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NMR Studies of Organic Thin Films

by

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## 1. INTRODUCTION

In many respects, the most exciting and important developments in science and technology often occur at interfaces. For technological advances this is because of the different backgrounds and views of the scientists involved. In the materials area, different species can be combined in ways which produce new materials whose properties can be significantly different from any component. In general, the properties of materials containing multiple phases are *not* necessarily the superposition of the properties of the components. The influence of the interfacial layer or layers, plays a significant role in the determination of the bulk properties in a wide range of materials.

The purpose of the present work is to review NMR studies of thin organic films--particularly those at the interface with solid substrates. These typically have relevance in composite materials used for structural applications, although other applications of these materials in catalysis, separations, and other surface modifications may also be important. For the purpose of this review, the term film implies something that is both semi-permanent and semi-continuous. Thus, this review will be restricted to organic materials strongly bound to a substrate, including those which are permanently attached to a surface. Adsorbed polymers and non-covalently bound surfactants are included, however, other small molecules that are simply "adsorbed" reversibly and discontinuously are not. For example, this excludes materials used as catalysts such as zeolites. A general discussion NMR studies focussing on polymer blends, interpenetrating networks, and multiphase (crystalline/amorphous) polymer systems has also been omitted.

The major goal of this work is to review how NMR can yield specific information on the structure and dynamics of the interfacial material and how this might be different from that in the bulk phase. In some respects, the number of papers in this area is not yet large--there are many more papers that deal with the interaction of small molecule

adsorbates. The lack of papers is probably because of the inherent insensitivity of the NMR technique and the limited ways in which one can distinguish between bulk and interfacial materials. However, for appropriate systems, the information obtained from NMR experiments is of exceptional importance in the understanding of microscopic properties of interfacial thin films.

## 2. BACKGROUND

### 2.1 Prior Reviews

Several authors have previously reviewed NMR studies of systems related to those included in this report. Resing (1) reviewed the relaxation effects of adsorbed chemical species and Pfeifer (2), the basic principles of NMR of surface adsorbed species focussing on how their absorption might effect common NMR parameters. Special emphasis was placed on phenomena such as exchange and its effects on the lineshapes, diffusion, and relaxation behavior. Examples of these included the i) silica/benzene, ii) surface hydroxyl groups interacting with adsorbates, and iii) NaX-zeolite/water systems. An extensive literature survey was also included as a table. Later Pfeifer et al. (3) extended this work to cover the NMR studies of molecules adsorbed on porous solids, with special emphasis on zeolites. Advances in cross-polarization (CP) and magic-angle spinning (MAS) have significantly increased the knowledge of the properties of both the adsorbate and substrate in these systems. Duncan and Dybowski (4) have reviewed catalytic and chemically adsorbed species. All three of these reviews have some overlap with the current topics, but none of them center on them.

More recently, a few reviews have been partly targeted at the characterization of surface-bound alkylsilanes (5-10) and/or polymers (10-15) adsorbed on solid surfaces. Zaper and Koenig (5) have reviewed the applications of high resolution solid-state NMR to both coupling agents and catalysts. For the coupling agents, coverage of  $^{13}\text{C}$  and  $^{29}\text{Si}$  chemical shifts, cross polarization and relaxation rates provided an initial picture of the structure and dynamics of these species. Boddenberg (6) has reported a variety of deuterium NMR studies of labelled chemical and physisorbed materials including a silane, but most of the material covered was from non-bonded small organic molecules. Blum (7) has focused on the use of isotopes in

surface-bound species such as silane coupling agents. The NMR-active isotopes provided the contrast and sensitivity necessary to probe the interface, even in composite materials. Albert and Bayer (8) have reported on the applications relative to bonded phases in chromatography focussing on the characterization and modifications of silica gel and silica. Legrand et al. (9) have a limited review of solid-state NMR of materials. Choli (10) has reported on the use of multinuclear NMR in industrial applications of polymeric materials. He covered a few select applications of coupling agents and also polymers and at interfaces.

The NMR behavior of polymers at interfaces has received less attention. Grandjean (11) has recently reviewed studies of interfacial phenomena with a focus on interfacial molecules, ions at the interface, and interphase components. This report included a few of the studies of polymers adsorbed at interfaces. Cosgrove et al. (12,13) have described NMR studies of interfacial polymers with particular emphasis on the work done at Bristol. Blum (14) has also reviewed experiments on polymers at interfaces in colloidal suspensions, composites, and surface coatings.

## 2.2 General NMR Considerations

The fundamental reason for using NMR to study thin films is to gain information on either structure or dynamics, or both. Structural studies are used to determine the composition and bonding of the interfacial species (perhaps across the interface). NMR is also one of the few ways to determine the molecular motion which occurs in this very thin layer. The relationship between the physical properties of polymers and molecular motion are established, but is difficult to probe the physical properties of interfacial layers that may be as thin as say 10-100  $\mu\text{m}$ . Consequently, it is hoped that the measurement of the mobility of the interfacial dynamics will allow the prediction of its physical properties.

There are several basic advantages that NMR has for the study of interfacial or interphase phenomena. One of the most significant is that the optical clarity of the sample is unimportant. This is contrasted with optical studies, where this is not the case. Because of this, NMR has the ability to probe the inside of composite materials for most nonferrous materials. For these heterogeneous materials, magnetic susceptibility effects usually do not create major complications in obtaining spectra.

A wide variety of different NMR experiments are available to the experimenter, although the choice of "solid-like" or "liquid-like" experiments are often dictated by the properties of the system. Advances in the application of solids NMR techniques (15) have significantly broadened the potential use of NMR to organic films. In general, most organic/interface systems offer a variety of nuclei to probe. Generally, different nuclei in the same system, even in the same molecule, provide complementary information. Different experiments on the same nucleus can be made to elucidate different surface features. The measurement of NMR parameters including: isotropic chemical shift and chemical shift tensor; relaxation and cross-polarization parameters; plus line shape analyses provide information on different aspects of the system.

In many cases, contrast in the NMR experiment can be achieved through the creative use of different pulse sequences. For example, the surface of the  $^{29}\text{Si}$  atoms in silica may be probed selectively through the use of cross polarization. The transfer of magnetization through the protons is only efficient near the surface because that is where the protons reside. Isotope enrichment can also provide the necessary contrast between bulk and interfacial material. Common nuclei for this include  $^2\text{H}$ ,  $^{13}\text{C}$ , and possibly  $^{15}\text{N}$  (7). Since these isotopes have low isotopic abundance, background from naturally abundant isotopes does not usually interfere in spectra with labelled species. For example, this contrast is needed to distinguish the carbons in a silane coupling agent on a silica surface from the carbon used in the matrix resin.

There are some serious limitations to NMR studies of interfacial species. The chief problem is sensitivity. The inherent insensitivity of NMR is such that high surface area materials need to be used as substrates. While many of those surfaces studied are indicative of the behavior in the actual application, it would be preferable to study the actual system. For example, studies of the polymer coating on an aluminum container may have to be simulated by studies of the polymer coating on high surface-area alumina.

### 3. Polymers at Interfaces

The adsorption of polymers at interfaces is rather different from that of small molecules. Polymers may associate with the surface through covalent or ionic bonds, polar, and even van der Waals forces. The range of these direct interactions with surface groups is quite short and on the order of a few Ångstroms. If this were the whole effect, the adsorption and dynamics of attached polymers would be similar to small molecules. Since the polymer segments attached to the interface are covalently bound to other segments, the surface binding may impact the entire chain. In fact, it may even impact neighboring chains. The two obvious effects of this interaction are restrictions of (i) overall motions of the adsorbed chain and (ii) conformational states and internal motions of the chain segments.

The importance of the adsorption of polymers at interfaces is such that a number of reviews exist on the structure, kinetics, and dynamics of adsorbed macromolecules (14,16-23). It is convenient to think of adsorbed polymers as either randomly or terminally attached. Polymers which randomly attach are usually homopolymers or random copolymers without "adsorbing" endgroups. These adsorb to solid surfaces with certain segments in direct contact with the surface and others not in direct contact. However, even though a particular segment may not be directly attached, its covalently-bonded neighbors may be, so that it may have more in common with directly attached segments than the other unattached segments. An example of this is shown in Figure 1 where portions of the chain are labelled trains, loops, and tails in accordance with current convention. Trains are polymer segments either directly attached or close to segments directly attached. The local motions of these segments are expected to be relatively restricted. Loops and tails are segments further away from the surface which end in either two or one train, respectively. It is generally accepted that these segments are more mobile than those in trains. However, they are

not necessarily less mobile than those in the corresponding bulk or solution systems (*vide infra*).

Terminally-attached polymers may be attached to the surface through a variety of mechanisms. Bonding with single (or at least small) points of attachment are possible through covalent bonding, ionic, zwitterionic, or polar groups normally attached at the end of the polymer chain. The use of anionic synthesis where the end groups of the polymer are controlled is convenient for making these polymers. Larger attachment points are possible through the use of block polymers. In most systems, the thermodynamics of mixing is such that one component selectively adsorbs at the surface.

For the adsorbed blocks, the distributions of segments into trains, loops, and tails depend on the specifics of the system. The attached block typically ends in an unattached block in the form of a tail. The conformation of the tail is a function of its length, interaction with the surroundings, and distance between neighboring terminally-attached chains. Following the accepted terminology (22), these segments are shown for terminally attached polymers in Figure 1 as "mushrooms" and "brushes". Generally mushrooms are expected for dilute systems while brushes are expected when the chains are tightly packed.

<Fig. 1>

Finally, in order to get an appropriate picture of polymers adsorbed to interfaces, it is necessary to compare their behavior to those in the parent systems. To this end, detailed knowledge from NMR is available and summarized in several reviews. Cheng (24) and Axelson and Russell (25) have reviewed solids and liquids characterization of polymers. Yu and Guo (26) and Volkel (27) have reviewed  $^{13}\text{C}$  solids studies of polymers. Roy and Inglefield (28) have reviewed studies of local motion in solids and Jelinski (29) has reported the use of deuterium in polymer chain

studies. Blümich et al. (30) and Spiess (31) have reviewed solid-state applications with special emphasis on multidimensional studies. Heatley (32) has reviewed relaxation studies of polymers in solution. The relationship between NMR parameters and mobility has been summarized by McCall (33) in terms of relaxation maps from various forms of spectroscopy. Of significance to the present work is the observation that the NMR  $T_g$  is typically on the order of 30-50 °C higher than that observed by differential scanning calorimetry (DSC)--reflecting the higher frequency of the NMR experiment. Several books (15,34,35) and collected works (36,37) also have good reference to polymer studies. These provide good starting points for understanding bulk properties so that the *differences* observed in adsorbed polymers can be understood.

### 3.1 Solid-Liquid Systems

Polymers adsorbed on solid surfaces in contact with a liquid are important for structural coatings, dispersion stabilizers and adhesives. The conformation and dynamics of the macromolecule at the interface are affected by the polymers interaction with the surface and the solvent(s) present. A variety of magnetic resonance techniques have been used to characterize these systems. If the polymer segments are extended into the solvent region or there is significant solvent penetration into the polymer layer, NMR solution techniques may be appropriate to characterize the material. If the polymer is tightly bound to the surface with little solvent penetration, this part of the system will be solid-like.

There are a variety of ways to characterize the adsorbed polymer (20). Generally, knowledge of the amount adsorbed, layer thickness, and density profile are useful, but not always easily determined. Spectroscopic methods for determining the bound fraction (trains) are important, but different techniques give somewhat different

estimates. Infra-red studies rely on changes in vibrational frequencies due to the interaction of a polymer moiety (e.g. carbonyl) with the surface. Deconvolution of the IR resonances give an accurate estimate of the fraction of bound groups, but this technique counts only those directly bound. In contrast, NMR, ESR and microcalorimetry, for example, are sensitive to those groups directly bound, plus those groups close enough to the directly bound groups to be similarly reduced in mobility. Thus IR and the other techniques provide complementary information.

Miyamoto and Cantow (38) were early users of NMR to study polymer adsorption for poly(methyl methacrylate) (PMMA) on silica adsorbed from deuteriochloroform. They found that at low coverages, no high resolution proton signals from the polymer were observed, but they did become apparent at higher coverages. With increasing polymer coverages, the surface polymer resonances became narrower. This is consistent with the polymer at low coverages being strongly attached and solid-like. Thus they were too broad to appear in a liquid-high resolution spectrum. Higher coverages produced more mobile material. They also found that the isotactic polymer is more motionally restricted than the atactic one at the interface. At low coverages, where the surface-PMMA signal in deuteriochloroform was not observable, the addition of deuteromethanol had the effect of producing relatively narrow polymer resonances. This is consistent with a more expanded and mobile polymer layer due to the interaction with deuteromethanol.

A number of ESR studies of surface attached polymers have been reported. While not the main focus of this report, these are of relevance because they employ very similar techniques and analysis. Central to the use of ESR is the incorporation of a stable unpaired electron, normally in the form of a nitroxide spin label. Use of spin labels in polymer systems has been reviewed (39). The main advantages are that the sensitivity of the electron is significantly greater than that of all NMR nuclei and that a similar apparatus can be used for many systems regardless of the mobility of the

labelled polymer. The disadvantage is that the spin label is not native to the chain and must be added in some fashion. Consequently, the potential perturbation of the polymer motion by the label, and the relationship between the motion reported by the label and that of the polymer must be considered. A comparison of ESR and NMR studies of the mobility of poly(vinyl acetate) (PVAc) has been made in the presence of several diluents (40). The correlation time estimates from both experiments were not equal, but showed similar trends. Consequently, it was concluded that these experiments were sensitive to the same types of motion.

Robb and coworkers (41-43) have used ESR to study both the interfacial dynamics of the polymer and as well as the adsorbed fraction. For the adsorption of poly(vinyl pyrrolidone) (PVP) on carbon black (and also silica) in chloroform, the fraction of segments in trains decreased with increased surface coverage (43). PMMA was found to be relatively flat under similar conditions. A comparison of calculations of train fractions from ESR and IR was made. Caution was given regarding the use of ESR spin labels which themselves may bind to the substrate. The segments of PVP in trains on silica also decreased with increasing thermodynamic quality of the solvent (42). Miller and coworkers (44,45) have used ESR to probe how the type of surface, amount adsorbed, and solvent used affect the dynamics of the adsorbed polymer. A deconvolution of the line shapes allow the separation of mobile (tails and loops) and somewhat immobile (trains) components. PVAc on alumina or titanium dioxide had little conformational freedom compared to that on silica regardless of the solvent quality (45).

The adsorption and dynamics of poly(ethylene oxide) (PEO) on silica have been studied using both ESR and NMR by Legrand, Hommel, et al. (46-55). PEO chains were end grafted on to silica by direct esterification of surface silanol groups. Analysis of the spectra based on division into mobile and immobile components allowed the

estimation of the segments that were adsorbed or free. In benzene, it was found (48) that oligomers behave like brushes and polymers like partially collapsed coils. An increase in the thermodynamic solvent quality results in greater swelling of the grafted PEO (49). In mixed solvent systems, the swelling increases with the fraction of good solvent (50). At high grafting levels, the hyperfine splitting was used to identify solvent partitioning in the adsorbed layer (51) and changes were found with grafting ratios (52,53).

High resolution  $^{13}\text{C}$  and  $^1\text{H}$  NMR relaxation time measurements of grafted PEO in benzene also showed two-component behavior in relaxation studies (54). An example of  $^{13}\text{C}$  relaxation behavior is shown in Figure 2. Both components show anisotropic motion with that of the less mobile component much more restricted in the direction perpendicular to the surface. The  $^1\text{H}$  relaxation times were also believed to be sensitive to the local concentration of segments. NMR, ESR and DSC were all used to probe the effect of the surface on a small molecule nematic liquid crystal (55). It was found that the grafted PEO layer caused the formation of a disordered region near the surface.

<Fig. 2>

In order to more fully exploit and characterize the mobility differences between attached and free polymer segments, Cosgrove and Barnet (56) developed the "driven equilibrium" method. This technique employs both a solid and liquid echo train to distinguish the proton spin density of the two species. Two examples are shown in Figure 3. Applications of this technique to PVP on silica in the presence of  $\text{D}_2\text{O}$  showed a bound fraction which decreased with increasing surface coverage (57). The results at low coverages were consistent with a relatively flat conformation of PVP on the surface. The bound fractions determined were also in good agreement with earlier experiments based on ESR studies. It was again noted that NMR and ESR yielded

similar results for the bound fraction while IR measured a fraction which was significantly lower. The results were consistent with magnetic resonance experiments being sensitive to mobility changes while IR is sensitive only to the carbonyls directly bonded to the silica. For comparison, terminally bonded polystyrene (PS) on carbon black with  $\text{CCl}_4$  showed a much lower fraction of bound segments (57).

<Fig.3>

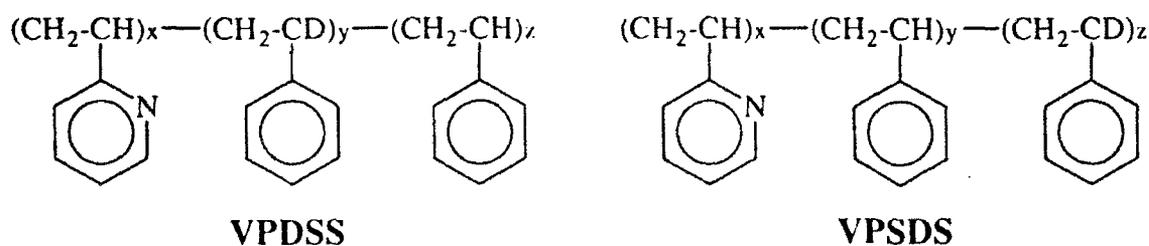
The driven equilibrium method has been applied to a number of systems and used in conjunction with neutron and light scattering to provide a fuller picture of the surface-adsorbed polymer (58-63). For random ethylene/vinyl acetate copolymers (58), the data suggest preferential adsorption of vinyl acetate groups on both methyl and cyclohexyl surface modified silica. There was reasonable agreement between the results from neutron scattering and NMR for the bound fraction. Further studies have identified preferential adsorption in polydisperse systems (59). Polystyrene latex particles have also been used as the surface. Adsorbed poly(vinyl alcohol) (PVA) in water had a small, but measurable value of the bound fraction while no bound material was found for terminally attached PEO (61,62). This was consistent with PEO having a highly extended conformation.

An alternate approach, combining the use of neutron scattering and NMR has been proposed by Cosgrove and Ryan (64-66). It was found that the solution  $T_2$  of PEO in water varied linearly with PEO concentration. The segment density profile from the neutron scattering experiments was then used to reproduce the  $T_2$  profile for the terminally-attached PEO. The comparison was based on the assumption that the  $T_2$  values would be the same for the solution and surface-bound polymer of the same local segment concentration. The good agreement between the predicted and experimentally measured  $T_2$  profile suggests the appropriateness of the assumption. The relaxation time approach was extended to poly(styrene sulfonate) (PSS)

adsorbed on silica (67). Since this is a non-absorbing system, the results were found to be useful in determining the thickness of the depletion layer.

The use of a solvent (water) as a probe of polymer adsorption and desorption at interfaces for PEO and PVP on silica (68) was also examined. The proton relaxation rate in water was enhanced (shorter  $T_1$ ) when polymer was adsorbed on a silica surface. The relative independence of the relaxation rate with polymer molecular weight was given as evidence that the solvent is mainly sensitive to the amount of polymer segments in trains. In addition, this method was also capable of measuring a critical displacer concentration in good agreement with other techniques. In contrast (69), the same technique applied to water in the poly(styrene sulfonate) (PSS) on a polystyrene latex yielded somewhat different results. The formation of a relatively flat PSS layer at the interface excludes solvent and the solvent is sensitive to only the segments in chains and loops. The calculation of bound fraction by this method was in agreement with ESR studies a similar system (70).

In some of the previous studies, measured relaxation times were related to the local segmental concentration of polymers adsorbed onto a silica surface. This was exploited by Blum et al. (14,71) who studied the relaxation behavior of deuterated styrene segments in adsorbed copolymers of 2-vinylpyridene (2-VP) and styrene (S). Two specifically deuterated polymers (VPDSS and VPSDS) were prepared with the deuteron on a different halves of the styrene part. This is shown below:



An example of the high resolution  $^{13}\text{C}$  spectra of the block copolymer in toluene and adsorbed on silica, swollen with toluene is shown in Figure 4. In solution, the resonances from all of the carbons are observed, while the spectrum from the surface bound material shows only high resolution resonances for the styrene. This is consistent with the 2-VP being rigidly adsorbed on the surface, while the styrene segments are mobile. Comparison of the deuterium relaxation times for the surface-bound and solution polymers allowed an estimate of the local concentration and thus the extension of the styrene segments to be made. It was found that the styrene segments were extended to 4 times their normal radius of gyration. This was in agreement with surface force studies.

A comparison of the relaxation times for these block copolymers is given in Table I. A surprising result was that when the relaxation times were compared at similar  $T_1$  values, the styrene surface segments had a  $T_1/T_2$  ratio closer to unity than in solution. This data is consistent with the notion that the styrene surface segments are locally *more mobile* than those in solution. This observation requires that some rethinking of how the surface packing of chains affects the local segmental motions be done. This phenomena was only observed in toluene, a good solvent for polystyrene. In poorer solvents, more reduced mobility was found (72,73).

<Fig. 4>

Relaxation times were also measured by Parker et al. (74) in the poly(vinyl pyrrolidone)-co-(vinyl acetate) (PVP-co-VAc) alumina system. Sedimentation studies showed that dispersion stability was increased with the amount of VAc present. Dispersion stability was also enhanced in the presence of *i*-propanol (good solvent for VP, poor for VAc) compared to toluene (good solvent for VAc, poor for VP). On alumina, the carbonyl  $T_1$  values for VP were longer in the presence of *i*-propanol than toluene. For the VAc carbonyl, the solvent quality didn't affect the  $T_1$  much. This was

consistent with the notion that the solvent doesn't displace VAc which is mainly associated with the surface. However, the solvent quality does seem to effect the layer (mostly VP) thickness in agreement with the dispersion stability.

### 3.2 Elastomer-Solid Systems

Most elastomers used for applications from balloons to tires are made from material which is filled with a solid species. Typical fillers include carbon black or silica. The interaction of elastomers with solid particles is reasonably well suited for NMR studies. Elastomers at room temperature have behavior which is in between solids and liquids. NMR studies on the bulk polymer systems have identified the motions responsible for the different behavior observed. Much of the earlier proton work prior to 1980 was reviewed by Douglass and McBrierty (75) for a number of different systems with interfacial effects. A more recent introduction to some of the previous work is given by Kenny et al. (76) and NMR studies of elastomers has been reviewed by Kinsey (77). The latter contains a small section on filled systems.

Schaefer first identified the anisotropic motions of *cis*-1,4-polyisoprene (*cis*-PIP) above its glass transition temperature for filled and unfilled system (78). He found that the presence of a carbon black filler produced an effect on the line widths, but not the  $T_1$ 's. Subsequent studies (79) employing low speed magic-angle spinning permitted the resolution of the methylene resonance and identified the inhomogeneous nature of the broadening. Dybowski and Vaughan (80) used multiple pulse proton NMR to remove dipolar broadening on similar *cis*-PIP samples. They were able to properly separate the relaxation and chemical shift effects, and the latter was determined to be the major contribution to the residual line widths in the filled rubber. Spin-spin relaxation rates were found to be an order of magnitude faster than in the corresponding unfilled rubber. It probably can be concluded that molecular motion is

homogeneous on the  $T_1$  timescale, but inhomogeneous on the  $T_2$  timescale (76).

More recently, a number of studies have more fully characterized bulk elastomers. English and Dybowski (81,82) have used a combination of techniques to show that the room temperature line width (a few hundred Hertz) of *cis*-polybutadiene (*cis*-PB) was caused by rapid anisotropic motion, restricted by chain constraints. Cohen-Addad et al. (83,84) have shown how some of these restrictions may relate to chain entanglements or crosslinks. Interestingly, there is enough motion in filled rubber systems that a combination of NMR techniques can ultimately provide quite narrow resonances for filled elastomers. The remaining widths are small enough that  $^1\text{H}$ - $^{13}\text{C}$  J-couplings were resolved by Kentgens et al. (85) for carbon black-filled natural rubber (*cis*-PIP). An example of the heteronuclear 2D J spectrum is shown in Figure 5 where the coupling is resolved. The carbon spectra under a variety of different conditions are shown in Figure 6. It is observed that the line widths can be reduced by an order of magnitude and the J-coupling can be resolved with the use of multiple pulse techniques.

<Fig. 5> <Fig. 6>

There have been a variety of studies which have attempted to characterize the physical inhomogeneity in filled elastomers (75, 86-88). Kaufman et al. (86) found that filled ethylene-propylene-diene rubber (EDPM) and *cis*-PB showed a two-component  $T_2$  behavior. The  $T_2$ 's varied by over an order of magnitude. The more immobile region was assigned to the rubber bound to the carbon black. The relatively free rubber was more motionally constrained than that in the bulk polymers. The authors also proposed that the motion of the bound polymers were somewhat less than isotropic. O'Brien et al. (87) have measured  $T_1$ ,  $T_2$ , and  $T_{1\rho}$  values and identified at least three different regions of polymer segments with differing mobilities. These are shown in Figure 7 and assigned to tightly-bound, more loosely-bound, and bulk-like rubber. Material balances suggested domain thicknesses of 6.6 nm for bound material

1.4 nm of which was tightly-bound material (75,87).

<Fig. 7>

Refinements of the above model have been made (76) and it was concluded that: (i) there is motional coupling between the tightly- and loosely-bound rubber molecules; (ii) a range of adhesion energies are indicated; and (iii) removal of bound polymer has Arrhenius behavior. These studies also implied that the glass transition temperature of the bound polymer was significantly greater than the bulk polymer. Similar results on motional differences have been found by Ito et al. (88) for silica-filled PIB and PIP. The effects of heat treatment on the materials showed that the fraction of bound rubber decreased irreversibly with heating. This was believed to be due to the degradation of the loosely-bound rubber. Simon et al. (89) have interpreted differences in relaxation time in terms of phantom network properties. Brown et al (90) have used both CW and FT-NMR to measure crosslink densities in filled and unfilled rubbers.

Several studies have been made on filled poly(dimethyl siloxane) (PDMS) (84,91,92). Cohen-Addad et al (84) have used relaxation experiments on solvent-swollen systems to characterize the network structure of the system. The silica concentration also was observed to control the superposition of relaxation data with a timescale shift factor (91). Litinov and Speiss (92) have used deuterium labelled PDMS to observe the behavior of various fillers on the interface. Deuterium powder patterns observed above the glass transition temperature were associated with the bound elastomer.

Imaging techniques may be sensitive to the interphase region in filled composites. Kuhn (93) and Koenig (94,95) have reviewed some of the applications in materials science. Chang and Komoroski (96) have demonstrated that contrast for elastomers can be obtained so that a 0.07 mm sheet of paper can be detected in a

sandwich of carbon-black filled *cis*-polybutadiene. In fact, upon removal of the paper, the feature is still observed where the two polymer layers are put together. It is possible that some of the contrast observed was due to the differences in  $T_2$  from the differences in mobility of the surface and bulk material. It does not appear that a detailed study of this effect has been made. Along similar lines, Sakar and Komoroski (97) have imaged tire cords and found differences between different rubbery regions. Differences in the  $T_2$ 's of carbon black/rubber differentiated good and poor dispersions. The reduced  $T_2$  value in a poorly dispersed sample may have been caused by the presence of "bound" rubber, though this was not observed directly.  $T_2$  weighted images made it possible to differentiate between "certain morphological and defect structures".

In elastomers filled with silica reinforcements, Garrido *et al.* (98) demonstrated the presence of an outer layer that appeared to have lower mobility, presumably due to both a lower concentration and mobility of the polymer in this layer. Subsequent density measurements confirmed a high density for this layer, consistent with a higher concentration of the more dense silica.

Even more convincing evidence of an interfacial layer with different mobility was identified by Blümmler and Blümich (99) who studied the aging and phase separation in elastomers. Upon aging for two hours, a ring on the outside of the polymer cylinder was formed with a thickness of about 70  $\mu\text{m}$ . With increased time, the width of the ring increased and was assigned to the aged fraction of the material. The contrast was proposed to be due to the decreased mobility of the polymer in the aged region. Interestingly, the sample did not show any physical signs of aging until after 8 hr, while the image showed noticeable effects after just 2 hr. Additional contrast for the interface was observed because the mobility of the polymer in the region next to the aged material had *higher* mobility than the unaged material. This material was identified

with chains which had been broken or possibly due to larger local concentrations of plasticizer excluded from the aged region.

### 3.3 Solid-Gas Interface

The coating of solid materials with polymers can be used to improve the surface properties of materials. In addition, these surfaces may serve as model systems for composites (with the matrix removed). Typically, these might be used in applications where the interfacial polymer layer would be in contact with a gaseous layer, usually air. These studies are often difficult to perform because polymers at an interface are typically rigid and consequently have broad resonances, although coherent averaging techniques can be used. They are also much more dilute than bulk systems so that sensitivity is of primary importance. An example of this for PVAc on silica is given in (14).

There have not been a large number of NMR studies of polymer films at the solid-air interface. ESR studies of adsorbed PS in the dry state at the air interface showed decreased mobility compared to that of the bulk material (44). The adsorbed polymer can be considered to have a higher glass transition temperature than that of the bulk polymer. ESR studies have the advantage of increased sensitivity over NMR.

The study of poly(*iso*-propyl acrylate) (PIPA) on silica has been performed by Blum et al. with  $^{13}\text{C}$  NMR (14,100-102). PIPA is a flexible polymer that is below its  $T_g$  at room temperature. With CP-MAS NMR of PIPA in bulk, it was possible that under the proper conditions that no high resolution resonances for the polymer backbone were observed. This is shown in Figure 8. When adsorbed on the surface, the CP-MAS spectra showed resolved resonances for all of the carbons (101). This behavior was similar to that of a glassy polymer where the rigid nature of the polymer backbone allows MAS and high power proton decoupling to sufficiently narrow the resonances.

As a function of increasing surface coverage, the resonances were observed to broaden. This was consistent with a view that there was increased mobility of the polymer with an increase in distance from the surface. A monolayer is roughly the amount of coverage that distinguishes surface-modified from bulk-like in terms of dynamics as observed from NMR. The use of a deuterium label allowed  $^2\text{H}$  NMR to be used for the surface adsorbed labelled polymer, although the sensitivity of these experiments was not good (103).

<Fig. 8>

For PDMS chains adsorbed on modified silica gel, Van Alsten (104) has shown that the  $T_1$ 's of the polymer increase with surface coverage. At a surface coverage of about 1.1 g PDMS/g silica, the  $T_1$  is comparable to that in the bulk polymer.

Chu and Murphy (105) have used  $^{15}\text{N}$ -labelled polyimides (PI) to study PI adhesion to alumina. For thin layers of 30-150 Å (2-10 monolayers), solid-state  $^{15}\text{N}$  chemical shifts provided evidence for amine production and PI backbone cleavage at 150-255 °C. Adhesion appears to be correlated with a higher temperature reaction which implies imide/alumina bonding. Treatment of the alumina with a silane coupling agent "passivates" the alumina towards this reaction.

Conformational changes of polypeptides on solid surfaces have been studied by Fernandez et al. (106). Carbon-13 chemical shifts were consistent with more extended structures (vs.  $\alpha$ -helices) on silica and hydroxyapatite than in the bulk material for poly-L-lysine and poly-L-glutamic acid. Deuterium NMR experiments were used to characterize the reduction of the mobility of the side chains on the surface. Spin-locking experiments also identified reduced mobilities of both the backbone and side chain upon adsorption.

Solid-state NMR studies have been used with some difficulty in the characterization of plasma polymers (107,108). These are often obtained as tenacious, thin films on low surface area substrates (e.g. glass slides).

Characterization with electron spectroscopy for chemical analysis (ESCA) has had good success with fluorine, but for carbon separation into  $sp^2$  and  $sp^3$  carbons is only achieved with deconvolution techniques. Carbon-13 studies by Kaplan and Dilks on hydrocarbons (109-111) and fluorocarbons (112) have shown the superiority of NMR in terms of resolution. Since the deposition rates were slow, polymer had to be collected using several runs between which the polymer was removed. Identification of specific chemical species such as methyls, methylenes, methines, and quaternary carbons was possible. Dipolar dephasing allowed non-protonated and weakly coupled (methyl) species to be separated from strongly coupled (rigid, protonated) species. The use of  $^{13}C$  labelled precursors also allowed the pathway to be followed. Gambogi et al. (113) used similar techniques to follow  $sp^2/sp^3$  ratios from ethane and methane plasmas. Dipolar dephasing allowed the identification of non-protonated aromatic or aliphatic carbons which could be precursors to diamond- or graphite-like regions.

Both  $^{13}C$  and  $^{15}N$  NMR were used on plasma polymers made from acrylonitrile (114). Acrylonitrile/nitrogen plasmas produced a variety of structures with C-N bonds. The type of material formed was dependent on the location in the cell. A variety of amide species, including heterocyclic rings were found with  $^{15}N$  NMR. A different approach has been used by Lock et al. (115) who used dynamic nuclear polarization (DNP) to transfer magnetization from unpaired electrons to  $^{13}C$  resonances. This technique offers the potential of performing experiments with substantially lower amounts of material. Unfortunately the authors reported the use of an 83 mg sample for  $^{13}C$  analysis which is about an order of magnitude more than a typical single plasma run produces. For the "diamond" films produced, the DNP derived spectra showed only one resonance at 36 ppm corresponding to "diamond-like" material. For this sample, a useful  $^{13}C$  spectrum could not be produced without DNP. The DNP

technique also offers the advantage of avoiding the long relaxation times of the diamond-like carbons.

It may ultimately be possible to study fairly thin organic films using NMR imaging. Applications of NMR imaging to materials science have been reviewed (93-95,116). Most commonly (as in medical imaging), the NMR signals from mobile components protons are responsible for the more intense signals while non-mobile species with short  $T_2$ 's provide little signal. Contrast is then due to differences in mobility. In many studies, this mobility difference is due to the presence or absence of relatively small molecules. These can be observed using liquid-like imaging techniques.

Early imaging studies have been applied to composite systems such as glass/epoxy by Rothwell et al. (117) where water was used to provide contrast. This approach was extended to glass/polyester and glass/nylon systems (118) where the uptake of water was also of prime interest. These studies demonstrated that the imaging technique could not only be sensitive to the amount of water uptake, but also to voids and imperfections in the composite. Extensions of these studies to polymer/solvent systems demonstrated that solvent fronts and inhomogenities could be observed and related to both the amount of solvent present, but also its mobility (119-121). The sharpness of the images of the front was sufficient to demonstrate case II diffusion behavior (119). Contrast between various regions in these materials was obtained via  $T_1$ ,  $T_2$ , or diffusion coefficient weighted images (120). While the mobility of the polymer was not directly imaged, the properties of the solvent are likely to be directly related to those of the polymer (122). Thin slices of poly(vinyl alcohol) and poly(vinyl acetate) were also imagable as glue lines between wood and ceramic tiles, though no attempt at identifying an interfacial layer was made (123). Cracks and voids which allow water penetration are also observable in ceramic tiles joint with styrene-acrylate adhesives (124).

The previously mentioned imaging studies were all performed on materials which had liquid-like resonances where more or less standard (medical like) imaging techniques could be used. For typical composite materials, this is not possible because the samples can be very solid-like. There have been some attempts at using combinations of multi-pulse and cross polarization to the imaging of true solids (125,126). These appear to be promising, but to date no detailed studies of relevance to thin organic films have been published.

### 3.4 Solid-Solid Systems

The solid-solid interface is of importance to composite materials in applications where a rigid matrix is required. In some cases, the presence of solid surfaces changes the behavior throughout much of the system (see sect. 3.2 and below). In others, the surface only appears to affect a thin layer. In that case, some technique which contrasts the interfacial material from that of the matrix is required. Isotope enrichment of surface active species such as coupling agents (7,127,128) and magnetization transfer (129,130) are both effective providing this contrast. The former will be discussed in section 4. The use of  $^{13}\text{C}$  NMR to probe composite materials containing solid polymers was realized about 10 years ago by Resing et al. (131). Unfortunately, none of the applications reported directly addressed the behavior of an *interfacial* polymer layer.

For composites made from poly(vinyl alcohol) and silica, Zumbulyadis and O'Reilly (129,130) found that the cross-polarization time constant,  $T_{\text{SiH}}$  for  $^1\text{H}$  to  $^{29}\text{Si}$  was shorter for the composite than the silica alone. This was interpreted as being due to the PVA making the surface hydroxyls more rigid and hence more effective at cross-polarizing silica. Deuteration of the exchangeable protons (surface and alcohol hydroxyls) resulted in a slower, but still measurable  $T_{\text{SiH}}$ . This showed that even the

backbone PVA protons could effectively cross-polarize the surface silicons. A rough distance estimate was also made from this data. The authors concluded that this was a "tightly coupled spin system".

Composites made from nylon-6 filled with glass were examined by Weedling et al. (132,133) using  $^{13}\text{C}$  chemical shift data. A comparison of bulk and glass-filled (including surface-treated) composites showed that a greater amount of  $\gamma$ -crystalline form was produced when the composite material was processed as compared with the original bulk polymer. In the absence of glass spheres, the  $\gamma$ -form reverted back to the  $\alpha$ -form (132). In follow-up studies, the effect of various processing and compositional variations were probed (133). An amorphous polymer layer was found to be intimately associated with the glass.

Parker et al (134) have probed the effect of the surface treatment of alumina on the properties of green tapes made with a polystyrene binder. Through measurements of the  $^{13}\text{C}$  cross-polarization times and  $^1\text{H}$   $T_{1\rho}$ 's that the mobility of the polystyrene varied as a function of surface treatment. The presence of n-octylsilane in the system increased the mobility of the plasticized tapes. The NMR measurements correlated with the expected densities and moduli of the tapes.

Proton  $T_{1\rho}$  studies of polyethylene (PE) have been studied by Natansohn (135,136) in composites with calcium carbonate and cellulose. For the  $\text{CaCO}_3$  composites, a "good" and "bad" sample had different relaxation behavior. The differences are believed to be due to physical differences in the samples as the  $\text{CaCO}_3$  was magnetically transparent. Yu and Guo (26) have also studied this system and found from  $^1\text{H}$   $T_{1\rho}$  values that the the PE was more rigid due to the presence of the filler.

To close this section, it is appropriate to note that the use of imaging to characterize surface species in composites would be an important accomplishment and is a major goal. New techniques based on multipulse NMR experiments

(137,138) have been applied to solid polymers. However, their resolution is not yet good enough to yield significant results on filled polymers. Some work has been done on composites used in propellents (139), green ceramics (140), and polymer sandwiches (141), but these have been limited to providing information on rather large structures.

#### 4. SURFACE ACTIVE AGENTS

Modifications of solid materials with small molecule surface-active agents are used to improve adhesion, dispersibility, wetting, and flocculation of solids. These materials may be added to the system such that they react at the surface or are just adsorbed. In the former case, the materials may form polymers or similar structures at the interface, however, these will be discussed here because they are typically applied as monomeric species. For the purpose of this review, discussion of chemically bonded species are separated from non-bonded ones.

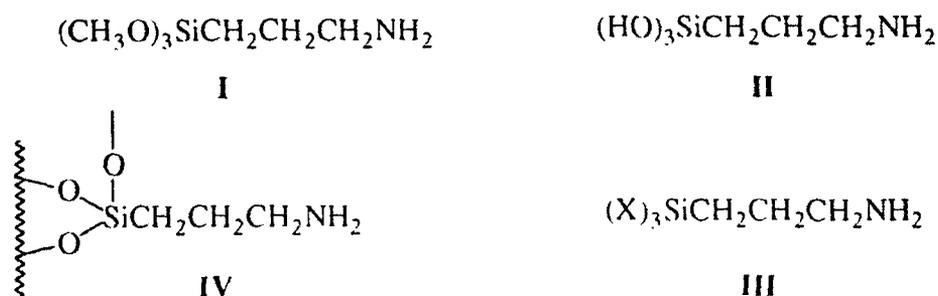
##### 4.1 Bonded Phases

The use of bonded surface species, particularly as used in composites and chromatography is well documented. In composites, these materials can form a bridge between an organic matrix and an inorganic filler. In chromatography, they modify the surface properties so specific binding may occur. The most common of these are based on silanes have been described by Plueddemann (142) and others (143). A variety of physical-chemical characterization tools have been applied to these species and have been reviewed by Ishida (144) in 1984. Since then a number of reviews have focused on the use of NMR to characterize these interfacially active species (5-10,14,26,101,102,145).

Silane coupling agents may be used in small amounts to treat glass and inorganic fibers and fillers. The major advantage of their use in polymer composites is the enhancement in physical properties such as strength when the composite is subjected to conditions which might degrade the interface. A common example of this is their use in glass/epoxy composites where good physical properties are maintained in the presence of water. While many aspects about how these interfacial species work are unclear, NMR has achieved good success at characterizing them.

In chromatography, the modification of surface properties are critical to the interactions responsible for chemical separation (146). The chemical structure and mobility of the agents at the surface are important for the effectiveness of the surface selectivity. In addition, the organo-functional end of the molecule provides a site for the attachment of other functional groups. This allows for the tailoring of the packing material for the specific separation required.

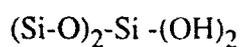
Silane coupling agents are normally obtained as chloro- or alkyl esters (typically methyl or ethyl). For example, 3-aminopropyltrimethoxysilane(I) (APMS) is shown below. Under anhydrous conditions these compounds can be relatively unreactive at room temperature. Addition of water to the sample causes the hydrolysis to a reactive silanol (II). Condensation of the silanols to form oligomers (III), where X may be another silane, occurs in competition with the formation of a surface-Si-O-SiR bond (IV). These are, of course, simplified structures. In general each of the functional groups reacts at its own rate and, in general, they may react with different species. Several workers have used NMR to identify the reaction products and rates (145,147,148), but this is beyond the scope of the present work.



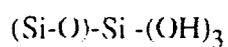
At low concentrations, most of the hydrolyzed coupling agents may be found as individual monomers, but oligomers form at higher concentrations. This formation does not appear to affect the adhesion,

however (148). The extent of interaction with the surface is often dependent on the functionality of the silane groups. For example, when a trifunctional silane is used, condensation of the silanol groups occur in addition to the surface reactions.

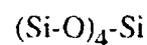
*<sup>29</sup>Si Studies.* The reaction of the silanes on the surface is conveniently followed by <sup>29</sup>Si NMR. In spite of the broad chemical shift range of silicon, the chemical shifts of different species in silica differ by only a small amount (8,149). Nevertheless, it is possible to identify silicon atoms with different substituents as:



Q<sub>2</sub>



Q<sub>3</sub>

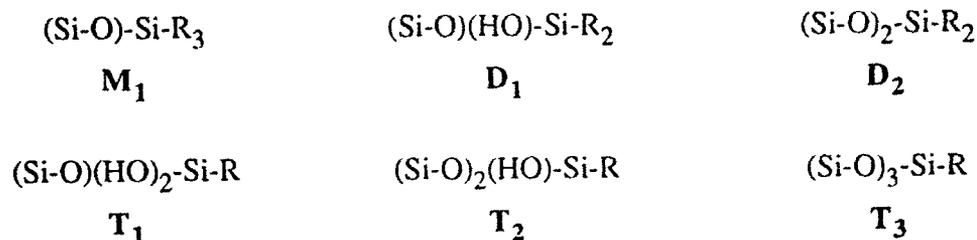


Q<sub>4</sub>

The chemical shifts for these are (150,151) -91, -100, and -109 ppm, respectively, for silica gel. The use of cross polarization from the surface hydroxyls make this a surface sensitive technique. Quantification of the various resonances is difficult because the T<sub>SiH</sub>'s are different with the Q<sub>4</sub>'s having the longest (150) CP time (15-20 ms). The types of species formed in silica gel were found to be dependent on the thermal and hydration history of the sample (151). Pfeleiderer et al (152) examined the <sup>29</sup>Si relaxation and cross polarization behavior of various silicas and found that various types of microdomains existed in the silica. Combined rotation and multiple pulse spectroscopy (CRAMPS) has also been used for surface proton characterization (153,154). These studies have identified hydrogen bonded silanols, isolated silanols, and adsorbed water. Various heat treatments were used to eliminate different species. Tuel et al. (155) have used <sup>29</sup>Si to differentiate between pyrogenic and precipitated silicas. The surface studies have not been limited to silica. Higgins and Ellis (156) have characterized high surface area alumina. At room temperature, aluminum atoms

in the first two layers were not observed in solid-state  $^{27}\text{Al}$  NMR spectra due to their large electric field gradients.

The reaction of silica with surface modifying alkylsilanes is conveniently followed with  $^{29}\text{Si}$  NMR. Loosely following the nomenclature of Albert and Bayer (8), trifunctional, T, difunctional, D, and monofunctional, M, silanes can be distinguished. These are shown below where the subscripts denote how many of the silicons bonds are to O-Si groups.



where the alkyl (R) groups need not be homogeneous and often contain functional moieties, and the silicons in parentheses may be either from the surface or from other silanes. Substitution of OR groups with OH groups is also possible. The alkyl substituent on the silicon conveniently shield the silicon resonances away from the surface hydroxyls.

The  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra of four modified silica gels were studied by Maciel et al. (157). These were typical of stationary phases used in chromatography. The  $^{29}\text{Si}$  spectra showed the presence of  $\text{Q}_3$  and  $\text{Q}_4$  species plus resonances due to the organosilanes. For trimethylchlorosilane reacted onto silica, the alkylsilane has a  $^{29}\text{Si}$  resonance at 15 ppm, well separated from the silica gel silanes. Well resolved resonances were also found for the  $^{13}\text{C}$  resonances.

The values of chemical shifts found in various studies will not be reproduced here. Several literature studies have been summarized (8). Sindorf and Maciel (158) have examined the details of the quantification of the structural features of

trimethylchlorosilane on silica gels. Shown in Figure 9 is the CP-MAS spectrum of silica gel and its reaction product with trimethylchlorosilane. Upon reaction it can be observed that the surface silanol sites  $Q_3$  (b in Figure 9) are converted to  $Q_4$  (a in Figure 9) sites. The species labelled c in the figure was assigned to geminal hydroxyls ( $Q_2$ ). The presence of the  $Q_2$  resonance was questioned for certain samples (159), although later spectra by the same authors show its presence (8). In addition, the  $M_1$  (d in Figure 9) resonance due to the reacted alkylsilane is clearly observed. Similar results were found for trimethylchlorosilane reactions with different silica gels. An alternative to CP-MAS studies was suggested by Fyfe et al. (160) who proposed the use of direct polarization MAS. Relaxation times,  $T_1$ , for the  $Q_4$  silica gel resonances were about 20 and 25 s for a silica gel and high surface area glass, respectively. Shorter relaxation times were found for silicons with hydroxyls. Silylation significantly increased the  $T_1$ 's of the support.

<Fig. 9>

Monodentate (M-type) silanes have one reaction site, but D and T have multiple ones. This adds to the complexity of the systems as the multifunctional silanes can react with each other in addition to silica, water and alcohols. Sindorf and Maciel (161) have done a detailed examination of the behavior of multifunctional silanes. Dimethyldichlorosilane, methyltrichlorosilane, dimethyldiethoxysilane, and methyltriethoxysilane were adsorbed on high surface area ( $750 \text{ m}^2/\text{g}$ ) silica gel. It was found that a variety of different structures were formed with time and air exposure. For example, for methyltrichlorosilane under anhydrous conditions a large  $T_1$  (single surface linkage) resonance was found. Upon exposure to air, loss of HCl and formation and condensation of silanols occurred. The reactions of the ethoxysilanes were similar to those of the chlorosilanes.

A series of mono- and tri-functional silanes on a number of different silicas were

studied by Bayer et al. (159) for a variety of chain lengths and functional groups. Both  $^{13}\text{C}$  and  $^{29}\text{Si}$  were deemed to be useful characterization tools for laboratory and commercial modified silicas. They compiled a  $^{13}\text{C}$  and  $^{29}\text{Si}$  chemical shift listing for a variety of silanes with different functionalities including commercial reversed phase systems. A similar multinuclear approach was also followed by Sudhölter et al. (162) for 3-chloropropyl- and 3-aminopropylsilane. Both nuclei provided evidence for different bonding of the reactive silanol groups. For  $\text{C}_{18}$  di- and trifunctional silanes on silica gel, Pfeleiderer et al. (163) have found that under dry conditions, monodentate and bidentate surface species are formed, respectively. Higher-dentate ligands are formed when a dry inert atmosphere is not used. Tuel et al. (164) focused their study of modified silicas to determine the amounts of reactive sites. Akapo and Simpson (165) examined the relationships between  $^{29}\text{Si}$  and  $^{13}\text{C}$  characterization and column performance. Reactions similar to those mentioned above also seem to occur for various silanes on the surface of zeolites (166).

A few detailed studies focussing on the  $^{29}\text{Si}$  characterization of 3-aminopropylsilane (APS) on silica have been performed (167-170). The influence of heat treatment and reaction conditions were probed for APS and 3-methacryloxypropyltrimethoxysilane (MPS) by de Hann et al. (167). For APS on both silica gel and Cab-O-Sil surfaces, reaction from dry toluene produces mostly monodentate structures, while heat treatment or the presence of water produces bidentate or tridentate linkages. For MPS, the spectra show the presence of bidentate and higher species, even under dry conditions.  $^{29}\text{Si}$  spectra taken from APS and 4-aminobutylsilane (ABS) on Cab-O-Sil show significantly poorer resolution than on silica gel (167,168) though they are sufficient to identify bonding. This is probably at least partially due to the lower surface area and perhaps even surface heterogeneity of Cab-O-Sil. Caravajal et al. (169) have made a detailed  $^{29}\text{Si}$  and  $^{13}\text{C}$  study on APS on

silica gel. Although the situation varied some with the exact conditions, it was generally observed that APS at room temperature was adsorbed mainly as mono-( $T_1$ ) or bidentate ( $T_2$ ) species. With heating, higher amounts of the  $T_3$  species were formed.

Hoh et al (170) have observed changes in the cross-polarization times for surface and bulk polymerized APS species. Shorter  $T_{SiH}$  values for the surface species was believed to be indicative of lower mobility of the surface species. In mixtures with epoxy resins, the  $T_{SiH}$  values were somewhat less conclusive. Gambogi and Blum (171) observed that the  $^{29}Si$  resonance from ABS got sharper with the addition of water to the interface of ABS/Cab-O-Sil and in a composite with bismaleimide. Vrancken et al. (172) determined that humidity could cause the partial hydrolysis of the surface APS layer.

Previous studies by the Eindhoven group have been extended to methoxytrimethylsilane, dimetoxymethylsilane, and trimethoxymethylsilane (173). They found that thionyl chloride was a more effective dehydration agent than heating. Some of the methanol produced in the hydrolysis reaction was adsorbed. Results similar to those in their earlier studies (167) were also found. Several studies have also followed the condensation reactions and adsorption with  $^{29}Si$  NMR (148,174-176). Detailed studies of chromatography supports are greatly aided by this technique (177,178).

**$^{13}C$  Studies.** Considering that the major differences between the reactive silanes are the organo groups,  $^{13}C$  studies have been crucial to the identification and characterization of the bonded surface species. The "business" end of the molecule is typically away from the silane. The functional group may be responsible for preferential binding, as in chromatography, or chemical bonding, as in adhesion promoters. In solventless situations, short chain alkyl groups are solid-like, while the

longer alkyl chains become more liquid-like with increasing chain length. For the solid-like chains, CP-MAS is an effective way to probe the interface. Reviews of this application on silanes exist (5,7,8,10,149)

One of the earliest reported  $^{13}\text{C}$  studies of silanes is that of Chang et al. (179) who reported the CP spectra of three different alkyl silanes on chrysotile asbestos. The importance of this work probably lies in the demonstration that natural abundance  $^{13}\text{C}$  studies were possible on the surface. In the early 80's a variety of CP-MAS  $^{13}\text{C}$  studies appeared. Additional work on the asbestos system (131) showed that the addition of MAS could significantly enhance the obtainable resolution. The identification of the carbons present in the reacted material was an important test to determine if various functional groups could survive the treatments.

Over the next several years a number of different surface bound silanes were characterized. Most of the systems studied were of relevance to chromatography. The aim was to identify the chemical shifts and any specific conformational or complexation effects present. The initial studies of Leyden et al (180,181) and Maciel et al. (157) demonstrated the usefulness of the technique and probably stimulated work on a number of systems. An example of the resolution obtainable is shown in Figure 10. Hayes et al. (182) reported the surface spectra of 12 different monofunctional silanes. The  $\text{C}_{18}$  material was noted to give broader resonances due to its mobility. A wide variety of other systems have been studied along by  $^{13}\text{C}$  in conjunction with  $^{29}\text{Si}$  (8,12,161,162,165,167) In addition, Jinno has characterized a number of commercial silica gel reverse phase materials with  $^{13}\text{C}$  (183).

<Fig. 10>

The work of Chiang et al. (184) was more oriented to the materials/composites applications. They compared the chemical shift values for for APS and N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS) on Cab-O-Sil silica, as a bulk polymerized polymer, and as a neat liquid. The chemical shifts were interpreted in

terms of structural changes believed to take place in the different systems. Zaper and Koenig (185) have extended these studies to mercapto-, amino-, epoxy-, methacrylate-, and vinyl- functional silanes. These were all either derived from the triethoxy- or trimethoxy- ester. Comparisons were made between Cab-O-Sil surface and bulk polymerized materials. Differences in line widths and chemical shifts were found. Carajaval et al. (169) did detailed studies on APS to determine how the reaction conditions affected the structures formed.

A few studies have used  $^{13}\text{C}$  to probe the dynamics of surface-bound species. Sindorf and Maciel (186) have measured  $T_{\text{CH}}$ ,  $T_{1\rho}$ , and  $T_1$  values for dimethyloctadecylchlorosilane (DMODCS,  $\text{C}_{18}$ ) and dimethyloctylchlorosilane on silica gel. The cross-polarization rates for carbons decrease away from the attached end, but level off after about 8 carbons. The rate of molecular motion increases away from the surface. Later studies on DMODCS on silica gel (187) identified differences in intensities between CP and single pulse spectra. At low coverages, the rate of reorientation of the silane groups was slow, but this rate increased with the addition of "wetting" solvents. Albert et al. (188) also probed  $\text{C}_{18}$  mobility on the surface in the presence of solvents. It was observed that both the loadings and solvents influence the mobility of the chains. For shorter chains of importance in composites, Nishiyama et al (189) that hydrolysis, adsorption, and condensation could be followed with solution state  $^{13}\text{C}$ , as well as  $^{29}\text{Si}$  NMR. Earlier studies (190,191) had previously identified the restricted mobility of APS on silica gel in  $\text{D}_2\text{O}$  with linewidth and relaxation-time measurements.

In order to characterize the behavior in solvent containing, modified systems, Gilpin and Gangoda (148,192-197) have performed experiments on a variety of  $^{13}\text{C}$  labelled silanes. In their initial studies, the labelling allowed them to observe the resonances from the labelled species at the interface. For  $\text{C}_9$  and  $\text{C}_{10}$  labelled

materials (192), the labels were far enough away from the silane end that they were mobile enough to be almost "liquid-like." Labels positioned nearer to the silicon atom were quite broad and very difficult to characterize with liquids techniques. Nevertheless, the motional gradient could be identified. For methyl end-labelled alkylsilanes on silica (195), the  $T_1$  relaxation times were more a function of loading than chain length.

Later studies by the same group demonstrated that the  $T_1$  values of an end labelled dodecyldimethylchlorosilane ( $C_{12}$ , monodentate attachment) varied linearly with the inverse of the solvent viscosity (196). Two distinct types of solvent behavior were found and ascribed to differences in solvent penetration into the  $C_{12}$  chains. The apparent energies of activation for the  $T_1$  process were also measured for the dry (ca. 13 kJ/mol) samples and compared to those soaked with ethylene glycol (15 - 19 kJ/mol), and carbon tetrachloride containing materials (197). The solvent-wet materials also showed greater sensitivity to the position of the  $^{13}C$  label on the silane. These results suggested to the authors that the silanes were more orientationally ordered in the presence of solvents than in their absence. It is believed that the mobility of the chain is related to the behavior as separation medium (194,198).

Van Alsten (104) has also used  $^{13}C$  methyl-labelled dodecyldimethylchlorosilane adsorbed onto silica gel in the presence of various solvents. The  $T_2$ 's of the label suggested heterogeneous broadening from different environments for the alkylsilanes. The  $T_1$  also decreased with increasing solvent viscosity. To the labelled coupling agent samples, poly(dimethyl siloxane) (PDMS) in deuterocyclohexane was added. At low coverages of PDMS, the  $T_1$  of the bound label increased with increased coverages, indicating greater motional freedom. This is possibly due to the conformational changes of the alkylsilane in response to the presence of the polymer. At higher polymer concentrations, the  $T_1$  decreased, went through a minimum and

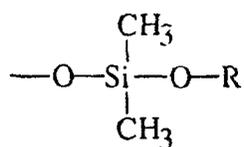
then increased with further addition of polymer. This is consistent with the environment of the alkylsilane becoming more motionally restricted as more polymer was added. In contrast, the mobility of the adsorbed polymer (and its  $T_1$ ) increased as the amount of adsorbed polymer increased. It appears that at low coverages, the polymer was in a relatively flat conformation on the surface. As the coverage increased, the number of segments in the more mobile loops and tails also increased. Changing the polymer molecular weight (199) had little effect on the silane mobility, but some on that of the polymer.

$^{13}\text{C}$  labelling has also been used to provide contrast between an interfacial APS layer on glass and a nylon-6 matrix (127). The position next to the amine was labelled. Even though relatively large spheres (5 mm) were used, there was still sufficient sensitivity to observe the coupling agent. CP-MAS spectra of the coupling agent on the glass beads: alone; in a composite with nylon-6; and after extraction of the polymer were taken. At the surface-air interface, the resonance due to the labelled species at 43 ppm was observed. At least two components of different mobility contributed to the signal intensity. Upon mixing with nylon-6 the  $\text{C}_1$  carbon of the nylon overlapped with the coupling agent resonance, but it was still possible to deconvolute the contributions to the relaxation behavior of each to some degree. After extraction of the free nylon in the composite, the resulting  $^{13}\text{C}$  spectrum showed the definite contribution of the coupling agent at 43 ppm plus nylon resonances due to material which had not been extracted. The fact that a considerable amount of polymer was not removed from the glass beads suggested a strong interaction between the polymer and the treated glass surface. Relaxation measurements on the coupling agent's labelled carbon suggested that the presence of the polymer reduced its mobility.

In a somewhat different, but related study, Tuel et al. (200) have studied the

behavior of  $\alpha$ - $\omega$  diols chemically bonded to silica. Measurements of relaxation behavior and intensities suggested to the authors that the conformation of the chains on the surface was relatively flat. In addition, there was an even/odd effect believed to be due to the conformation of the molecules on the surface.

*<sup>2</sup>H Studies.* Deuterium labelling has been used in a number of cases to provide contrast and also a spectrum which can be interpreted in terms of motional dynamics. Kelusky and Fyfe (201) have reacted perdeuteroalkoxydimethoxychlorosilanes with silica gel to probe mobility in the presence and absence of solvents. The coupling agents studied had the general formula:



V

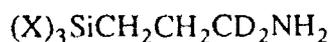
and included R = -CD<sub>3</sub>, -CD<sub>2</sub>CD<sub>3</sub>, -CD(CD<sub>3</sub>)<sub>2</sub>, -(CD<sub>2</sub>)<sub>7</sub>CD<sub>3</sub>, and -(CD<sub>2</sub>)<sub>15</sub>CD<sub>3</sub>. For the dry, treated surfaces, the deuterium lineshapes were superpositions of sometimes unresolved resonances. The mobility of the alkyl CD's increased with distance away from the surface. Differences in mobility with differing solvents was also found. Because of the overlap of resonances, quantifying the dynamics was impossible.

To overcome the problems associated with overlapping resonances, selectively deuterated silanes have been used (7,101,128,145,147,168,171,202-205). The structure of these was similar to V with an R in place of the OR. The labelled compounds are designated by C<sub>x</sub>(D<sub>y</sub>), where x is the total length of the R group and y is the position of the deuterium label with carbon number 1 next to the silicon. Gangoda et al. (202,203) have prepared C<sub>7</sub>, C<sub>10</sub>, and C<sub>12</sub> dimethylalkylsilanes and bonded them to silica gel. Another material without the capability of surface bonding

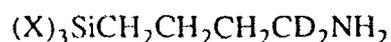
was used for comparison. The bonded silanes had more restricted mobility with the labels further away from the surface being more mobile. Spin lattice relaxation times were in accord with that expected from the lineshapes. Deuterium labelled  $C_{12}(D_{11})$  was used to probe the surface mobility of the bound silane in the presence of various diluents including simple and binary solvent systems, surfactant solutions and nematic liquid crystals. In methanol and hexane, the silane moved faster than in the dry state. In a water/methanol mixture, the mobility was similar to that of the dry state. In a dispersion containing surfactant, the silane moved slower than in the dry state and a further reduction was found in the presence of the nematic liquid crystal. Boddenberg et al. (205) have studied the behavior of the deuterated trimethyl species and found that the methyl rotation was fast while the O-Si motion much slower.

Several deuterated  $C_{18}$  species were studied by Zeigler and Maciel (204). Specifically  $C_{18}(D_{9,10})$  and  $C_{18}(D_1)$  were studied as a function of temperature, loading and solvents. Anti-gauche jumps and more complicated motions were required to simulate the experimental data. At "high" loadings the mobility of the silanes was decreased compared to that at low loadings. The expected motional gradient extending out from the surface was found. Cyclohexane and acetonitrile significantly increased the segmental mobility, while water increased it only marginally. Quantitative rates for reorientation were provided with the use of a computerized spectral simulation program.

In the authors laboratory studies have been made on deuterated coupling agents, specifically deuterioaminopropylsilane (VI, DAPS) and deuterioaminobutylsilane (VII, DABS) because of their use in composites. Their structure is shown below and their synthesis, hydrolysis, and exchange described (147):



VI



VII

where the X groups depend on the reactions which occurred. The adsorption isotherms for the APS on silica have been determined (145) and the coupling agent adsorbed and reacted on Cab-O-Sil silica surfaces at sub-monolayer and multi-layer levels. Shown in Figure 11 are the deuterium quadrupole spectra for aminopropylsilane at various coverages (168). At sub-monolayer coverages, the mobility of the surface-bound coupling agent was greater than that at monolayer coverage. At higher coverages, the mobility of the material starts to resemble that of the bulk polymer made by condensing the coupling agent alone. The spectra were consistent with a large amplitude, anisotropic, rotational motion plus conformational jumps. Interestingly, the behavior of DABS (butyl group) is similar to that of DAPS (propyl group) on silica at low coverages. At higher coverages the behavior of the coupling agent layer approaches the behavior of the bulk condensed polymer. Thus, at high coverages the DABS is more mobile than DAPS. This may be why ABS is preferred over APS for glass/epoxy applications.

<Fig. 11>

The deuterium label can provide the contrast necessary to probe the mobility of the bonded layer in the presence of an overlayer of polymer. Shown in Figure 12 are spectra of DABES on silica at roughly monolayer coverage in air and after reaction with bismaleimide (BMI) (128,145). It was found that the overpolymerization with BMI inhibited the motion of the coupling agent at the interface and *also* changed the way it moved. The spectra were consistent with the freezing out of the rotational motion chain in the composite--leaving only conformational jumps. The effect of water on the deuterium spectra of the labelled coupling agent at the air interface, and also in the composite, was consistent with the coupling agent moving 3-4 times faster than in the dry state (171). Consequently the water affects the interface in these composites. Upon drying, the interface returns to its original state. This is believed to be important

in how coupling agents provide enhanced performance in wet composites.

<Fig. 12>

*<sup>15</sup>N Studies.* Solution and solid-state experiments have been made on <sup>15</sup>N enriched APS by Chu et al. (206). Based on comparison with other known chemical shifts, they determined that different structures are present depending on conditions. For example on alumina, from propanol or *n*-methylpyrrolidone, the amine, "closed form", and "unique form" are found. From water at neutral pH (10-11), only the "unique form" and amine cation are found. The unique nitrogen form found is non-amine like and possibly bonded to a heteroatom. The closed form is a ring structure suggested by Plueddemann (142). On silica, the amine, amine cation, and closed form are found. The authors suggest that a "flip" mechanism likely occurs when reaction of the amine and polymer occurs.

*<sup>1</sup>H Studies.* Proton studies are valuable to study the kinetics of silane hydrolysis (147), etc., and the surface hydroxyl characterization (153,154). However, there appear to be few reports of their use in the characterization of the surface-bound species. Gerasimowicz, et al. (207) have reported the use of multiple-quantum (MQ) proton experiments to count the number of spins in the "spin system". For the trimethylsilyl system the MQ experiment had a plateau at about 10 spins. This is roughly in agreement with the spin system being confined to a single molecule (9 protons). For a C<sub>8</sub> chain, a spin system of about 25 is observed consistent with the protons on a single molecule.

#### 4.2 Non-Bonded Phases

There appear to be only a few reports of NMR of thin organic films that are not

permanently bound to the substrate. In the last two years, three groups have reported on surfactant groups at interfaces (208-211). Interestingly, all three involved the use of deuterium NMR of specifically labelled surfactants. Söderlind and Stilbs (208) have labelled dodecyltrimethylammonium bromide (DoTAB) and decyltrimethylammomium bromide (DTAB) with deuterons in various locations and probed the behavior of aqueous dispersions with Cab-O-Sil using deuterium NMR lineshapes and relaxation times. The spectra were consistent with fast exchange between the surfactant in solution and that on the surface. The surfactant on the surface exhibited a motional gradient with the groups near the ionic head group being more motionally restricted than the tails. This was consistent with the head group being most associated with the surface. No resolved quadrupolar splitting was observed and the mobility of the surfactant was greater than that of chemically attached chains.

Macdonald and coworkers (209-211) have prepared three choline-methyl-deuterated surfactants with different alkyl chains to probe the interaction of the surfactants with polystyrene lattices in aqueous dispersions. For dodecyl- (DDPC), tetradecyl- (TDPC), and hexadecyl- (HDPC) phosphocholine- $d_6$ , the spectra of surfactant/latex dispersions consisted of "free" and "bound" surfactant resonances (209). The largest quadrupole splitting was found with HDPC. The interaction of the surfactant with the latex was ascribed to the hydrophobic effect and hence the association was believed to be through the surfactant tails. Quadrupolar splittings were observable only at higher surface concentrations. It was concluded that the "bound" surfactant was in slow exchange with the solution phase in spite of the small quadrupolar splitting observed (<500 Hz). The quadrupolar splitting of HDPC was also sensitive to the ionic environment of the latex surface (210). This suggested that this probe might be an effective "molecular volt meter" for the surface. Relaxation time measurements (210) were used to infer that the motional state of the head group was

similar to that found in the gel state.

Finally, Söderlind and Blum (213) studied the adsorption of head group deuterated sodium 4-(1'-heptylnonyl)benzenesulfonate (SHBS) on alumina. At saturation they found that the inner (surface-bound) layer had dynamics similar to that found in the lamellar liquid crystal including quadrupole splitting on the order of about 10-12 kHz. Consequently, this layer was believed to be in slow exchange with the other layer or aqueous surfactant. The outer layer, which was unsplit, was believed to be in fast exchange with the aqueous surfactant. At lower coverages, a monolayer of surfactant was formed and was in fast exchange with the aqueous surfactant. Thus the presence of the outer surfactant layer impeded the exchange of the inner (surface) layer.

## 5. CONCLUSIONS

NMR was found to be a very powerful technique for examining the structure and mobility of thin organic films. It usually requires the use of high surface area materials because the effects of the surface are not usually very long range. Isotope substitution can sometimes provide the necessary increases in sensitivity to obtain useful surface spectra. It also can provide the contrast necessary in determining the properties of the interface, even in the presence of similar material, e.g. organic composites. Proton, deuterium, carbon and silicon experiments are to date the most informative.

NMR characterization of bonded interfacial species can be used to identify the species that have been reacted and determine the type of surface bonding. The mobility of the surface species may also affect the behavior of the material in use in applications like chromatography and composites. The use of NMR to characterize chromatographic gels should continue to be strong, while that related to composites and small non-bonded molecules should continue to increase.

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Table I Comparison of deuterium relaxation times for VPDSS and VPSDS polymers in the presence of toluene. (from reference 71)

material	T <sub>1</sub> , ms	T <sub>2</sub> , ms	T <sub>1</sub> /T <sub>2</sub>
VPDSS			
surface	3.63	3.38	1.07
solution	3.63	2.75	1.32
VPSDS			
surface	3.94	3.60	1.09
solution	3.94	3.25	1.21

## FIGURE CAPTIONS

- Fig. 1. Idealized representation of polymers attached to a solid surface: A) randomly attached showing trains, loops and tails; and B) terminally attached chains showing the two extremes of brushes and mushrooms.
- Fig. 2.  $\{^1\text{H}\}^{13}\text{C}$  inversion recovery spectra of 2000 g/mol PEO grafted on silica in benzene. Reprinted with permission from reference 54, copyright 1984, American Chemical Society.
- Fig. 3. Solid and liquid echo spectra for a) PVP on Aerosil in  $\text{D}_2\text{O}$  and b) terminally attached polystyrene on Philblack "O". The intensities for the B regions are representative of the liquid-like resonances while A is representative of both liquid- and solid-like spins. Reprinted with permission from reference 57, copyright 1981, American Chemical Society.
- Fig. 4.  $\{^1\text{H}\}^{13}\text{C}$  spectra of poly(2-vinyl pyridine-co-styrene) in toluene solution (top) and on silica swollen with toluene (bottom). The absence of liquid-like signals for 2-vinyl pyridine on the silica surface implied that it was firmly held, while the styrene segments are quite mobile. Reprinted with permission from reference 71, copyright 1990, American Chemical Society.
- Fig. 5. Heteronuclear 2D J spectrum of carbon-black filled *cis*-PIP with magic angle spinning and high power proton decoupling during detection. Reprinted with permission from reference 85, copyright 1987, American Chemical Society.
- Fig. 6. Carbon-13 spectra of filled *cis*-PIP under a variety of conditions. (A) no decoupling, no MAS; (B) high power proton decoupling, no MAS; (C) MAS, no decoupling; (D) MAS, multiple pulse decoupling; (E) MAS, high power proton decoupling. Reprinted in part with permission from reference 85, copyright 1987, American Chemical Society.

Fig. 7. Diagram of regions different mobilities in filled elastomers. the boundaries of tightly bound chains are given by the dashed lines. Reprinted with permission from reference 87, copyright 1976, American Chemical Society.

Figure 8. Spectra of PIPA (from bottom to top) in bulk, at 1/4 monolayer, at 1/2 monolayer, and at monolayer coverage on silica. Reprinted from reference 101 with the permission of Plenum Publishing.

Figure 9.  $^{29}\text{Si}$  CP-MAS spectra of A) silica gel and B) the product of its reaction with trimethylchlorosilane. Reprinted with permission from reference 158, copyright 1982, American Chemical Society.

Figure 10.  $^{13}\text{C}$  CP-MAS spectrum of a trifunctional silane on silica gel. Reprinted with permission from reference 181, copyright 1982, American Chemical Society.

Fig. 11. Deuterium NMR spectra and simulations of deuterium-labelled  $\text{C}_3(\text{D}_3)$  aminopropylsilane on silica. The material was deposited with solution concentrations of A) 0.5%, B) 1.0%, C) 2.0%, D) 3.5% and E) 10%; 2% corresponds to approximately monolayer coverage. Reprinted with permission from reference 168, copyright 1991, American Chemical Society.

Fig. 12. Deuterium NMR spectra of deuterium-labelled  $\text{C}_4(\text{D}_3)$  aminopropylsilane on silica, A) treated surface and B) treated surface overpolymerized with bismaleimide. Reprinted in part with permission from reference 128, copyright 1992, American Chemical Society.

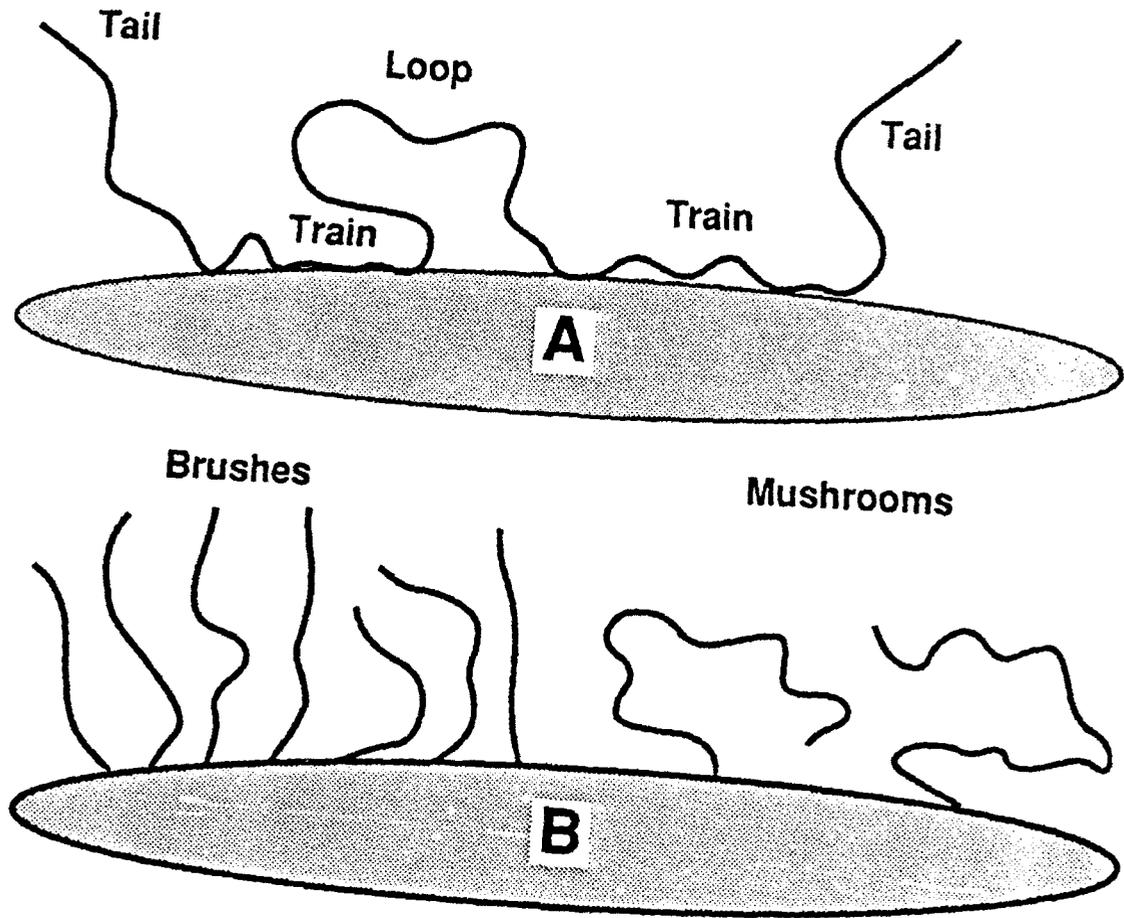


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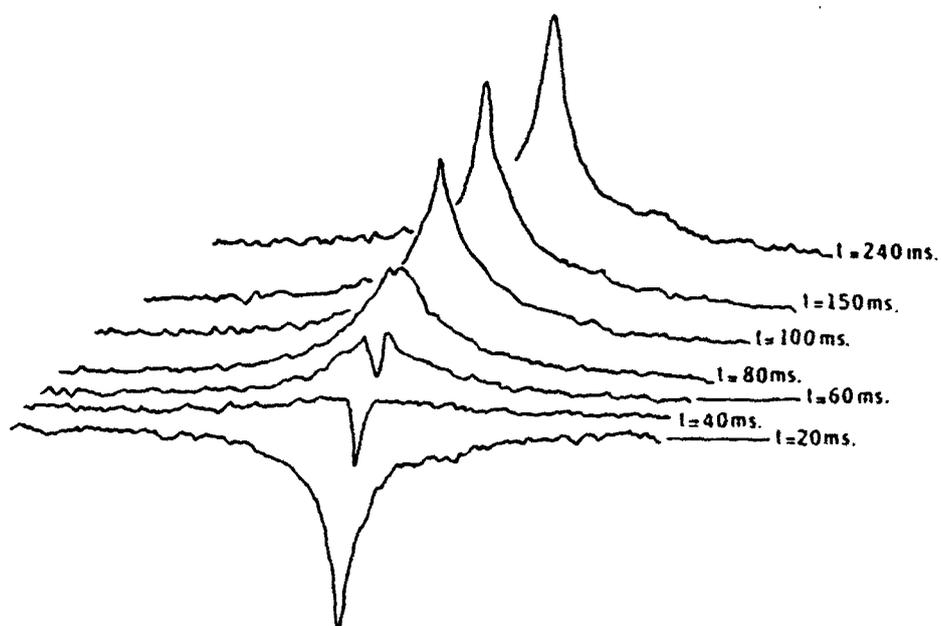


Fig. 2.  $\{^1\text{H}\} ^{13}\text{C}$  inversion recovery spectra of 2000 g/mol PEO grafted on silica in benzene. Reprinted with permission from reference 54, copyright 1984, American Chemical Society.

Blum Fig 2

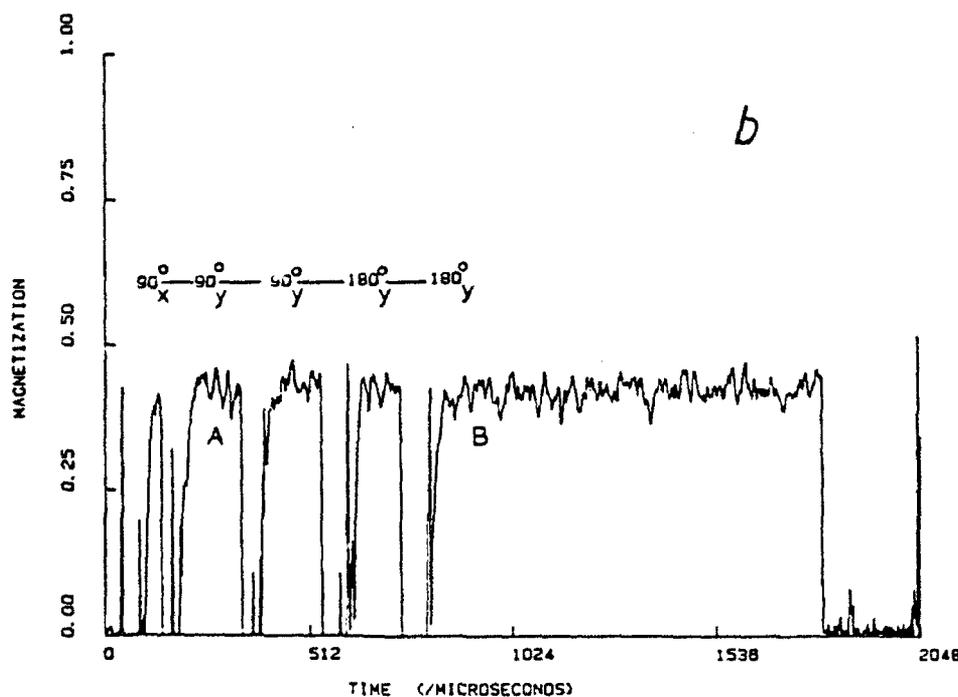
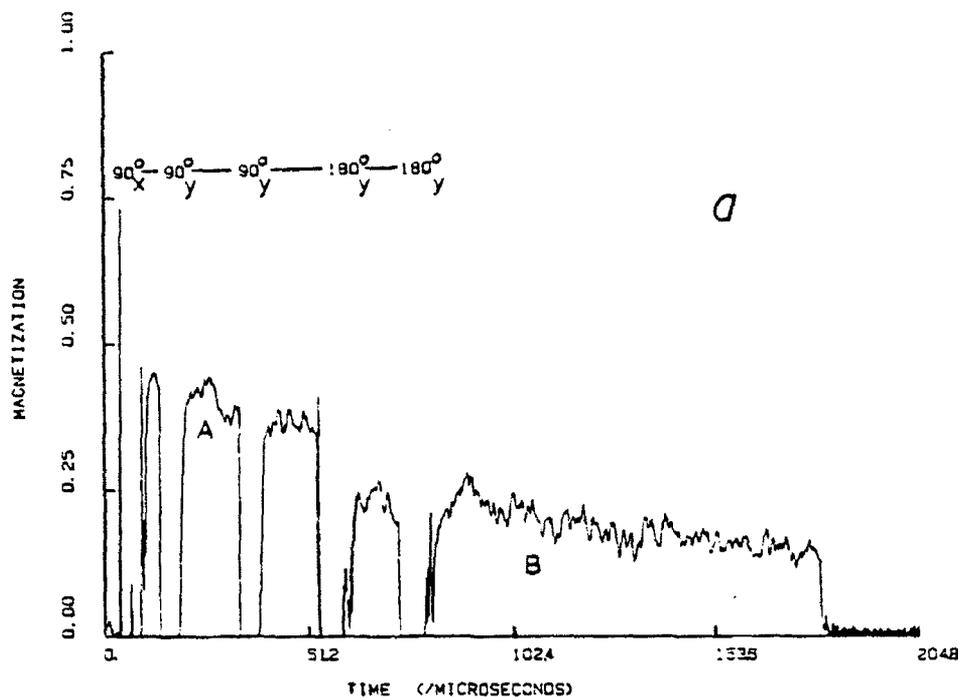


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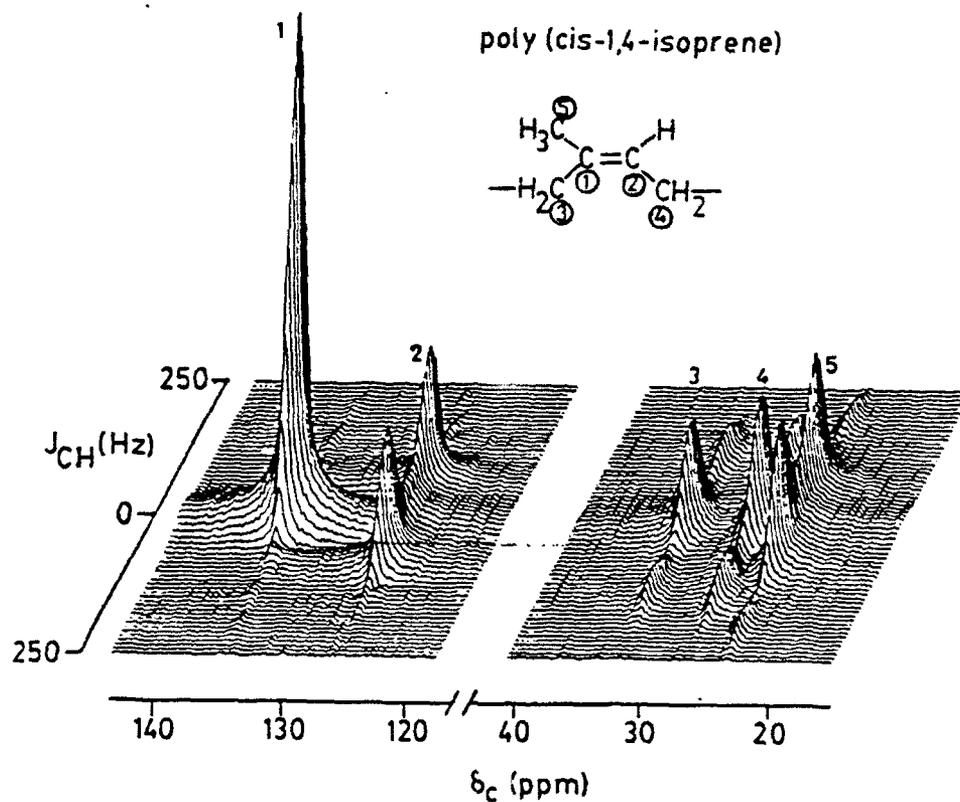
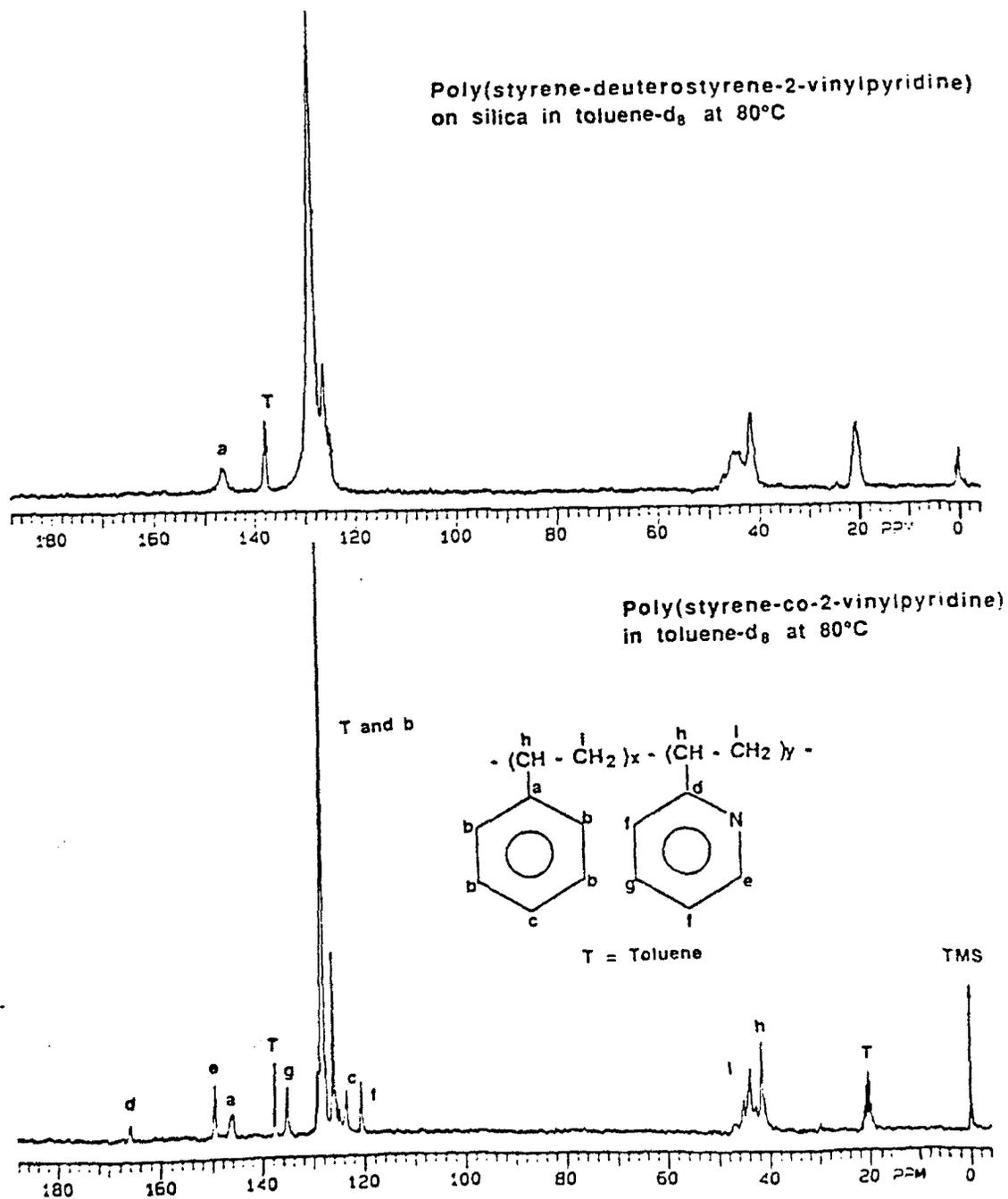


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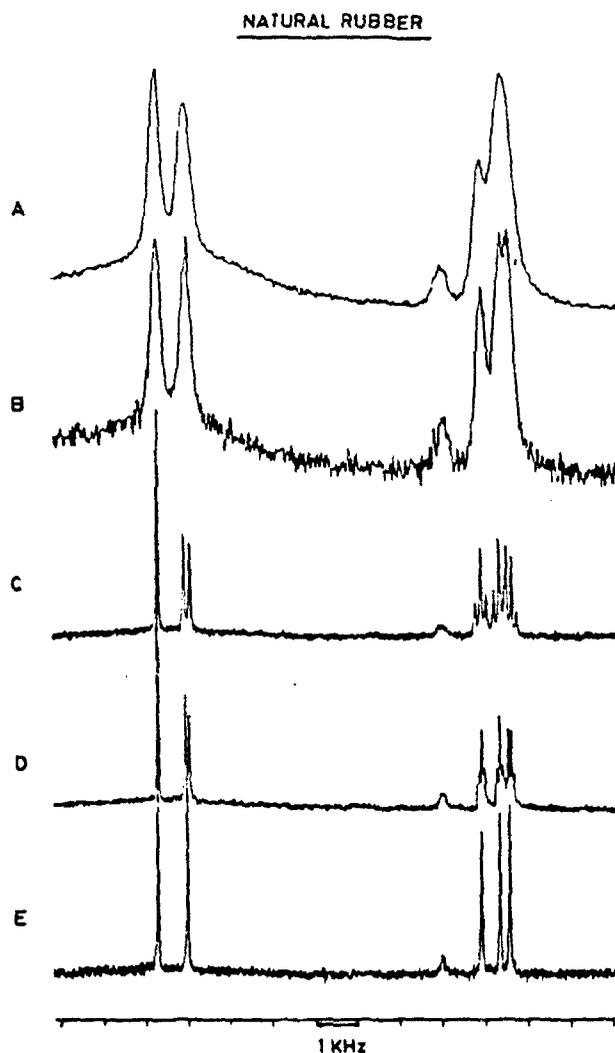


Fig. 6. Carbon-13 spectra of filled *cis*-PIP under a variety of conditions. (A) no decoupling, no MAS; (B) high power proton decoupling, no MAS; (C) MAS, no decoupling; (D) MAS, multiple pulse decoupling; (E) MAS, high power proton decoupling. Reprinted in part with permission from reference 85, copyright 1987, American Chemical Society.

Blum Fig 6

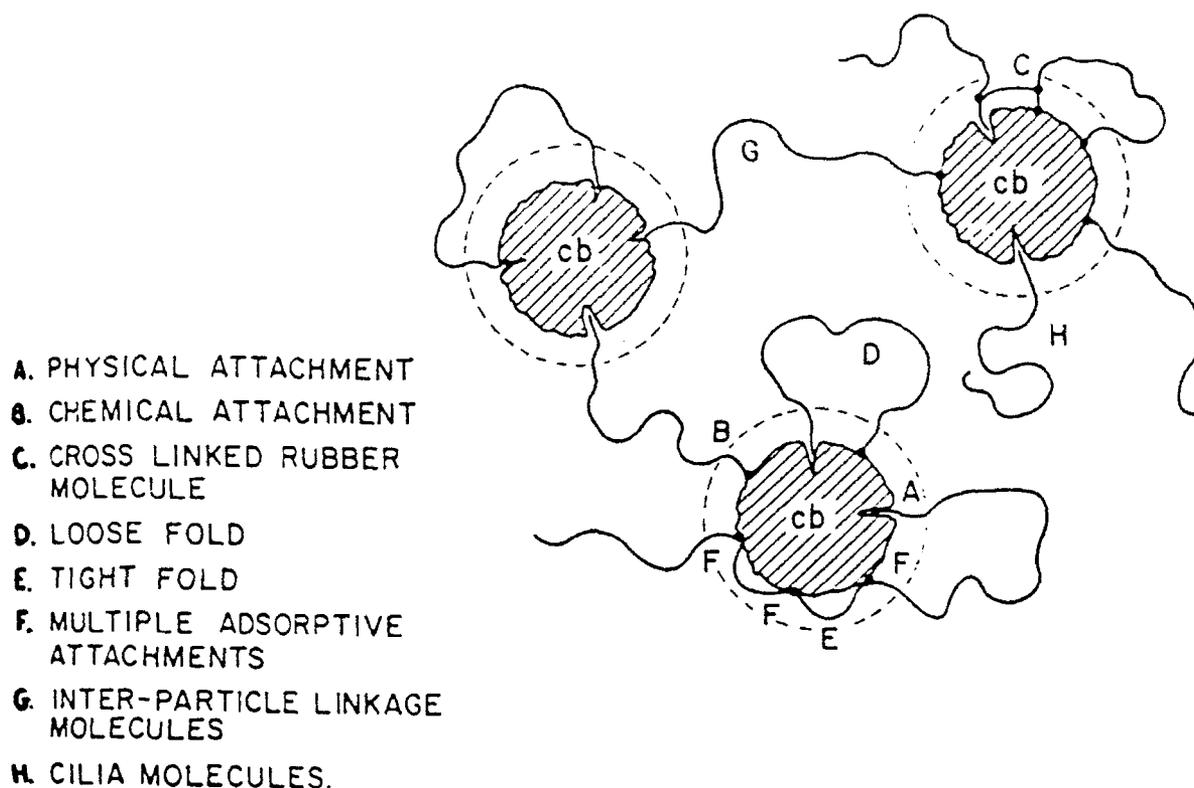


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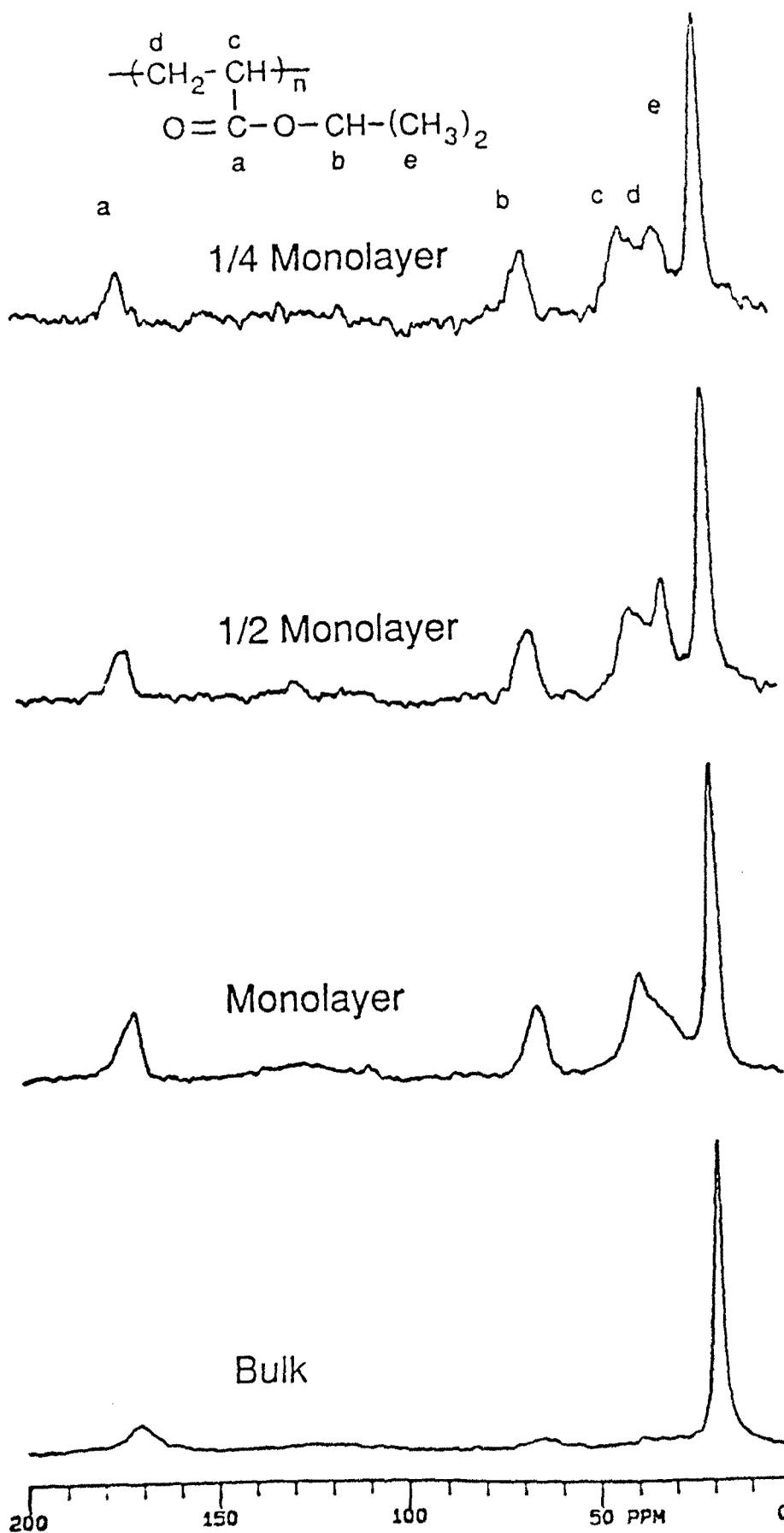


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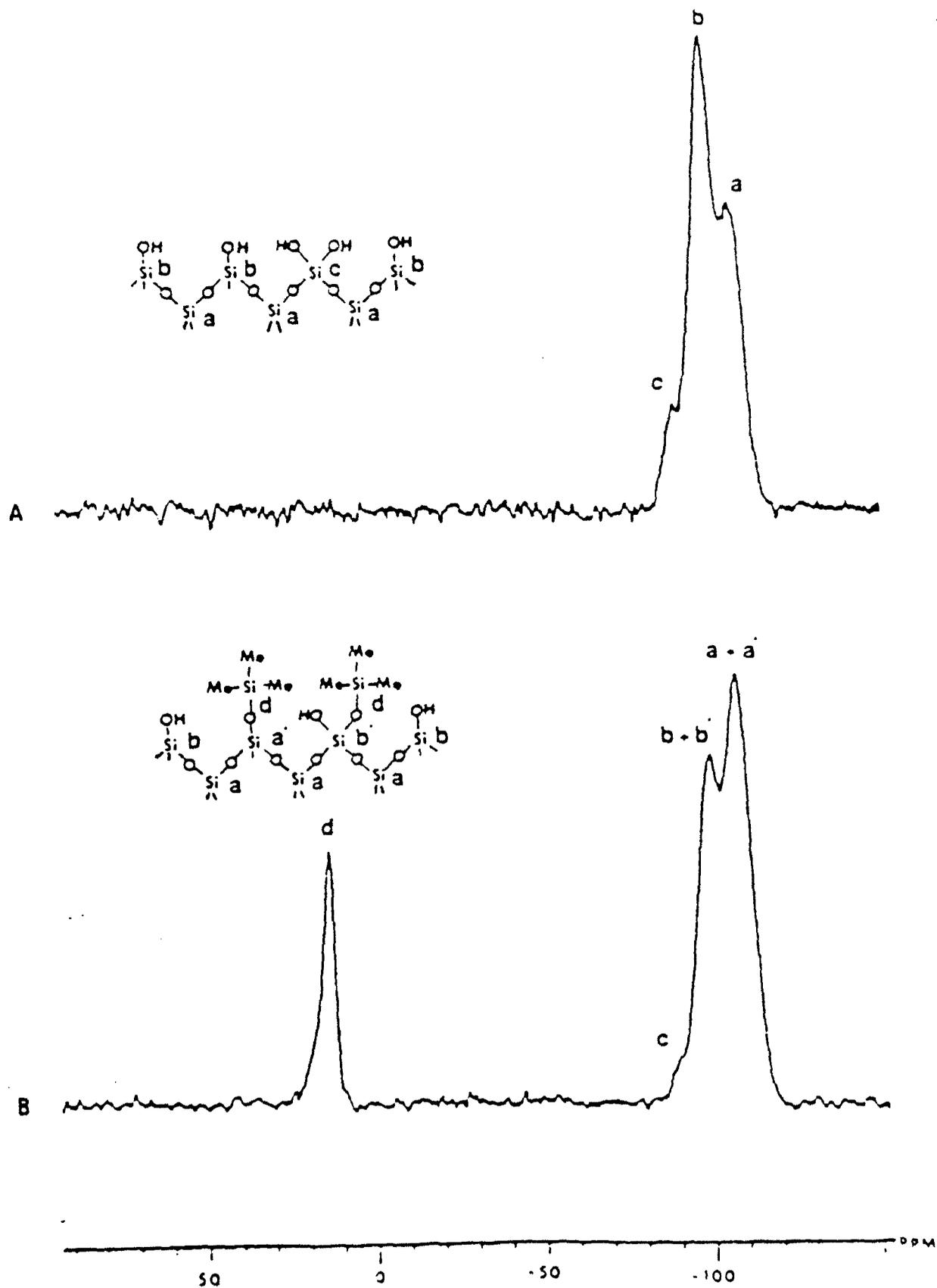


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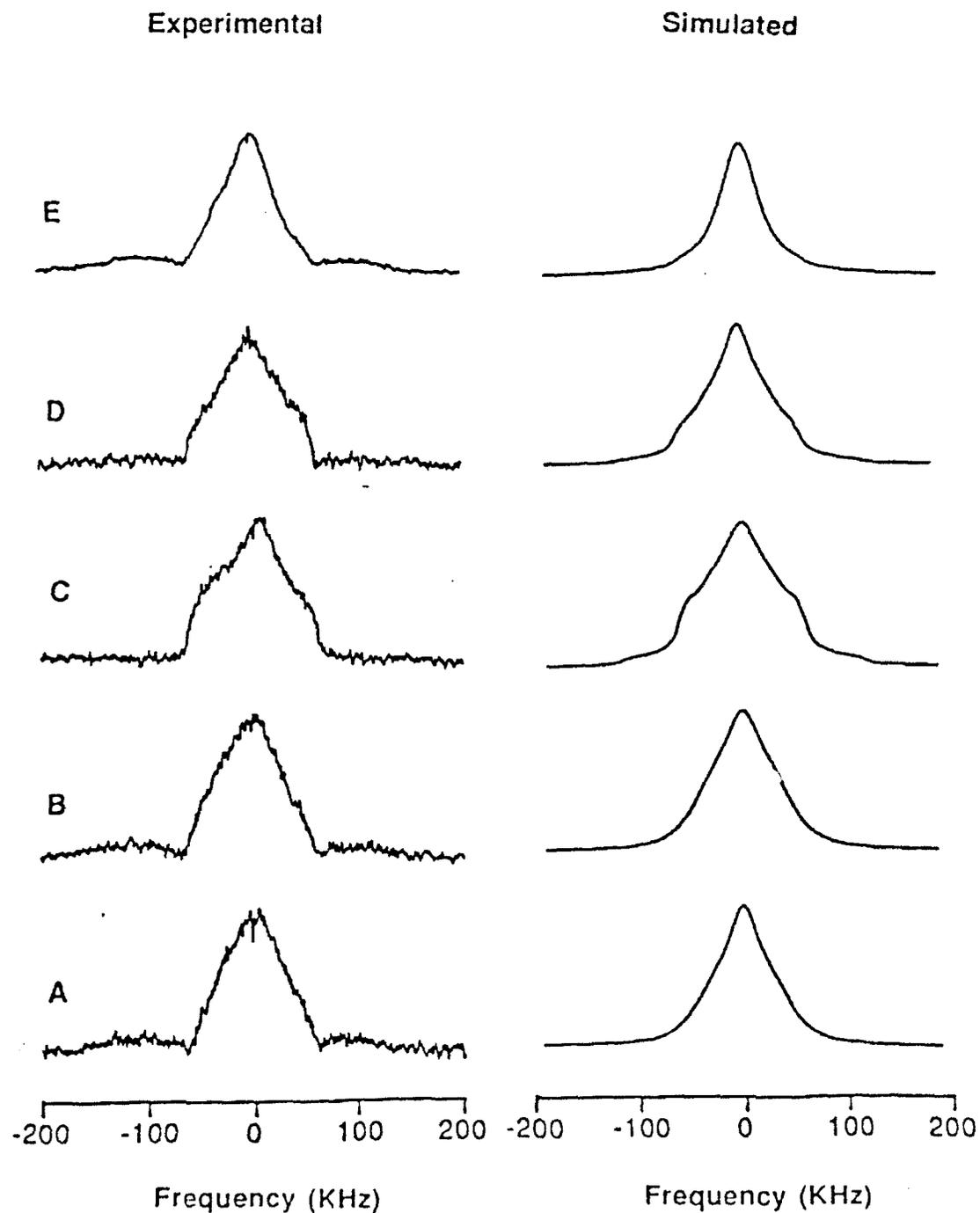


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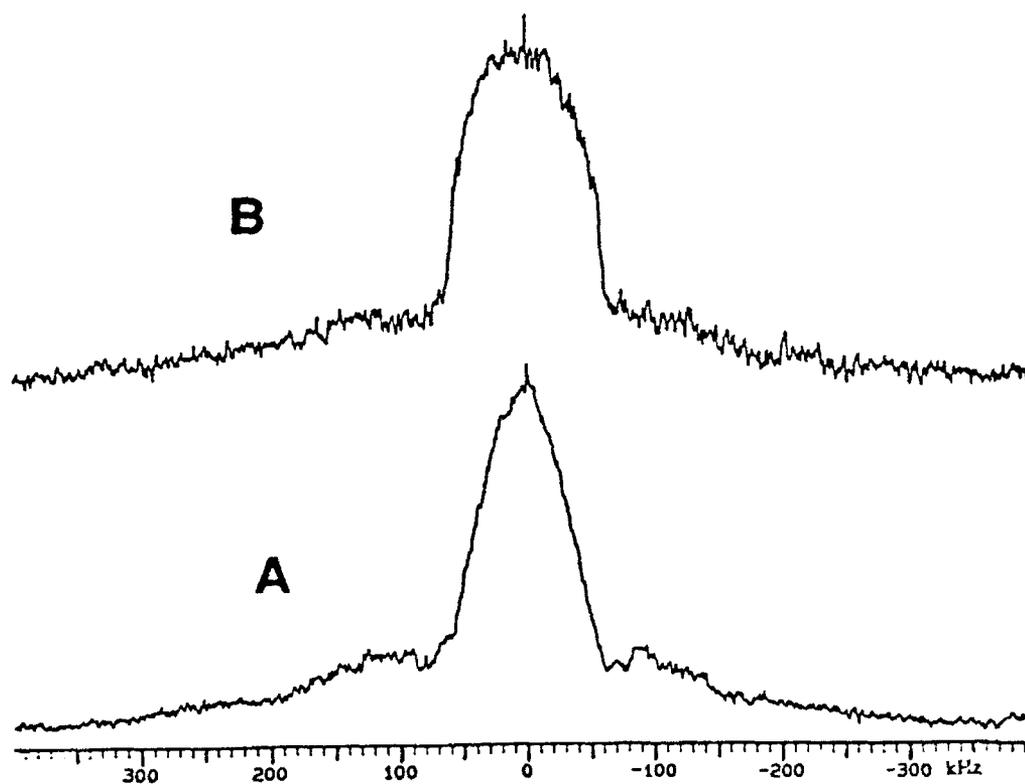


Fig. 12. Deuterium NMR spectra of deuterium-labelled  $C_4(D_3)$  aminopropylsilane on silica, A) treated surface and B) treated surface overpolymerized with bismaleimide. Reprinted in part with permission from reference 128, copyright 1992, American Chemical Society.

Blum Fig 12