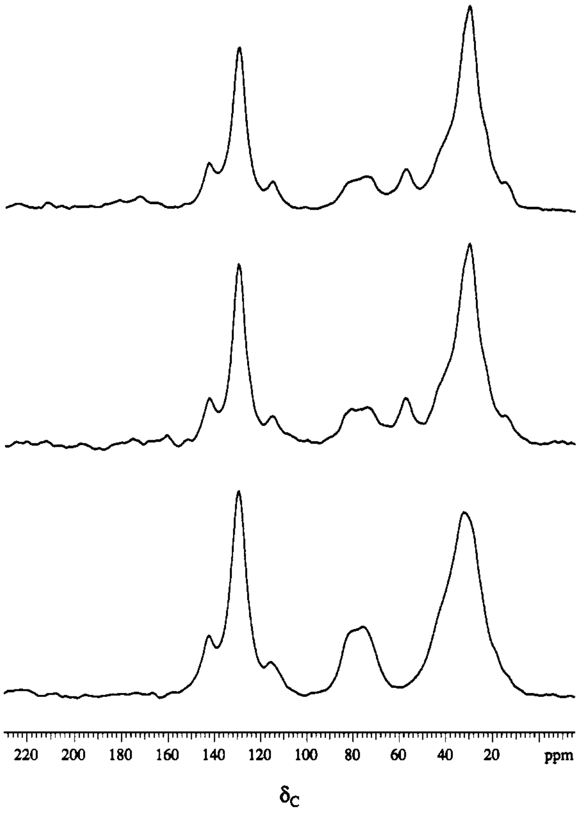

Figure 6. CPMAS ^{13}C NMR spectra of Unisphere alumina particles coated with cross-linked PBO in which the PBO polymer was further modified after being cross-linked: (bottom) fully hydrolyzed PBO, 366 mg, 60 000 transients; (middle) decylamine-modified PBO, sample weight = 401 mg, 50 000 transients; (top) undecyl alcohol-modified PBO, sample weight = 410 mg, 125 000 transients. All experimental conditions are as described in the caption to Figure 1.

hydrolyzed (Figure 6, bottom), the 55-ppm resonance is assigned to epoxide carbons and the 77-ppm signal to hydroxyl carbons which result from hydrolysis of some of these epoxides.

Figure 6 shows CPMAS ^{13}C spectra of PBO-coated alumina particles in which the PBO polymer was further modified after being cross-linked. Figure 6 (bottom) shows the spectrum of fully hydrolyzed PBO, in which all of the epoxides have been converted to hydroxide functions. Compared with the spectrum of PBO (Figure 5), the epoxide-carbon signal at 55 ppm has disappeared, while the hydroxide-carbon signal at 77 ppm has been enhanced. Figure 6 (middle and top) show the spectra of cross-linked PBO which has been reacted with decylamine and undecyl alcohol, respectively. Enhancements of the aliphatic-carbon region of the spectra relative to the spectrum of PBO reflect signals due to the C_{10} and C_{11} chains. The difference spectra of these particles before and after reaction with the amine/alcohol (differences not shown) consist entirely of aliphatic-carbon signals from the attached hydrocarbon chains, with the remainder of the spectra being unaffected by the reaction of PBO with the amine/alcohol. In particular, the absence of observable negative-going difference signals for the epoxide carbons indicates that only a small fraction of these sites actually react.

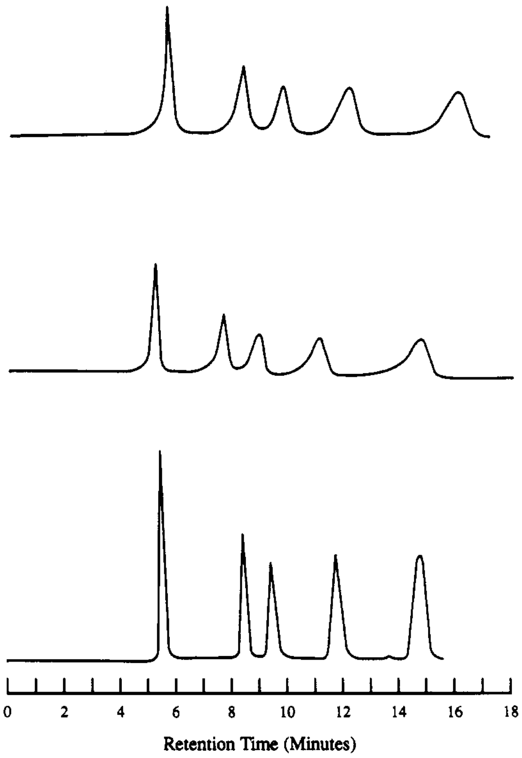

Figure 7. RPLC plot of theophylline, *p*-nitroaniline, methyl benzoate, phenetole, and *o*-xylene vs retention time for Unisphere alumina particulate stationary phase coated with cross-linked, modified PBO: (bottom) decylamine modified; (middle) undecyl alcohol modified; (top) fully hydrolyzed.

Chromatographic Performance. The geminal glycol-, C_{10}-, and C_{11}-containing coated aluminas were evaluated for RPLC chromatographic performance as described previously. The chromatograms and derived chromatographic parameters are listed in Figure 7 and Table III, respectively. The apparent hydrophobicities of the PBO-derived coatings compare favorably with the PBD alumina. Considerable peak broadening and fronting is observed for the fully hydrolyzed and C_{11}-alcohol modified films. These effects are likely due to the presence of highly polar hydroxyl groups. The presence of free hydroxyl groups in silica-based RPLC media, primarily in the form of silanol groups, has long been associated with detrimental mixed-mode interactions.[40] The chromatographic performance of the C_{10} amine modified PBO is superior, in terms of hydrophobicity and is substantially free of mixed-mode effects, despite the presence of one equivalent each of free hydroxyl and secondary amine for every C_{10}. This surprising result clearly indicates that the connection between free hydroxyl functionality in the stationary phase and diminished RPLC performance is not absolute. In fact there has been speculation that the presence of a hydrophilic underlayer, below the hydrophobic side chains, might result in a net improvement in the balance of properties for RPLC.[41,42]

Summary

The molecular structure versus chromatographic-property performance of a series of polymer-coated alumina particles has been evaluated. The coatings examined include cross-linked PBD, cross-linked PBO, and derivatives thereof. Solid-state ^{13}C NMR spectra of the coated alumina particles provide detailed structural information about the cross-linked polymers. Several key RPLC parameters were found to depend strongly on polymer composition. Among the factors which are important in determining the RPLC performance of coated-alumina particles are olefinic- vs aliphatic-carbon content of the cross-linked polymer, its percentage of 1,2 vs 1,4 olefin units, the presence of hydroxyl and amino functionality, and the polymer loading level.

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