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Poly(vinylbutyral-*co*-vinyl alcohol) Tacticity and Aluminum Oxide Surface Adsorption

Anthony A. Parker[†]

Aluminum Company of America, Alcoa Center, Pennsylvania 15069

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ABSTRACT: Solution-state ^{13}C NMR was used to study the mobility of poly(vinylbutyral-*co*-vinyl alcohol) (PVB) carbons in acetone-d_6, both in the presence and absence of aluminum oxide (α-alumina, Al_2O_3) powder. Apparent activation energies taken from variable-temperature T_1 spin−lattice relaxation measurements indicate that the dynamics of the aliphatic side chains and vinylbutyral backbone carbons are not affected by the presence of alumina. However, the dynamics of the vinyl alcohol sequences are influenced by alumina, which indicates that the alcohol groups experience an interaction with the alumina powder surfaces. This interaction is accompanied by a spectral line-shape change for the meso (isotactic) methine carbon triads, which shows that tacticity has an influence on the adsorption process.

Introduction

Poly(vinylbutyral-*co*-vinyl alcohol) (PVB) is well-known for use as a binder in alumina-based ceramic applications,[1,2] as well as an interlayer in safety glass applications.[3] In both cases, polymer interactions at the inorganic interface are of primary importance for controlling adhesion. In the case of ceramics, these polymer interactions can also influence slip rheology, ceramic green body properties, and binder burn-out behavior. Sacks et al.[4] have illustrated through FTIR studies that the vinyl alcohol (VA) groups in PVB are preferably adsorbed onto alumina. Roosen et al.[5] used synthetic variations of PVB to show that adsorption increases as the overall VA content increases and as the fraction of syndiotacticity increases.

PVB is generally synthesized by a two-step process involving first the hydrolysis of poly(vinyl acetate) (PVAc) to yield poly(vinyl alcohol) (PVA), followed by reaction with butyraldehyde. The resultant polymer is essentially a copolymer of vinylbutyral and vinyl alcohol as shown in Figure 1, with a small residual concentration of unreacted vinyl acetate. Hence, the microstructure of the final polymer is a complex reflection of the microstructure of the starting materials—PVAc and PVA. Thus, although Roosen's studies could be applied to polymers of known and pure tacticity, commercial grades of PVB contain a wide array of stereosequences which makes it difficult to separate the effects of microstructure with conventional analytical techniques. Given that ^{13}C NMR can be used to study polymer functional group dynamics in slurries that contain powders like alumina,[6] an attempt was made in this study to determine the effect of alumina on the dynamics and on the conformational behavior of VA stereosequences in a commercial PVB copolymer.

Experimental Section

Poly(vinylbutyral-*co*-vinyl alcohol) (PVB) containing approximately 14% vinyl alcohol by weight (35 mol % VA) was obtained as the commercial product "B-79 Butvar" from the Monsanto Chemical Co. The PVB was dissolved at a concentration of 22% by weight in acetone-d_6 from Aldrich and was then placed into 10-mm-o.d. glass NMR tubes for subsequent ^{13}C NMR analyses. Deuterated acetone was chosen as the solvent since it served as a field lock and as a chemical shift reference with no resonance overlap in the VA methine carbon region. Low-power proton scalar decoupling was used during the acquisition of all ^{13}C spectra.

Fast inversion−recovery experiments (180°−τ−90°−acquire−recycle)[7] were performed on the 22% PVB solution (without and later with alumina powder) to measure ^{13}C T_1 spin−lattice relaxation values using a Varian XL-200 NMR at a ^{13}C frequency of 50 MHz. Unlike standard inversion−recovery, fast inversion with short recycle times leads to a quasi-equilibrium condition where the spin populations of the upper and lower energy levels (for spin $^1/_2$ nuclei) are closer to equality. This results in a lower signal intensity since less nuclei are available for resonance excitation. However, the spins still decay to the lattice with the same exponential relaxation rate constant, T_1. Thus, fast inversion−recovery can yield the same motional dynamics information with a significant reduction in experimental time. Measurements were made between the temperatures of 0 and 40 °C using a ^{13}C 90° pulse of 18.0 μs and a recycle time of 1 s with an average of 64 transients per delay time (τ). A total of 10 delay times was called in a random sequence ranging from 0.005 to 4.0 s. T_1 values were then calculated from single-exponential fitting of the integrated intensity vs delay time data with resulting correlation coefficients of 0.98 or better using Varian software.

In a separate set of variable-temperature experiments, the same 22% PVB solution was slurried with 3% Alcoa A-4000 alumina powder by weight (α-Al_2O_3, 5-μm diameter, 0.8 m^2/g surface area) to determine the effect of alumina on T_1 relaxation times. As in previous studies,[6] all experiments (with and without alumina) were performed without sample spinning to avoid complications due to centrifugal separation of the powder. Also, only a small percentage of alumina was used to minimize its potential effect on solvent viscosity,[8] which could indirectly influence polymer dynamics.

In addition to fast inversion−recovery, quantitative spectra were also obtained (with long recycle delays of 5 times the longest T_1) for PVB in acetone-d_6 at 20 and 40 °C and for the same sample in the presence of alumina at 20 °C.

Results and Discussion

Vinyl Alcohol Carbons in PVB. Spectral Assignments. The ^{13}C spectrum for PVB in acetone−d_6 is shown in Figure 1 with peaks referenced to the acetone septet at 29.8 ppm. Although the fundamental peak assignments for PVB carbons have been made,[9,10] the exact chemical shift effects due to cotacticity sequencing of vinylbutyral (VB) with vinyl alcohol (VA) groups have not been quantified. PVB is actually a copolymer of VB and VA monomeric units, where the VA units in PVB have been shown to display the same triad microstruc-

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[†] Present address: Libbey Owens Ford Co., 1701 E. Broadway, Toledo, OH 43605.

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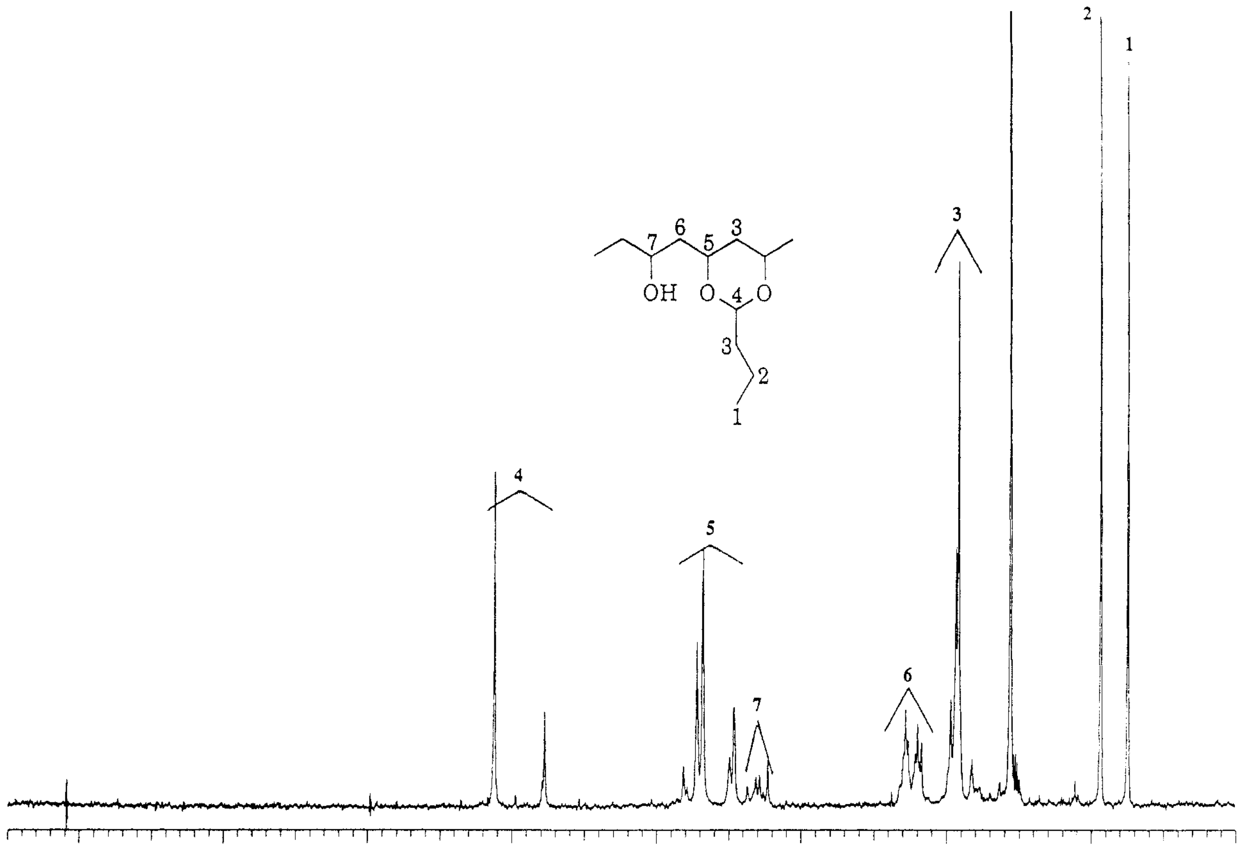

Figure 1. ^{13}C solution spectrum of PVB, 22% in acetone-d_6 at 20 °C.

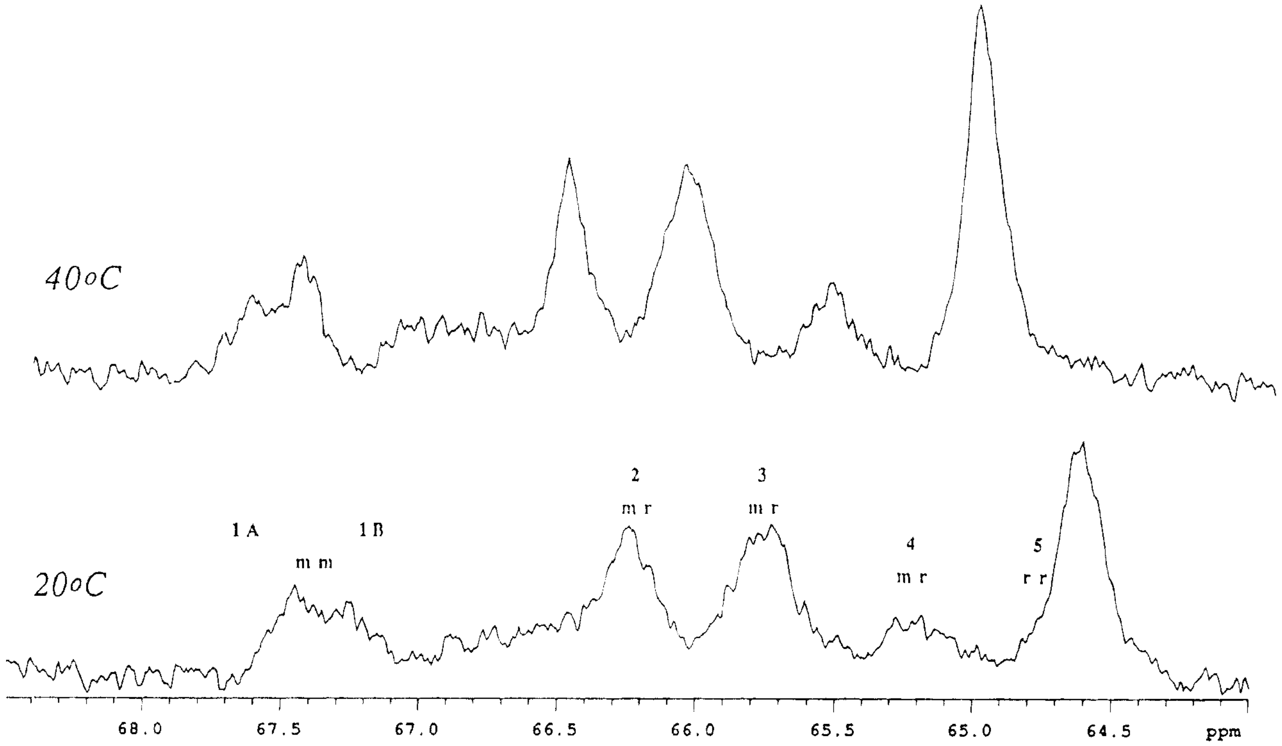

Figure 2. ^{13}C solution spectra of the VA methine carbon region at 20 and 40 °C, 22% in acetone-d_6.

ture as was previously noted for the poly(vinyl alcohol) homopolymer (PVA).[9,11] Despite the low molar percentage of alcohol units in the PVB analyzed both by Bonesteel[9] and by our group (34 mol % VA, B-79 Butvar in this case), it appears that the VA groups exhibit triad block structure as evidenced by the fine splitting in the VA methine regions between 64 and 68 ppm. This implies that "blocks" of alcohol groups are available for adsorption onto the surface of inorganic materials like aluminum oxide.

Figure 2 provides specific spectra of the VA methine carbons at 20 and 40 °C. The complicated triad structure is evidenced by five separate peaks between 64 and 68 ppm. Although the entire spectrum is observed to shift as the temperature is increased, the spectral changes are reversible, and the relative identity of the

Table 1. Mole Percentages of Methine Alcohol Groups as a Function of Sequencing, Based on Integrated Intensities from the VA Methine Carbon Region As Shown in Figures 3–9 for PVB in Acetone-d_6[a]

VA carbon peak	sequence	mol % VA
1A + 1B[b]	mm = mmmm + mmmr	5 = 3.3 + 1.7
2	mr	6.9
3	mr	6.9
4	mr	3.3
5	rr	11.9
total		34

[a] Intensities are normalized to account for a total of 34 mol % VA in the PVB copolymer. [b] Peaks 1A and 1B are contained within meso mm triads, but their relative intensities may provide information about pentad microstructure concentrations.

Table 2. Moles of Triad and Pentad Sequences per PVB Chain[a]

peak	sequence	no. per chain	peak	sequence	no. per chain
1	mm	5	3	mr	7
1A	mmmm	2	4	mr	3
1B	mmmr	1	5	rr	13
2	mr	7			

[a] (1) PVB M_n = 100 000, 1.66 × 10^{-19} g/chain. (2) 14% VA by weight = 2.32 × 10^{-20} g/chain = 5.28 × 10^{-22} mol/chain = 317 VA groups/chain. (3) Mole % triads = (mol % VA group)/3. (4) Mole % pentads = (mol % VA group)/5. (5) Number of triads per chain = (mol % triad/100)(317)/3. (6) Number of pentads per chain = (mol % pentad/100)(317)/5.

peaks remains unchanged. The peak at highest field (peak number 5 near 64 ppm) and the peak at lowest field (peak number 1 near 67 ppm) are characteristic of syndiotactic (rr) and isotactic (mm) VA triads, respectively.[11] The other three peaks at intermediate fields are associated with "atactic" (mr) VA sequences. Unlike PVA homopolymer which displays only one atactic triad peak, the VA sequences in PVB display three peaks (peaks 2–4) since the alcohol groups can be sequenced in cotactic form with vinylbutyral groups (either m**r**, m**m**, or r**m**, where the underlined bold designation refers to one VB methine carbon). The exact assignments for these cotacticity carbons have not been determined. However, peaks 1 and 5 can still be unambiguously assigned to the mm and rr VA triads.

Effect of Temperature on Alcohol Sequence Conformations. The molar percentage of each type of alcohol carbon is shown in Table 1 based on integrated intensities and based on the total mole percentage of alcohol carbons in the polymer (34 mol %). The splitting of the mm peak could be consistent with sequencing of mmmm and mmmr VA pentads for the low- and high-field components, respectively (peaks 1A and 1B as shown in Figure 2).[11] However, given that isotactic VA monomer sequences are preferentially reacted with butyraldehyde during the synthesis of PVB,[9] the probability of finding residual isotactic pentads of pure VA monomeric sequences will be very low. This argument is illustrated in Table 2, where, based on the integrated intensities, only two mmmm VA pentads on the average can exist per PVB chain. Thus, it is more probable that the splitting of the mm peak is consistent with a sequence-dependent variation in backbone chain conformation.[9]

The relative intensities of the mm peaks 1A and 1B are also observed to change reversibly upon heating and cooling, whereas the other VA sequences do not appear to change shape. This phenomenon can be linked to a reversible change in motional dynamics with temperature; either from motional components that affect T_2 and hence line shape[13] or from a trans–gauche conformational change, where a change from an all-trans conformation to a conformation with more trans–gauche character can result in an upfield shift due to the γ carbon shielding effect.[12]

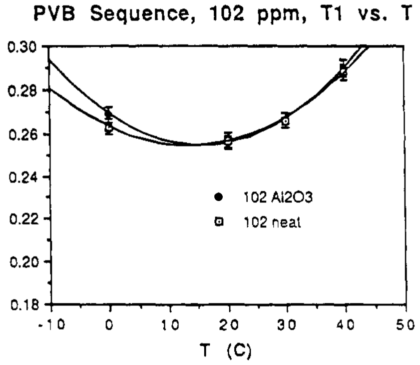

Figure 3. T_1 spin–lattice relaxation time vs temperature for the VB backbone carbon at 102 ppm, in the presence and absence of alumina.

Normally, the rotational barriers for macromolecules in solution are sufficiently low (ca. 2 kcal/mol for polyethylene) to allow for an isotropically averaged signal on the time scale of the NMR experiment, so that the γ shielding effect from rotational isomerization is not observed.[12] However, in the solid-state where multiple packing environments can exist or even in the liquid state when the potential energy barrier for backbone rotation is high (i.e., when the rate of exchange between trans and gauche conformations is slow), rotational isomeric splitting will be observed in an NMR spectrum. At its full extent with no exchange on the megahertz NMR time scale, the γ shielding effect would result in a −5.3 ppm chemical shift separation between conformers (in this case, the separation is approximately 0.3 ppm). However, the actual extent of separation will depend on the equilibrium fraction of gauche bonds (which in turn depends on the potential barrier to backbone rotation) and on the rate of exchange between the conformers. Higher temperatures could increase the probability of gauche conformations and thus account for the increase in 1B intensity at the expense of a slight diminution in 1A intensity.

Since this process is reversible with temperature, a conformational change would be an acceptable mechanism for the change in line shape. However, independent of the exact mechanism, it is important to note that this phenomenon is restricted to the mm (isotactic) triads. This will be important when considering the effects of Al_2O_3 on the motional dynamics of the VA sequences.

Effect of Alumina on VB Motional Dynamics. The results of the T_1 spin–lattice relaxation experiments show that the motional dynamics of VB sequences are not affected by the presence of alumina. On the other hand, the motional dynamics of the VA sequences are influenced by alumina, as would be expected based on the previous studies by Sacks et al.[4] Figure 3 shows T_1 as a function of temperature for the PVB backbone carbon at 102 ppm. This particular carbon has been shown to be representative of VB backbone motional behavior without complications from tacticity.[10] With the exception of data at 0 °C, there is a clear overlap between T_1 values, independent of the presence of alumina.

Further evidence for the lack of interaction between VB sequences and alumina comes from an analysis of

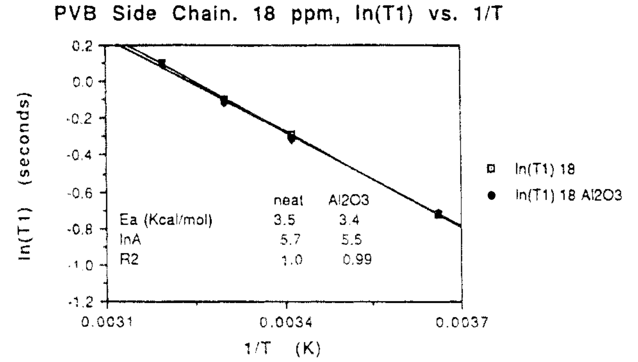

Figure 4. T_1 spin–lattice relaxation time vs temperature for the VB aliphatic side-chain methylene carbon at 18 ppm, in the presence and absence of alumina.

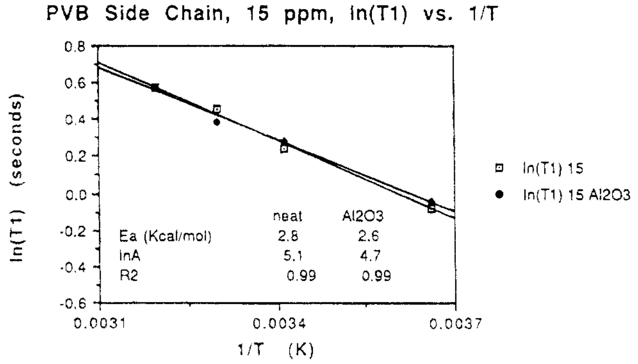

Figure 5. T_1 spin–lattice relaxation time vs temperature for the VB aliphatic side-chain methyl carbon at 15 ppm, in the presence and absence of alumina.

the temperature-dependent T_1 behavior of the VB side-chain carbons at 18 and 15 ppm as shown in Figures 4 and 5, respectively. These data plots show that both the activation energies and Arrhenius prefactors are unchanged by the addition of alumina.

Previous NMR studies of PVB have shown that the 15 ppm methyl group motion is sensitive to free volume and hence can serve as an internal measure of the change in viscosity due to any alteration of the PVB chain's environment. For example, the activation energy for PVB methyl group motion in the solid state has been found to be 2.7 kcal/mol (±0.2) independent of the presence of plasticizer, which shows that the character of the methyl group motion is unchanged by the presence of plasticizer in its environment.[14] However, the Arrhenius prefactor decreases in the presence of plasticizer, which shows that the frequency of the motional process can change as a function of its environment.

Interestingly, the activation energy for methyl group motion in acetone-d_6 also remains at about 2.7 kcal/mol independent of the presence of alumina as shown in Figure 5. Since the prefactors are also not significantly different, it appears that the dynamics near the VB sequences are not influenced by alumina. This indicates that the VB units are not interacting with alumina and that the addition of 3% alumina by weight is not dramatically changing solvent viscosity and hence polymer viscosity in the vicinity of VB groups.

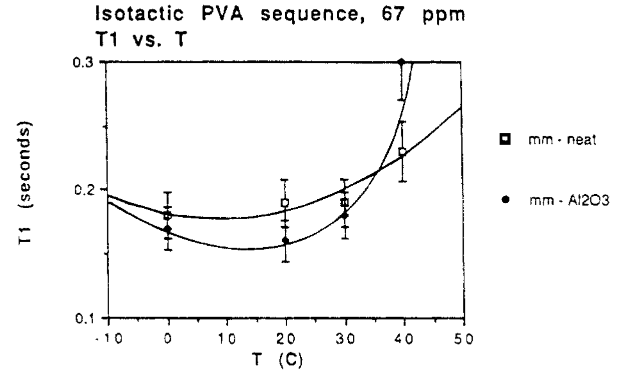

Figure 6. T_1 spin–lattice relaxation time vs temperature for the VA mm methine triad (isotactic carbons 1A and 1B), in the presence and absence of alumina.

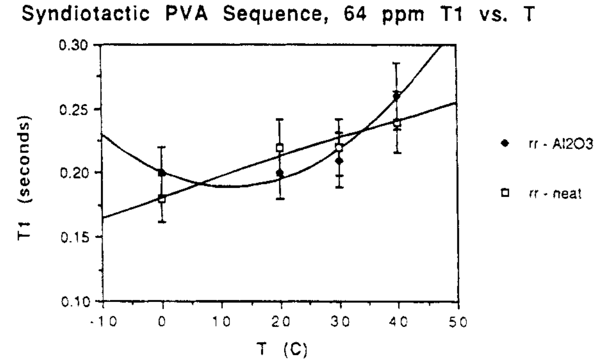

Figure 7. T_1 spin–lattice relaxation time vs temperature for the VA rr methine triad (syndiotactic carbon 5), in the presence and absence of alumina.

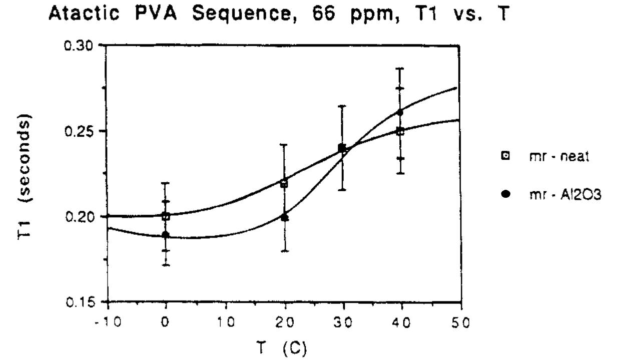

Figure 8. T_1 spin–lattice relaxation time vs temperature for the VA mr methine triad (atactic carbon 2), in the presence and absence of alumina.

Effect of Alumina on VA Motional Dynamics. As shown in Figures 6–8, the addition of alumina results in a change in the T_1 temperature dependence for the mm, rr, and mr VA sequences, respectively. Although the motional dynamics of all VA sequences appear to change, the isotactic mm sequence near 67 ppm exemplifies the most significant change after considering the amount of overlap due to error. Because of the complex temperature-dependent behavior for all of these sequences, it is difficult to equate these changes with specific changes in motion. However, VA motion is hindered by the presence of alumina at 20 °C since T_1 values are shorter and since the process is occurring on the "fast" motional side of the T_1 minimum.[13]

Figure 9 shows quantitative spectra for comparison of the VA methine carbons in the presence and absence of alumina at 20 °C. All of the sequences become slightly broadened in the presence of alumina which shows the sensitivity of the line width and hence T_2 to these interactions. However, the isotactic mm peaks (1A and 1B) show the most distinctive line-shape changes of all the VA sequences. The relative shift in the intensities of peaks 1A and 1B at 20 °C in the presence of alumina appears similar to the line-shape change which was generated by heating the neat polymer in solution to 40 °C as shown earlier in Figure 2.

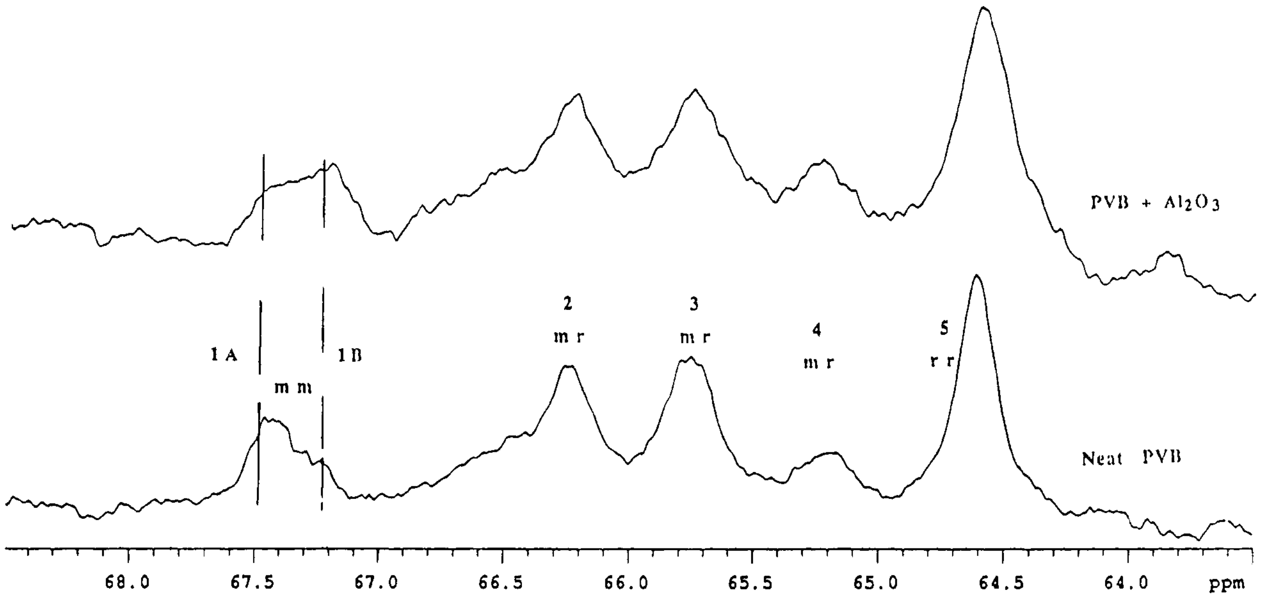

Figure 9. ^{13}C solution spectra of PVB vinyl alcohol methine carbons at 20 °C, 22% in acetone-d_6, in the presence and absence of alumina.

Based on the previously discussed reasons for the temperature dependence of the mm VA line shape in the absence of alumina, there are at least two possible reasons for the change in line shape which occurs in the presence of alumina. First, the change in line shape could be due to a change in motional dynamics which influences T_2 and hence the line width. Thus, the decrease in 1A intensity could be related to the preferential adsorption of isotactic-rich VA sequences. Such preferential adsorption would hinder the mobility of the meso methine carbons and would thus broaden the line width.

Second, however, the change in line shape could be due to a conformational change upon adsorption. In this case, the adsorption of mm sequences would favor a trans to gauche conformational change, which would explain the increase in 1B intensity along with the decrease in 1A intensity. This is the most probable mechanism since it would be consistent with an alternating placement of alcohol groups on the alumina surface and it would be consistent with the observed change in dynamics for the rr and mr sequences, both of which contain alternating alcohol groups. This would also be consistent with Roosen's finding that higher levels of syndiotacticity and hence alternating alcohol placement result in higher adsorption levels of PVB onto alumina.[5] However, independent of the exact mechanism, the data indicate that the isotactic sequences undergo a specific motional change in the presence of alumina, hence supporting the general hypothesis that tacticity is an important variable which affects the adsorption process.[15]

Finally, although NMR generally shows that VA sequences are influenced by the presence of alumina, these results cannot be used to strictly differentiate between carbon moieties on solution extended tails, on loops, or on surface-bound species. Instead, it must be remembered that all of these T_1 values (as well as the line shapes) represent dynamic time averages of carbon nuclei which are in equilibrium with adsorbed, partially desorbed, and completely desorbed species.

Impact of PVB Tacticity on Adsorption and Ceramic Slip Processing. It is generally understood that polymer adsorption on ceramic powders can have a dramatic influence on the rheology and hence on the processability of high solids ceramic slurries. Given that the degree of PVB adsorption will determine the degree to which it behaves as a steric stabilizer during ceramic slip processing, it follows that the vinyl alcohol content and tacticity can have a dramatic influence on the properties of ceramic slips. In our prior work with sedimentation experiments,[16] we showed with a model series of dispersants that trifunctional alcohol "anchoring" groups are more efficiently adsorbed on the alumina powder surface than both diol and monoalcohol anchoring groups. In fact, octanetrimethylol, octanoic acid, and hydrolyzed octyltriethoxysilanol will completely adsorb at very low solution concentrations—equivalent to concentrations of 5–10 μmol/m^2 in a noncompetitive solvent medium. These coverage levels are consistent with strong surface adsorption where all of the available surface sites are saturated on the time scale of a sedimentation test. On the other hand, octanediol requires higher solution concentrations, equivalent to 30 μmol/m^2 for effective adsorption, and 1-octanol must be present in solution concentrations which exceed 2000 μmol/m^2 in order to get similar degrees of adsorption. These results indicate that monoalcohol adsorption is not efficient and that a much higher solution concentration is required to drive the equilibrium toward complete adsorption.

Given that PVB is composed of monoalcohol carbons (which are inefficient adsorbers) and given that the NMR data suggest that these alcohol groups interact with alumina, it follows that the adsorption behavior of PVB will be sensitive to variations in the total molar percentage of alcohol groups. Also, regardless of the exact mechanism for the isotactic VA sequence adsorption (trans to gauche conformation change vs motional dynamics change), the NMR data suggest that the tacticity of the vinyl alcohol groups will also be important in the adsorption process.

Table 3 shows the approximate number of moles of each sequence that is availabe for surface adsorption for the case of the NMR samples (3% by weight alumina) and for the case of a typical high solids slip for producing a ceramic green body, which can contain up to about 70% powder by weight. In the case of the production slip, the concentrations of available sequences are critically below the levels required for driving the

Table 3. Moles of VA Triads and Pentads per Square Meter of Powder Surface Area for Samples Analyzed by NMR and for a Typical Production Slip

		moles of VA sequence/m^2	
peak	sequence	NMR sample	typical slip
1A + 1B	mm triad	4.8×10^{-4}	4.2×10^{-6}
1A	mmmm pentad	1.9×10^{-4}	1.6×10^{-6}
1B	mmmr pentad	9.9×10^{-5}	8.5×10^{-7}
2	mr triad	6.7×10^{-4}	5.8×10^{-6}
3	mr triad	6.7×10^{-4}	5.8×10^{-6}
4	mr triad	3.2×10^{-4}	2.5×10^{-6}
5	rr triad	1.2×10^{-3}	9.9×10^{-6}

[a] Notes: (1) NMR samples contain 22% PVB, 3% alumina, and 75% acetone-d_6 by weight. This equates to 0.029 mol of VA groups/m^2 of alumina. (2) A typical production slip contains 4.42% PVB, 1.48% plasticizer, 23.6% solvents, and 70.5% powders by weight. This equates approximately to 2.5×10^{-4} mol of VA groups/m^2 of powder surface. (3) (Moles of VA sequence/m^2) = (mol of VA groups/m^2)/(monomer units per sequence).

monoalcohol adsorption equilibrium to complete surface coverage.[16] Even in the NMR case, where the ratio of polymer to alumina is higher, the concentrations of various sequences are low compared to the equilibrium adsorption concentration that seems to be required for monoalcohol carbons. This in part explains why the VA relaxation behavior is sensitive to the addition of only a small amount of alumina.

Taken collectively, the results of these studies imply that macroscopic properties such as ceramic slurry rheology will be extremely sensitive to minor variations in the microstructure of the dispersant/binder. In the case of PVB (a polymer that can perform the role of both binder and dispersant), any variation in hydroxyl content and tacticity will have an influence on adsorption and hence on macroscopic rheological properties.

Conclusions

Temperature-dependent T_1 experiments show that the motional dynamics of VB backbone carbons are not affected by the presence of alumina. Furthermore, the activation barriers and prefactors for VB side-chain motions remain unchanged in the presence of alumina. On the other hand, the dynamics of vinyl alcohol sequences are influenced by alumina, which suggests that the alcohol groups are preferentially involved in the adsorption process. Tacticity also plays a role in this process as can be seen from a preferential change in the line shape of the mm VA triad peak in the presence of alumina, which is consistent with either a change in conformation and/or a change in motional dynamics upon adsorption of the isotactic sequences. Thus, this research has shown that functionality and tacticity are important variables that can influence polymer interactions with inorganic surfaces like aluminum oxide. Although the relative ranking of these variables may be system dependent, both variables should be considered when studying the interactions between polymers and inorganic surfaces.

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