by the rinse judging from the small change in infrared band intensity. However, the amino groups can interact rather strongly with the wetting liquids, especially those capable of hydrogen bonding. Such interaction would lower the contact angles and in a way that would not be a systematic function of the liquid surface tension, thus obviating any linear γ_{LV}–cos θ relationship.

Conclusion

The trialkoxysilane films were found to be essentially polysiloxane coatings, part of which could be rinsed away by acetone, but in all cases there remained a more firmly held polymer network. Among the four silanes examined, the polyvinylsiloxane films were the most severely depleted by this rinse. The residual coating was composed of patches of spherical polymer particles deposited on a thin, uniform polymer film. On a molecular scale this film had an open structure easily penetrated and swelled by water and organic liquids. In applying the silanes from various solvents the only major difference was that the films from cyclohexane were generally thicker than those from the more polar solvents. As far as the substrate was concerned, there were no distinguishable differences between the films formed on steel, glass, or the atr plates.

In technical practice the silane-adhesion promoters are applied to adherend surfaces by evaporation from solutions, as was done here. The solvent is usually water (or alcohol–water mixtures), although nonaqueous solvents have been employed. Presumably, the coating material found here to be easily removed by acetone would dissolve into the adhesive resin and the resin molecules would penetrate the polysiloxane network. It is known that too thick a coating of the silane can be detrimental to the bond strength, so the use of nonpolar solvents does not seem advisable. It is not immediately obvious why the application of thin, penetrable polysiloxane films should give better bond strength than just thoroughly cleaning the adherend surface. It would be incorrect to view the siloxane films as protective barriers, since they are not dense enough to block the diffusion of water molecules. Explanations based on the silanes forming covalent bonds to the adherend are inconsistent with the ability of these finishing agents to improve the wet strength of resin-to-metal adhesion, if we take account of the low water stability of metal–oxygen–silicon bonds.[7]

It is possible that in reacting with water to form the siloxane film the silanes serve as water scavengers. Also, it has been suggested[18] that the functional group of the film (vinyl, aminopropyl, chloropropyl) influences the resin polymerization and thereby the resin structure near the interface. The end result could be an improvement in the mechanical properties and/or the moisture resistance of the resin in the interfacial region.

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Magic-Angle Carbon-13 Nuclear Magnetic Resonance Spectra of Filled Rubber

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ABSTRACT: Line narrowing by a factor of 3–4 has been achieved in the ^{13}C nmr spectra of a carbon-black-filled, vulcanized *cis*-polyisoprene by 1-kHz sample rotation at the magic angle. The narrowing permits the resolution of a new methylene-carbon line not present in the spectrum of an unfilled, nonvulcanized, otherwise comparable *cis*-polyisoprene.

An analysis of the ^{13}C nmr spectra of carbon-black-filled *cis*-polyisoprene, $-\!(CH_2CCH_3{=}CHCH_2)\!-_x$, has indicated that the line broadening of the filled polymer relative to the unfilled polymer can be attributed to incomplete motional narrowing of the nmr lines.[2] By this analysis the broadening results from low-frequency motion, described by long correlation times, associated with the residual dipole remaining from an incomplete spatial average. When line broadening is due to dipolar interactions with long correlation times, it is reasonable to expect that line narrowing can be achieved by any of several techniques including multiple-pulse schemes,[3,4] high-speed sample rotation[5] at the "magic angle," or strong decoupling (double resonance) experiments.[6] We have, in fact, achieved substantial line narrowing in the ^{13}C nmr spectra of carbon-black-filled *cis*-polyisoprene by use of magic-angle spinning.

Experiments under magic-angle conditions were performed on a solid, 60-pph HAF carbon-black-filled, sulfur-vulcanized,

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(1) (a) Monsanto Co.; (b) Washington University.

(2) J. Schaefer, *Macromolecules*, **5,** 427 (1972).

(3) (a) See, for example, U. Haeberlen and J. S. Waugh, *Phys. Rev.*, 185, 420 (1969); (b) J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.*, **48,** 662 (1968).

(4) P. Mansfield, *Progr. Nucl. Magn. Resonance Spectrosc.*, **8,** 41 (1971).

(5) E. R. Andrew, *ibid.*, **8,** 1 (1971).

(6) F. Bloch, *Phys. Rev.*, **111,** 841 (1958).

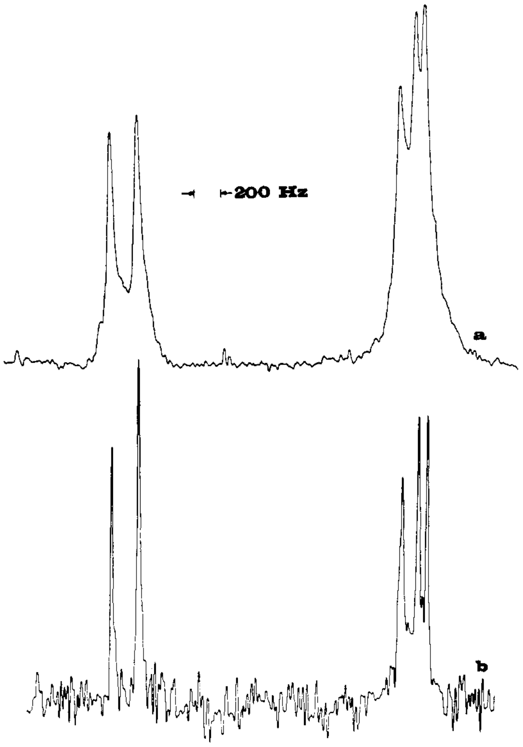

Figure 1. Fourier transforms of noise-decoupled (^{1}H, $\gamma H_2/2\pi$ = 1000 Hz), natural-abundance ^{13}C free-induction decays of a carbon-black-filled, sulfur-vulcanized *cis*-polyisoprene (a) nonspinning and (b) spinning at about 1 kHz at the magic angle. The nonspinning sample was a 15-mm long by 13-mm diameter cylinder while the spinning sample was a specially machined rotor, 6 mm long by 4 mm in diameter. The delay time between 90° pulses was 1.5 sec for a and 0.5 sec for b. These delay times are too short to permit complete relaxation of all the carbons between pulses. A total of 512 free-induction decays was accumulated for a and 1600 for b.

standard tread-stock sample of *cis*-polyisoprene.[2] The rotor design introduced by Lowe[7] and developed by Kessemeier and Norberg[8] was used. The rotor consisted of a cylinder, 6 mm long and 4 mm in diameter, and fitted with sapphire bearings. The rotor was made from the carbon-black-filled polymer and was itself the analytical sample. It was suspended by a horizontal phosphor-bronze axle attached to a Teflon support and was driven by compressed nitrogen from a glass jet directed onto precision notches cut into the rotor perpendicular to the spinning axis. Maximum spinning speeds of about 1 kHz were achieved. The rotor did not spin well at speeds much below 600 Hz. The rotor and its support assembly were placed in a 15-mm tube which was located in the nmr probe in the usual way. The spinning axis of the rotor lay in a plane perpendicular to the cylindrical axis of the nmr tube, and the angle which the spinning axis made with the magnetic field was chosen by rotating the nmr tube to the desired value. Determination of this spinning angle was made with a simple protractor attached to the nmr tube and was accurate to about ±3°.

An example of the line narrowing realized by performing the ^{13}C nmr experiment under magic-angle conditions is shown in Figure 1. These spectra were obtained by Fourier transform techniques using a Bruker HFX spectrometer operating at 22.6 MHz. Figure 1a shows the proton-decoupled ($\gamma H_2/2\pi$ = 1 kHz) natural-abundance ^{13}C nmr spectrum of a standard size, 13 × 15 mm nonspinning cylindrical sample of the filled, vulcanized rubber. The five lines observed in the spectrum arise from the five chemically different carbons of the repeating unit in the chain. Assignments are discussed in detail elsewhere.[9] All of these five lines are about 70 Hz wide at 35°. The line widths are temperature dependent and, in fact, can easily be narrowed by a factor of about 2 by the approximately 15° increase in temperature resulting from an increase of $\gamma H_2/2\pi$ to 4 kHz.[2] As shown in Figure 1b, the lines are narrowed by a factor of 3–4 at 35° when the free-induction decay is obtained from a sample spun at the magic angle at a rate of about 1 kHz. The extent of the narrowing depended on the angle of the spinning axis with the applied magnetic field. The narrowing was most pronounced in the vicinity of the magic angle of 54°44′. (This angle reduces to zero the $(3\cos^2\theta - 1)$ dependence of dipolar interactions.) For an angle of about 30° much of the narrowing was lost, while for an angle of about 60° very little of the narrowing was lost. The widths of the narrowest lines observed, the quaternary- and methine-carbon lines, were 18 and 23 Hz, respectively.

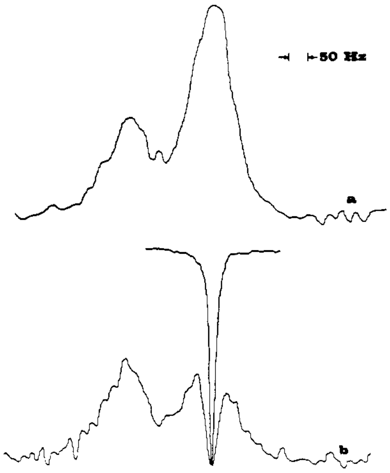

Figure 2. (a) An inhomogeneously broadened, proton-decoupled ^{13}C nmr spectrum of the vinyl carbons of filled, vulcanized *cis*-polyisoprene observed by Fourier transform techniques. (b) The same spectrum observed the same way except that preceding the usual sampling pulse, a 500-msec, 1-mW burst of single-frequency ^{13}C rf has been introduced at the center of the higher field line. The width of the hole burned into the inhomogeneously broadened line depends on the natural dipolar line width. The hole is three to four times broader than a typical 20-Hz-wide line shown inverted for comparison.

The fact that this observed line narrowing was genuine was established by a determination of the homogeneous line width of the nonspinning, filled, vulcanized sample. This was accomplished by burning a hole into an artificially broadened line of the nonspinning sample and observing the shape of the hole.[2] The experiment is illustrated in Figure 2. The two proton-decoupled low-field lines in the spectrum of the nonspinning sample were broadened by about a factor of 2 by altering the gradients of the homogeneity coils (Figure 2a). Then a 500-msec, 1-mW burst of single-frequency ^{13}C irradiation was introduced immediately preceding the normal sampling pulse. In this situation, the ^{13}C spins (connected to proton spins only through the lattice[2] and isolated from one another by their low natural abundance) whose Larmor frequency matched that of the long ^{13}C rf burst were satu-

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(7) I. J. Lowe, *Phys. Rev. Lett.*, 2, 285 (1959).

(8) H. Kessemeier and R. E. Norberg, *Phys. Rev.*, 155, 321 (1967).

(9) M. W. Duch and D. M. Grant, *Macromolecules*, 3, 165 (1970).

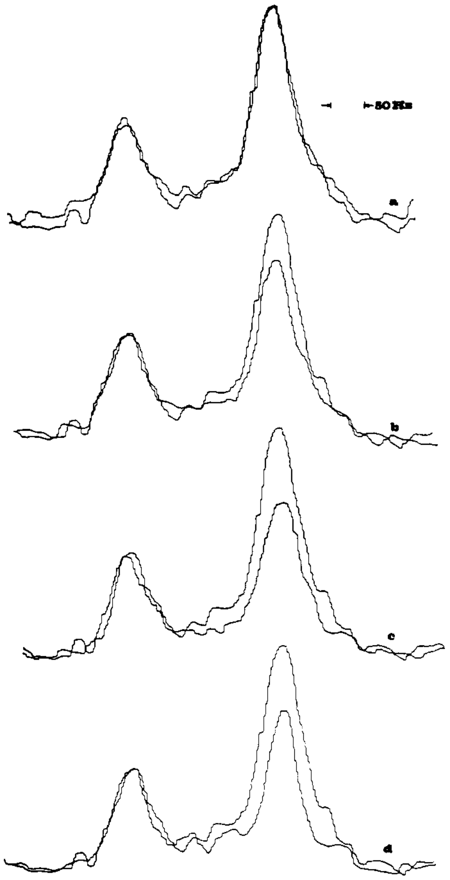

Figure 3. Selectively saturated Fourier transform ^{13}C nmr spectra of vinyl carbons of the same carbon-black-filled, vulcanized, *cis*-polyisoprene sample used in the magic-angle spinning experiments. The prepulse 500-msec ^{13}C rf burst is close to resonance relative to the high-field line in a, b, and d, with approximate power levels of 0.0, 0.1, and 0.4 mW, respectively. A prepulse 500-msec, 0.3-mW ^{13}C rf burst is off resonance about 30 Hz in c. The selectively saturated spectra are shown superimposed on a spectrum obtained in the usual fashion. The delay time between 90° sampling pulses was too short to permit the low-field, quaternary carbon line to display full intensity.

rated. The width of the resulting hole depends on the true dipolar line width.[10] The observed hole has a width which is about four times that of a typical, 20-Hz-wide line (comparable to the narrowest line observed in the spinning experiment) inverted for purposes of comparison (Figure 2b). The width of the hole was the same when the frequency of the ^{13}C rf burst was changed by 50 Hz (although the position of the hole was naturally shifted), and was also the same, within experimental error, when the irradiating power was reduced by a factor of 2.5. In the latter experiment, the amplitude of the hole was substantially reduced, indicating that full saturation at the ^{13}C burst frequency had not been achieved.[11] Figure 3 shows the results of a similar selective saturation experiment performed on the same sample under normal conditions of homogeneity. Regardless of the power level, and independent of the ^{13}C prepulse burst frequency, the selectively saturated, high-field line decreases in intensity while maintaining approximately the same center, symmetry, and width at half-height. (The line width is measured from this experiment as 65 ± 10 Hz.) Similar results were obtained even when burst lengths comparable to but shorter than T_1 were used.

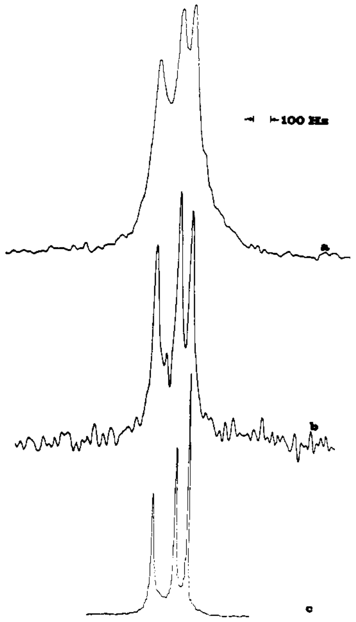

Figure 4. Spectra of the high-field methylene- and methyl-carbon regions of the carbon-black-filled, vulcanized *cis*-polyisoprene (a) nonspinning and (b) spinning at about 1 kHz at the magic angle. The corresponding spectrum of nonspinning, unfilled, nonvulcanized, otherwise comparable *cis*-polyisoprene is shown in c. The delay times between 90° pulses used in obtaining the three spectra were not the same. This has affected the integrated intensity of the methyl-carbon line at highest field.

The results of these selective saturation experiments are consistent with the absence of significant line broadening due to either micro- or macroscopically inhomogeneous magnetic fields. If the microscopic inhomogeneities generated by susceptibility variations arising from the presence of the carbon-black filler particles determined the line width (rather than incomplete motional narrowing), an apparently homogeneous and temperature-dependent ^{13}C line width would be possible only if molecular diffusion permitted each ^{13}C spin to sample, although not necessarily average, all values of the inhomogeneous magnetic field. In the filled polyisoprene used in these nmr experiments, the carbon-black particles form regions on the order of 1000 Å in diameter and spaced many diameters apart.[12] Translational motion of several times 1000 Å in a time comparable to T_1, or 100 msec, corresponds to a self-diffusion constant on the order of 10^{-8} cm^2/sec. A diffusion constant this large can be reasonably associated only with the translational self-diffusion of short chains (with molecular weight less than 5000) and not with high polymers entangled in solids.[13]

The narrowing of the ^{13}C nmr lines of the filled, vulcanized *cis*-polyisoprene permits the resolution of at least one additional line. This is illustrated in Figure 4. A weak line appearing between the two lower field methylene-carbon lines is visible in a spectrum obtained at the magic angle, but not

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(10) C. P. Poole and H. A. Farach, "Relaxation in Magnetic Resonance," Academic Press, New York, N. Y., 1971, Chapters 5 and 13.

(11) Saturation away from the burst frequency, which tends to broaden the hole, is present here, but is not a major factor. Using the same irradiating power levels and about the same prepulse burst lengths in selective saturation experiments on an intentionally inhomogeneously broadened line, which was normally 20-Hz wide, a hole was produced whose width was about one-third that of the hole burned in the filled, vulcanized polyisoprene (see ref 2).

(12) G. Kraus, *Advan. Polym. Sci.*, **8**, 155 (1971).

(13) J. E. Tanner, *Macromolecules*, **4**, 748 (1971).

in the spectra of either the nonspinning sample or of an unfilled, nonvulcanized, otherwise comparable, *cis*-polyisoprene. This line appeared in every spectrum obtained at the magic angle and its position and intensity were reproducible. Qualitative indications of its spin–lattice relaxation time suggested a longer value than for normal main-chain methylene carbons, but shorter values than for normal methyl carbons in *cis*-polyisoprene. Several kinds of lines arising from structural and steric defects in the polymer chain can occur in this region,[2] so an unambiguous assignment is not possible at this time. One possibility is that the line arises from methylene carbons which have been removed from the main chain during vulcanization, remain bonded to carbons still in the chain, but are now also covalently bonded to sulfur and so form part of the cross-linking network. On the other hand, the line may simply arise from carbons in independent chain fragments, either formed during the milling or vulcanization processes, or part of the oil additives usually found in rubber formulations.

Magic-angle spinning experiments on solid rubbers have been reported before. In fact, the proton nmr line of a cross-linked silicone rubber has been successfully narrowed in both magic-angle spinning[14] and multiple-pulse experiments.[15] These earlier results were interpreted in terms of the net slow motion of the chains, generating a distribution of interchain interactions which occurred almost entirely at low frequencies. In the carbon-black-filled polyisoprene system, low-frequency interactions probably arise from filler–chain entanglements. That is, the filler excludes the bulk polymer from some spatial orientations resulting in low-frequency dipolar interactions which are not averaged to zero in a time T_2. The nmr lines are therefore subject to incomplete motional narrowing. Since the ^{13}C line widths of the filled polyisoprene obtained under magic-angle conditions are greater than the homogeneous line widths of the unfilled polymer, the average correlation frequency of the low-frequency interactions resulting from the influence of the filler, while small compared to the 22.6-MHz measuring frequency, must still be large compared to the 1-kHz spinning frequency. Thus, the broadened line can be only partially narrowed by magic-angle spinning.[8a]

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(14) M. Cohn, A. Kowalsky, J. Leigh, and S. Maricic, "Magnetic Resonance in Biological Systems," Pergamon Press, Elmsford, N. Y., 1967, p 45.

(15) L. M. Huber, unpublished results, as cited in ref 3a.

Electron Spin Resonance Studies of Frequencies of *Intra*molecular Collisions between the End Groups of a Hydrocarbon Chain

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ABSTRACT: The frequency of *intra*molecular collisions between two groups linked to a polymer chain depends on chain flexibility, length of the polymer segment separating them, temperature, viscosity of the solvent, bulkiness of the attached groups, etc. We developed an esr technique which permits us to determine the frequency of such collisions and its dependence on the above parameters. This has been achieved by attaching two groups of relatively high electron affinity to the ends of the chain. Reduction of one of them to the respective radical anion yields a paramagnetic species characterized by its esr spectrum. Collision with the other end group results in electron transfer, and this affects the shape of the spectrum. A mathematical procedure has been described by means of which the frequency of collisions can be calculated from the shape of the experimental spectra. The results obtained at various temperatures for $X-(CH_2)_j-X$ chains with j equal to 3, 4, 5, 6, and 12 are reported.

Most polymeric molecules are flexible. This property arises from internal rotations around the covalent bonds of a polymeric chain that change its conformation. The flexibility of polymer chains endows these materials with their most valuable and useful properties. It makes many polymers plastic, provides elastic properties for rubbers, and permits many biopolymers to fulfill their vital biologic functions. Therefore, studies of the kinetics of conformational changes of polymer chains are important, and a novel approach to this problem is outlined in the present paper.

Consider a hydrocarbon chain, *e.g.*, one formed through linkage of j CH_2 units and terminated by some groups X, *viz.*, $X-(CH_2)_j-X$. Continuous changes of conformation lead to collisions between the end groups, and the frequency of such *intra*molecular encounters depends on the flexibility of the chain, its length as determined by the value of j, temperature, viscosity of the solvent, bulkiness of the end groups, etc. A method of counting the frequency of such intramolecular collisions and its dependence on the above factors is therefore valuable in studies of kinetic problems associated with the chain's flexibility. The following technique led us to this goal.

Hydrocarbons having the general structure $(\alpha\text{-N})-(CH_2)_j-(\alpha\text{-N})$ with j varying from 3 to 12 were synthesized,[1] α-N

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(1) P. Caluwe, K. Shimada, and M. Szwarc, *J. Amer. Chem. Soc.*, in press.